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# The influence of electronic structure on hydrogen absorption in palladium alloys

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## Abstract

The influence of the electronic structure and the lattice constant on hydrogen absorption in bulk Pd<sub>3</sub>M<sub>1</sub> (M = Cd, Ag, Au, Pd, Cu, Ni, Pt, Pb, Sn, Fe, Rh, Ru) has been studied by density-functional calculations. We have assumed face-centred cubic structure for all the alloys, and hydrogen has been placed in the octahedral site surrounded by six Pd atoms. We have calculated the absorption energy of hydrogen in the alloys, and found that the influence of the electronic structure is much more important than that of the lattice constant. The results demonstrate that Miedema's empirical rule is also satisfied in this system, i.e., the higher the binding energy of the host alloy, the less stable the hydride. We have also calculated the detailed electronic structures of the alloys and their hydrides. We found that more stable hydrogen absorption is correlated with the hydrogen 1s electrons, palladium s electrons, palladium s-like electrons and the palladium d electrons moving higher in energy towards the Fermi level. The two latter relations have previously been described for bulk systems and surfaces respectively, while this study is apparently the first to point out the correlation between the position of the hydrogen band and the stability of the hydride, i.e., the deeper the hydrogen band, the less stable the hydride.

(Some figures in this article are in colour only in the electronic version.)

## 1. Introduction

In our previous studies on hydrogen absorption in bulk palladium–silver alloys, maximum hydrogen solubility was found for the silver concentration is around 25% [1, 2]. Whether this is a geometric or an electronic effect is still a subject of debate in the literature. Since the lattice constant of Pd<sub>3</sub>Ag is larger than that of pure Pd, it has been suggested that a geometric effect may be the main reason for the higher absorption energy [3]. When two different absorption sites have the same co-ordination (in our case, as described below, the absorption sites are

always surrounded by six Pd atoms), different absorption energies may also be ascribed to an electronic effect caused by the next-nearest neighbours of the adsorption site. This would correspond to the ligand effect in the adsorption on alloy surfaces [4, 5]<sup>3</sup>.

In this paper, our main motivation is to understand the reason for the large hydrogen absorption energy in the Pd<sub>3</sub>Ag alloy (compared with the hydrogen absorption in the pure Pd). This is an unresolved and fundamental problem. This may be useful for guiding us to find a suitable element to make Pd-based alloys (or other metallic alloys) for the purpose of H storage or membrane separation. There has been some effort to study the stability of various metallic hydrides [6–12]. Gelatt *et al* [6] investigated the stability of hydrides in terms of the metal–hydrogen bonding band, the d-band shift and the shift of Fermi energy. Nørskov [7] proposed a formula for the heat of a solution based on the effective-medium theory, in which the chemical bonding between the hydrogen 1s and the metal 3d orbitals was taken into account. A recent study of the LaNi<sub>4</sub>M system (M=Mn, Fe, Co) shows that the hydride stability can be attributed to lattice expansion [8]. Another study of the TiMn system shows that hydride stability is primarily governed by the equilibrium volume and the bulk modulus of the host alloy [9]. A systematic analysis of the stability of MH<sub>x</sub> (M = alkali, earth alkali or transition metal hydrides) has demonstrated that the electronic structure of the host metal is a key factor in determining the stability of the hydride [12]. According to these previous studies, it seems that the stability of the hydride depends on either the electronic structure or the lattice expansion.

This study of Pd-based alloys shows that lattice expansion cannot increase the absorption energy of hydrogen significantly, and some of the hydrides with large lattice constants are even unstable compared with the gas phase of the H<sub>2</sub> molecule, indicating that the influence of the electronic structure on the stability of the hydrides may be more important than that of the lattice constant (geometric effect).

To get a better understanding of the significance of the geometric or electronic effect on the Pd<sub>3</sub>Ag alloy and related systems, we have performed density-functional theory (DFT) calculations on a series of Pd<sub>3</sub>M alloys (M = Ru, Rh, Pd, Ag, Cd, Sn, Pt, Au, Pb), and put hydrogen in such a way (surrounded by six Pd atoms) that the ‘ligand effect’ can be isolated. This made it possible to investigate four relations between the detailed electronic structure and the hydrogen absorption energy of these alloys and found that the electronic effect is indeed more important than that of geometry. One of these relations, that stating that the deeper the hydrogen band, the less stable the hydride, has not to our knowledge been described previously.

Due to the low mass of hydrogen, the zero-point (ZP) vibrational energy of H in the hydrides may be important and contribute significantly to the absorption energy. We have therefore performed quantum-mechanical calculations on the ZP vibrations of H in the octahedral site of the hydrides by solving the time-independent Schrödinger equation based on a three-dimensional adiabatic potential. For lower hydrogen concentrations, the phenomenon of self-trapping as a result of local lattice relaxations reportedly plays some role [13–17]. We did not consider this effect, but experiments have shown that this affects the ZP energy by <0.02 eV in the PdH system [1] (see figure 3(b) there). We thus expect that the self-trapping phenomenon does not influence our results significantly.

## 2. Model and simulation methods

For the alloy structures, experiments have shown that the majority of the binary alloys of Pd with neighbouring elements in the periodic table have face-centred cubic (fcc) lattices [18]. Among

<sup>3</sup> These papers explained that ‘ligand effects loosely describe changes in the chemical properties of the atoms in the surface due to alloys, while ensemble effects refer to changes in the catalytic properties of an ensemble of atoms in the surface when the chemical composition of the ensemble changes’.

them, Pd<sub>3</sub>Fe, Pd<sub>3</sub>Pb and Pd<sub>3</sub>Au (with some uncertainty) have L1<sub>2</sub> structure [19]. For the other alloys, either a precise knowledge is lacking or the structure is complicated. For computational convenience, L1<sub>2</sub> structure has been assumed for all the alloys (Pd<sub>3</sub>M<sub>1</sub>, M = Ru, Rh, Pd, Ag, Cd, Sn, Pt, Au, Pb). There are two types of octahedral sites for hydrogen occupation. One is surrounded by six Pd nearest neighbours and the other is surrounded by four Pd and two M nearest neighbours. We chose the first configuration (surrounded by six Pd) to isolate the ligand effect.

The density-functional calculations were performed using two packages: the Amsterdam density functional band-structure package (ADF-BAND) [20] and the Vienna *ab initio* simulation package (VASP) [21, 22]. The ADF-BAND uses linear combinations of atomic orbitals as basis functions. The core is frozen and described by numerical atomic orbitals (NAOs). The valence part is described by a combination of NAOs and Slater-type orbitals (STOs). The electron density is calculated at the local density approximation level, and the gradient corrections are included after convergence of the density. The exchange and correlation corrections are from Becke [23] and Perdew [24] respectively. Scalar relativistic effects have been included by the zeroth-order regular approximation [25].

In the ADF-BAND, in practice we use the frozen-core approximation, which may have some impact on the results if the frozen core is too large. We have checked for the effects of making the frozen core smaller, and concluded that this approximation has negligible effect on the resulting absorption energy and electronic structure. We have also checked carefully the total-energy convergence. All basis sets have triple zeta quality (the basis sets contain three basis functions for each valence electron). The basis functions for Pd, Cd, Ag, Au, Cu, Ni, Pt, Pb, Sn, Fe, Rh and Ru were frozen up to the 3d, 3d, 3d, 4f, 2p, 2p, 4f, 4f, 4p, 2p, 3d and 3d shells, respectively. The accurate quadratic tetrahedron procedure [26] was used for Brillouin-zone (BZ) integrations, and integration parameters were chosen to achieve convergence well within 50 meV.

We also used VASP to calculate the binding energy of the alloys for comparison. VASP carries out DFT calculations using Vanderbilt-type pseudopotentials [27] and a plane wave basis set. The functional is from Perdew and Wang [28]. BZ integrations were performed on an 8 × 8 × 8 mesh through the Monkhorst–Pack procedure [29]. The cut-off energy for the plane waves was chosen to be 400 eV for all the elements. The partial density of states (PDOS) evaluated by VASP depends on the Wigner–Seitz radius to some extent. To avoid possible artifacts from this procedure, all band structures including DOS and PDOS in this paper were calculated by the ADF-BAND package.

Due to the light mass of hydrogen, the ZP vibrational energy of H may be important to the absorption energy. To treat this quantum-mechanical problem, we used the ANHARMND package [30]. This package can solve the time-independent Schrödinger equation based on the adiabatic potential energy. The potential was fitted with a three-dimensional polynomial. To obtain the adiabatic potential of the hydrogen vibrations in Pd<sub>3</sub>M, a 7 × 7 × 7 mesh with 343 data points in each octahedral site was calculated and the step size of displacement of hydrogen was 0.06 × *a* (*a* is the lattice constant).

### 3. Results and discussions

We have calculated the binding (formation) energy of Pd<sub>3</sub>M alloys with respect to infinitely separated spin-polarized atoms:

$$E_b = \frac{1}{4}(E_{tot}(\text{Pd}_3\text{M}) - 3E_{\text{Pd}} - E_{\text{M}}), \quad (1)$$

**Table 1.** The lattice constants, binding energies, absorption energies and ZP vibrational energies of hydrogen in the various alloys.  $a_0$  and  $a_H$  represent the lattice constants of Pd<sub>3</sub>M and Pd<sub>3</sub>MH respectively,  $E_b$  (eV per atom) represents the binding energy of Pd<sub>3</sub>M,  $E_{abs}$  (eV per H atom) is the absorption energy of hydrogen in Pd<sub>3</sub>MH and  $E_{zp1}(H)$  (eV per H atom) the ZP energy of hydrogen vibrations in octahedral site of Pd<sub>3</sub>M. The contribution of ZP energy to absorption energy is  $\Delta E_{zp}(H) = E_{zp1}(H) - E_{zp2}(H)$ .  $E_{zp2}(H)$  is the ZP energy of H vibrations in H<sub>2</sub>.

System	$a_0$ (Å)	$a_H$ (Å)	$a_H - a_0$ (Å)	$E_b$	$E_{abs}$	$E_{zp1}(H)$	$\Delta E_{zp}(H)$
Pd <sub>3</sub> Ru	3.925	3.987	0.062	-4.262	0.337	0.109	-0.025
Pd <sub>3</sub> Sn	4.049	4.101	0.052	-3.924	0.139	0.104	-0.030
Pd <sub>3</sub> Rh	3.934	3.995	0.061	-4.222	0.103	0.106	-0.029
Pd <sub>3</sub> Pb	4.120	4.169	0.049	-3.662	0.083	0.089	-0.046
Pd <sub>3</sub> Fe	3.904	3.932	0.066	-4.157	0.120	0.127	-0.008
Pd <sub>3</sub> Ni	3.873	3.943	0.070	-3.796	-0.015	0.121	-0.014
Pd <sub>3</sub> Pt	3.964	4.019	0.055	-4.044	-0.098	0.099	-0.036
Pd <sub>3</sub> Cu	3.896	3.962	0.066	-3.609	-0.094	0.121	-0.014
Pd <sub>4</sub>	3.959	4.018	0.059	-3.601	-0.126	0.099	-0.036
Pd <sub>3</sub> Au	4.019	4.065	0.046	-3.429	-0.214	0.092	-0.043
Pd <sub>3</sub> Ag	4.008	4.063	0.055	-3.329	-0.300	0.096	-0.039
Pd <sub>3</sub> Cd	4.043	4.092	0.049	-3.096	-0.453	0.098	-0.036

where  $E_{tot}$  is the total energy of the fully relaxed lattice of the alloys.  $E_{Pd}$  and  $E_M$  are the energies of the spin-polarized Pd and M atoms, respectively. The absorption energy of hydrogen in Pd<sub>3</sub>M is defined as

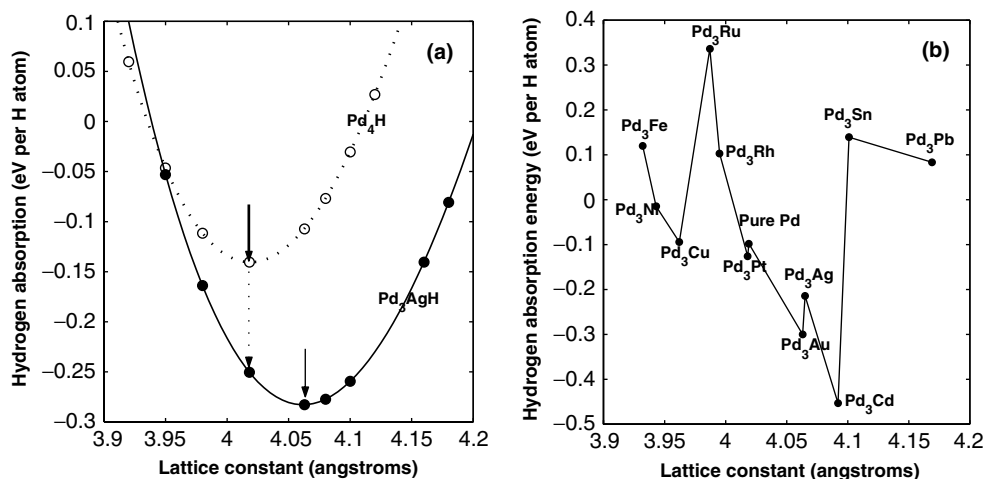
$$E_{abs} = E_{tot}(\text{Pd}_3\text{MH}) - E_{tot}(\text{Pd}_3\text{M}) - \frac{1}{2}E_{\text{H}_2} + E_{zp1}(\text{H}) - E_{zp2}(\text{H}), \quad (2)$$

where  $E_{tot}$  is the total energy of the fully relaxed lattice.  $E_{\text{H}_2}$  is the total energy of the H<sub>2</sub> molecule ( $E_{\text{H}_2} = -6.8037$  and  $-6.557$  eV for VASP and ADF-BAND calculations respectively).  $E_{zp1}(\text{H})$  is the ZP energy of H in the octahedral site of the alloys.  $E_{zp2}(\text{H})$  is the ZP energy of H in the H<sub>2</sub> molecule ( $E_{zp2} = 0.1347$  eV per H atom in our calculation). For an H<sub>2</sub> dimer, the calculated cohesive energy is  $-4.42$  eV, which compares with the commonly used value of  $-4.79$  eV [31]. A negative  $E_{abs}$  means that the hydride is stable compared with a free hydrogen molecule.

The lattice constants, binding energies, ZP energies and absorption energies are presented in table 1. It seems that the ZP energy depends mainly on the lattice constant (as well as on the electronic structure). As a whole, the contribution of ZP energy to absorption energy ( $E_{zp1}(\text{H}) - E_{zp2}(\text{H})$  in equation (2)) is almost constant (see the last column of table 1). Table 1 shows that the calculated absorption energy of hydrogen in Pd<sub>4</sub>H is  $-0.126$  eV per H atom, which is in good agreement with the experimental value of  $-0.100$  eV per H atom [32]<sup>4</sup>. The experiments show that the solubility of H in PdPt and PdRh alloys is lower than that in the pure Pd, and that the solubility of H in PdAg (20–40% Ag content) is greater than that in PdAu (20–40% Au content), which in turn is greater than that in pure Pd [18, 33]. This trend is reproduced in table 1, where the most stable hydrides correspond to the alloys with largest hydrogen solubility. All these indicate that the calculated absorption energies have reasonable accuracy.

We have examined the effect of changing the lattice constants on the absorption energy of hydrogen (take Pd<sub>3</sub>Ag and Pd<sub>4</sub> as an example). The absorption energies of H in Pd<sub>4</sub> and Pd<sub>3</sub>Ag as a function of the lattice constant are plotted in figure 1(a). It shows that the energy

<sup>4</sup> The experimental value is given by hydrogen in the heat solution.

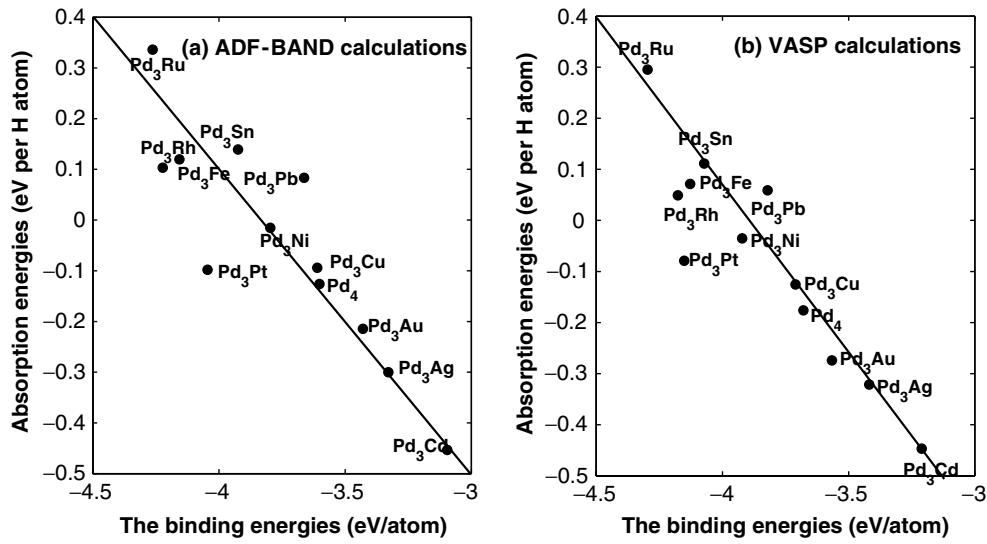


**Figure 1.** (a) The absorption energy (in eV) of H in Pd<sub>4</sub> (○) and Pd<sub>3</sub>Ag (●) as a function of the lattice constant (in Å). The energies of the equilibrium structures Pd<sub>4</sub> and Pd<sub>3</sub>Ag are chosen as reference energies for Pd<sub>4</sub>(H) and Pd<sub>3</sub>Ag(H), respectively. The energies in the equilibrium positions are denoted by arrows. The data were calculated using the VASP package. (b) The absorption energies of hydrogen as a function of lattice constants of Pd<sub>3</sub>MH.

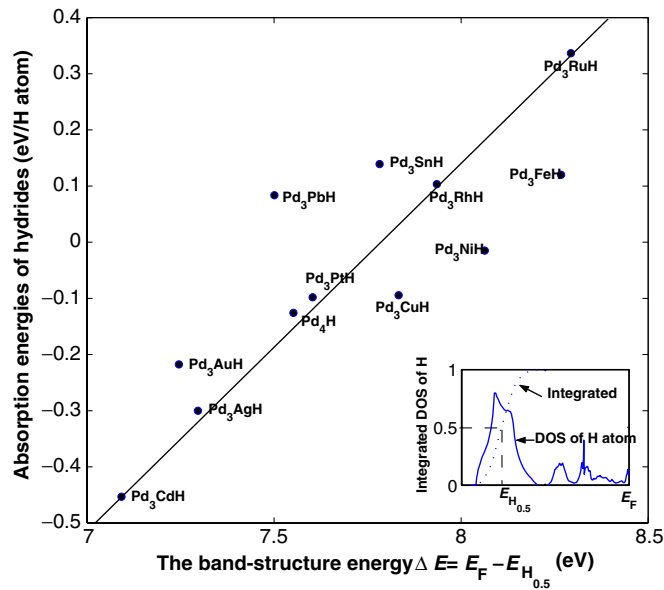
profiles near the equilibrium positions are quite flat. It can be seen from figure 1(a) that even if hydrogen absorption in Pd<sub>3</sub>Ag becomes less stable when the lattice constant decreases (to the equilibrium lattice of Pd<sub>4</sub>H), it is still significantly more stable than absorption in pure Pd. Thus, it seems that electronic effects should be most important in an explanation of the larger absorption energy in the alloy. Figure 1(b) shows the absorption energy of hydrogen as a function of the lattice constant, in which the lattice constant corresponds to the respective equilibrium lattice of the alloys. Both table 1 and figure 1(b) show that there is no clear correlation between the absorption energy and the lattice constant. For instance, we see that the lattice constant of Pd<sub>3</sub>Pb is the largest among all the alloys, while the corresponding hydride is not even stable compared with the gas phase.

We have subsequently investigated the correlation between the absorption energy  $E_{abs}$  of hydrogen in the alloy and the following parameters obtained from total energy and PDOS calculations: (i) the binding energy  $E_b$ , (ii) the half-band hydrogen energy  $\Delta E_H$  (see equation (3) and the inset in figure 3 for the definition), (iii) the lowest (*s*-like) valence band of Pd in Pd<sub>3</sub>M alloys  $\Delta E_s$  (see equation (4) and the inset in figure 4 for the definition) and (iv) the *d*-band centre  $\Delta E_d$  in the Pd<sub>3</sub>M alloy. Among them, the first correlation is the well-known Miedema empirical rule [34]. The second is raised by us. The third has been described by Griessen *et al* [35, 36], while the fourth has previously been applied only to adsorbates on surfaces [4, 37].

We have plotted the correlation between  $E_{abs}$  and (i)–(iv) in figures 2–5 respectively. We see in figure 2 that there is a clear correlation between  $E_{abs}$  and  $E_b$ . We have in figures 2(a) and (b) shown the results obtained by the ADF-BAND and VASP packages, respectively. Both of them show that the absorption energy decreases almost linearly as the binding energy increases. This is a justification for Miedema's 'reverse stability', i.e. the more stable the host metal, the less stable the hydride [34]. This has been explained in terms of breaking of metal–metal bonds: for the more stable metal it is harder to replace some of these bonds by metal–hydrogen bonds [12, 34]. This can also be understood qualitatively by a simple argument: a stronger



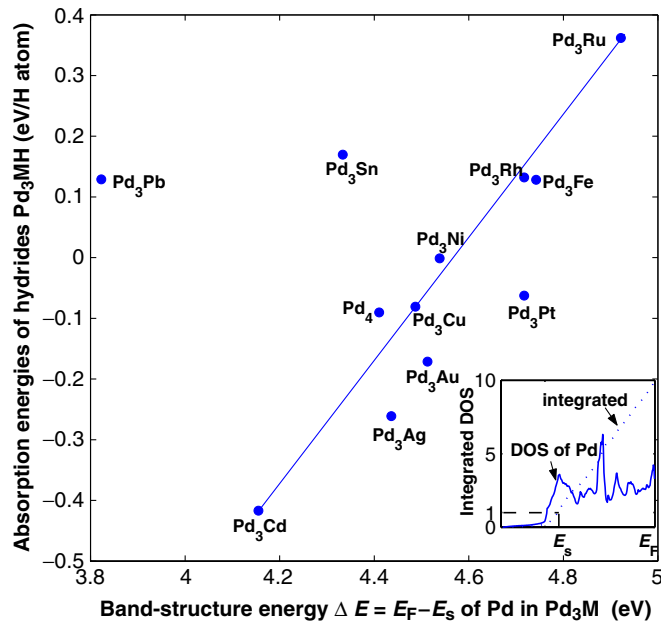
**Figure 2.** Correlation between the absorption energy of hydrogen and the binding energy of Pd<sub>3</sub>M; (a) and (b) were calculated using the ADF-BAND and VASP packages respectively.



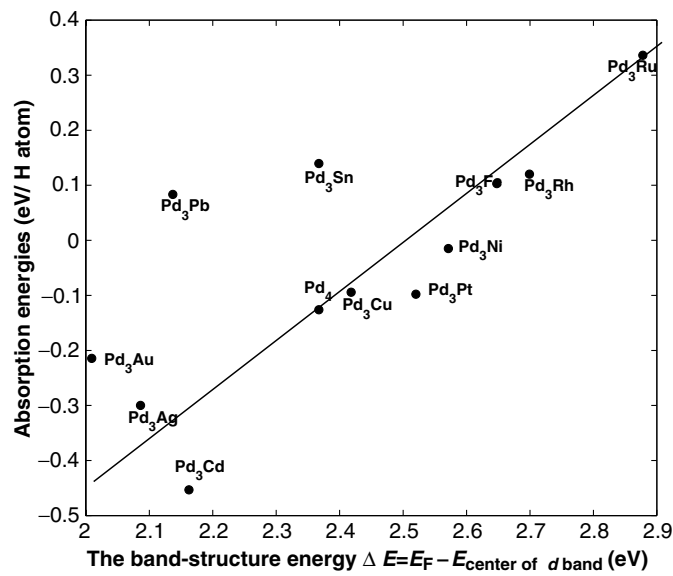
**Figure 3.** Correlation between the absorption energies of hydrogen in Pd<sub>3</sub>M and the band-structure energy of H in Pd<sub>3</sub>MH. The inset shows the definition of  $\Delta E = E_F - E_{H_{0.5}}$ , in which the solid line is the DOS of the hydrogen atom, and the dotted line is the integrated DOS of the hydrogen.  $E_{H_{0.5}}$  is the energy for which the integrated DOS of the hydrogen atom in Pd<sub>3</sub>MH is equal to 0.5 electron.

binding between the metal atoms makes it more difficult for the hydrogen atom to find ‘partner’ electrons that can participate in the binding of hydrogen in the lattice.

We also know that  $E_b$  is correlated with the location of the valence band relative to the Fermi level, i.e. the higher the binding energy of the host metal, the lower the



**Figure 4.** Correlation between the absorption energies of hydrides and the lowest (s-like) valence band energy ( $\Delta E = E_F - E_s$ ) of the Pd atom in  $\text{Pd}_3\text{M}$ . The inset shows the definition of  $\Delta E = E_F - E_s$ , in which the solid line is the DOS of the palladium atom, and the dotted line is the integrated DOS of palladium.  $E_s$  is the energy for which the integrated DOS of the palladium atom in  $\text{Pd}_3\text{M}$  is equal to one electron per atom.



**Figure 5.** Correlation between the absorption energies of hydrogen in  $\text{Pd}_3\text{M}$  and the energies of the d-band centre of the Pd atom in  $\text{Pd}_3\text{M}$ .



valence band. When the host metal valence band is lower, the location of the hydrogen s-band is brought lower in the hydride, due to the interaction between the hydrogen electrons and the valence band. Since  $E_b$  is correlated with  $E_{abs}$ , we should expect that  $E_{abs}$  is correlated with the location of the hydrogen s-band. A common way to quantify this is to define the half-band energy of hydrogen in Pd<sub>3</sub>M as follows:

$$\Delta E_H = E_F - E_{H_{0.5}}, \quad (3)$$

where  $E_F$  is the Fermi energy and  $E_{H_{0.5}}$  the energy for which the integrated DOS of the H atom in Pd<sub>3</sub>MH is equal to 0.5 electron (see figure 3, inset). Figure 3 shows the correlation between the absorption energies of hydrides and  $\Delta E_H$ . It shows that the absorption energy of hydrogen decreases with increasing  $\Delta E_H$ . This means that the hydrides become more stable as the hydrogen electrons move higher in energy, towards the Fermi level.

The lowest (s-like) valence band energy was proposed by Griessen *et al* [35, 36], as a relevant parameter from electronic band structure calculations. The energy is defined as

$$\Delta E_s = E_F - E_s, \quad (4)$$

where  $E_s$  is the energy for which the integrated DOS of the Pd atom in Pd<sub>3</sub>M is equal to one electron per atom (see figure 4, inset). It was shown in [35, 36] that there is an almost linear relationship between the heat of formation and  $\Delta E_s$  for binary hydrides. Figure 4 shows the absorption energy of hydrogen as a function of  $\Delta E_s$ . It shows that the relationship is almost linear for our ternary hydrides as well, except for the hydrides of Pd<sub>3</sub>Pb and Pd<sub>3</sub>Sn. This relationship, to some degree, also coincides with the first correlations. This can again be understood by noting that  $E_b$  is correlated with the position of the valence band.

We have also examined the relationship between  $E_{abs}$  and the centre of mass of the electronic density of states projected on the atomic  $d$  orbitals of the metal before adsorption ( $\Delta E_d$ ).  $\Delta E_d$  is defined relative to the Fermi energy, and is calculated from the  $d$ -electron density of Pd in the Pd<sub>3</sub>M alloys. Nørskov and co-workers [4, 37] previously demonstrated a general relationship between the adsorption energy of an adsorbate on an alloy surface and the  $d$ -band centre of the metal atom of the adsorbate-free surface to which the adsorbate bonds. They showed that adsorption becomes more stable (the reactivity of the surface increases) as the centre of the  $d$ -band moves towards the Fermi level. It is not obvious that the same relationship holds when we move from the surface into the bulk. However, we can see that indeed it does: figure 5 shows how  $E_{abs}$  correlates quite well with  $\Delta E_d$  in our alloys. Corresponding to the case of adsorption on alloy surfaces, the rule is that the deeper the centre of the Pd  $d$ -band, the less stable the hydride.

It is interesting to see whether these correlations can be applied to other systems. For Miedema's rule, Smithson *et al* [12] have, for instance, demonstrated that the binding energy of the host metal is an important factor in determining the stability of the hydride—this was based on a systematic investigation of the stability of MH<sub>*x*</sub> (M = alkali, earth alkali and transition-metal hydrides,  $x = 1$  and 2). But it should be noted that this rule is not truly universal for all the systems. Even for the binary hydrides, the rule is not valid; the cohesive energy (2.50 eV) of the pure Ag fcc lattice is much smaller than that (3.68 eV) of the pure Pd fcc lattice. Nevertheless, the hydride of AgH<sub>*x*</sub> is much less stable than the palladium hydride, it is even unstable compared with a free hydrogen molecule. As discussed above, we think that the second correlation closely relates to the binding energy: the stronger the binding energy of the host alloy, the deeper the hydrogen band, and thus the less stable the hydride. Since the first correlation has its limitations, we thus expect that the universality of the second correlation is also restricted. The third correlation was raised by Griessen *et al* [35, 36], who made considerable effort to apply it to various compounds; this has, to some extent, been

successful. But we have seen that the correlation is not perfect in our system: there is a large discrepancy for Pd<sub>3</sub>Pb (particularly) and Pd<sub>3</sub>Sn in figure 4. This discrepancy is also seen for the correlation raised by Nørskov and co-workers [37] in figure 5. These indicate that the s-like state and the d-band centre do not always represent the nature of the hydrogen–metal bond.

#### 4. Conclusions

The influence of the electronic structure and of the lattice constant on hydrogen absorption in the bulk Pd<sub>3</sub>M<sub>1</sub> (M = Cd, Ag, Au, Pd, Cu, Ni, Pt, Pb, Sn, Fe, Rh, Ru) has been studied by DFT. Our results show that the influence of the electronic structure on the absorption energy of hydrogen is much larger than that of the varying lattice constant. Four correlations have been investigated and the results are summarized as follows:

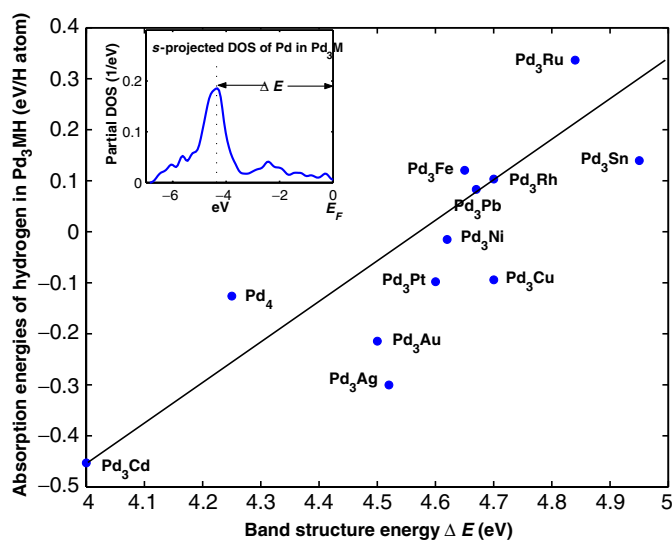
- The higher the binding energy of the host alloy, the less stable the hydride.
- The deeper the hydrogen band (relative to the Fermi level), the less stable the hydride.
- The deeper the lowest (s-like electrons) valence band, the less stable the hydride.
- The deeper the Pd d-band centre, the less stable the hydride.

The correspondence between these effects can be understood from the common notion that stronger binding is related to electrons farther below the Fermi level. This could also be expected in other alloys. The present study indicates that the stability of Pd hydrides can be improved by alloying other metals to change the electronic structure.

In this study, we have for the first time demonstrated a correlation between the position of the hydrogen band (relative to the Fermi level) and the stability of the hydride. Since this correlation belongs to an empirical rule, it is difficult to explain the reason for this correlation. We think that this may be interpreted in terms of the binding energy of the host metals: for hydrogen in metals the position of the hydrogen band is usually below the valence band of the host metal (relative to the Fermi level). A higher binding energy of the host metal usually has a wider valence-band width. Thus, once a hydride is formed, the higher binding energy (of the host metal) indicates the hydrogen band will be located to the deeper position. According to Miedema's rule, the higher the binding energy the host metal, the less stable is the hydride. Therefore, the deeper the hydrogen band, the less stable the hydride. According to the rule, in principle, the stability of the hydrides can be identified by locating the peak position of the hydrogen band, e.g. figure 3 in [12] shows that the deeper the hydrogen band, the less stable the hydride. This is in accordance with this correlation.

There are important exceptions from the correlations discussed in this study; particularly Pd<sub>3</sub>Pb and, to some extent, Pd<sub>3</sub>Sn do not fit into the overall scheme (particularly for the third and fourth correlations). This may be due to the influence of the 5s electrons of the Pd atom. Following the suggestion of the referee, we plotted the correlation between the absorption energies of hydrogen in Pd<sub>3</sub>M and the band-structure energy of the s-projected DOS of Pd in Pd<sub>3</sub>M in figure 6, where the inset shows that the definition of  $\Delta E$  is the energy between the Fermi level and the peak position of the s-projected DOS. Indeed, figure 6 shows that the discrepancies for Pd<sub>3</sub>Pb and Pd<sub>3</sub>Sn now disappear. Overall, it shows that the deeper the s-projected band, the less stable the hydride.

We conclude that for the ternary Pd alloys, the electronic effects are most important to explain the variation in hydrogen stability, but that the proposed correlations only give a simplified view of hydrogen bonding in such compounds.



**Figure 6.** Correlation between the absorption energies of hydrogen in Pd<sub>3</sub>M and the band-structure energy of the s-projected DOS of Pd in Pd<sub>3</sub>M. The inset shows that the definition of  $\Delta E$  is the energy between the Fermi level and the peak position of the s-projected DOS of Pd in Pd<sub>3</sub>M.

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