



Ni-doping effect of Mg(0001) surface to use it as a hydrogen storage material



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ABSTRACT

A detailed study of Ni-doped Mg(0001) surface performed by PAW method and the gradient corrected density functional GGA-PBE within the framework of generalized Kohn–Sham density functional theory (DFT) is presented in this work. Structural and electronic properties of magnesium surface interaction with nickel for the purpose of such compounds use for creation of hydrogen storage matrixes were investigated here. Choice of the PBE functional was caused by the good accordance of its prediction of the cell parameters with experimental results. It was shown that Ni atoms prefer to substitute for Mg atoms. Using NEB method, the diffusion barrier was calculated, and the most probable reaction path was established. In particular, when the Ni atom dopes the magnesium surface, it can migrate to the bulk and substitute for Mg in subsurface layers. Also a possibility of nickel cluster formation on clean surface of magnesium was examined. The kinetic factors hinder the movement of the nickel atoms to each other and make problematic the formation of clusters. The studies presented here showed that the diffusion barriers of the nickel atom migration from the cluster on the surface to the bulk of magnesium are 1.179 eV and 1.211 eV for the forward and reverse reactions, respectively. Therefore an improvement of the hydrogenation properties of Ni-doped magnesium surface depends on deposition not of the individual atoms, but their clusters. Hydrogenation of Ni cluster doping the magnesium surface was investigated. Initially Kubas complexes arise on the Ni cluster with hydrogen–hydrogen bond lengths equal to 0.80–0.87 Å. Next the cluster needs to be saturated by hydrogen atoms to allow them later to migrate from cluster to magnesium.

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1. Introduction

In the new century society needs highly efficient transport utilizing the renewable and clean energy. Use of hydrogen is a possible way to meet future energy needs of the population because this is the most widespread element in the universe, and it contains the highest energy density and can be burned clean, producing water only. Therefore hydrogen has great potential for wide use in the energy sector, particularly as a fuel for vehicles. The US Department of Energy (DOE) published technical system targets for hydrogen storage applications relative to light-duty fuel cell vehicles. The predicted minimum hydrogen storage capacity here should be 5.5 wt% and 40 g/L at the operating ambient temperature between –40 and 60 °C [1]. Also low temperatures of

hydrogen desorption and low pressures of hydrogenation are required. Furthermore, the financial cost and toxicity properties of storage materials need to be carefully considered before realization of their practical use.

Hydrogen storage in a solid state phase offers several benefits as compared with other means of storing hydrogen. MgH₂, AlH₃, NaAlH₄, LiH and other metal hydrides can be used as a matrix for hydrogen storage with varying success. Magnesium is one of the most promising metals in this set, because it has low cost, low molecular weight, availability and non-toxicity.

However, there are some serious challenges to use magnesium as reversible sorbent. Most of them are associated with the occurrence of diffusion limitations in magnesium hydride, where hydride phase formed initially creates a “surface shield” that blocks further hydrogen sorption [2]. This delays diffusion of the hydrogen atoms into the bulk of metal. Furthermore, there is a strong ionic Mg–H bond in magnesium hydride, which is caused

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by a relatively high enthalpy of formation ($\Delta H = -75$ kJ/mol). This bond leads to the increase of the temperature of hydrogen desorption out of the hydride phase and as a result to the decrease of a rate of this process [3]. Finally, the high barrier of the hydrogen molecules dissociation on the magnesium surface is another problem [4–7]. Therefore using magnesium and magnesium hydride in a pure form is not possible. However, the particle size reduction is the promising way to overcome challenges.

In recent years, special attention is paid to magnesium nanoparticles due to their novel properties different from those of bulk materials [8–11]. Usually, nanoparticles are prepared by two main methods such as milling in a ball mill and gas phase condensation [6,8,11]. It should be noted that there are some other methods of nanoparticles synthesis such as the preparation in tetrahydrofuran by the reduction of the lithium magnesium salt [12] and as the sonochemical method which is based on the use of ultrasound [13]. Another modern approach of the preparation of ultrafine nanoparticles of magnesium (size about 40 nm) is the arc melting of magnesium in the acetylene plasma [14]. The application of these methods reduces the particles size of magnesium, and improves the diffusion and kinetics of the hydrogenation/dehydrogenation of Mg nanoparticles.

At the same time it is advisable to consider the possibility of magnesium modification by various transition metals. Numerous studies are aimed at overcoming kinetic limitations by adding a catalyst to increase the rate of hydrogen dissociation on the magnesium surface [2,15]. The most of studies published previously show the improvement of the absorption/desorption reaction kinetics at addition of transition metals. However, the mechanism of such reactions remains obscure. An implementation of one or another mechanism is dependent on many conditions such as the deposition temperature, the rate of atoms feed and other factors. The determination of these mechanisms is experimentally difficult or extremely resource-expensive. In this situation the quantum-chemical methods seem preferable to study the processes occurring in the systems during these reactions.

The barriers of the hydrogen dissociation on the transition metals atoms, which were situated on the magnesium surface, were theoretically calculated earlier [16–20]. Du et al. [18] have shown that using of titanium as the modifying component makes such barrier quite low. However, titanium forms a strong stable hydride bond, which, to be broken, requires a lot of energy. Therefore diffusion of these two dissociated hydrogen atoms into the bulk of magnesium is very complicated [19]. Palladium as catalyst makes dissociation quick, and diffusion from palladium into the bulk of magnesium is not difficult [18]. Unfortunately, this metal possesses effective catalytic activity as compared with nickel and titanium only at high temperatures. On the other hand, Pozzo and Alfè [20] have investigated the dissociation and the followed diffusion of the hydrogen atoms on the magnesium surface (0001) modified by the different transition metals (Ti, V, Zr, Fe, Ru, Co, Rh, Ni, Pd, Cu, Ag). The results showed that insertion of the atoms Fe, Ni, Rh, and (to some extent) Co and Pd can lead to the low hydrogen dissociation and diffusion barriers, but the most effective alloying component is Ni. Experimental results confirm these theoretical conclusions. In other words hydrogenation occurs quickly and efficiently in magnesium doped by nickel. However, despite the experimental development and theoretical approaches to overcome the restrictions of the use of magnesium, including its modification by transition metals, its practical use as the hydrogen storage matrix remains problematic.

According to the theoretical and experimental results [16–23] it can be assumed that the following processes can occur due to the nickel adsorption precipitation on the magnesium surface: clustered and epitaxial growth of transition metal on the surface, inclusion of d-metal atoms into the metal-sorbent lattice interstices,

placement of transition metal atoms into the vacancies, formation of the intermetallic compound. In this case, an essential step in the interaction mechanism determination of transition metal with magnesium is detailed consideration of these processes and description of compounds that are generated on the surface and the subsurface layers depending on the synthesis conditions.

In the present study, the low index magnesium surface Mg(0001) has been studied computationally with help of DFT method. The behavior of nickel atoms at the surface and subsurface layers of magnesium has been investigated by quantum-chemical simulation. A possible reaction pathway for nickel atom diffusion from surfaces into the bulk has been chosen, and its potential barriers have been computed using the nudged elastic band (NEB) method. Next, a possibility of cluster formation and nickel diffusion from cluster into the bulk of magnesium has been examined.

2. Computational method

Quantum-chemical calculations were performed with the Vienna *ab initio* simulation package (VASP) [24–27] and within the density functional theory (DFT) [28,29]. The Perdew–Burke–Ernzerhof functional was used for the calculation of the exchange–correlation energy [30]. The electron–ion interactions were described by the projector augmented wave (PAW) method [31]. The plane wave cutoff energy for all calculations was set at 400 eV. An energy difference of 10^{-4} eV was set as the convergence criterion between successive ionic steps during the geometries relaxation.

The equilibrium geometry of the magnesium unit cell with the space group symmetry P63/mmc has been calculated at the work initial stage to study the interaction of the Mg surface with atoms and clusters of nickel. The *k*-point samplings of the first Brillouin zone (1BZ) have been chosen as $12 \times 12 \times 12$ according to the Monkhorst–Pack scheme [32]. It was detected that these values are sufficient for a correct description of the lattice parameters (calculated values of *a* and *c* are 3.10 and 5.00 Å, when experimental values are 3.22 and 5.23 Å [33], respectively).

The investigation of the processes on the surface was the following stage, where a slab consisting of the hexagonal cells with surface index (0001) and translation vector of 3.10 Å was used in the calculations. The structures with a different number of layers were examined to find the optimal thickness of the slab. It was detected that difference of a surface energy density between the slabs containing of 7 and 8 layers, respectively, is less than 0.01 eV/Å. Thus the seven atomic layers is enough thickness of the slab for the accurate modeling of the surface processes, therefore this model was used for the next steps of the investigation. A vacuum space was equal to 15 Å to guarantee a sufficient separation between the periodic images.

Using the optimized slab geometry, a supercell with a size of $7 \times 7 \times 1$ of the unit cells of the slab was modeled to exclude an interaction of the nickel atoms between neighboring images. The *k*-point samplings of the first Brillouin zone (1BZ) were chosen as $2 \times 2 \times 1$. In the case of the surface processes' simulation four different positions of the Ni atom were examined: above the Mg atom (top), above the Mg–Mg bond (bridge), above the tetrahedral (hcp) and octahedral (fcc) hollows (Fig. 1(a–d)). In the case of a penetration the nickel atom was placed into the tetrahedral and octahedral hollows of the surface layer (Fig. 1(e and f)). Also a substitution of the Mg atom in the first, second and third layer by the Ni atom was examined (Fig. 1(g–i)).

3. Results and discussion

The specific binding energies of supercell with nickel atoms at the doping and the substitution (Table 1), respectively, were defined as

$$E = \frac{E_T - E_S - nE_{Ni}}{n}, \quad (1)$$

$$E = \frac{E_T - E_S - nE_{Ni} + nE_{Mg}}{n}, \quad (2)$$

where E_T is the total energy of the magnesium supercell with *n* atoms of nickel, E_S is the energy of the magnesium supercell separately, E_{Ni} is the energy of the Ni atom in its bulk crystal structure, E_{Mg} is the energy of the Mg atom in its bulk crystal structure.

According to the specific binding energies the most stable structures are those where the magnesium atoms are replaced by the nickel atoms. However, there is no substitution solution at the

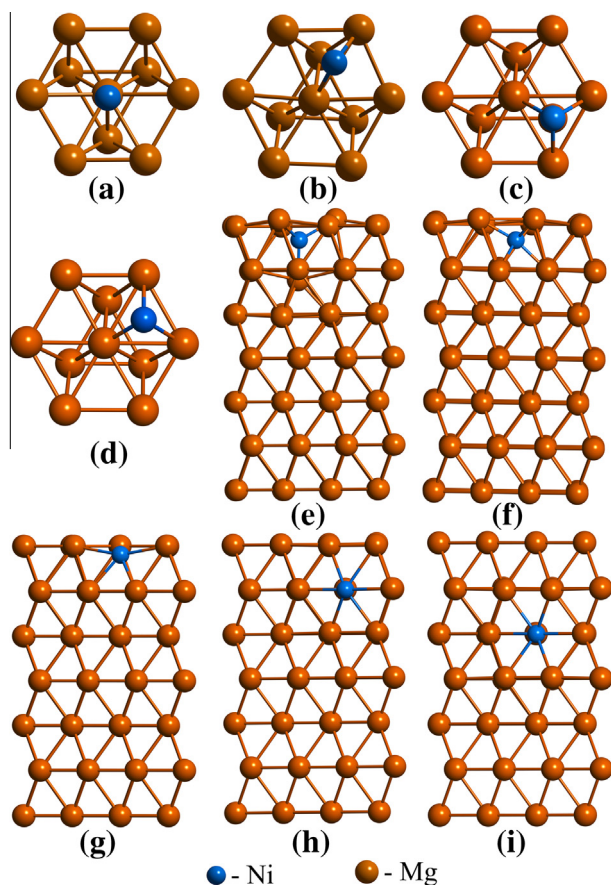


Fig. 1. The equilibrium geometry positions of the nickel atom on the surface and in the subsurface layers of magnesium: a – top, b – bridge, c – hcp, d – fcc, e – in the tetrahedral hollow, f – in the octahedral hollow, g – substitution of the Mg atom in the first layer, h – substitution of the Mg atom in the second layer and i – substitution of the Mg atom in the third layer.

Table 1
The binding energies of the nickel atom with the magnesium supercell, eV.

Ni position	Binding energy
<i>On surface</i>	
fcc	1.37
Bridge	1.28
Top	1.91
hcp	1.33
<i>Substitution</i>	
First layer	–0.38
Second layer	–0.67
Third layer	–0.77
<i>In the bulk</i>	
Octahedral	0.32
Tetrahedral	1.06

phase diagram in the relevant concentrations area [34]. A possibility of its formation was examined by the calculation of the periodic structure consisting of plane supercell with the size of $7 \times 7 \times 1$ of the unit cells where one magnesium atom is replaced by the nickel atom. Namely, substitution was in the bulk of magnesium. The length of a supercell translation vector was 18.57 Å. Such replacement was found not favorable in terms of energy, because the binding energy of the Ni atom with magnesium supercell is positive and equal to 0.04 eV. Thus, it indicates the existence of the subsurface substitution effect of the atom of one type by the atom of another type, extending to several layers from the surface.

A possibility of nickel migration from the surface into the volume of the structure was also examined. It was carried out with help of the NEB method [35,36], calculating the potential barriers of the nickel atom migration on the surface and from the surface into the bulk of the crystal lattice, and the magnesium atom substitution in the second layer (Table 2). Seven images were used here for NEB calculations. The calculated distance between two energetic minimums came out short. Therefore it should not be two pathways here.

The values of the potential barriers of the Ni migration from “bridge” position to “fcc” or “hcp” positions are very low. It indicates that nickel atom can move freely along the magnesium surface. The potential barriers of the Ni diffusion from the surface into the bulk (fcc-bulk (octahedral)) and from the bulk in place of Mg are also low. Thus, for example, if the nickel atom occupies position on the magnesium surface from which its migration into the bulk becomes difficult, it can move to the better place and then go into the bulk from there. The diffusion of the Ni atom from the surface to the “hcp” position was not examined, because there is the magnesium atom under the nickel, and it prevents the penetration of the last one. Therefore such transition is hardly probable for the substitution reaction.

A possibility of the nickel atoms to aggregate, producing the cluster by substitution in the surface layer, was examined by the modeling of the mini-cluster consisting of three nickel atoms in the angles of triangle. The calculated specific binding energy of the nickel here is equal to 0.27 eV. Therefore the probability of cluster formation in the surface layer is very low, and the nickel atoms prefer to stay separately in the bulk. At the same time the aggregation of the Ni atoms on the surface can occur complicating their diffusion into the bulk. A possibility of such situation was estimated by the comparing the binding energies of the nickel atoms in the cluster at “hcp” and “fcc” positions and of the single atom with surface with help of the equation

$$E = 3E_{1Ni} - (E_{3Ni} + 2E_S), \quad (3)$$

where E_{1Ni} is the binding energy of the single nickel atom with magnesium surface, E_{3Ni} is the formation energy of the Ni cluster consisting of three atoms and having the same position as the single atom, E_S is the total energy of magnesium supercell.

It was detected that formation of the cluster at “fcc” position is preferable than the existence of the separated nickel atoms there. The specific binding energy of the Ni atom in the cluster is larger on 0.19 eV than in the case of the single atoms on the surface. The opposite situation is observed for the “hcp” position. The specific binding energy of the separated Ni atom on the surface is larger on 0.72 eV than in the cluster.

Ni clusters on Mg(0001) surface have been previously studied by Churilov et al. [37] **MC comment: Ignore Q3 response.** Authors calculated the binding energies of one and two layers of Ni clusters contained 16 atoms. It was shown that nickel prefers to form multilayer covering by mechanism of island growth. However paper does not contain information about interaction of Ni atoms with

Table 2
The values of the potential barriers of the nickel atom diffusion, eV.

Initial-final positions of the Ni atom migration	Potential barrier	
	Direct	Reverse
<i>On the surface</i>		
Bridge-fcc	0.171	0.086
Bridge-hcp	0.128	0.079
fcc-bulk (octahedral)	0.448	1.502
<i>In the bulk</i>		
Bulk (octahedral)-replacement	0.162	0.082

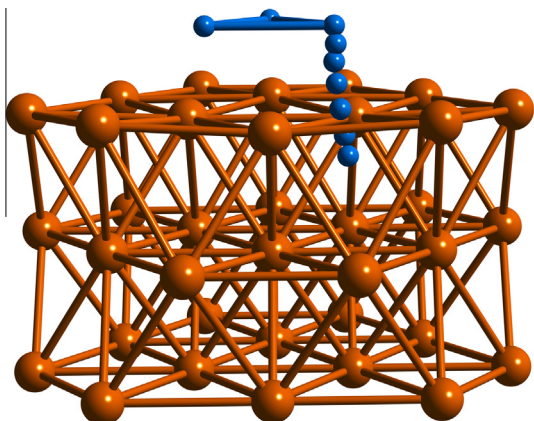


Fig. 2. Location of diffusing nickel atom in the simulation of the migration process from the cluster on the surface to the bulk of magnesium.

slab, about possibility of their diffusion, and about cluster formation on the Mg(0001) surface.

Next, the diffusion of the nickel atom from the cluster onto the surface into the “fcc” position was examined (Fig. 2). A bond breakage must have a place in this process, so the diffusion barriers were 1.179 eV and 1.211 eV for the forward and reverse reactions, respectively. It indicates that cluster breakage allowing to the nickel atoms to go into the bulk is very complicated.

Table 3
The binding energies of the H₂ with the supercell (with Ni–fcc), eV/H₂.

H ₂ position	Binding energy
Bridge	–0.07
Top	–1.13
Center	0

However, there is also a kinetic factor of Ni atoms approach to each other on the Mg(0001) surface, influencing on the cluster formation. Cluster is formed by passing a set of intermediate states. In this case, the atoms have to pass a number of states and their stability will be influence on the cluster formation. A step by step diagram of the formation of the mini-group consisting of three nickel atoms was calculated with help of Eq. (3) and constructed to estimate this influence (Fig. 3). Such mini-group formation was modeled by the approaching of a nickel atom to another one or to a cluster of them. Calculated energies of all intermediate states turned out very high. It implies a problem for the nickel cluster formation on the magnesium surface, i.e. the growth of cluster on the surface will be complicated.

Thus, the formation of the intermetallic compound is the more probable process at the covering the magnesium surface by the small amount of nickel. In this case, the nickel atoms will be accumulating in the surface and subsurface layers up to the formation of the transition into the Mg₂Ni phase, which will be not contributing into the process of hydrogenation [2,38].

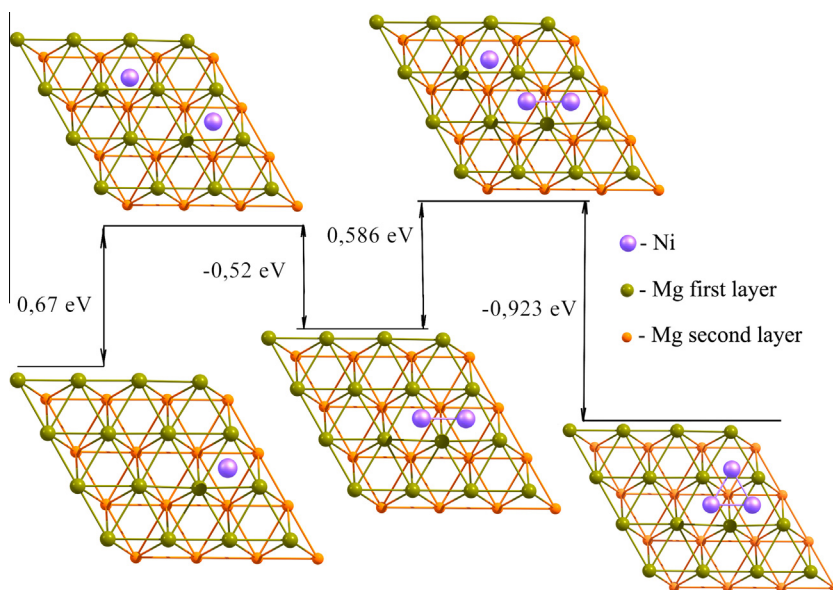


Fig. 3. Step by step diagram of mini-cluster formation on the magnesium surface. Nickel atoms are situated at “fcc” positions.

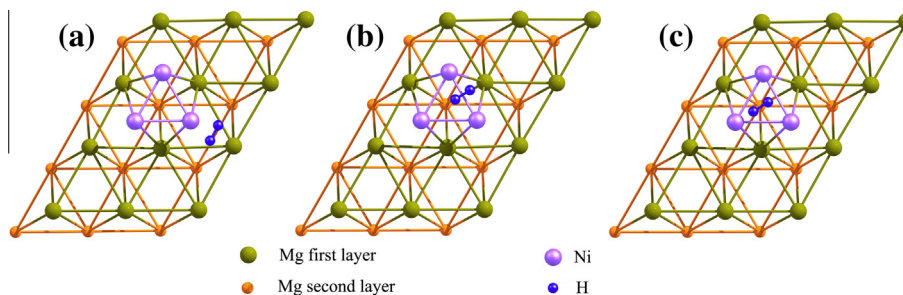


Fig. 4. The positions of hydrogen molecule on the Ni cluster: a – top, b – bridge and c – center.

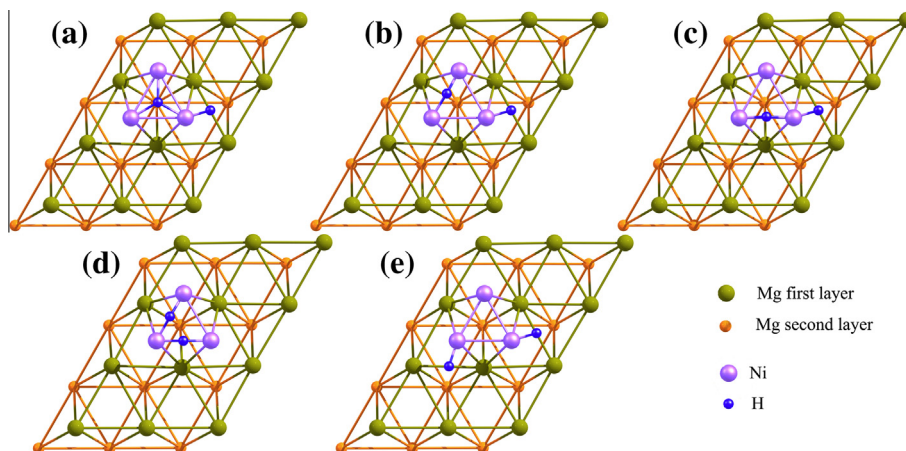


Fig. 5. The positions of hydrogen atoms on the Ni cluster: a – top-center, b – top-bond 1, c – top-bond 2, d – bond-bond and e – top-top.

Table 4

The binding energies of two H atoms with the supercell, eV/H₂.

H position	Binding energy
Top-top	–0.01
Top-center	–1.31
Top-bond 2	–0.47
Top-bond 1	–0.57
Bond-bond	–0.29

The next step was the investigation of a hydrogenation process on the Ni cluster. Three different positions of the H₂ were examined: above the Ni atom (top), above the Ni–Ni bond (bridge), above the center of the cluster (Fig. 4). Different orientations of hydrogen molecule in those positions were calculated. The calculations show that binding energy of H₂ slightly depends on its orientation.

The specific binding energies of supercell (with Ni cluster in fcc) with hydrogen molecule (Table 3) were defined as

$$E = \frac{E_T - E_S - nE_{H_2}}{n}, \quad (4)$$

where E_T is the total energy of the supercell (with Ni-fcc) with n molecules of H₂, E_S is the energy of the magnesium supercell with Ni-fcc cluster, E_{H_2} is the energy of the H₂.

According to the values of binding energies the structure with hydrogen molecule situated in top position is the most stable. It is worth noting all positions of H₂ form Kubas complexes with H–H bond length of 0.80–0.87 Å.

The most probable five positions of two hydrogen atoms on the cluster surface were also examined (Fig. 5): top-center, top-bond 1, top-bond 2, bond-bond, top-top. The values of binding energies of supercell (with Ni cluster in fcc) with H atoms (Table 4) were

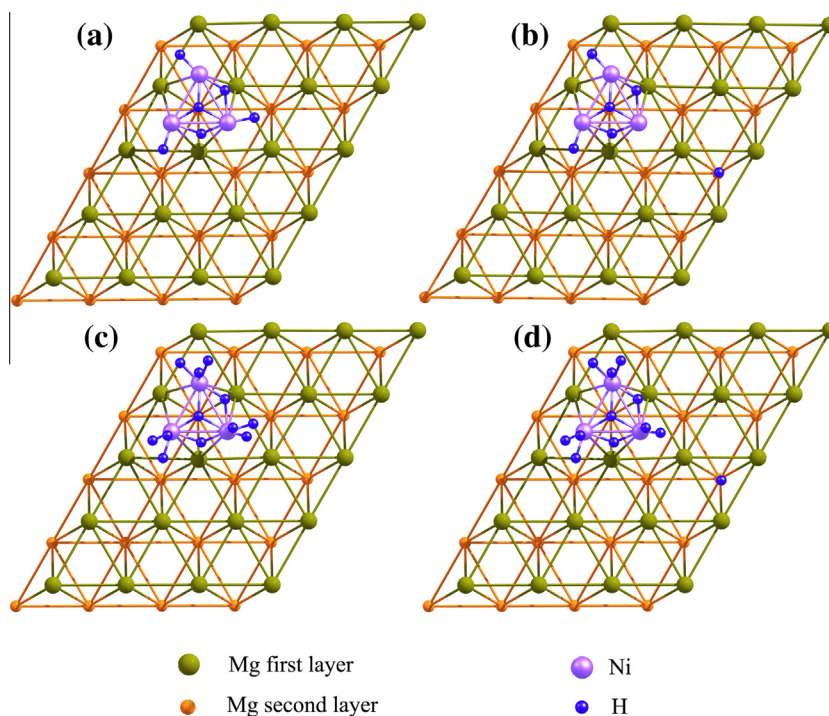


Fig. 6. The positions of 6 and 12 hydrogen atoms in the system: a – 6H on Ni cluster, b – 5H on Ni cluster + 1Mg hcp, c – 12H on Ni cluster and d – 11H on Ni cluster + 1Mg hcp.

estimated with help of Eq. (4). The values of binding energies indicate that structure with hydrogen atoms situated in “top” and “center” positions is the most stable.

Potential barrier, calculated by NEB method, of the H atom migration between “top” and “center” positions is low and equals 0.197 eV. It indicates that hydrogen atom can move freely into center of cluster.

Also binding energies were calculated when one H atom was situated on magnesium and another one was situated on the Ni cluster. It was detected that hcp position of H atom is preferable than all other positions on magnesium. The specific binding energy of the hydrogen atom in the hcp position is equal to -1.17 eV.

Next the cluster was saturated by occupying the top–bond and then the top–top positions by 6 and 12 hydrogen atoms (Fig. 6). It was two cases examined here. In the first one all H atoms were situated on cluster, in second case one of them was situated on magnesium in hcp position. The values of binding energies of 6 hydrogen atoms are equal to -1.16 and -1.07 eV/H₂ respectively for two considered cases. At the same time the values of binding energies of 12 hydrogen atoms are equal -0.77 and -0.75 eV/H₂.

Thus the difference between initial and final points of hydrogen position decreases with increasing the number of H₂ molecules in the system. In this case, accumulating the hydrogen atoms on the cluster up to the formation of the transition into the Mg is the most probable outcome.

4. Conclusion

In summary, the detailed study of Ni-doped Mg(0001) surface was performed by PAW method and the gradient corrected density functional GGA-PBE within the framework of generalized Kohn–Sham density functional theory. It was shown that substitution of a magnesium atom in the subsurface layer is the most likely position for the nickel atom after the doping. A general reason for that are the low potential barriers of the nickel atom migration on the magnesium surface, from the surface into the bulk of the crystal lattice, and next replacing the magnesium atom in the second layer.

Also the possibility of the nickel cluster formation on the clean magnesium surface was examined. It was shown that such formation is hindered due to kinetic factor of the nickel atoms approach to each other. At the same time, the potential barriers of the nickel atoms diffusion from the cluster, located on the surface, into the bulk of magnesium also are very high. Therefore the formation of the intermetallic compound is the more probable process at the covering the Mg(0001) surface by the small amounts of nickel. From this point of view if it is necessary to put the nickel clusters onto the magnesium surface the special methods must be chosen which allow to spray directly the clusters, but not the separated atoms. In the last case it can be done only at special diapason of temperatures which are not too high to allow the nickel atoms to diffuse into the bulk.

Hydrogenation of Mg(0001)/Ni cluster must be occurring easily. And the first step here is formation of the Kubas complexes on the Ni cluster, where hydrogen–hydrogen bond length becomes equal to 0.80–0.87 Å. Next the cluster needs to be saturated by hydrogen atoms to allow them later to migrate from cluster to magnesium.

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