

Comparison of Bonding Characteristics of Hydrogen in Ti_2Pd and Pd_2Ti Alloys

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The electronic structure and bonding in Ti_2Pd and Pd_2Ti alloys with and without hydrogen as an interstitial atom were studied by performing extended Hückel tight-binding band calculations. The hydrogen absorption near an octahedral site is found to be a favorable process in Ti_2Pd rather than in Pd_2Ti . In metal hydrides, the metal-hydrogen bonding contribution is crucial to the stability of the system. The stronger interaction of hydrogen with Ti atoms in Ti_2PdH_2 than with Pd atoms in Pd_2TiH_2 is analyzed by perturbation theory.

Key Words : Hydrogen storage materials, Electronic structure, Extended Hückel calculations

Introduction

There is a substantial technological interest in the inter-metallic compounds as materials for hydrogen storage, particularly for a viable hydrogen fuel in vehicular applications.¹⁻⁴ Compared with other technologies such as gas compression or liquefaction, solid-state materials such as metal alloys can store hydrogen at relatively low pressure and ambient temperatures.

The traditional interstitial metal hydrides have been successfully utilized.⁵ Over the past few decades, a major challenge which still remains is to identify optimal inter-metallic for such purposes. The hydrogen sorption properties of these alloys are very much dependent on the constituents and metal-hydrogen bonding interactions play a major role for the stability of the hydrides. A better understanding of the role of individual alloy constituents in relation to the presence of hydrogen and the subsequent influence on electronic and structural properties may eventually lead to more efficient devices with higher storage capacities.

Several members of the A_2B intermetallic compound family with the tetragonal $MoSi_2$ -type crystal structure can absorb hydrogen to produce ternary metal hydride phases.⁶ We use the Ti-Pd intermetallic compounds, Ti_2Pd and Pd_2Ti , as model systems. Ti_2Pd is known for its hydrogen storage capability,⁷ whereas for Pd_2Ti , this property still needs to be proven.^{8,9} The compound Ti_2Pd readily forms a hydride to give a nominal composition Ti_2PdH_2 . Surprisingly, Pd_2Ti does not form a hydride under normal condition although both Ti and Pd are good hydride forming metals. It is of interest to try to understand the reasons for the hydrogen inertness of this compound.

In the present work we examine the origin of this puzzling behavior. It will be useful to eliminate the possibility of geometrical considerations first, since hydrogen occupation is not restricted by geometrical criteria for the minimum hole size and intersite distance in the lattice of Pd_2Ti . Thus, the different hydriding behaviors of the two intermetallics, Ti_2Pd and Pd_2Ti , can be understood in terms of their electronic structures and bonding characteristics. Since Pd_2TiH_2 does

not exist, its crystal structure is assumed to reveal the factors that disfavor hydride formation in this compound. These computational results may be helpful for designing new A_2B -type hydrogen storage alloys with high efficiency.

We use the extended Hückel tight-binding (EHTB) method^{10,11} to determine the influence of hydrogenation on the electronic structures of the Ti_2Pd and Pd_2Ti alloys and to discuss the electronic consequences of the relevant orbital interactions of incorporating H with the intermetallics. Double zeta expansions of the metal d orbitals were employed; the parameters used for all atoms are listed in Table 1. Although the EH method is quite approximate, the analysis of orbital interactions by perturbation theory seems to be reasonably reliable. The CAESAR package¹² was used to calculate the density of states (DOS) and the crystal orbital overlap population (COOP) spectra of pure and hydrogenated Ti_2Pd and Pd_2Ti structures. While the DOS provides information about the band structure and the distribution of various orbitals in energy, the COOP curves describe the nature of the bonds between constituent atoms, with positive and negative values indicating bonding and antibonding states, respectively. Looking at the COOP, we may analyze the extent to which specific states contribute to a bond between atoms.

Crystal Structure

Both Pd_2Ti and Ti_2Pd crystallize in the $MoSi_2$ -type

Table 1. Parameters used for EHTB calculations

Atom	Orbital	H_{ii} (eV)	ζ_1	ζ_2	c_1	c_2
Ti	4s	-6.3	1.5			
	4p	-3.2	1.5			
	3d	-5.9	4.55	1.40	0.4206	0.7839
Pd	5s	-7.32	2.190			
	5p	-3.75	2.152			
	4d	-12.02	5.983	2.613	0.5535	0.6701
H	1s	-13.6	1.3			

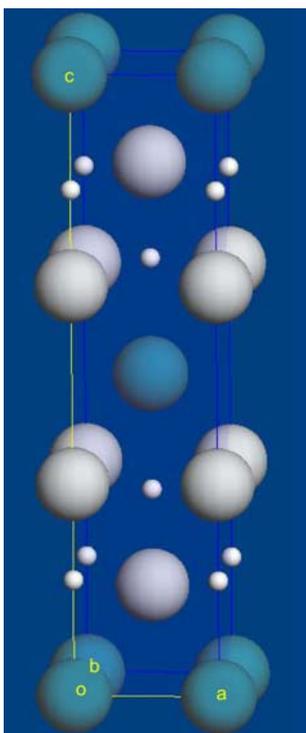


Figure 1. The tetragonal unit cell of Ti_2PdH_2 . Large white, large blue, and small white spheres are for Ti, Pd, and H, respectively.

structure (space group $I4/mmm$). The latter compound has a body-centered tetragonal structure with lattice constants $a = 3.09 \text{ \AA}$ and $c = 10.054 \text{ \AA}$.¹³ There are two formula units of Ti_2Pd per unit cell with a single $2a$ Pd site $(0,0,0; 0.5, 0.5,0.5)$ and a single $4e$ Ti site $(0,0,z; 0,0,1-z; 0.5,0.5,0.5+z; 0.5,0.5,0.5-z)$. The Ti ($4e$) and Pd ($2a$) sites have an axial symmetry around c -axis (see Figure 1).

The hydrogen atom occupies an octahedral interstitial site formed by four titanium atoms in its base bicapped with Ti and Pd atoms, which provides an optimum environment satisfying the geometrical criteria for hydride formation. Such criteria have been established empirically.^{14,15} They imply minimal values for the H-H distances and the interstitial hole radii of about 2.1 and 0.4 Å , respectively, for stable hydrides. Examination of the unit cell shows, as indicated in Figure 1, that there are four octahedral sites per unit cell surrounded completely by metal atoms. These are found to be the preferred sites for hydrogen occupation.¹⁶ A complete filling of those sites in the lattice corresponds to a composition of Ti_2PdH_2 . For the purpose of comparison with the case of Ti_2PdH_2 , we assume that the hydride form of hypothetical Pd_2TiH_2 can be stabilized in MoSi_2 -type structure. Ti_2Pd and Pd_2Ti retain their MoSi_2 structure when they absorb hydrogen, but the insertion of hydrogen in the metal matrix causes highly anisotropic lattice changes; a large expansion along c and a small contraction in the a direction.¹⁶

In order to understand why Ti_2Pd forms a stable hydride in contrast with Pd_2Ti , the same MoSi_2 -type structure for these hydrides was adopted in the calculations. The theoretically

Table 2. Lattice constants a and c (Å) and atomic parameter z of Ti-Pd intermetallics. For Ti_2Pd and its hydride, Pd is in $2a$ and Ti and H in $4e$ positions. The Ti and Pd positions are exchanged in Pd_2Ti and its hydride.

Parameter	Ti_2Pd ¹³	Pd_2Ti ⁸	Ti_2PdH_2 ¹⁶
a	3.09	3.24	2.85
c	10.054	8.48	12.508
z (Ti)	0.333		0.3406
z (Pd)		0.333	
z (H)			0.8139

determined cell and structure parameters for the investigated compounds, along with the experimental values obtained from X-ray diffraction measurements, are given in Table 2.

Results and Discussion

Electronic Structure of the Intermetallic Compounds Ti_2Pd and Pd_2Ti . We start with the pure intermetallics. The total and projected density of states (DOS) for Ti_2Pd and Pd_2Ti are shown in Figure 2. The Pd 4d states are found at low energies with the main peaks corresponding to rather localized states situated between -13 and -11 eV, while the Ti 3d states, which are more delocalized, result in a broad structure located at higher energies between -9 and -1 eV. This feature is reminiscent of the relative position of the atomic d levels. The Ti 3d and Pd 4d states are of course fairly mixed, and hybridized with metal s, p states. This

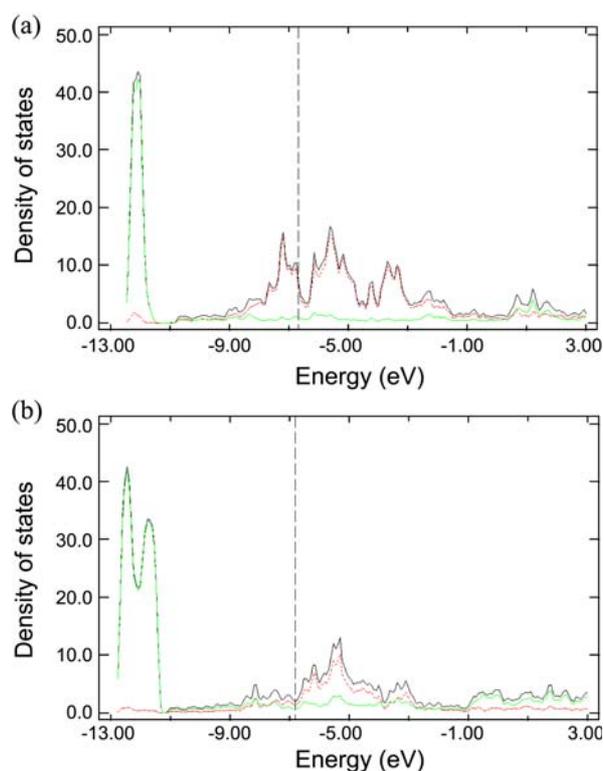


Figure 2. Total and projected DOS plots on Ti atoms (red line) and Pd atoms (green line) of (a) Ti_2Pd and (b) Pd_2Ti alloys. The Fermi level refers to the vertical dashed line.

mixing leads to a partly covalent character of the Ti-Pd bonds. The Ti to Pd charge transfer and the filling of the Pd d bands require that a late Pd atom has as many Ti atoms as its nearest neighbors as possible to facilitate the charge transfer and bonding interaction. The contribution of the Ti states at the Fermi level (E_F) is larger than that of the Pd states. There are two common features in the DOS profiles for these compounds, indicating that the Pd 4d bands are fully occupied and the states near the Fermi level are mainly the broad Ti 3d bands. The bandwidth of the filled Pd d bands in Pd_2Ti is much wider than that of Ti_2Pd . This is due to the more Pd-Pd interactions between the metal atoms in the unit cell of Pd_2Ti .

Regarding the bonding, the COOP curves in Figure 3 show that a substantial part of Ti-Ti bonding states in Ti_2Pd is occupied at E_F (Fig. 3(a)), while in Pd_2Ti both the lower Pd-Pd bonding and the upper Pd-Pd antibonding states are well below E_F (Fig. 3(b)). Therefore, the Ti-Ti interaction in Ti_2Pd is much higher than Pd-Pd one in Pd_2Ti . The Ti-Pd, Ti-Ti, and Pd-Pd overlap populations are summarized in Table 3.

Electronic Structure of the Hydrides Ti_2PdH_2 and Pd_2TiH_2 . In Figure 4, we show the DOS profiles of Ti_2PdH_2 and Pd_2TiH_2 . One can see that absorption of hydrogen atoms within the host intermetallic lattices introduces new s bands associated with H atoms in the low-energy region (from -16.5 to -14 eV). The H s states have moderate mixing with the d states from the Ti and Pd atoms, reflecting the

Table 3. Overlap population (OP), charge, and distances for Ti_2Pd and Pd_2Ti alloys

Compound	Atom or Bond type	Charge	OP	Distance (Å)
Ti_2Pd	Ti	0.61		
	Pd	-1.22		
	Ti-Ti		0.379	2.749
	Ti-Pd		0.170	2.755
Pd_2Ti	Ti	1.98		
	Pd	-0.99		
	Pd-Pd		0.098 ^a	2.689/2.832
	Pd-Ti		0.180 ^a	2.693/2.824

^aOP: Average overlap population

hydrogen-metal interaction. This low-energy bonding states show a strong hydrogen character, while the corresponding high-energy antibonding states contain more pronounced Ti and Pd contributions. In both cases, a new structure associated with metal-hydrogen bonding states appears below the Pd 4d bands. For Ti_2PdH_2 , they are mainly derived from the Ti-H interaction which leads to an important energy lowering of the Ti 3d states located above the Fermi level in the pure intermetallic Ti_2Pd , an important factor which is crucial to the stability of the hydride. In this hydride, the Ti-H interaction is strong enough to stabilize below E_F Ti d states that were mostly empty in the pure intermetallic compound. The contribution of Pd 4d to this bonding is very weak, even

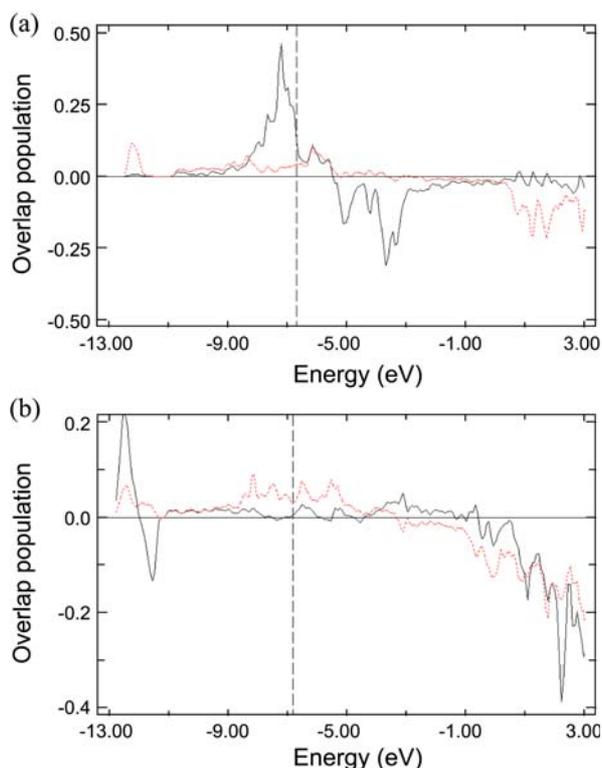


Figure 3. COOP plots of (a) Ti_2Pd and (b) Pd_2Ti alloys: a Ti-Ti bond of Ti_2Pd and a Pd-Pd bond of Pd_2Ti (black solid line) and a Ti-Pd bond (red dotted line). The Fermi level refers to the vertical dashed line.

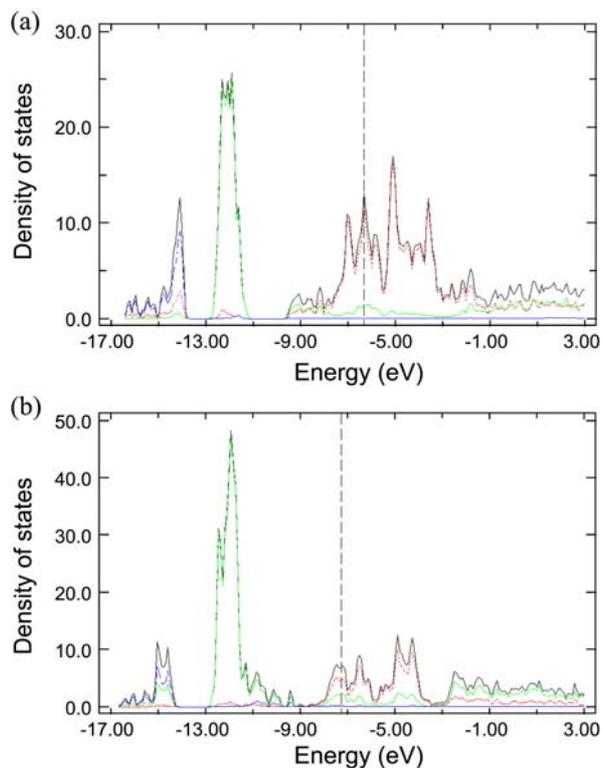


Figure 4. Total and projected DOS plots on Ti atoms (red line), Pd atoms (green line), and H atoms (blue line) of (a) Ti_2PdH_2 and (b) Pd_2TiH_2 hydrides. The Fermi level refers to the vertical dashed line.

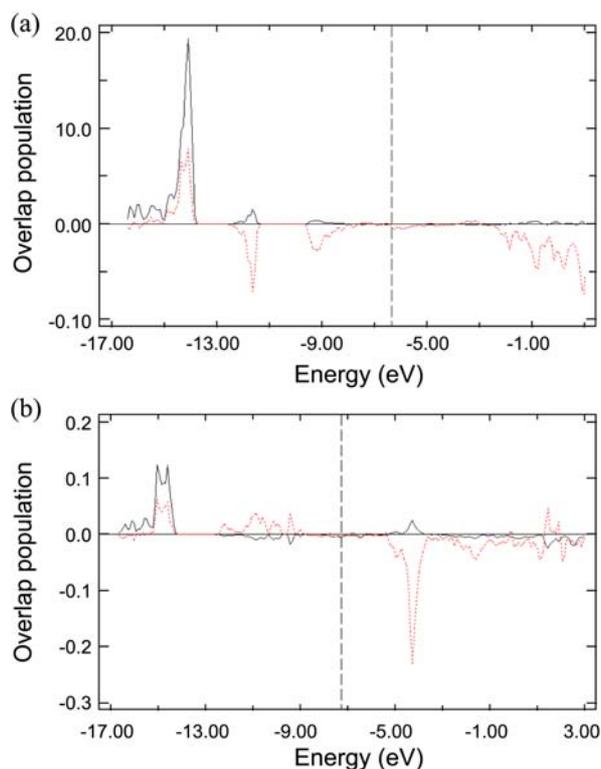
Table 4. Overlap populations (OP) for H-Ti and H-Pd bonds in Ti_2PdH_2 and Pd_2TiH_2 . BL denotes the bond length between two given atoms

Hydride	H-Ti		H-Pd	
	BL (Å)	OP	BL (Å)	OP
Ti_2PdH_2	2.042/1.932	0.128 ^a	2.327	0.002
Pd_2TiH_2	2.327	0.082	2.042/1.932	0.092 ^a

^aOP: Average overlap population

though it is lower in energy than Ti 3d states, as shown in Figure 4. This is due to a very low coordination number of H with Pd in the octahedral sites.

In hypothetical Pd_2TiH_2 the metal-hydrogen bonding states occur at lower energies than in Ti_2PdH_2 , which seems to be favorable for hydride formation. However, as seen in Figure 5, these states are formed from the interaction of hydrogen with the lower lying Pd 4d states; the antibonding counterparts also lie below E_F . Therefore, there is no net gain in energy to stabilize the hydride. This is in contrast to the case of Ti_2PdH_2 where mostly empty Ti 3d states in the pure intermetallic Ti_2Pd are lowered in energy to form metal-hydrogen bonding states. The most important difference observed in the bonding of H with Pd and Ti is that the Pd d states are already occupied in the pure intermetallic while a majority of the Ti d states are located above E_F . The occupation of metal-hydrogen antibonding states in hypothetical Pd_2TiH_2 thus does not favor the hydride formation.

**Figure 5.** COOP plots for Ti-H (black solid line) and Pd-H (red dotted line) of (a) Ti_2PdH_2 and for Pd-H (black solid line) and Ti-H (red dotted line) of (b) Pd_2TiH_2 . The Fermi level refers to the vertical dashed line.

These results are in good agreement with the calculated energy of hydrogen absorption which is strongly endothermic (123.1 kJ/mol H_2) for Pd_2TiH_2 .¹⁶

To gain a deeper understanding of the interaction between the host metal atoms and H atoms, we performed a Mulliken population analysis of the Ti_2Pd and Pd_2Ti hydrides. The theoretical results are listed in Table 4. The overlap populations (OP) in Table 4 demonstrate that the average value for H-Ti bonds in Ti_2PdH_2 is higher than that for H-Pd bonds in Pd_2TiH_2 , reflecting the stabilizing effect of titanium-hydrogen bonding. H increases its bond strength when H is absorbed in Ti-rich octahedral sites. Typically, a high positive OP value indicates strong covalent interaction. The COOP curves in Figure 5 show the bonding/antibonding nature of the interaction in question. Interactions between H and metal atoms are taken into account. Most Ti-H interactions show a bonding character below E_F and push its antibonding states above the E_F . It is likely that this factor is important in determining the stability of the lattice with the interstitial H. Many Pd-H antibonding states wind up higher in energy than the Pd d-block states in the intermetallic, but still below the Fermi level after interaction with the H. These levels are populated. The result is that the Pd-H bonding is weakened, as attested to by the lower OP value (Table 4). It should be emphasized that negative Pd-H COOP occurs below E_F . This prevents effective bonding between Pd and H atoms at the octahedral interstitial sites with five Pd neighbors in Pd_2TiH_2 and thus plays a role in anomalous absence of hydride formation in Pd_2Ti .

Conclusion

In this study, we find that the difference in the H absorption properties of Ti_2Pd and Pd_2Ti is related to the presence of both bonding and antibonding combinations of new dominant metal-hydrogen interactions below E_F that is unfavorable to the formation of the hydride. This occurs in Pd_2Ti , while in Ti_2Pd the Ti-H bond interaction leads to the pushing of its antibonding states above the E_F . Only the bonding combination remains filled. It can be suggested that this metal-hydrogen bonding should play a role in the stability of the alloy. Our results illustrate why Ti_2Pd forms a stable hydride and Pd_2Ti does not.

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