

ENERGETICS OF THE ADSORPTION AND DIFFUSION OF HYDROGEN MOLECULES IN A (001) PLATE OF NANOCRYSTALLINE ALUMINUM

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The energetics of the adsorption and diffusion of hydrogen molecules in the surface of an Al plate bounded by the (001) atomic plane has been investigated by the density-functional method. The spatial configuration of hydrogen atoms and surface layers of the plate corresponding to the most stable structures was determined. It has been established that the energies of the physical and chemical adsorptions of hydrogen are equal to -0.049 eV and -0.080 eV respectively. It is shown that, as a result of the chemisorption, two stable spatial configurations with energies differing by 0.33 eV are formed. A bridge arrangement of hydrogen atoms between the apical atoms of aluminum is characterized by a minimum energy. The energy barrier of transformation of a hydrogen molecule from the physical into the chemisorbed state comprises 0.438 eV. An H_2 molecule does not dissociate completely in the process of adsorption and diffusion. On the surface and in the bulk of the metal being considered there arise diagonal-chain structures, in which the distance between the hydrogen atoms does not exceed 2.86 Å.

Introduction. Materials capable of adsorbing hydrogen reversibly are of interest for designing systems for its storage. It is known that a number of hydrides based on alkaline, alkaline-earth, and transition metals and intermetallic compounds [1–4] can be used for this purpose. It was shown in [5–7] that aluminum and its binary compounds with alkali metals are among the most effective adsorbents of hydrogen. These materials are of practical interest because they have a high adsorbability, reaching 10 wt. %, and a relatively low desorption temperature.

The main method of obtaining aluminum hydrides is the chemical synthesis of them in the reaction of lithium aluminum hydride with aluminum chloride in a diethyl-ether medium [8, 9]. As a result of this reaction, at least seven known polymorphic aluminum-chloride modifications of different stability are formed [5]. Another popular method of production of aluminum hydrides is the treatment of the surface of an aluminum plate by molecular beams of hydrogen ions, having different energies [10, 11]. Depending on the method used, different hydride structures are formed. Every so often, contradictory results were obtained when these structures were analyzed and, on the basis of these results, contradictory conclusions on the mechanisms of interaction of hydrogen with the metal were made.

It is difficult to investigate the adsorption and diffusion of hydrogen experimentally because hydrogen molecules have small sizes and high mobility. Because of this, experimental investigations of the indicated processes are complex and laborious and their results are insufficiently reliable. Therefore, it is best to study the processes being considered by theoretical methods that, due to the development of density-functional theory [12] and computer simulation [13], open up wide possibilities for investigating the energetics of the adsorption interaction and the structure of the surface compounds [14].

The aim of the present work is to investigate, "from the first principles," the energetics of the adsorption and diffusion of hydrogen molecules in the surface and bulk of an atomic-thin crystalline- aluminum plate bounded by the (001) plate and to determine the geometrical configurations of stable surface structures of nonstoichiometric aluminum hydrides.

Computational Procedure. The adsorption and diffusion of a hydrogen molecule in a thin atomic plate bounded by the (001) plate was simulated and the optimum geometric parameters of the system were determined with

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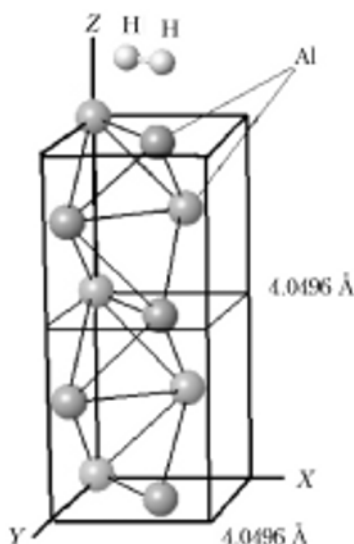


Fig. 1. Periodic cell for simulation of the interaction of a hydrogen molecule with a five-layer Al plate bounded by the (001) plane.

the use of the ABINIT (v.4.2.3) package [15] allowing one to calculate the complete energy, geometrical configuration, and electron structure of molecular-crystalline systems. The software used was developed on the basis of the density-functional theory and the pseudopotential theory and, therefore, makes it possible to determine the energy of the main state of an atomic-molecular system by optimization of the spatial arrangement of atoms.

The plate being considered was simulated by a periodic atomic cell consisting of five atomic layers containing two atoms each. This cell is shown in Fig. 1. The dimensions of the periodic cell in the (001) plane corresponded to the experimental parameters of the aluminum structure: $4.0496 \times 4.0496 \text{ \AA}$ ($7.6526 \times 7.6526 \text{ bohr}$). The height of the cell was 24.2988 \AA (45.918 bohr). The vacuum region, where the hydrogen molecule was initially located, comprised 16.2 \AA (30.612 bohr). The surface density of hydrogen molecules in the indicated cell was $1.01 \cdot 10^{-5} \text{ mole/m}^2$, which corresponded to the coating of approximately 0.4 parts of a monolayer.

The complete energy of the system was calculated in the local-density (LD) approximation with the correlation exchange energy formalized in [16]. The interaction of electrons with the atomic core was calculated using the Troullier–Martins pseudopotentials [17]. An analysis of the correspondence of the total energy of the system to its geometry has shown that the calculation of aluminum nanoplates in the LD approximation gives a crystal-lattice parameter close to the experimental one.

The size of the basis of plane waves (BPW), determining the simulation efficiency and accuracy, was calculated in advance. Calculation of the dependence of the total energy of the system on the kinetic energy of electrons, varied within 10–30 hartree (5500–21,100 plane waves), has shown that the geometry and energy of the system relative to the basis of 30 hartree are adequately determined in the BPW of 15 hartree. In this case, the length of a bond is estimated with an accuracy of 0.5–1.0%. Since the length of a bond, given by the LD approximation, is smaller by approximately 2–3% than the experimental value of this quantity, it may be concluded that the calculation parameters selected correspond to the desired accuracy of simulation. The criterion restricting the cycles of the self-coordinated calculations was the maximum force acting on the relaxing atoms; this force was taken to be equal to $1 \cdot 10^{-3} \text{ hartree/bohr}$ ($1 \text{ hartree} = 27.211 \text{ eV}$, $1 \text{ bohr} = 0.529177 \text{ \AA}$).

The geometry of the system was optimized with the use of the algorithm proposed in [18]. The calculations were carried out for the case of relaxation of the coordinates of the hydrogen atoms and two atomic layers of the Al plate and the complete relaxation of the degrees of freedom of the whole system. Comparison of the calculation data on the partially and completely relaxing systems allowed us to estimate the long-range interactions arising in the process of hydrogen adsorption and diffusion.

The plane waves in the surface Brillouin zone were integrated by the method of special points [19] with account for the temperature dependence of the electron population determined by the "cold spreading" scheme [20]; in

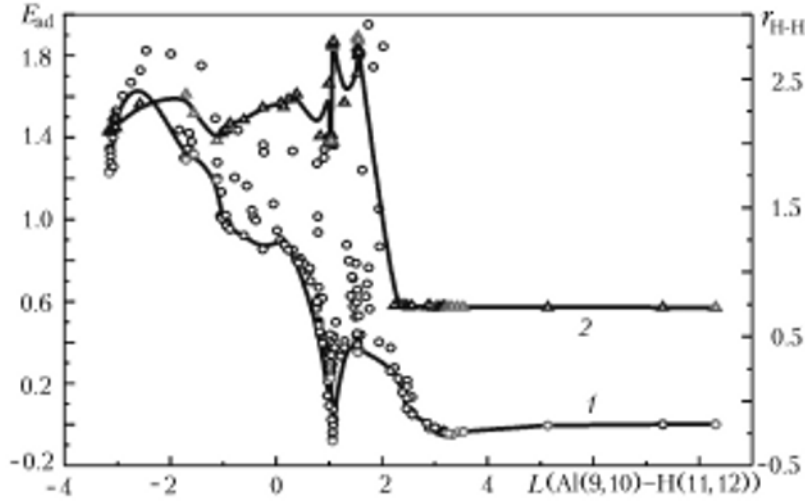


Fig. 2. Dependence of the energy of the 10Al-2H system (1) and the bond distance in the hydrogen molecule (2) on the distance between the molecule and the surface of the plate.

this case, the BPW broadening was taken to be 0.025 hartree. To increase the calculation efficiency, we investigated the convergence of the total energy of the system relative to a number of k-points. As a result, for integration of the Brillouin zone, four k-points were selected: $(1/8, 1/8, 0)$, $(3/8, 3/8, 0)$, $(-3/8, 1/8, 0)$, $(-1/8, 3/8, 0)$. The values of the complete energy of the system, calculated at 4 k-points, differed from the analogous values calculated at 36 k-points by 0.0001 hartree.

The adsorption of hydrogen in the Al plate was simulated by calculating different geometric configurations of the system arising as a hydrogen molecule sequentially approaches the surface of the plate. The minimum energy of the system was determined in the space region of size $\sim 0.02 \text{ \AA}^3$. Initially the H_2 molecule was oriented parallel to the surface of the plate. To improve the convergence of the complete energy of the system, in investigating the interaction of this molecule with the surface of the plate at a distance of 1.0–2.5 Å from it, an overstated value of the bond distance in the H_2 molecule (0.76 Å) was used; the experimental value of this distance is 0.741 Å.

The adsorption and diffusion energies of the molecular and atomic hydrogen were calculated by the formulas

$$E_{\text{ad}} = E(10\text{Al} + 2\text{H})_L - E(10\text{Al} + \text{H}_2)_{\text{inf}}, \quad (1)$$

$$E_{\text{d}} = E(10\text{Al} + 2\text{H})_L - E_{\text{ch}}(10\text{Al} + 2\text{H}). \quad (2)$$

Discussion of Results. Figure 2 presents the dependences of the energy of the system $\text{H}_2\text{-Al}$ and the length of the H–H bond in a hydrogen molecule on the distance of the center of mass of this molecule from the surface atoms of the Al plate. The calculated dependences show that both the energy of the system and the bond distance in the hydrogen molecule change nonmonotonically. When the H_2 molecule is displaced at a distance larger than 5–6 Å from the surface, the energy of the system does not change, i.e., the molecule does not interact with the surface of the plate. The length of the H–H bond in the hydrogen molecule far removed from the surface, calculated in the LD approximation, is equal to 0.727 Å; this length does not change when the surface is approached as long as the distance between it and the molecule becomes equal to 2.5 Å. The energy of the system decreases insignificantly when the distance between the H_2 molecule and the surface of the Al plate increases to 3.0–3.4 Å. Since the bond distance in the molecule remains unchanged, the decrease in the energy of the system to -0.0496 eV corresponds to the physical adsorption of hydrogen in the surface of the (001) aluminum plate. When the hydrogen molecule further approaches the surface of the Al plate, the energy of the system increases gradually and the interatomic distance in the H_2 molecule increases abruptly to 2.81 Å. The distance between the hydrogen atoms is practically equal to the length of the bond (2.86 Å) between the surface aluminum atoms located in the (001) plane.

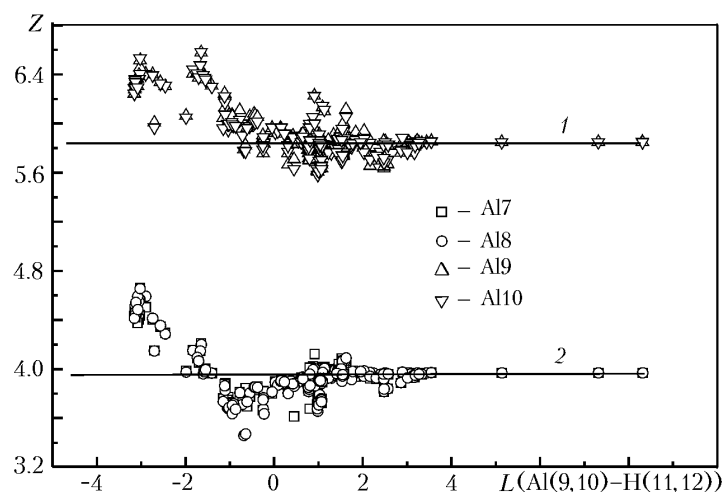


Fig. 3. Dependence of the Z coordinates of the atoms of the surface (1) and subsurface (2) mobile layers of the plate on the distance between the hydrogen molecule and the surface of the plate.

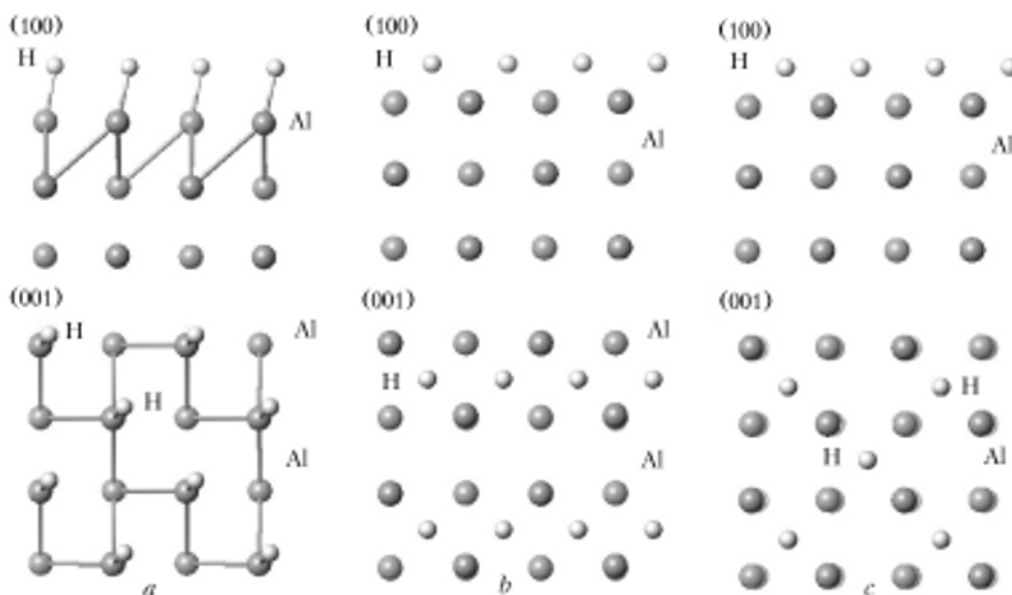


Fig. 4. Structure of the surface hydrides in the transition state (a) and in the process of chemisorption (b, c): a) H atoms are positioned above the surface atoms of aluminum; $L = 1.563 \text{ \AA}$, $E_{\text{ad}} = 0.355 \text{ eV}$, $r_{\text{H-H}} = 2.798 \text{ \AA}$; b) and c) two types of bridge structures of H atoms on the surface of the aluminum plate; $L = 1.067 \text{ \AA}$, $E_{\text{ch}} = -0.0806 \text{ eV}$, $r_{\text{H-H}} = 2.746 \text{ \AA}$ and $L = 1.043 \text{ \AA}$, $E_{\text{ch}} = -0.228 \text{ eV}$, $r_{\text{H-H}} = 2.016 \text{ \AA}$ respectively. The atomic plane of the cross section of the plate is indicated above each fragment of the figure.

At a distance of 2–3 \AA , the energy of the system increases to 0.3 eV with no marked change in the bond distance in the H_2 molecule, which, evidently, is due to the change in the positions of the Al atoms or the deformation of the surface layers of the plate. Figure 3 shows the dependence of the Z coordinates of the atoms of the upper layers of the plate on the distance between it and the H_2 molecule. It follows from this figure that, when this molecule is at a distance smaller than 3 \AA from the plate, it causes the Z coordinates of the Al atoms to shift by 0.25 and 0.1 \AA in the bulk of the plate, i.e., a compression of the surface and subsurface atomic layers. Thus, the hydrogen mole-

TABLE 1. Z Coordinates of the Two Upper Layers of an Al Plate and of the Atoms of an H₂ Molecule (Å) Found at Different Distances from the Surface of the Plate (different adsorption states)

Atom	$L, \text{Å}$			
	1.04	1.06	1.54	3.05
Al 7	3.9073	3.7248	3.9517	3.9678
Al 8	3.8973	3.731	3.9538	3.9679
Al 9	5.8155	5.6372	5.7516	5.8485
Al 10	5.8293	5.6278	5.7481	5.8485
H 11	6.8628	6.7002	7.2944	8.8765
H 12	6.8582	6.6989	7.2971	8.8999

cule, coming out from the space region corresponding to the physical adsorption, causes a deformation of the plate and an increase in the energy of the system.

When the physical adsorption is transformed into the chemical one, an equilibrium apical structure is formed at a distance of 1.54 Å from the plate (Fig. 4a). Since the energy of the transition state substantially exceeded the energy of the physical and dissociative adsorption, the apical structure should be unstable. As the optimization of the structure in the transition state has shown, the shift of the atoms and, accordingly, the deformation of the surface layer of the plate are very small in this case.

The character of change in the energy of the system in the case where the hydrogen molecule approaches the plate at distances smaller than 1.5 Å points to the fact that, in this case, the H₂ molecule is transformed into the chemisorbed state with a substantial increase in the bond distance. Calculations of different geometrical configurations have shown that two types of structures stable in energy are formed on the surface of the plate as a result of the dissociation adsorption. The lowest-energy state with an energy of -0.0805 eV is formed at a distance $L = 1.067 \text{ Å}$. The second chemisorption state, having a much higher energy (0.228 eV), is formed at a distance of 1.038 Å from the surface. In these states, the interatomic distance H-H comprises 2.747 and 2.016 Å respectively.

Analysis of the geometry of the system in the chemisorption state shows that its energy decreases to a minimum as a result of the formation of a bridge arrangement of hydrogen atoms between the apical atoms of aluminum (Fig. 4) leading to a compression deformation of the surface layers of the plate. Two types of bridge structures can be formed in the process of chemisorption; they have different energies and, in them, atoms are arranged differently in the {001} plane of a space cell. In one of these structures, characterized by the lowest energy, H atoms are arranged along the diagonal of the cell (Fig. 4b), and, in the other structure (Fig. 4c), H atoms form a linear chain along the {001} direction. The distance between the nearest aluminum and hydrogen atoms in the diagonal structure is equal to 1.78–1.79 Å, which points to the formation of the linear surface complexes (AlH)_n. In the chain structure, the length of the Al-H bond ranges from 1.74 to 1.75 Å, and the distance between the hydrogen atoms comprises 2.01–2.03 Å, which is explained by the incomplete dissociation of the hydrogen molecule and the formation of the zigzag-like surface complexes (AlH-HAl).

Analysis of the changes in the Z coordinates of the H atoms in the process of the physical and chemical adsorption (Table 1) shows that the surface layer of the plate is deformed most significantly ($\epsilon \approx 4\%$) in the case of formation of a bridge configuration, where the H atoms are positioned practically at the center of the diagonal connecting the surface atoms of aluminum. The minimum deformation of the surface layer $\epsilon \approx 0.34\%$ corresponds to the chemisorption of the H atoms forming a chain structure in the {100} and {010} directions. When a transition complex with an apical structure, in which the length of the Al-H bond is 1.598 Å, is formed, the compression deformation of the surface layer of the plate comprises $\epsilon \approx 1.7\%$.

The calculation data obtained point to the fact that the diffusion of hydrogen atoms is an endothermic process. The energy of the system increases rapidly to 0.9 eV when the hydrogen atoms intersect the boundary of the surface and reaches 1.3 eV when they pass through the surface layer. The diffusion of H atoms in the bulk of the plate leads to the formation of energy-stable zigzag-like chain structures between the surface and subsurface atomic layers (Fig. 5). The chain structure, characterized by the lowest energy $E_{\text{ad}} = 1.19 \text{ eV}$, includes H-H bonds of length 2.021 and 2.065 Å that (Fig. 5a) are almost equal to half the face-centered lattice parameter (4.0496 Å) of aluminum. Each H atom is bonded to the nearest aluminum atom such that it is positioned at the center of the distorted tetrahedron formed by

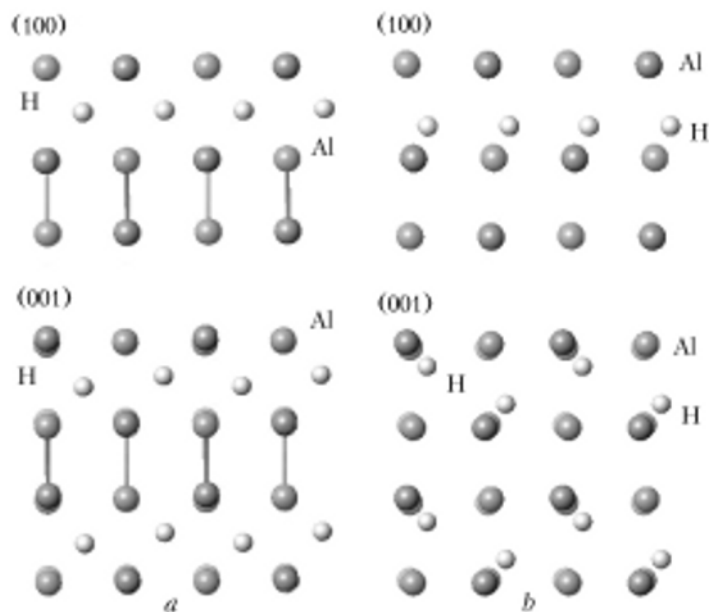


Fig. 5. Arrangement of hydrogen atoms in the process of hydrogen diffusion through the surface layer of the aluminum plate: a) $L = -1.11 \text{ \AA}$, $E_d = 1.192 \text{ eV}$, $r_{\text{H-H}} = 2.021 \text{ \AA}$; b) $L = -1.55 \text{ \AA}$, $E_d = 1.318 \text{ eV}$, $r_{\text{H-H}} = 2.232 \text{ \AA}$.

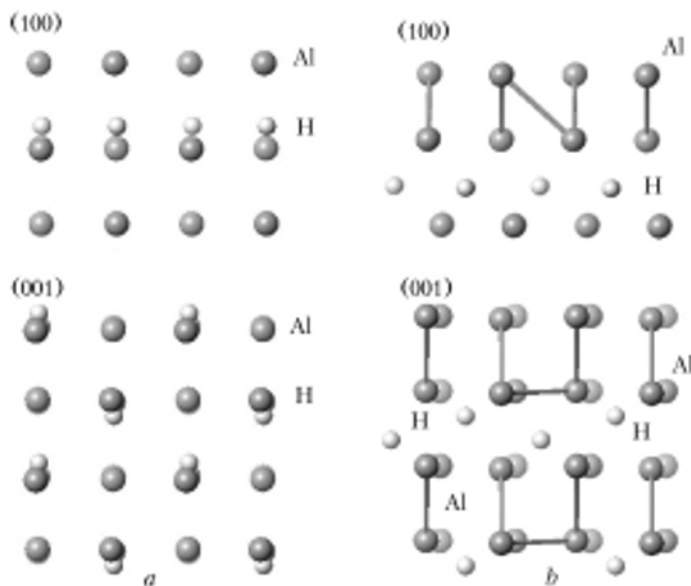


Fig. 6. Diagonal-chain arrangement of hydrogen atoms in the process of hydrogen diffusion through the subsurface layer of the plate: a) $L = -1.70 \text{ \AA}$, $E_d = 1.290 \text{ eV}$, $r_{\text{H-H}} = 2.380 \text{ \AA}$; b) $L = -3.15 \text{ \AA}$, $E_d = 1.318 \text{ eV}$, $r_{\text{H-H}} = 2.110 \text{ \AA}$.

atoms of the surface and subsurface layers of the plate. For one of the hydrogen atom being considered the length of the Al–H bond with the surface and subsurface Al atoms comprises, respectively, 1.84, 1.93 and 2.01, 1.85 Å, and, for the other hydrogen atom, this length is equal to 1.84, 1.90 and 2.09, 1.82 Å. Analysis of the geometry of this structure allows the conclusion that, at the initial stage of diffusion, Al_4H_2 complexes, structured in the form of polymeric chains, are formed in the surface layer.

TABLE 2. Energetics of the Adsorption and Diffusion of a Hydrogen Molecule in the Nanocrystalline (001) Plate of Aluminum in the Case where Three Atomic Layers of the Plate Have Fixed Coordinates and in the Case of Complete Relaxation of the Atomic Coordinates. Calculation by Formulas (1) and (2)

Adsorption state	Fixed three layers, E_f , eV	Relaxation of coordinates, E_r , eV	$\Delta E = E_f - E_r$, eV	$r_{\text{H-H}}$, Å	
				Fixed three layers	Relaxation of the coordinates of all atoms
Molecule remote from the plate	0	0	0	0.7273	0.7262
Physical adsorption	-0.0497	-0.0437	-0.006	0.7283	0.7306
Energy barrier	0.4010	0.3806	0.0204	2.01—2.23	2.02—2.03
Chemical adsorption, apical	0.3513	0.3369	-0.0217	2.8313	2.8492
Chemical adsorption, bridge	-0.0805	-0.0377	-0.0428	2.7468	2.8254
Energy of diffusion in the surface layer	1.3180	0.8622	0.4486	2.2324	2.3157
Energy of diffusion in the subsurface layer	1.3081	1.1825	0.1256	2.1102	2.09615

It was established that the second equilibrium arrangement of H atoms with an energy of 1.32 eV (Fig. 5b) is formed at a depth of 1.55 Å from the surface of the plate. In this case, the hydrogen atoms are arranged in an extended chain structure in the (001) plane with H–H bonds of length 2.232 and 2.267 Å. In this spatial configuration, the hydrogen atoms are bonded to three atoms of aluminum. The lengths of the Al–H bonds are equal respectively to 1.749, 1.807, 1.930 Å and 1.756, 1.823, 1.937 Å for the first and second hydrogen atoms. In this case, the shortest bond is formed between the hydrogen atoms and the surface atoms of the plate, and the longer Al–H bonds are formed as a result of the interaction of the hydrogen atoms with the atoms of the subsurface layer. In this case, an Al_6H_2 complex is formed in the surface layer.

When the distance between the hydrogen atoms and the subsurface layer decreases to 1.7 Å (Fig. 6a), a structure with a practically diagonal arrangement of hydrogen atoms in the (001) plane is formed. As in the previous case, the hydrogen atoms are bonded to the surface atoms of aluminum by shorter bonds of length 1.764 Å; the lengths of the bonds of the hydrogen atoms with the Al atoms of the subsurface layer are equal to 1.819, 1.826, 2.189, and 2.132 Å. It follows herefrom that the hydrogen atoms form a surface Al_4H_2 complex with an energy of 1.29 eV.

The energy of diffusion of hydrogen atoms through the subsurface layer ($L = -3.15$ Å) reaches 1.8 eV. When the hydrogen atoms overcome the energy barrier, a chain structure is formed in the bulk of the plate (Fig. 6b); this structure is more stable in energy than the diagonal structure. It has an energy of 1.227 eV close to the energy of the chain structure of hydrogen atoms positioned between the surface and subsurface layers of the plate. The structure of hydrogen bonded to aluminum includes H–H bonds of length 2.110 and 2.138 Å; in this structure, the length of the bonds of hydrogen atoms with Al atoms of the fixed layer fall within the range 1.84–1.85 Å and the length of the bonds of hydrogen atoms with Al atoms of the subsurface layer are equal to 1.856, 1.868, 2.179, and 2.106 Å. Thus, in the bulk of the plate there arises an Al_4H_2 complex identical in geometry to the structure formed as a result of the diffusion of hydrogen atoms through the surface layer of the Al plate.

The chain structure, formed at the initial stage of the diffusion as a result of the passage of H atoms through the surface of the plate, causes a smaller deformation of the surface layer as compared to the deformation caused by the formation of the diagonal structure. Comparison of the energies of the chain and diagonal structures shows that the deformation energy of the lattice is higher by approximately 0.1 eV in the case where a diagonal structure of hydrogen atoms is formed in the surface layer. The hydrogen passing through the subsurface layer displaces the Al atoms of the surface and subsurface layers in the (001) plane. The subsurface layer of the plate experiences a stretching deformation, while its surface layer is subjected to a smaller deformation (Fig. 3).

The results of calculations of the energetics of the adsorption and diffusion of hydrogen in the aluminum plate, leading to the formation of stable geometrical configurations, presented in Table 2, allowed us to determine the main stages of the interaction of hydrogen with aluminum.

The physical adsorption occurs with a small energy release and represents, in essence, a weak exothermic process. For a transition complex to form, an energy necessary for the stretching of the H–H bonds and formation of surface AlH hydrides should be supplied to the system. When hydrogen atoms overcome the energy barrier of the order of 0.4 eV (endothermic process), a strong exothermic effect arises as a result of the formation of the diagonal bridge AlH structures. The formation of the chain AlH–HAl structures as a result of the transformation of the hydrogen molecule from the chemisorbed to the diffusion state occurs with an energy absorption of the order of 0.35 eV.

The diffusion of hydrogen atoms is an endothermic process (an energy of the order of 1.32 eV is absorbed) that proceeds in two stages, at one of which the bridge Al–H bonds are disrupted and diagonal-chain hydrogen complexes are formed in the surface layer of the plate. The subsequent diffusion of the hydrogen atoms in the bulk of the plate leads to the formation of diagonal and chain Al₄H₂ structures with absorption of a somewhat smaller amount of energy. The diffusion in the bulk of the plate, estimated relative to the activation energy of the hydrogen diffusion in the surface layer, occurs without absorption and it is possible even with an energy release.

The influence of the relaxation of the atomic coordinates of the nanocrystalline plate on the characteristics of the hydrogen adsorption and diffusion can be judged by the data presented in Table 2. The system of several atomic layers of the plate with fixed coordinates is used for simulation of the influence of the deep atomic layers of the metal, found in the equilibrium state, on the indicated processes; these layers cannot interact with the adsorbate and change their space positions because the adsorption and diffusion forces act at a distance of the order of two atomic layers. The difference between the energies E_r and E_f is evidence that the energy parameters of the systems with fixed and free atomic coordinates differ substantially. The largest differences were obtained when the diffusion state of the interaction was simulated. The diffusion energy in the surface layer of the completely relaxing plate is smaller by approximately a third than that of the partially fixed system. The latter allows the conclusion that the accumulation of hydrogen by nanostructure metals, in particular, ultrathin films or metal clusters, should be effective in energy as compared to that of macroscopic objects.

Conclusions. On the basis of simulation, "from the first principles," of the adsorption and diffusion of a hydrogen molecule in a thin atomic plate of aluminum, bounded by the (001) atomic plane, the energetics of the interaction of hydrogen with aluminum and the geometrical configurations of the equilibrium structures of surface aluminum hydrides have been determined.

Our calculations have shown that an H₂ molecule does not dissociate completely in the process of adsorption and diffusion. The physical adsorption is an exothermic process occurring with an insignificant energy release. The transition state between the physical and chemical adsorption is characterized by the potential barrier of 0.4 eV arising as a result of the formation of surface hydrides including H–H bonds of maximum length. In the process of chemisorption, two types of equilibrium structures are formed: a bridge AlH structure and a chain (AlH–HAl) structure; the formation of these structures occurs, respectively, with release of energy and energy absorption.

The diffusion of hydrogen atoms is accompanied by an energy absorption of the order of 1.3 eV with the result that the chemisorption bridge bonds are disrupted and diagonal-chain hydrogen structures are formed in the surface layer of the plate. The diffusion of hydrogen atoms into the bulk of the plate is realized through the formation of diagonal and chain structures with an energy absorption of the order of 1.2 eV.

NOTATION

E , total energy of the system, hartree; $E(10Al + 2H)_L$, total energy of the system in the case where a hydrogen molecule is at a distance L from the surface of the plate, hartree; $E(10Al + 2H)_{inf}$, total energy of the system in the case where a hydrogen molecule is at a maximum distance from the plate, hartree; E_{ad} , energy of adsorption, eV; E_{ch} , chemisorption energy, eV; E_d , diffusion energy, eV; E_r , energy in the case of complete relaxation of the atomic coordinates, eV; E_f , energy of the system of three atomic layers with fixed coordinates, eV; $L(Al(9, 10) - H(11, 12))$, average distance between the hydrogen atoms and the atoms of the surface layer of the aluminum plate, Å; r_{H-H} , distance between the hydrogen atoms, Å; X, Y, Z , coordinates of the hydrogen atoms and the atoms of the plate; ϵ , relative deformation of the surface layers of the plate. Subscripts: ad, adsorption; inf, disposition of a hydrogen molecule at a large distance from the plate; ch, chemisorption; r, relaxation of the atomic coordinates; f, partially fixed atomic coordinates; d, diffusion.

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