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Molecular dynamics simulation of hydrogen atom diffusion in crystal lattice of fcc metals

The study of diffusion of hydrogen atoms in crystal lattice of fcc metals Pd, Ni, Al, Ag was performed by the method of molecular dynamics. The diffusion characteristics of hydrogen impurity (activation energy of hydrogen atom migration and pre-exponential factor in the Arrhenius equation) in the considered metals were calculated. It is shown that the prevailing mechanism of the over-barrier hydrogen diffusion in fcc metals consists of successive migration through octahedral and tetrahedral pores. During migration, as a rule, the hydrogen atom is not delayed in tetrahedral pores.

Keywords: Molecular dynamics; Metal; Hydrogen; Diffusion; Diffusion mechanism

1. Introduction

The interaction of hydrogen with metals has been the subject of intensive study over the last century. On the one hand, this is due to the practical interest in using the metal–hydrogen system: creation of radiation-resistant materials, filters for obtaining of pure hydrogen, including for isotope separation, accumulation and storage of light gases in metals and alloys and the problem of hydrogen transportation. On the other hand, this is due to the undesirable effects of hydrogen on the properties of materials (embrittlement, corrosion, cracks spreading) [1, 2].

Hydrogen atoms have a unique small mass and size in comparison with other interstitial atoms in metals, and for this reason have extremely high diffusion mobility [3, 4]. The diffusion coefficients of hydrogen in solid metals are almost the same as in liquids. This feature, in addition to the small size and mass of the hydrogen atom, is also associated with the dissociation of a hydrogen molecule into individual atoms upon ingress into the metal [5, 6]. In metal crystals, hydrogen atoms are in interstitials and in the diffusion process they pass from one interstitial site to another. In fcc lattice, hydrogen can occupy two types of interstitial sites: octahedral and tetrahedral. At the present time, the question of the mechanism of hydrogen diffusion in the crystal lattice of metals remains. Even in a pure crystal, transitions between interstitials of different types are possible, which entails, in particular, the ambiguity of the activation energy of hydrogen diffusion. In addition, as noted in [7], the redistribution of hydrogen atoms in interstitial sites of various types due to changes in external conditions, for

example, deformation, can lead to a change in the diffusion parameters. It should be noted that other factors may also lead to deviations from the Arrhenius law, in particular, the possibility of diffusion jumps of different lengths and the effect of crystal lattice defects [1, 5].

The aim of the present work is to study the mechanism of hydrogen atom diffusion in the crystal lattice of fcc metals using the molecular dynamics method and to calculate the diffusion parameters: the activation energy and the pre-exponential factor in the corresponding Arrhenius equation. Typical fcc metals with different sorption capacity with respect to hydrogen were chosen for consideration: Pd (exceptionally high), Ni (medium), Ag and Al (weak).

Solving these problems with the help of real experiments is currently very difficult, taking into account the high mobility of hydrogen atoms in metals. In this case, the most effective is the application of the method of computer simulation, which allows with sufficient accuracy within the model to consider and control the parameters of a phenomenon under study, to investigate in the dynamics processes occurring at the atomic level using various demonstrative structure visualizers. The method of molecular dynamics, in comparison with other methods of computer simulation, is more suitable for studying the processes associated with the dynamics of the atomic structure, in particular, for modeling diffusion processes.

It is well known that the distinguishing features of hydrogen diffusion in metals, compared to other heavier interstitial atoms, in addition to exceptionally low activation energy, is the quantum nature of diffusion at low temperatures which is manifested in pure crystals up to room temperature [2, 5, 8]. For instance, at superlow temperatures a predominantly quantum diffusion mechanism is possible, which consists of under-barrier quantum tunneling of hydrogen atoms between the neighboring interstitial sites. With increased temperature and imperfections of the crystal lattice, the contribution from the under-barrier diffusion is sharply decreased and the classical over-barrier mechanisms are predominantly realized. At temperatures above the room temperature, hydrogen diffusion occurs via over-barrier mechanisms [2, 5, 8]. This allows us to investigate diffusion of light interstitial atoms by classical molecular dynamics at comparatively high temperatures.

2. Description of the model

Interactions between metal atoms were described by the many-body Cleri–Rosato potentials [9], built within the

tight-binding model. Potential energy of the i -th atom in this case is found using the following expressions:

$$U_i = \sum_j A \exp\left(-p\left(\frac{r_{ij}}{r_0} - 1\right)\right) - \sqrt{\sum_j \xi^2 \exp\left(-2q\left(\frac{r_{ij}}{r_0} - 1\right)\right)} \quad (1)$$

Here A , p , q , ξ , r_0 are the potential parameters and r_{ij} is the distance between the i -th and the j -th atoms. Parameters of the Cleri–Rosato potentials were taken from [9]. The using of this potential has proven efficient in a number of calculations performed by the method of molecular dynamics [10–12].

The Morse pair potentials were used to describe the interactions of hydrogen atoms with each other and with metal atoms:

$$\varphi(r_{ij}) = D\beta e^{-\alpha r_{ij}}(\beta e^{-\alpha r_{ij}} - 2) \quad (2)$$

Here α , β , D are the potential parameters, r_{ij} is the distance between the i -th and the j -th atoms. The Morse pair potentials are used relatively often by various researchers to describe interatomic interactions in metal–hydrogen systems. To model the interaction of hydrogen atoms with each other and with metal atoms in Pd–H, Ag–H, Al–H systems, the Morse potentials were taken from [13] and [14]. When testing these potentials, it was found that they do not satisfactorily describe certain characteristics of hydrogen in the considered metals (for example, the binding energy with defects). Therefore, in addition to them, we have previously developed our own interatomic potentials for Pd–H and Ni–H systems [15]. The choice of Pd and Ni is due to increased attention to these fcc metals and a relatively large amount of experimental data available for them. When determining the parameters of the H–H potential, the potentials and results of first-principles calculations of other authors were taken into account. The potentials of Pd–H and Ni–H interactions were constructed in such a way that they could simultaneously describe well the experimentally obtained values of the energy of absorption, the activation energy of the over-barrier diffusion of hydrogen in the metal and the binding energy with point defects.

The number of atoms in the simulated calculation blocks in the present work was about 25 000. The conditions at the block boundaries were periodic. The time step of integration of atomic motion in the method of molecular dynamics was equal to 0.5 fs. The temperature of the calculation blocks was set via the initial atomic velocities in accordance with the Maxwell–Boltzmann distribution (wherein the total momentum and the angular momentum of atoms in the calculation block were equal to zero).

The activation energy of point defect migration in the molecular dynamics model can be found by static and dynamic methods [10]. By the static method, with knowledge of the trajectory of the defect migration, the magnitude of the energy barrier on the migration path is determined. The dynamic method consists of finding the temperature dependence of the diffusion coefficient $D(T)$ at the introduction into the computational block of a certain number

of defects of the considered type (in this case, hydrogen atoms) during a sufficiently long molecular-dynamic experiment. The migration energy of the hydrogen atom E_m can be found with help of the dependence $\ln D(T^{-1})$ by the slope of the straight line to the abscissa axis α :

$$E_m = -k \tan \alpha = -k \frac{\partial \ln D}{\partial (T^{-1})} \quad (3)$$

where k – Boltzmann constant. The dynamic method is more complicated than the static method, but it has several advantages [10, 16]. First of all, the dynamic method allows us to find the effective value of the activation energy in the case of the possible presence of several variants of elementary diffusion mechanisms, whereas the static method makes it possible to determine the probability of implementing different mechanisms only indirectly. The dynamic method also allows determining the pre-exponential factor in the Arrhenius equation. It is proportional to the defect concentration as follows [10]:

$$D_0 = \frac{c}{c'} D'_0 = \frac{Nc}{n} D'_0 \quad (4)$$

Here c is the defect concentration, for which we calculate the pre-exponential factor; c' is the concentration of the defects in the calculation block during the computer experiment ($c' = n/N$, where n is a number of the introduced defects, N is a number of atoms in the calculation block); D'_0 is the pre-exponential factor obtained in the computer experiment from the dependence $D'(T)$ in the case of introduction of n defects (is found on the intersection of the curve $\ln D(T^{-1})$ with the ordinate axis).

The activation energy of the over-barrier diffusion of hydrogen was calculated in the work by both methods. When determining the diffusion coefficient, computer experiments had a duration of at least 200 ps. The diffusion coefficient was calculated as follows:

$$D = \frac{1}{6tN} \sum_{i=1}^N \left[(x_{0i} - x_i)^2 + (y_{0i} - y_i)^2 + (z_{0i} - z_i)^2 \right] \quad (5)$$

where x_{0i} , y_{0i} , z_{0i} are the coordinates of the initial position of a hydrogen atom and x_i , y_i , z_i are its positions in the point of time t . In order to rule out atomic displacements while calculating the diffusion coefficient via Eq. (5), the computational block in the end of the computer experiment was cooled down to the temperature close to 0 K.

3. Results and discussion

It is well known that a hydrogen atom in metals is positioned in the interstitial sites and during diffusion moves from one interstitial into the other. In the fcc lattice, according to numerous data, hydrogen is predominantly located in the octahedral pores [1–3, 5, 8].

Shown in Fig. 1 are possible migration trajectories of a hydrogen atom from one interstitial into the other. When moving between the octahedral pores along a straight-line path (trajectory 1), as is evident in Fig. 1, it bumps into a relatively high energy barrier – in the point on the trajectory

between two metal atoms along $\langle 110 \rangle$. Trajectory 2 – migration of a hydrogen atom through the center of a triangle formed by three metal atoms in the (111) type plane. In this case the path is longer than in the first case, hydrogen would migrate from one octahedral pore into the other across a tetrahedral pore. As can be seen in Fig. 1, there are two energy barriers on trajectory 2, but apparently smaller than in the first case.

Mechanism 1 seems less possible than mechanism 2 due to the lower height and relative closeness of the energy barrier corresponding to trajectory 2. However it should be taken into account that, firstly, the equilibrium distance between the metal and hydrogen atoms is much less than that between metal atoms (about one and a half times [15]). Secondly, as a result of the thermal oscillations of atoms, the barrier ratio can vary, due to which the probability of realization of the mechanism 1 is nonzero.

To determine the leading mechanism for the hopping of a hydrogen atom between two octahedral pores, the activation energy of the hopping was found using static and dynamic methods. The static method was used to calculate the activation energies separately for all the mechanisms under consideration. The dynamic method, as mentioned earlier, allows us to obtain the effective value of the activation energy (i.e. the average value taking into account the probability of realizing of all possible mechanisms). Comparing the effective value of the activation energy with the values obtained by the static method, we can judge the predominance of one or another diffusion mechanism.

The values of the activation energy for trajectories 1 and 2, found by the static method, are given in Table 1. Trajectory 2 was divided into two stages: hydrogen migration from an octahedral pore to a tetrahedral one, and from a tetrahedral into an octahedral pore. The activation energy was

calculated as the difference between the energies of the computational block containing a hydrogen atom occupying the initial position (in one of the pores) and in the position of saddle point (between the atoms along $\langle 110 \rangle$ or in the center of the triangle in the (111) plane). In all these cases, before calculating the energy of the calculation block, a dynamic relaxation of the structure with following cooling to 0 K was held.

It is evident from Table 1 that the tetrahedral-to-octahedral pore transition requires almost no energy. Overall, the activation energy for the transition of hydrogen along trajectory 2 is lower than that along trajectory 1. We might assume that in the metals under study hydrogen is predominantly diffused following trajectory 2, in other words, it consecutively crosses octahedral and tetrahedral pores.

When calculating the hydrogen migration energy using the dynamic method, we introduced several hydrogen atoms into the computational block. The hydrogen diffusion coefficient in the crystal lattice of a metal was obtained for different values of the temperature of the computational block. Shown in Fig. 2 are the curves $\ln D(T^{-1})$ obtained in the work for considered systems Pd–H, Ni–H, Ag–H, Al–H. Table 2 lists the values of activation energy and pre-exponential factors estimated using these curves, and also, for comparison, data from the experimental works [5, 17–24].

Hydrogen concentration in metals can naturally be different. In order to allow a comparison of our data with those of the experimental studies, hydrogen concentration used to

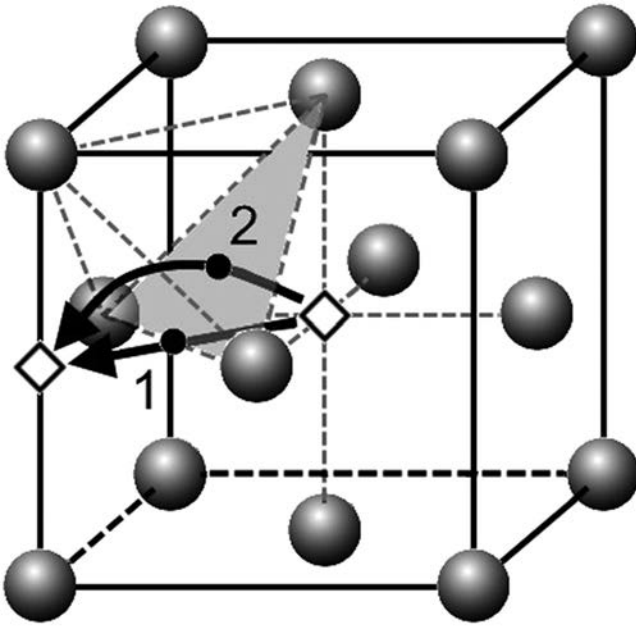


Fig. 1. Two possible trajectories of migration of a hydrogen atom from one octahedral pore into the adjacent pore: in a straight line along $\langle 110 \rangle$ (1) and across a tetrahedral pore (2). Position of the octahedral pores is indicated by rhombus. Dots on the trajectories are the positions of the hydrogen atom where it possesses the maximum potential energy in the course of migration.

Table 1. Hydrogen migration energies in Ag, Al, Pd, Ni along the different trajectories calculated by the static method (eV).

Metal	oct. $\rightarrow$ oct.	oct. $\rightarrow$ tet.	tet. $\rightarrow$ oct.
Ag	0.09	0.05	0
Al	0.16	0.12	0.02
Pd	0.29	0.18	0.01
Pd*	0.36	0.24	0
Ni*	0.52	0.37	0.01

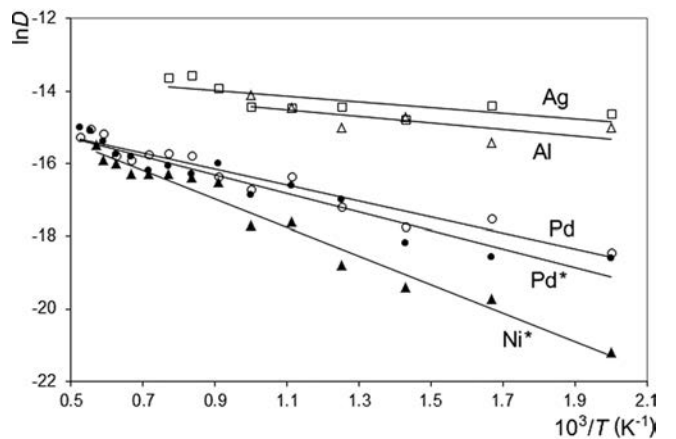


Fig. 2. Dependences of $\ln D$ on T^{-1} obtained by simulation of hydrogen diffusion in metals Pd, Ni, Ag, Al. The asterisk denotes metals for which our potentials from [15] were used.

Table 2. The migration energy and the pre-exponential factor for hydrogen diffusion in the considered metals obtained using the dynamic method (the asterisk denotes metals for which our potentials from [15] were used).

Metals	Model results		Data from other works	
	E_H^m (eV)	$D_0 \cdot 10^{-7}$ (m ² s ⁻¹)	E_H^m (eV)	$D_0 \cdot 10^{-7}$ (m ² s ⁻¹)
Ag	0.06	4.1	0.08 [22]	2–8 [22]
Al	0.08	8.1	0.07–0.13 [23, 24]	5–12 [17, 22]
Pd	0.19	4.6	0.22–0.25 [5, 17–19]	2–8 [5, 17–19]
Pd*	0.23	9.2		
Ni*	0.34	15.1	0.33–0.42 [19–21]	5–9 [19–21]

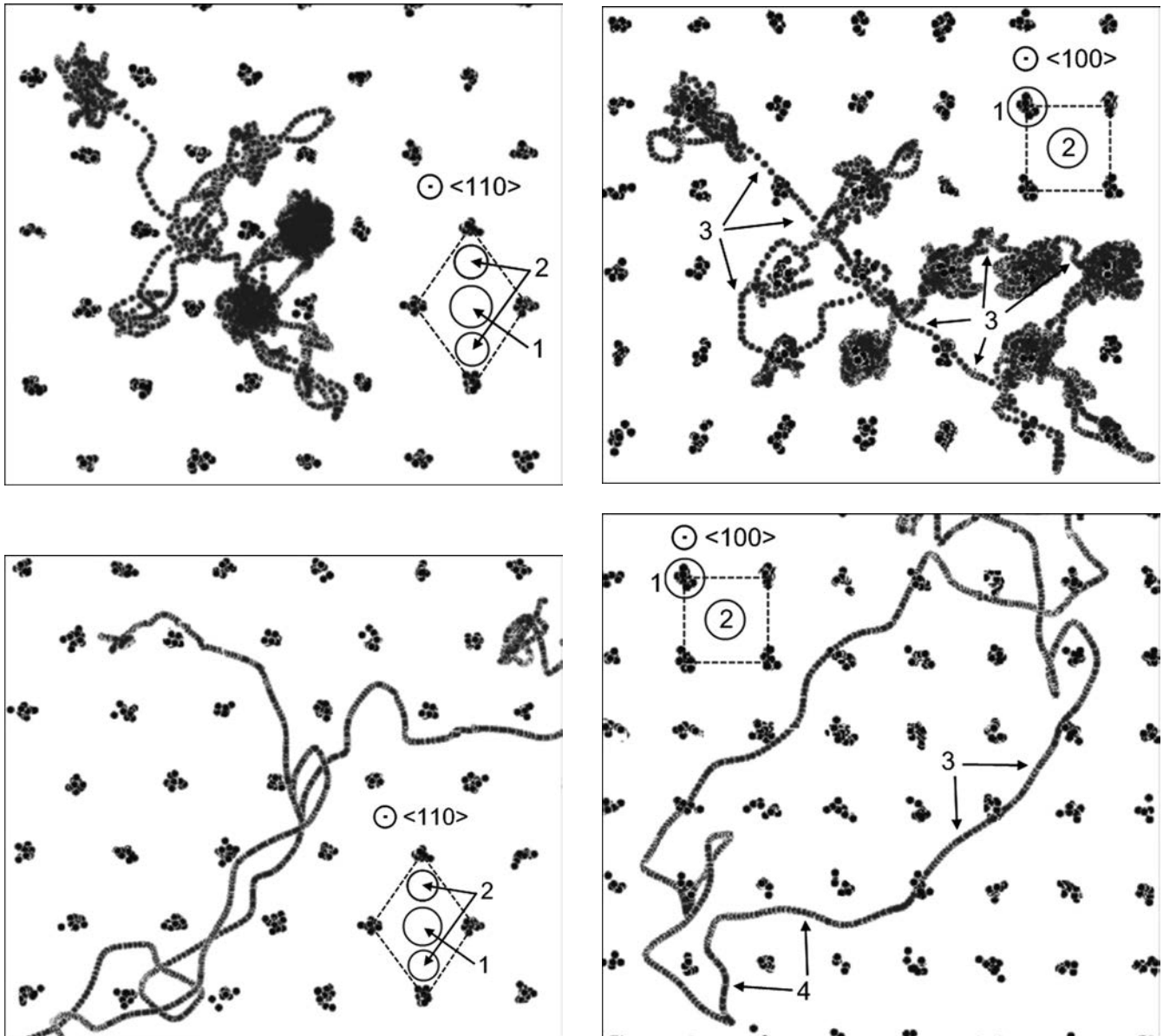


Fig. 3. Trajectories of the hydrogen atom migration in Pd (a, b) and Ag (c, d) projected onto the (110) (a, c) and (100) (b, d) planes. 1 – positions of octahedral pores; 2 – positions of tetrahedral pores; 3 – hydrogen migration with alternating crossing of the octahedral and tetrahedral pores; 4 – hydrogen migration only through tetrahedral pores. The trajectories were obtained at the temperature 350 K.

calculate pre-exponential factors by Eq. (4) was taken from works with which the comparison was made: for Pd – 0.5 % [5, 17–19], for Ni – 0.5 % [19–21], for Ag – 0.07 % [22], for Al – 0.6 % [23, 24].

As can be seen from the table, the values of the activation energy and the pre-exponential factor of the over-barrier diffusion of hydrogen in Pd, Ag, Al, Ni obtained in the present work are consistent with the experimental data. It is also seen from the table that the activation energies obtained by the dynamic method (i.e. from the $\ln D(T^{-1})$ dependencies) are less than the activation energies of the hydrogen migration along trajectory 1 calculated by the static method (Table 1). At the same time, the obtained values are close or equal to the sum of the energies of the hydrogen transition from an octahedral pore to a tetrahedral one and then from the tetrahedral pore to the other octahedral pore (trajectory 2). On the basis of this, it can be asserted that the second mechanism is basically realized in the fcc metals, i.e. a hydrogen atom consecutive crosses octahedral and tetrahedral pores.

In order to determine the leading mechanism of hydrogen diffusion in the metals under study, the visualizer of trajectory of hydrogen atom migration was used. The most informative are projections of the hydrogen atom trajectory onto the (110) and (100) planes: in this case hydrogen positions in octahedral and tetrahedral pores are readily distinguishable. Figure 3 illustrates hydrogen migration trajectories in Pd (Fig. 3a and b) and Ag (Fig. 3c and d). Hydrogen solubility in Pd and Ag is very different: Pd is a good absorber of hydrogen, while Ag absorbs it poorly. This difference is quite evident in the reported trajectories of hydrogen migration: in Pd it is often retained in octahedral pores. In Fig. 3a and b this is readily seen from the typical “bundles” in the trajectories in the octahedral pore positions.

The main mechanism of hydrogen diffusion in Pd consists of consecutive crossing of octahedral and tetrahedral pores (i.e., trajectory 2 in Fig. 1) with the hydrogen being generally delayed in octahedral rather than tetrahedral pores. As the temperature is increased, the delays of hydrogen in octahedral pores were increasingly less frequent and more rectilinear sections of its trajectory were observed.

The energy of hydrogen absorption for Ag is much higher than for Pd (0.7 eV and –0.1 eV respectively [1, 25, 26]). Moreover, the difference in the absorption energies in Ag in the octahedral and tetrahedral pores is small (0.06 eV), whereas in Pd this difference is 0.16 eV [25, 26]. In this connection the hydrogen trajectories in Ag (Fig. 3c and d) suffer fewer delays in octahedral pores, and have parts evidencing of hydrogen migration only through the tetrahedral pores without crossing the octahedral ones.

4. Conclusion

The primary mechanism of over-barrier hydrogen diffusion in fcc metals, according the results obtained by the method of molecular dynamics, consists of a consecutive crossing of octahedral and tetrahedral pores. It has been noted that the higher the temperature, the more seldom hydrogen delays in octahedral pores during its migration, whilst in tetrahedral pores it nearly never delays. In the metals where hydrogen energies in octahedral and tetrahedral pores differ only slightly (e.g., Ag), in addition to the above mechanism

hydrogen migration can occur via tetrahedral pores without crossing the octahedral ones: the activation energy of this mechanism is lower than in the case of consecutive crossing of both pore types.

Using the method of molecular dynamics, in this work we have obtained the values of activation energy and pre-exponential factor of over-barrier hydrogen diffusion in metals Pd, Ni, Ag, Al. The results are well consistent with the data obtained in the experimental studies.

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