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## Determination of Activation Energy of Surface Diffusion Based on Thermal Oscillations of Atoms

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This paper covers calculations of the activation energy of surface diffusion of ad-atoms on the substrate surface from the point of view of thermal oscillations of substrate atoms and ad-atoms. The main characteristic of oscillations of atoms and geometric mean frequency was calculated based on statistical approximation of the Debye model using the reference values of entropy and heat capacity of metals. The basic principle of the model of activation energy calculation presented in the paper is the formation of potential wells and barriers during oscillations of atoms localized in the sites of the lattice. Oscillations of atoms were considered in the framework of quasiclassical quantum approximation as the oscillations of harmonic oscillators in the potential parabolic wells. Dimensions of the negative part of values of the potential well energy were determined by the amplitude of thermal oscillations of atoms. Positive values constituted a significant part of the potential well energy values. Barriers were formed owing to interaction of positive values of the energy of parabolic wells of adjacent atoms. Therefore, in order to make the ad-atom jump, it is necessary to get out of the potential well having the negative values, and to overcome the potential barrier. The energy required for the ad-atom jump on the substrate surface was the activation energy of surface diffusion. The results obtained in this paper agree satisfactorily with the results of another method, which is based on determining the energy of ad-atom binding with the substrate atoms.

**Key words:** activation energy, ad-atom, thermal oscillations of atoms, geometric mean oscillation frequency, amplitude of oscillations, heat energy, potential well, potential barrier.

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### Introduction

Surface diffusion, which consists in the transfer of a substance on the surface of the solid-state body, plays an important role in many surface processes and chemical reactions, such as adsorption, desorption, crystallization, wetting, thin-film growth, and formation of nanostructures [1-3]. Surface atoms become mobile ones owing to random thermal fluctuations. The important characteristic of surface diffusion, which determines the rate of thermo-active process at a given surface temperature, is the activation energy of surface diffusion  $E_a$ . Surface diffusion is studied experimentally using the methods which allow recording the result of the atom movement (labeled atoms, measurement of work function, field

emission microscopy) [4, 5]. However, the experimental evaluation is associated with a number of problems related to purity of samples, capacity of indicator elements, surface oxidation and so on.

Theoretical calculation of  $E_a$  is a difficult task, since the real surface of the crystal exhibits inhomogeneous structure. As a result, the surface energy relief of "substrate-ad-atom" system changes [6], creating the difficulties for determination of the diffusion coefficient and  $E_a$ . Existing theoretical methods for  $E_a$  calculation are mostly based on the energy of ad-atom binding with the atoms of the substrate surface (for example, the embedded atom method, or EAM) [7]. This method represents the total energy of the system as a sum of the atom penetration energy and electrostatic energy. The penetration energy is

calculated using the method of the local density functional, which determines the atom binding energy and depends only on the local density of electrons. The use of this method requires a fitting procedure [7, 8] and in some cases leads to inaccurate results [9]. Another method presented in [10, 11] allows to calculate  $E_a$  without fitting procedure. This method consists in correlating  $E_a$  of ad-atoms with the change in cohesion energy of these atoms with the nearest neighbors of the crystal at the time of jumping from one position to another. In [10]  $E_a$  is calculated for the self-diffusion of ad-atoms of all transition and rare-earth metals on the tungsten surface (110). As a result, the values, which agreed satisfactorily with the experimental data, were obtained. The most accurate method of theoretical calculations of  $E_a$  [12] is the development of cohesive approximation. This method is based on the calculation of the total energy of ad-atom with the substrate in each position of the ad-atom diffusion. The diffusion activation energy was determined as a difference of this energy in the equilibrium adsorption position and in the transition saddle point. The total energy was calculated using the density functional theory [13] with high accuracy of the results. Calculation of  $E_a$  for ad-atoms of nickel, copper, zinc and iron on the surface of the copper substrate is given in [12].

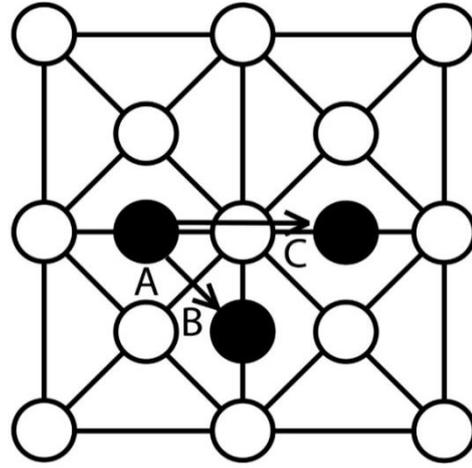
This paper proposes the theoretical method for calculation of the activation energy of surface diffusion of ad-atoms on the substrate surface, which considers the amount of heat energy required to perform the movement of the ad-atom on the surface, instead of the change in binding energy. This energy can be found based on the model of thermal oscillations of oscillators of ad-atoms and substrate atoms in the potential wells, which are formed by propagation of the Coulomb field of ions of the substrate crystal lattice. Results of  $E_a$  for ad-atoms of nickel, copper, zinc and iron on the surface of the copper substrate obtained in this paper are compared with the results of [12].

## I. Calculation models and methods

Surface diffusion of ad-atom on the substrate surface can be represented as a movement over the distances of the appropriate levels between the adjacent adsorption positions. Adsorption positions of ad-atom on the substrate surface are in places of energy minimums. Therefore, ad-atom surface diffusion can be represented as a sum of ad-atom jumps between the sites of the crystal lattice at the level of distance.

Let's consider surface diffusion of ad-atoms on the copper surface, which has fcc lattice, in the plane (100). Ad-atom is located in the lattice site A in the plane (200) at the distance of  $0.5c$  ( $c$  – parameter of crystal lattice) (Fig. 1). We shall investigate the diffusion of ad-atom from site A in two directions: to position of site B and to position of site C. The distance between sites A and B is  $c\sqrt{0.5}$ , and jump length between sites A and C is equal to  $c$ .

At the given temperature of the system  $T$ , atoms of the crystal lattice of copper and ad-atom located on the substrate perform thermal oscillations and have a



**Fig. 1.** Diffusion of ad-atom on the surface of crystal with fcc lattice: A – initial position, B, C – end positions.

corresponding heat energy of oscillations. The jump of ad-atom to the adjacent position in the site B or C is carried out in the case if it has the sufficient energy for this. The difference between this energy and the energy of thermal oscillations of ad-atom at temperature  $T$  is the activation energy of ad-atom surface diffusion. The energy required for the ad-atom jump will be calculated based on model representations of oscillations of the atom oscillators. We represent copper atoms and ad-atom as oscillators performing thermal oscillations at a given temperature of the system with certain frequency, and consider the geometric mean frequencies of these oscillations. The geometric mean oscillation frequency  $\varpi$  is expressed as follows [14]:

$$\ln \varpi = \frac{\sum_a \ln(\omega_a)}{3N\nu}, \quad (1)$$

where  $\omega_a$  – oscillation frequency of the oscillator  $a$ ,  $3N\nu$  – quantity of oscillators. Now we shall calculate geometric mean oscillation frequencies of copper atoms and ad-atom, based on macro-parameters. The Helmholtz free energy of distributed oscillators takes the form [14]:

$$F = k_B T \sum_a \ln \left( 1 - \exp \left( -\frac{\hbar \omega_a}{k_B T} \right) \right) \approx k_B T \sum_a \ln \left( \frac{\hbar \omega_a}{k_B T} \right), \quad (2)$$

where  $\hbar$  – the Planck constant,  $k_B$  – the Boltzmann constant.

For high temperatures in the Debye approximation ( $T > \theta/4$ ,  $\theta$  – the Debye temperature) the exponent indicator can be considered a small value and it is possible to expand the exponent into series to the first term:

$$F = \frac{3N\nu k_B T}{3N\nu} \sum_a \ln \left( \frac{\hbar \omega_a}{k_B T} \right) = 3N\nu k_B T \ln(\hbar \varpi) - 3N\nu k_B T \ln(k_B T), \quad (3)$$

From equation (3) we express the energy using the relation  $E = F + TS$ ,  $S = -\frac{\partial F}{\partial T}$ , where  $S$  is the entropy. We obtain:

$$E = 3N\nu k_B T, \quad C_V = \frac{\partial E}{\partial T} = 3N\nu k_B, \quad (4)$$

where  $C_V$  – heat capacity at a constant volume. Expression (4) agrees with the Dulong-Petit law, where  $C_V$  at high temperatures is equal to  $3R$ ,  $R$  – gas constant. Then in expression (4) the value  $3N\nu k_B$  can be correlated with the value  $3R = C_V$ .

On the other hand, using expression (3) and the relation  $S = -\frac{\partial F}{\partial T}$  we can write:

$$S = 3N\nu k_B \left( \ln(k_B T) - \ln\left(\frac{\hbar\omega}{e}\right) \right) = C_V \ln\left(\frac{k_B T e}{\hbar\omega}\right), \quad (5)$$

From this, we obtain the geometric mean oscillation frequency of oscillators:

$$\omega = \frac{ek_B T}{\hbar \exp\left(\frac{S}{C_V}\right)}, \quad (6)$$

Therefore, taking from the reference data [15] the heat capacity and entropy of substances at the corresponding temperature (in our case  $T = 295$  K), we can calculate the geometric mean oscillation frequency of copper atoms and ad-atom.

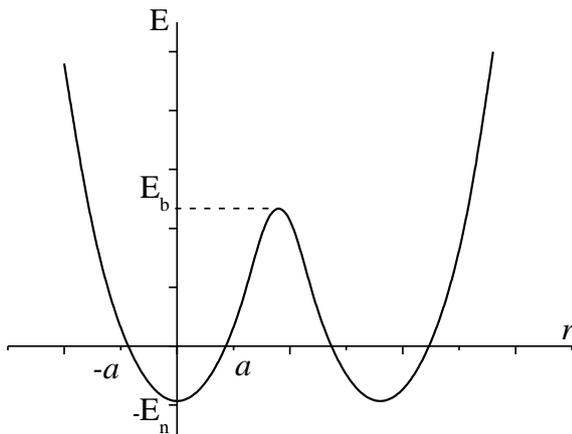
Let's represent the ad-atom and copper atoms as harmonic oscillators which perform the oscillations with the amplitude  $a$ . The amplitude of oscillations of copper atoms and ad-atom is calculated from the heat energy  $E_t$ :

$$E_t = C_V T = \frac{1}{2} m \omega^2 a^2, \quad (7)$$

where  $m$  – mass of atom.

We consider oscillations of the oscillators within the framework of quasiclassical quantum approximation in the potential parabolic wells of width  $2a$  (Fig. 2). Despite the fact that atoms are large, we'll consider the oscillations of atoms in potential wells as point ones, as presented in [16].

Energy of the oscillator in the potential well takes the form [17]:



**Fig. 2.** Parabolic potential wells with the width of  $2a$  and depth of  $E_n$  of adjacent atoms, formation of the barrier in the interaction of positive values of parabolas.

$$E_n = \hbar\omega \left( n + \frac{1}{2} \right), \quad (8)$$

where  $n$  – principal quantum number. In order to determine the stationary states of a particle in the quasiclassical case and find  $n$ , we write the Bohr quantization rule [17]:

$$\frac{1}{\hbar} \int_{-a}^a p dx = \pi \left( n + \frac{1}{2} \right), \quad (9)$$

where  $p$  – particle momentum. Since  $p = \sqrt{2mE_n} = \sqrt{2m\hbar\omega \left( n + \frac{1}{2} \right)}$ , expression (9) can be presented as:

$$\frac{1}{\hbar} \sqrt{2m\hbar\omega \left( n + \frac{1}{2} \right)} 2a = \pi \left( n + \frac{1}{2} \right), \quad (10)$$

where  $n$  – positive integers.

Therefore, calculating  $n$  from (10), we can determine the energy level of a particle in the potential well and depth of the well from (8). It should be noted that the use of quasiclassical quantum mechanical approximation in the above calculations is possible since the condition of Wentzel-Kramers-Brilluen quasiclassicality is met [17]:

$$\frac{d}{dx}(\lambda) = \frac{d}{dx} \left( \frac{\hbar}{p} \right) = -\frac{\hbar \frac{dp}{dx}}{p^2} = -\frac{\hbar m \left( -\frac{\partial E_n}{\partial x} \right)}{p^2 \sqrt{2m(E_t - E_n)}} = \frac{\hbar m F_c}{p^3} \ll 1, \quad (11)$$

where  $\lambda$  – de Broglie wavelength,  $p$  – atom momentum; size of the well is considered as  $x$ . In our case (11) will have a value of the order of  $\sim 10^{-3}$ , which is less than unity.

It is to be noted that the energy of the parabolic potential well where the structural copper atom is located has insignificant negative values equal to (8), which is generally determined by the amplitude of thermal oscillations of copper atoms in the crystal lattice. This region of the spatial oscillation of atoms is formed due to generalized distribution of valence electrons. However, significant part of energy of the potential well, in which the atoms are localized, has positive values:

$$E = \frac{m\omega^2}{2} (x - b)^2 - E_n, \quad (12)$$

where  $x$  – current coordinate,  $b$  – coordinate of the parabola center.

Adjacent parabolic potential wells of harmonic oscillators of the copper atoms of the crystal lattice form an energy barrier [18, 19] determined by the structure of adjacent parabolic wells and the distance between them. The potential barrier is directly formed outside the negative values of the well in two directions at the interaction of positive energy values of adjacent atoms of the crystal lattice (Fig. 2) [19]. Owing to interaction of the similar positive charges of copper ions, the structural stability of the crystal lattice of the substrate is built, since the atoms under the action of the field remain localized in the space of the lattice sites [20]. At the same time, the adjacent potential wells of atoms will interact in a way that the total flux of vectors of Coulomb field strength is proportional to the total ion volume charge density, i.e. the Poisson equation of electrostatic fields is fulfilled [21]. It will lead to mutual weakening of the interacting strengths of the charge fields as the boundaries of potential wells converge according to the law corresponding to the

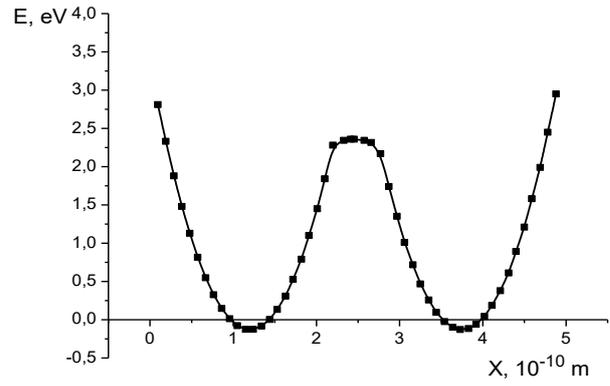
relation  $\sim \Delta E = -\frac{\alpha}{(\Delta r)^2}$ , where  $\alpha$  – energy determined by the fluctuation processes,  $\Delta r$  – distance between the boundaries of adjacent parabolic wells. We assume that  $\alpha = \frac{m\omega^2}{2}(\Delta x)^2$ , where  $\omega$  is the geometric mean oscillation frequency of the atom in the well,  $\Delta x$  is small shift of the parabola coordinate by means of fluctuations of the charges. Since  $\Delta x$  is determined by the fluctuation processes, we can use the Heisenberg uncertainty ratio for its calculation. In our case,  $\Delta x$  is  $0.055 \cdot 10^{-10}$  m on average. In order for the correction  $\Delta E$  to have the energy dimension, we shall normalize  $\Delta r^2$  to the full distance between the coordinates of the centers of parabolas  $r^2$ . Therefore, correction to the energy values of parabolas is as follows:

$$\Delta E = -\frac{m\omega^2(\Delta x)^2 r^2}{2(\Delta r)^2}. \quad (13)$$

When sufficiently small distances between coordinates of parabolic dependencies of energies are reached, their values disappear completely because of correction (13). Thus, the final energy values of potential barriers are determined taking into account the correction (13).

## II. Results and discussion

Let's consider the direction of ad-atom movement AB. We will assume that ad-atom in its initial position A has four nearest neighbors of copper atoms; at the time of jump, ad-atom has two neighbors of copper atoms. The geometric mean oscillation frequency of ad-atom, when it is placed on the substrate, will change insignificantly compared to the geometric mean frequency calculated for this atom by formula (6), since the entropy and heat capacity of the atom at a given temperature will change slightly. For ad-atom movement from the initial position A to position B, it should have additional energy, i.e. activation energy. This energy should be sufficient firstly for the exiting the potential well, the depth of which is determined by formula (8), and then for overcoming the potential barrier formed by two ions of the copper substrate at the time of the jump. After that, ad-atom again enters the potential well in position B. Using formulas (6 - 10) we calculate the geometric mean frequencies, amplitude of oscillations, quantum numbers and depth of the wells for the ad-atoms of nickel, copper, zinc, iron, and copper substrate atoms. The results are given in table 1. Next, we shall consider the barrier of two atoms of the



**Fig. 3.** Potential barrier formed by positive values of energies of two parabolic wells of copper atoms located at the distance of  $r = c/\sqrt{2}$ .

copper substrate, which are located at a distance  $r = c/\sqrt{2}$ , where  $c$  is the parameter of the crystal lattice of copper. We construct two parabolas (12) with the distance between the centers equal to  $r = c/\sqrt{2}$ , taking into account the correction (13) (Fig. 3). Fig. 3 shows that, when the parabolas converge, the energy values exceeding 2.0 eV will disappear. That is, height of the barrier taking into account the correction (13) will remain at 2.0 eV. However, ad-atom passes at the distance of  $c/2$  from the surface of crystal lattice of the substrate, whereas the value of the formed potential barrier is determined at the level of the substrate surface. Therefore, the energy of the potential barrier acting on ad-atom will be lower by the magnitude equal to the energy function determined by (12) from the coordinate  $c/2$ , taking into account the correction (13):

$$\varepsilon = \frac{m\omega^2}{2}(c/2)^2 - E_n - \Delta E, \quad (14)$$

where the correction  $\Delta E$  was calculated at the nearest point of the parabola to the vertex. Therefore, in the direction of AB, ad-atom should overcome the barrier  $E_b$  equal to 0.13 eV. The final values of the activation energy of ad-atoms  $E_a$  in the direction of AB:

$$E_a = E_n + E_b - E_t, \quad (15)$$

are presented in Table 1.

Let's consider the direction of AC of the ad-atom diffusion. As in the previous case, ad atom in position A has four nearest neighbors of copper atoms (Fig. 1) and is localized in a potential well, the depth of which is determined by (8). At the moment of jump, the ad-atom passes over the copper atom. Like the copper atom, ad-

**Table 1**  
Values of thermodynamic and oscillatory parameters of ad-atoms, calculated values of the activation energy of surface diffusion of ad-atoms in the directions of AB and AC

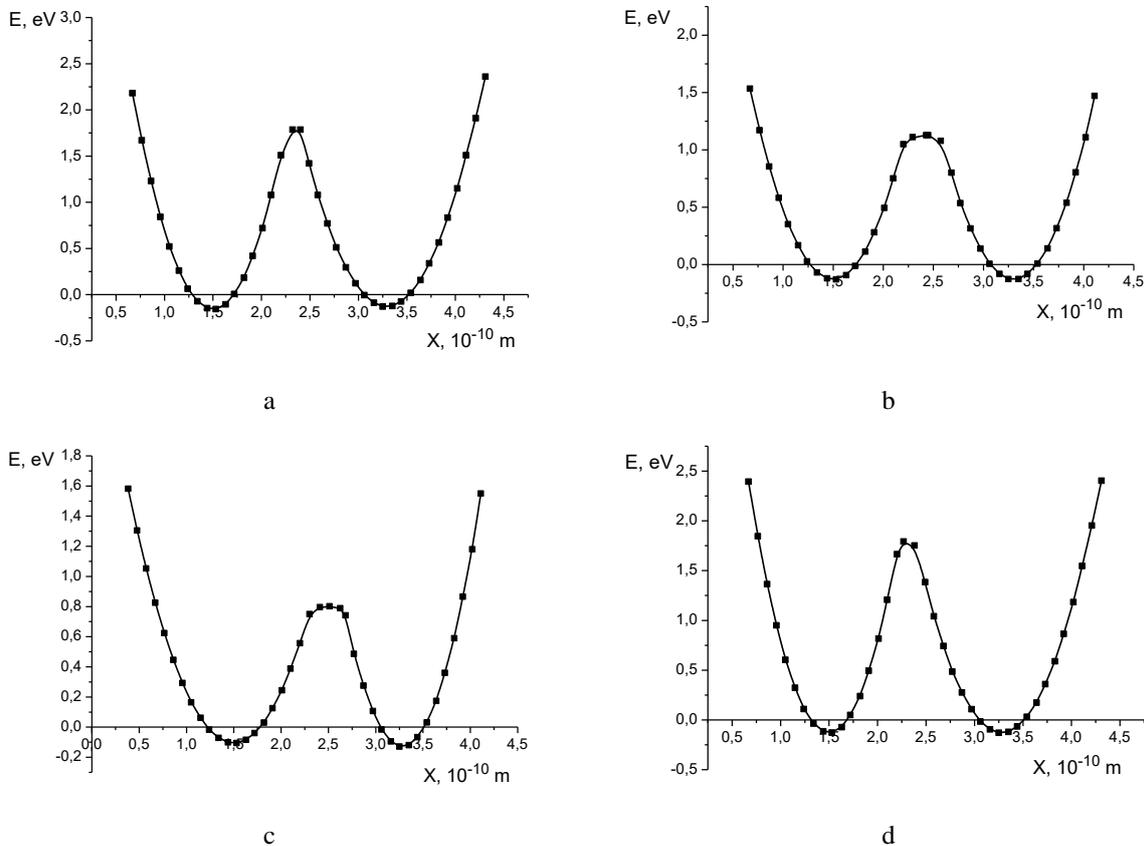
	$C_v$ , J/mol·K	$S$ , J/mol·K	$\omega$ , $10^{13}$ rad/s	$a$ , $10^{-11}$ m	$n$	$E_t$ , eV	$E_b$ , eV AC	$E_a$ , eV		$E_a$ , eV [12]	
								AB	AC	AB	AC
Zn	25.40	41.6	2.03	2.36	8	0.078	1.16	0.16	1.19	0.15	1.30
Cu	24.44	33.1	2.70	1.75	7	0.075	1.04	0.18	1.09	0.16	1.13
Ni	26.10	29.9	3.33	1.54	7	0.08	1.70	0.21	1.78	0.24	1.90
Fe	25.14	27.1	3.55	1.45	5	0.077	1.11	0.18	1.16	0.18	1.30

atom also has four neighbors (Fig. 1) and for the certain period of time, at the moment of transition, ad-atom and copper atom will be localized in the potential field formed by four copper ions. Consequently, for some time between ad-atom and a copper atom in the given field a potential barrier repelling the atoms can be created. However, action of the energy of the potential field on ad-atom will compensate for the action of the potential barrier between atoms. Therefore, for exiting the energy action of the potential field of four copper ions, ad-atom should have the energy equal to the energy of the potential barrier. In order to move from position A to position C, ad-atom should have the activation energy sufficient for exiting the potential well to A and overcoming the energy action of the field equal to the energy of potential barrier created by copper atom when interacting with ad-atom.

The depth of the potential well of ad-atoms of nickel, copper, zinc and iron in position A is calculated as in the previous case. Let's consider the potential barrier at the time of ad-atom movement over the copper atom. The distance between ad-atom and copper atom is equal to  $c/2$ . Constructed barriers taking into account the correction (13) and the distance between wells  $c/2$  are presented in Fig. 4. On the left there is a parabolic dependence of the ad-atom energy, whereas on the right the parabolic dependence of the energy corresponding to the copper atom is shown. As can be seen from Fig. 4, when the coordinates of the parabolic dependencies converge, the values of energy exceeding certain level begin to disappear. Constructed parabolic dependencies of energy

of copper atom and ad-atom are non-symmetric. As a result, the magnitude of the energy of the ad-atom repulsion from the copper atom varies depending on the position of the barrier asymmetry in relation to the ad-atom. Therefore, we assume for simplicity that the energy of the potential barrier which the ad-atom should have to overcome the action of the copper ion field changes. In case of ad-atoms of nickel and iron (Fig. 4, a, d), point of the center of the barrier is to the left by  $0.05 \cdot 10^{-10}$  m and  $0.1 \cdot 10^{-10}$  m. Therefore, the change in the value of the parabolic function (12) at these intervals was subtracted from the obtained value of energy of the barrier formed by ad-atoms of nickel and iron with copper atoms. In case of ad-atom of zinc (Fig. 4, c), point of the center of the barrier is to the right by  $0.13 \cdot 10^{-10}$  m from the point of the center of the distance between coordinates of parabolas. Thus, change in the values of the parabolic function of energy at these coordinates was added to the obtained value of energy of the barrier formed by ad-atoms of zinc and copper atom. Obtained values of energy of the barriers and activation energy of ad-atoms in the direction of AC (15) are shown in Table 1.

As shown by Table 1, obtained activation energies of surface diffusion of ad-atoms of nickel, copper, zinc and iron on the copper substrate surface in the plane (100) in the directions of AB and AC agree satisfactorily with the values given in [12]. Therefore, using the method of thermal oscillations of oscillators presented in this paper, it is possible to determine the activation energy of surface diffusion of ad-atom on the metal surface, having fcc



**Fig. 4.** Potential barriers formed by positive values of energies of two parabolic wells located at the distance of  $r = c/2$ : a – nickel and copper atoms, b – two copper atoms, c – zinc and copper atoms, d – iron and copper atoms.

lattice, along with the method of [12]. It should be noted that the main parameter, which allows making calculations by this method, is the determination of the geometric mean oscillation frequency of atoms from macro-parameters such as entropy and heat capacity. Advantage of the method described in the paper is that there is no need for the construction of complex models and calculation of energy of ad-atoms' binding with atoms of the substrate in several coordination spheres, and the method does not require machine computation.

Underlying principles of this method can also be used to calculate the activation energy of surface diffusion of ad-atoms on the surface of the metal with BCC lattice, as well as in other planes, for example (110). The basic principles of the model of thermal oscillations of oscillators are preserved when using this method to calculate the activation energy of surface diffusion around the growth step. It should also be noted that this method can be used for making calculations at other temperatures.

## Conclusions

The method for determination of the activation energy of surface diffusion based on thermal oscillations of oscillator atoms, which are localized in some space of the

lattice sites, has been developed. The main characteristic of the oscillatory motion of atoms is the geometric mean frequency determined by the approximation of the Debye model.

Considering oscillations of oscillators within the framework of quasiclassical quantum approximation in the potential parabolic wells, we determined the depth of these potential wells and height of potential barriers formed owing to the positive values of energies of two parabolic wells of adjacent oscillator atoms.

The results obtained for the activation energy of ad-atoms of nickel, copper, zinc and iron on the surface of the copper substrate agree satisfactorily with the results given in using the density functional theory. Underlying principles of presented model of thermal oscillations of oscillators can be used for the activation energy calculations in case of BCC lattice of the substrate, other diffusion planes, diffusion around the growth step and diffusion at other temperatures, which will be the subject of further research.

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## Визначення енергії активації поверхневої дифузії з позицій теплових коливань атомів

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В роботі представлено теоретичний розрахунок енергії активації поверхневої дифузії ад-атомів по поверхні підкладки як теплової енергії, визначеної методом, що оснований на теплових коливаннях атомів кристалічної решітки. Коливання атомів розглядаються з позицій квазикласичної квантової механіки як коливання гармонічних осциляторів з деякою середньгеометричною частотою та амплітудою в параболічній потенційній ямі. При цьому потенційна яма має невелику від'ємну частину, розміри якої визначає амплітуда коливань. Значну частину параболічної ями складають позитивні значення енергії. Потенційний бар'єр формується при взаємодії позитивних значень енергії параболічних ям поряд розташованих атомів кристалічної решітки. Ад-атом при перескоку у сусіднє положення на поверхні підкладки повинен мати необхідну енергію щоб вийти з потенційної ями, що має від'ємні значення енергії, та при русі подолати потенційний бар'єр, що створюють позитивні значення енергій ям сусідніх атомів. Таким чином була розрахована тепла енергія, необхідна для переміщення ад-атома, що складає енергію активації. В роботі показано, що отримані результати енергій активації поверхневої дифузії нікелю, міді, цинку та заліза по поверхні мідної підкладки задовільно співпадають з результатами, що розраховані іншим методом.

**Ключові слова:** енергія активації, ад-атом, теплові коливання атомів, середньгеометрична частота коливань, амплітуда коливань, тепла енергія, потенційна яма, потенційний бар'єр.