
MATERIALS FOR
GENERAL PURPOSE

Advanced Materials for Hydrogen Storage Based on Iron–Palladium Intermetallic Alloys

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Abstract—The article discusses first-principles calculations of hydrogen solubility in various interstitial positions in L1₀ ordered FePd alloy. It is demonstrated that the predominant localization of hydrogen in solid solution is in octahedral positions in the Fe and Pd planes, where the position in the Fe plane is somewhat more favorable (by 0.13 eV). It is also demonstrated that addition of a hydrogen atom to an FePd crystal results in modification of the magnetic moment of the system by approximately one Bohr magneton.

Keywords: hydrogen, iron, palladium, dissolution.

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INTRODUCTION

The possibility of solid-state hydrogen accumulation is seriously considered in modern technologies of storage and transportation of hydrogen fuel. It is well known that certain metals, such as palladium or platinum, are able to efficiently absorb hydrogen. Even better absorption efficiency is attained in intermetallic alloys, mainly on the basis of light metals (aluminum, magnesium) and semimetals (boron). In such metals and alloys, the hydrogen atoms are predominantly trapped in interstitial positions. At relatively low concentrations, hydrogen remains in the form of a solid solution, but after reaching the levels of tens of atomic percent, there occurs formation of chemical compounds (metal hydrides).

When metals are used as hydrogen accumulators, the necessary condition for reaching high capacity of a hydrogen accumulator is the efficiency of hydrogen trapping by the solid. This high efficiency has a reverse side of making problematic hydrogen extraction from an accumulator for further utilization. High energy of hydrogen binding with a solid, required for its accumulation in high amounts, means that discharge of an accumulator by conventional methods requires high operating temperatures that cannot be applied for practical purposes (for example, in automotive applications). Therefore, there is a continuing search for materials that could combine sufficiently high capacity with the capability of efficient control of hydrogen

solubility. A possible method of solution of this problem could be the use of magnetic materials, where the hydrogen solubility would be controlled by the level of the intrinsic or external magnetic field.

As possible candidates for such a material, we propose to consider ordered binary alloys of the type “transition metal (Fe, Cr, Ni)—noble metal (Pt, Pd),” which seem very promising for further investigations. Indeed, an ordered alloy of AB type consisting of alternating atomic planes of transition and noble metals (structure of L1₀ type) would presumably possess high efficiency of hydrogen trapping, characteristic of pure noble metals. At the same time, ordered intermetallic compounds of the aforementioned type possess pronounced magnetic properties, not characteristic of pure noble metals. Therefore, the combination of a metal with good magnetic properties and a metal with high affinity to hydrogen can provide a synergetic effect of high efficiency of hydrogen accumulation and capability of subsequent control of its content by magnetic field variation.

Quantitative justification of these expectations obviously requires the knowledge of energy parameters characterizing solubility and mobility of hydrogen atoms in the ordered intermetallic compounds. However, at present, such published information is extremely limited. In particular, according to earlier calculations within the framework of modified generalized extended Hückel tight-binding (EHTB) theory

[1], hydrogen atoms in $L1_0$ ordered FePd alloy are mainly located in tetrahedral interstitial positions between the Fe and Pd planes. Localization of hydrogen atoms in tetrahedral positions is quite unusual, because pure Pd [2, 3] and face-centered cubic (FCC) Fe [4] are characterized by hydrogen localization in octahedral interstitial sites. Moreover, the predominant localization of hydrogen atoms in octahedral interstitial positions is predicted by the same EHTB method in the case where Fe and Pd atoms are positioned in accordance with the B_1 ordering type, though with significantly lower (by 2.2 eV) energy gain than upon addition of hydrogen to an ordered crystal [1]. Unfortunately, the reliability of even qualitative predictions of the tight-binding technique is low. For quantitative predictions of hydrogen parameters in metals (such as the solution energy), more accurate methods are certainly required.

This work presents a theoretical estimate of the energies of dissolution of hydrogen in various interstitial positions in ordered intermetallic compound Fe–Pd by means of a first-principles approach, which currently is the most reliable method of calculation of energy parameters of impurity atoms in crystals.

SIMULATION TECHNIQUE

The calculations of equilibrium parameters of the FePd: $L1_0$ system and its interaction with hydrogen were performed using density functional theory and the PAW (Projector Augmented Wave) method [5]. All calculations explicitly considered spin polarization, because neglecting it can significantly distort the calculated results, especially for the atoms of iron and hydrogen, possessing nonzero magnetic moments.

Since there were no earlier systematic investigations of convergence of the calculation results for the system considered in this work, the adequacy of the applied approximations and their parameters was tested. Most of all, this concerns the adequacy of selection of calculation cell size.

The atomic structure of the ordered FePd alloy is illustrated in Fig. 1. This system is a 50 : 50 intermetallic alloy with FCC crystal lattice, which is characterized by alternation of atomic planes consisting of atoms of one component (Fe or Pd). As a result of such alternation, there appears elastic heterogeneity, resulting in a decrease in cubic symmetry, inherent to nonordered Fe–Pd alloy, and violation of the relation $c = a$ (where a and c are the lattice parameter in the monatomically packed planes and the distance between these planes, respectively). As can be seen, a nearly cubic elementary cell of the alloy includes four atoms (2Fe + 2Pd). It is obvious that, for calculations of the parameters of single hydrogen atoms, it is insufficient to use the minimum cell of four atoms of metal. Ideally, the number of elementary cells in a simulated crystal should be such that overlapping of elastic strains and electron orbitals introduced by a hydrogen

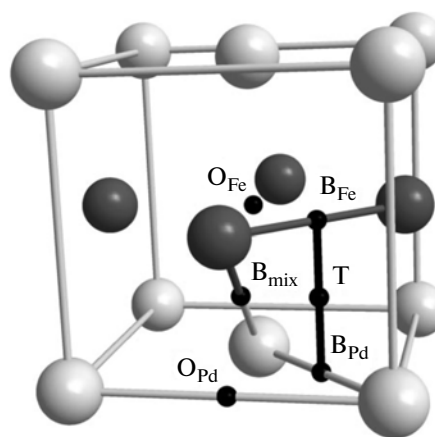


Fig. 1. Schematic representation of atomic structure of $L1_0$ ordered FePd alloy and high-symmetry interstitial positions in it. Atoms of iron and palladium are shown as dark and light spheres, respectively; interstitial positions, as black dots.

atom with its “images” resulting from the application of periodic boundary conditions is avoided. On the other hand, strong restrictions on the maximum simulation cell size are imposed by significant computational time and computer resources as a result of explicitly accounting for d electrons of iron and palladium in calculations of the system energy. As a compromise, the calculations of hydrogen parameters were performed using a relatively small (32 metal atoms) supercell, which, however, provides an adequate description of the behavior of interstitial hydrogen.

In addition to the supercell size, the convergence of results depends on the adequacy of selection of calculation parameters, such as the maximum considered kinetic energy of electrons (so-called cutoff energy E_{cut}) and the position and number of points in the Brillouin zone used for integration in the reciprocal space. These parameters were estimated using the smallest supercell (2 atoms of Fe + 2 atoms of Pd) and for the two most widely used approximations of the exchange–correlation functional—local density approximation (LDA) and generalized gradient approximation (GGA) [5].

Figure 2 illustrates the total energy as a function of the cutoff energy and the number of k points for the LDA approximation (the results obtained for the GGA approximation are similar). As can be seen in Fig. 2a, convergence of the total energy is achieved for $E_{\text{cut}} \geq 450$ eV. Correspondingly, further convergence estimates and all subsequent calculations of hydrogen parameters in the FePd system were performed with the value of cutoff energy $E_{\text{cut}} = 450$ eV. To study the convergence of the total energy of the system as a function of the number of k points, the Brillouin zone was sampled according to the Monkhorst–Pack scheme [6] with the grid varying from $6 \times 6 \times 6$ to $20 \times 20 \times 20$. Figure 2b illustrates that, for the smallest size

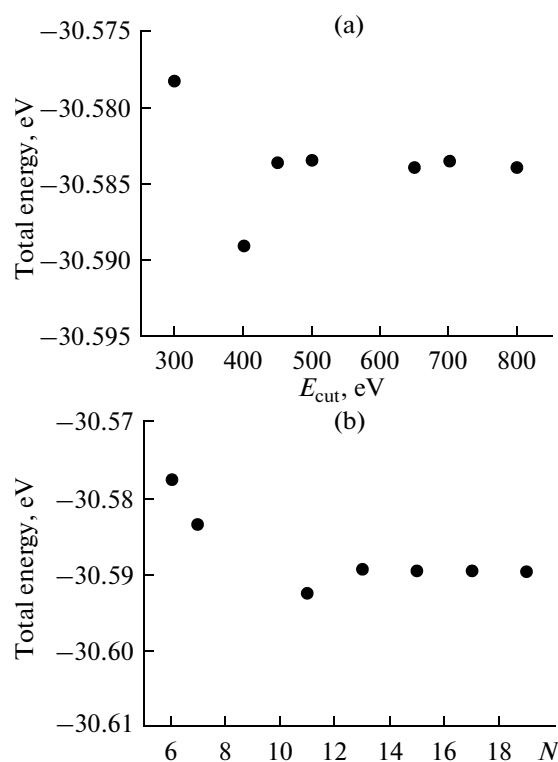


Fig. 2. Total energy of four-atom FePd simulation cell as a function of cutoff energy E_{cut} (a) and of the number of k points in the Monkhorst–Pack grid $N \times N \times N$ (b).

supercell, the convergence is achieved for the Brillouin zone grid containing $15 \times 15 \times 15$ points. With the increase in simulation cell size, the required density of the Brillouin zone grid can be decreased. In particular, for the supercell containing 32 atoms ($2 \times 2 \times 2$ elementary cells), the convergence is already achieved for the $8 \times 8 \times 8$ grid.

The effect of addition of a hydrogen atom on the convergence of total energies was examined using 32-atom cell with the hydrogen atom in the O_{Pd} position (Fig. 1). The sampling of the Brillouin zone was performed by applying the Monkhorst–Pack scheme with grids from $8 \times 8 \times 8$ to $14 \times 14 \times 14$. Table 1 summarizes the results of calculations for the GGA approximation. As fol-

Table 1. Total energy (in eV) and total magnetic moment (in Bohr magnetons) for 32-atom supercell of FePd alloy containing hydrogen atom in O_{Pd} position

Number of k points	Total energy, eV	Total magnetic moment, μ_B
$8 \times 8 \times 8$	-220.978	52.41
$10 \times 10 \times 10$	-220.980	52.38
$11 \times 11 \times 11$	-220.981	52.39
$12 \times 12 \times 12$	-220.979	52.40
$14 \times 14 \times 14$	-220.979	52.39

lows from the table, the $8 \times 8 \times 8$ grid provides convergence of the total energy and total magnetic moment of the system in both the absence and the presence of a hydrogen atom in the cell.

Therefore, further calculations for various positions of interstitial hydrogen were performed with the cutoff energy $E_{\text{cut}} = 450$ eV and Monkhorst–Pack sampling with the grid density of $8 \times 8 \times 8$. We applied only the GGA approximation.

RESULTS AND DISCUSSION

The calculations of equilibrium lattice constants, c and a , were performed with the smallest supercell, consisting of four metal atoms. The sampling of the Brillouin zone involved a Monkhorst–Pack $15 \times 15 \times 15$ grid, in agreement with the aforementioned convergence test. Relaxation was performed until all residual forces became lower than 0.01 eV/ \AA^3 , and the external pressure achieved reasonably low values (<5 MPa). The performed calculations predict that the equilibrium FePd:L1₀ lattice constant has the value of $a = 3.86$ \AA , and the c/a ratio corresponds to 0.98, in good agreement with the experimental data ($a = 3.852$ \AA , $c/a = 0.97$ [7]). These values were applied in all subsequent calculations.

According to the performed calculations, without hydrogen the energy per (Fe–Pd) atom pair equals -13.6 eV. The ground state of the system is ferromagnetic, with total magnetic moment per (Fe–Pd) atom pair $\mu = 3.3 \mu_B$, where μ_B is the Bohr magneton. The latter agrees both with the earlier theoretical calculations performed under similar calculation conditions [8] and with the available experimental data [9].

The considered interstitial hydrogen configurations in the ordered FePd alloy are shown in Fig. 1. They include two octahedral positions O_{Fe} and O_{Pd} located in the monatomic Fe and Pd planes, respectively; tetrahedral interplane position T; and three additionally considered positions B_{Fe} , B_{Pd} , and B_{mix} . The positions B_{Fe} and B_{Pd} are located at the midpoints of the bonds connecting atoms within the Fe and Pd planes, respectively, whereas B_{mix} corresponds to the midpoint of the bond between neighboring Fe and Pd atoms.

Table 2. Hydrogen solution energy U (in equilibrium with molecular gas H_2) and the change in total magnetic moment $\Delta\mu$ of simulation cell (with respect to magnetic moment change in O_{Fe} , $x = 0.77 \mu_B$) upon addition of hydrogen atom in various interstitial positions

Position	U , eV	$\Delta\mu/\mu_B$
O_{Fe}	0.16	x
O_{Pd}	0.29	$x + 0.18$
B_{Fe}	0.77	$x - 0.17$
B_{Pd}	1.15	$x + 0.05$

According to the performed calculations, hydrogen added to the inter-plane positions T and B_{mix} drifts to the positions B_{Fe} and O_{Fe}, respectively, whereas the remaining four configurations are equilibrium and stable with respect to small displacements of the hydrogen atom from local minima of potential energy. The values of hydrogen solution energy are summarized in Table 2. The hydrogen solution energy U was estimated using the following equation:

$$U = E_{\text{tot}}(\text{FePd} + \text{H}) - E_{\text{tot}}(\text{FePd}) - E_{\text{ref}}(\text{H}),$$

where $E_{\text{tot}}(\text{FePd} + \text{H})$ and $E_{\text{tot}}(\text{FePd})$ are the total energies of the simulation cells with and without hydrogen atoms, and $E_{\text{ref}}(\text{H})$ is the energy of a hydrogen atom outside of the alloy. The latter obviously depends on which type of hydrogen (atomic or molecular) in the environment is considered. For typical experimental conditions, when hydrogen solubility is determined in equilibrium with molecular hydrogen gas under pressure, the most adequate for $E_{\text{ref}}(\text{H})$ is half of the energy of a hydrogen molecule. In the framework of the employed calculation approximations, we obtain $E_{\text{tot}}(\text{FePd}) = -217.86$ eV and $E_{\text{ref}}(\text{H}) = -3.4$ eV.

The most energetically favorable position for hydrogen in FePd is the octahedral position O_{Fe}, but the octahedral position O_{Pd} is only slightly (by 0.13 eV) worse in energy. At the same time, the stable positions at the midpoints of interatomic bonds have markedly higher energies. In other words, the interstitial hydrogen in the ordered FePd alloy should be predominantly positioned in the Fe planes and, to a lesser extent, in the Pd planes. The preferential hydrogen location in octahedral sites agrees with the general trend for FCC metals [10]. It should also be noted that, even in the most energetically favorable position, the energy of hydrogen dissolution in FePd is positive, so that the process of saturation of the ordered alloy with hydrogen is endothermic.

In addition to total energy of the crystal, the addition of a hydrogen atom to an interstitial position results in modification of the magnetic moment (Table 2). In the most energetically favorable position, this change is approximately $\Delta\mu \approx 1 \mu_{\text{B}}$. The change in the magnetic moment of the alloy upon addition of a hydrogen atom implies the possibility of modification of the energy of hydrogen dissolution by application of a magnetic field.

CONCLUSIONS

The solubility of hydrogen in various interstitial positions in L1₀ ordered FePd alloy was studied using

first-principles methods. It is shown that the predominant positions of hydrogen localization in the solid solution are octahedral location in the Fe and Pd planes, the hydrogen position in the Fe plane being 0.13 eV more favorable than in the Pd plane. It is also shown that addition of a hydrogen atom to an FePd crystal results in modification of the magnetic moment by approximately one Bohr magneton, indicating the potential capability to control the hydrogen dissolution by application of an external magnetic field.

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