



The adsorption of hydrogen on face centered tetragonal FePd surfaces

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Received 22 March 2004; received in revised form 19 April 2004; accepted 28 April 2004 by E.L. Ivchenko

Available online 13 May 2004

Abstract

Adsorption of hydrogen on the ordered FePd face centered tetragonal alloy is investigated using a tight binding theoretical method. The changes in the electronic structure and bonding in the (100), (110) and (111) surfaces are analyzed. A simplified model for H diffusion to the bulk is also developed. The H-surface bond is achieved at the expense of the metal–metal bond being the Pd–Pd the more affected in the (100) and (110) cases.

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PACS: 73.20At; 73.20Ht; 71.20Be

Keywords: A. Surface and interface; A. Transition metal alloy; D. Electronic structure; D. Adsorption

1. Introduction

Transition metals (TM) bimetallic surfaces might exhibit chemical and catalytic properties that are very different from those of the pure metal surfaces [1]. Recently, extensive studies have been carried out on binary alloy surfaces both experimentally [2] and theoretically [3]. TM alloys consisting of a combination of ‘early’ and ‘late’ TM with a significantly different d-band occupation are of the particular interest not only because of their catalytic properties but also from a basic Surface Science point of view [2]. The practical uses of metal–hydrogen system include the ability of some metals and alloys to store hydrogen [4].

It is well known that the changes in the electronic structure of a Pd (111) surface through alloying with an early TM have dramatic effects on its surface chemical reactivity [5].

The interaction of hydrogen with the B2TiFe (001) and (110) surfaces and the changes in the electronic structure have been reported by Lee et al. [6]. The formation of surface oxide layer on the TM can be prevented by the usage of a thin layer of Pd as a cover [7]. It is assumed that Pd

coating or alloying will be beneficial for hydrogen uptake because the Pd is a catalytically active element [8]. The absorption of hydrogen on TiFe surface covered by a Pd monolayer has been studied using the full potential augmented plane wave method (FP-LAPW). The results show that in all considered cases H is located below the Pd surface. Furthermore, hydrogen located between Fe atoms can cause a weakening of the interatomic bonds [9].

On the other hand, Pd and its alloys have been extensively studied because they absorb hydrogen reversibly [10].

Nowadays, great attention has been paid to binary and ternary Pd alloys [11]. Hayashi et al. have reported experiments where Pd-coated Fe films show practically null permeability to hydrogen [12–15]. That is the reason why interfacial Fe–Pd studies have a critical technological importance. Furthermore, Fe/Pd multilayers are of particular interest because of an abnormally Pauli susceptibility of the Pd atoms. There is no visible interdiffusion of Fe into the Pd layers either. However, at higher growth temperatures an essential interdiffusion of Fe into Pd has been reported [16].

The aim of the present paper is to study the effect of hydrogen on the metal–metal bond on different surfaces. There are two stable 1:1 structures for Fe–Pd alloys. One is called the high temperature phase which is face-centered

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cubic (fcc); and the other, the low temperature phase which is face-centered tetragonal (fct). We have focused our research on the fct structure.

2. Computational details

Our calculation was performed using the atom superposition and electron delocalization tight-binding method (ASED–TB) [17]. This is an approximate molecular orbital scheme implemented within the modified YAeHMOP program [18]. Double zeta expansion of the metal d orbitals was employed. The parameters are those listed in our previous paper [19]. The off diagonal Hamiltonian matrix elements were computed with the modified Wolsberg–Helmholtz formula [20]. A manually generated set of 32 k was used to sample the irreducible wedge of the Brillouin zone defined by $0 \leq k_a \leq \pi/2$, $0 \leq k_b \leq \pi/2$, $0 \leq k_c \leq \pi/2$ for a tetragonal supercell.

The energy was computed as the difference ΔE between the Fe–Pd–H composite system when the H atom is either absorbed or adsorbed at a specified geometry and when it is far away from the Fe–Pd alloy. It can be expressed as

$$\Delta E_{\text{Total}} = E(\text{FePdH}) - (E(\text{FePd}) + E(\text{H}))$$

where E is the electronic energy, $E(\text{FePd})$ corresponding to the pure surface alloy and $E(\text{H})$ is the hydrogen 1s ionization energy.

To understand the Fe–Pd–H interaction we used the concept of density of states (DOS) and crystal orbital overlap population (COOP) curves. The DOS curve is a plot of the number of orbital per unit volume per unit energy. The COOP curve is a plot of the overlap population weighted DOS vs. energy. The integration of the COOP curve up to the Fermi level (E_F) gives the total overlap population of the bond specified and it is a measure of the bond strength.

The Fe–Pd alloy is a CuAu(I)-type structure with lattice parameters $a = 3.86 \text{ \AA}$ and $c = 3.73 \text{ \AA}$ [21,22]. In metallurgical nomenclature, it is known as the $L1_0$ phase. The crystal space group is $P4/mmm$. The structure of the alloy is shown in Fig. 1.

We have studied the H absorption on the (100), (110) and (111) surfaces (Fig. 1). The thickness of the slab (five layers) is such that it approximates the electronic structure of the 3D solids in the most inner layer. We have mapped the H adsorption energy on each surface at 0.01 \AA steps. After that, the H-surface height was optimized. We have also studied the absorption energy along a linear path along the slab layers, in a direction perpendicular to the surfaces.

3. Results and discussions

The most stable plane for the H adsorption is the (100),

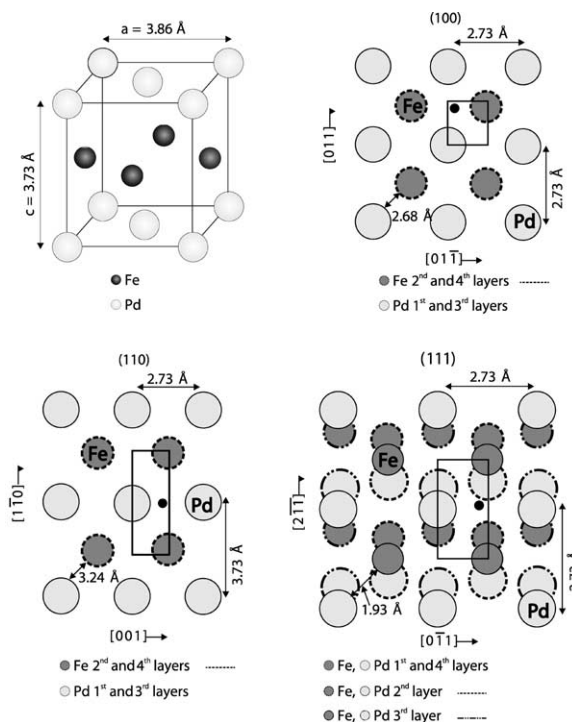


Fig. 1. Schematic view of the FePd fct structure and the planes (100), (111) and (110). The energy was evaluated on the region inside the box. The small circle in black indicates the H location.

which is close in energy to the (110). It can be seen in Fig. 1 that these planes have similar adsorption geometries being the (110) much more open.

The H is located at 0.80 \AA above the top metal layer on the (100) surface in a bridge position. However, in the (110) case the H is located 0.80 \AA below these metal layers, also in a bridge position. The H-adsorption on the (111) plane is almost 50% less stable in energy than in the former planes.

The computed Pd–H distance on the (100) plane is 1.578 \AA , which is consistent with the sum of the atomic radii. The optimum Pd–H distance obtained by LEED for the fcc Pd(111) is 1.78 \AA . For a surface fcc hollow site on pure Pd(111) is from 1.78 to 1.80 \AA , which corresponds to a vertical height of 0.80 – 0.85 \AA for H [23]. Experimental photoemission measurements show that the H atoms prefer the hollow site at a bonding Pd–H distance of 1.67 \AA [24]. Also, our computed Pd–H distances are close to that reported by Skottke et al. [26]. The energy difference between H on Pd(001)—at 1.6 \AA above the top metal layer—and H on the alloy surface gives 0.84 eV , which means a 16.5% change.

The computed Fe–H distance is longer than those of H on pure bcc Fe(110) [25]. This fact is not unexpected because Fe's belongs to the second metal layer in the alloy.

The total energy curves for H-alloy interactions when the H diffuses from the surface through the metal layers are

shown in Fig. 2. The represented energies are relative to the minimum value for H location. The activation barriers are much higher going in from the (111) surface. The (100) and (110) cases are similar, with activation barriers from 0.81 to 1.20 eV. This activation barriers are indicated in Fig. 2.

Let us discuss first the electronic structure of the Fe–Pd alloy free of hydrogen. In the DOS of the reference bulk solids (Fe bcc and Pd fcc), the metals d states form a band between -12 and -7 eV for Fe and between -13 and -10 eV for Pd [19]. The detailed compositions of states for the FePd fct alloy are shown in Table 1. In the alloy, the Fe atoms become positively charged and the Pd and H atoms negatively charged in all considered surfaces.

The orbital composition of Fe and Pd atoms shows little changes after H adsorption. However, in the FePd(110)–H case the Pd 5s orbital changes by ≈ -0.30 with respect to the clean surface. The Fe atoms remain the same except in the (111) case, in which the 4p and 3d populations decrease by 0.15 and 1.00, respectively.

The Total DOS for the planes (100) and (110) are similar being the (111) case much more dispersed (Fig. 3(a)). A comparison with the hydrogen free alloy shows that the most prominent feature is hydrogen induced split off state below the d metal band (Fig. 3(b) and (c)). This state is more developed in the Pd projection in all the surfaces (Fig. 3(c)). The (100) and (111) planes show Fe–Pd hybridization which can be seen in the Fe projections. The Total DOS for (110) surface is almost the sum of the individual contributions.

Regarding the bonding, Fig. 4 shows the COOP curves for metal–metal atoms close to H and the metal–H bonds. The interaction between Pd and H is stronger than that of Fe and H. There is almost no Fe–H bonding on (100) and (110)

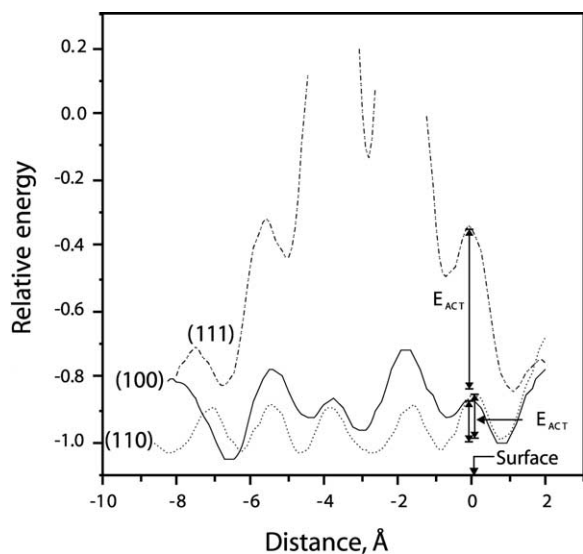


Fig. 2. H-adsorption/absorption relative energy vs. depth in a perpendicular direction to the slab surface. The arrows indicate the activation barriers (ΔE_{ACT}).

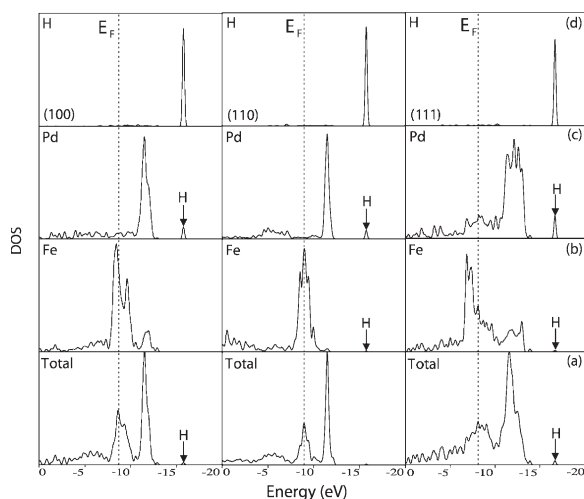


Fig. 3. Total DOS (a), Fe PDOS (b), Pd PDOS (c), and H PDOS (d) for all surface considered after H adsorption.

surface, however in the (111) plane the Fe–H overlap population (OP) is 1/3 of the Pd–H OP. The Pd–H interaction is always almost bonding. The H–metal bond is achieved at the expense of weakening the metal–metal bond. For the (100) surface, the Fe–Fe bond OP is not affected (which is consistent with no Fe–H bond and a long metal–H distance of about 2.994 Å, Table 1). In addition, the intermetallic Fe–Pd bond decreases 27% while the Pd–Pd bond decreases 70%. A similar Pd–H OP is obtained on the (110) plane with a small Fe–H OP. In this plane, the Fe–Fe bond decreases only 1%. The intermetallic bond is more affected than in the former case with a decrease of 73% in this OP. On the other hand, the Pd–Pd bond OP is similar to

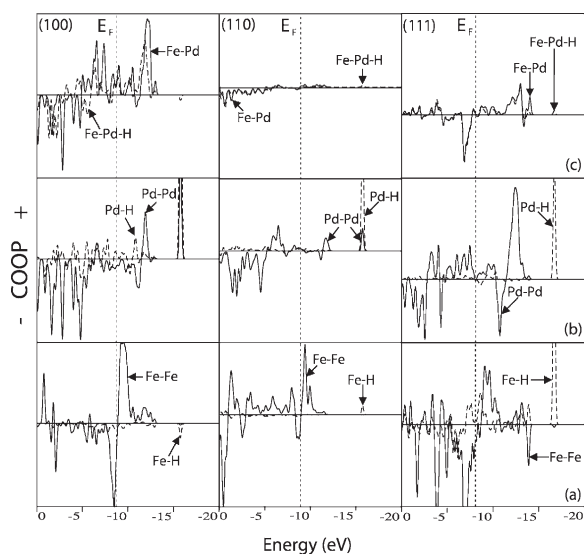


Fig. 4. COOP curves Fe–Fe and Fe–H (a); Pd–Pd and Pd–H (b); Fe–Pd and Fe–Pd–H (c) for all the surfaces after adsorption. The scale in (111) plane has been magnified for a better viewing.

Table 1
Electron density, overlap population, charge and distances for FePd fct structure after H adsorption

Structure	Electron density			Charge	OP ^a	%ΔOP ^b	Distances (Å)	E _F (eV)	
	s	p	d						
FePd(100)–H									
Fe–H	H	1.32	0.00	0.00	–0.319	0.000	–	2.994	–8.71
	Fe	0.58	0.21	5.02	2.190				
Pd–H	H	1.32	0.00	0.00	–0.319	0.427	–	1.578	
	Pd	0.73	0.69	9.63	–1.059				
Fe		0.58	0.30	5.92	1.194	0.243	–	2.729	
Fe–Pd	Fe	0.58	0.21	5.02	2.190	0.144	–27	2.684	
	Pd	0.73	0.69	9.63	–1.059				
Pd		0.70	0.70	9.67	–1.068	0.062	–70	2.729	
FePd(110)–H									
Fe–H	H	1.28	0.00	0.00	–0.281	0.039	–	2.590	–8.93
	Fe	0.52	0.19	5.33	1.950				
Pd–H	H	1.28	0.00	0.00	–0.281	0.451	–	1.507	
	Pd	0.69	0.37	9.86	–0.926				
Fe		0.46	0.18	5.38	1.976	0.486	–1.2	2.729	
Fe–Pd	Fe	0.52	0.19	5.33	1.950	0.016	–72	3.576	
	Pd	0.69	0.37	9.86	–0.926				
Pd		0.72	0.32	9.88	–0.922	0.110	–67	2.729	
FePd(111)–H									
Fe–H	H	1.16	0.00	0.00	–0.165	0.116	–	1.525	–8.10
	Fe	0.52	0.29	5.26	1.926				
Pd–H	H	1.16	0.00	0.00	–0.165	0.284	–	1.434	
	Pd	0.68	0.78	8.77	–0.227				
Fe		0.50	0.17	4.22	3.456	0.062	–25	2.463	
Fe–Pd	Fe	0.50	0.17	4.22	3.456	0.295	–11	1.930	
	Pd	0.68	0.78	8.77	–0.227				
Pd		0.91	0.76	9.57	–1.248	0.633	–	1.985	

^a OP: overlap population.

^b %ΔOP: percentage change in the OP of a specified bond when H is adsorbed. The negative sign indicates a decrease in the strength of the bond.

that of the (100) plane. Finally, when H is adsorbed on the (111) surface, the Pd–H distance is shorter than the other cases. However, the Pd–H OP is ≈40% lower. In this plane, H is also close to the Fe atom developing an OP of 0.116. Both Fe–Fe and Fe–Pd OP decrease while the Pd–Pd bond is not changed. This fact is consistent with a higher hybridization of Fe and Pd in the (111) surface which is a consequence of the geometrical array shown in Fig. 1. Accordingly, more Fe and Pd are in contact at shorter distance (1.930 Å).

The present calculations allow to predict the preferable surface location of H and orbital composition of electronic states. The H bonds mainly to Pd atoms and the more affected metal–metal bond is Pd–Pd on the (100) and (110) surfaces. The differences between hydrogen absorption/adsorption relative energy for the considered planes is a consequence of the major differences in the geometries of the planes.

Acknowledgements

This work was supported by ANPCyT (PICT 12-09857B), UNS-Física and Fundación Antorchas. A Juan and N. Castellani are members of CONICET. E. Gonzalez and P. Jasen are fellows of that organization. We thank the valuable suggestions made by the referee.

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