Origin of the Anomalous Absence of Hydride Formation by $ZrPd_2$

Michèle Gupta,[1] Raju P. Gupta,[2] and David J. Singh[3]
[1]*EA3547, Bâtiment 415, Institut des Sciences des Matériaux, Université de Paris-Sud, 91405 Orsay, France*
[2]*Service de Recherches de Métallurgie Physique, Centre d'Etudes Nucléaires de Saclay, 91191 Gif sur Yvette, Cedex, France*
[3]*Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6032, USA*
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Intermetallic compounds based on hydrogen absorbing elements usually form stable hydrides. This is the case for $PdZr_2$. Surprisingly, $ZrPd_2$ does not absorb hydrogen although both compounds have the same crystal structure and satisfy the empirical geometrical criteria for hydride formation. Results of *ab initio* calculations reveal an unanticipated purely electronic origin. These results have implications in the search for new intermetallics for hydrogen storage.

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There is strong current interest in materials for reversible storage of hydrogen as a clean fuel [1–3]. Hydrogen storage in gaseous or liquid forms poses challenging handling and safety problems in vehicular applications. The safest way to store hydrogen is in the form of a metal hydride, and, in some metal hydrides, the volumetric hydrogen storage capacity [3] can be more than twice that of liquid H_2. However, there are only a few elemental metals, such as Pd, that can be used and have suitable thermodynamic properties [4–6]. Others, such as Zr, V, Mg, etc., readily absorb hydrogen but are unsuitable because the hydride is far too stable for easy hydrogen recovery. Much attention has been focused on intermetallic compounds [7,8]. Although a number of intermetallic compounds currently used for hydrogen storage, e.g., $LaNi_5$, have excellent charge and discharge capabilities, they suffer from low weight storage capacities, and so are not suitable for onboard applications.

To find new materials with desirable thermodynamic properties, it is important to understand the basic mechanisms of hydrogen absorption. Besides the experimental observation that at least one of the elements constituting the alloy should be a hydride former, there are mainly two empirical geometrical observations that have guided the search. These are that the minimum size of the interstitial hole to accommodate hydrogen [9] should not be less than 0.40 Å and that the minimum H-H separation [10] should be larger than 2.1 Å. These criteria work reasonably well, though exceptions to the second rule have been reported recently [11]. However, some puzzling cases have been reported where they are fully satisfied but hydride formation still does not occur. This is the case for $ZrPd_2$ which is formed from two elements, Zr and Pd that readily form hydrides. $ZrPd_2$ does not form a hydride even under high pressure [12]. Even more striking is the fact that a similar compound, $PdZr_2$, formed from the same elements and with a similar crystal structure forms an excellent hydride, $PdZr_2H_2$ [12]. Here, we examine the origin of this puzzling behavior in the hydrogen absorption properties of $PdZr_2$ and $ZrPd_2$. This may have important implications in the selection of intermetallic compounds for hydrogen storage.

Both $PdZr_2$ and $ZrPd_2$ form [13] in the $MoSi_2$-type body-centered tetragonal (bct) structure, space group 14/mmm, no. 139. In the $MoSi_2$ structure type, a bilayer of Si atoms in the bct stacking sequence is inserted between two layers of Mo atoms also in the bct sequence. Neutron powder diffraction data [13] on $PdZr_2D_x$ ($x = 1.70$, $x = 1.96$) showed that the metal atoms in the deuteride have the same structure as $PdZr_2$ with space group 14/mmm. The D atoms occupy 4*d* tetrahedral sites, which provide an optimum environment according to the criteria above. Each D is then surrounded by 4 Zr atoms. A complete filling of those sites corresponds to a composition of $PdZr_2D_2$. Further, $PdZr_2$ forms other hydrides, $PdZr_2H_x$, up to $x \sim 4.75$, including a $PdZr_2H_3$ with a different structure [14]. Jacob *et al.* [15] have examined in detail the geometrical considerations for hydrogen occupation in $ZrPd_2$, and concluded that there are no geometrical considerations that prevent a similar hydride in $ZrPd_2$.

To understand this unexpected behavior, we studied the electronic structure and energetics of the two intermetallic compounds $PdZr_2$ and $ZrPd_2$ and their hydrides, $PdZr_2H_2$ and hypothetical $ZrPd_2H_2$. Since $ZrPd_2H_2$ does not exist, a crystal structure had to be assumed to bring to light the factors that disfavor hydride formation in this compound. All three possible octahedral and the four possible tetrahedral sites were considered for hydrogen occupation. The lattice constants and the internal coordinates were obtained from energy minimization. None of the sites was found to be energetically favorable for hydrogen accommodation but of them the 4*d* tetrahedral site was the least unfavorable. This is the same site that is occupied in $PdZr_2H_2$. A structural relaxation starting from this site was performed, yielding a lower symmetry structure, but still hydride formation was found to be highly disfavored. In the following, we present well converged local density approximation (LDA) results for full occupancy of the 4*d* sites in both compounds. These were performed using the full potential linearized augmented plane wave (LAPW) method with local orbital extensions to treat high lying semicore states and relax linearization errors [16]. Well converged basis sets of more than 800 functions were used with LAPW sphere radii of 2.2 and 1.2 Bohr radii for metal and H atoms, respectively. The zone sampling for iteration to self-consistency was done with 752 special **k** points in the irreducible wedge. Tests confirmed sub-meV convergence in the total energy with respect to these parameters. The crystal structure data for the intermetallic $PdZr_2$ and the hydride $PdZr_2H_2$ were taken from Maeland *et al.* [13], while for hypothetical $ZrPd_2H_2$ it was necessary to determine the lattice parameters $\boldsymbol{a}$ and $\boldsymbol{c}$ and the internal coordinates by energy minimization. For consistency in calculating the formation enthalpy, the same procedure was followed for $ZrPd_2$, although, as seen below, these choices are not significant considering the large energies involved.

We start with the pure intermetallics. Figure 1 shows the densities of states (DOS) and projections onto LAPW spheres. Two distinct $4d$ subbands are clearly seen, the higher lying one from the more electropositive element, Zr. In both compounds, the Pd $4d$ bands hybridized with Zr $4d$ states are filled and the Fermi energy E_F falls in the broad Zr $4d$ bands. The filled Pd $4d$ bands are much broader, $\sim$4 eV wide, in $ZrPd_2$ than in $PdZr_2$ where their width is $<$2 eV. This is expected in the $MoSi_2$ structure where the interactions between the atoms located in the Si_2 biplanes (here the two adjacent Pd planes in $ZrPd_2$) are dominant. This leads to the formation of bonding and the antibonding Pd-Pd states in $ZrPd_2$ and similar Zr-Zr states in $PdZr_2$. The antibonding Zr states in $PdZr_2$ are above E_F, while in $ZrPd_2$ both the bonding and antibonding peaks in the Pd DOS are well below E_F. In $PdZr_2$, E_F falls $\sim$3 eV above the filled Pd-$4d$ bands, while in $ZrPd_2$, E_F falls at less than 1 eV above the top of the broad Pd $4d$ peak. These results are in good agreement with spectroscopy data [17]. A charge analysis was done using Bader's atoms in molecule approach [18] as implemented in the WIEN2K code [19]. For $ZrPd_2$ we obtain an excess Bader charge of $0.78e$ on each Pd, while for $PdZr_2$ the excess Pd Bader charge is $1.36e$.

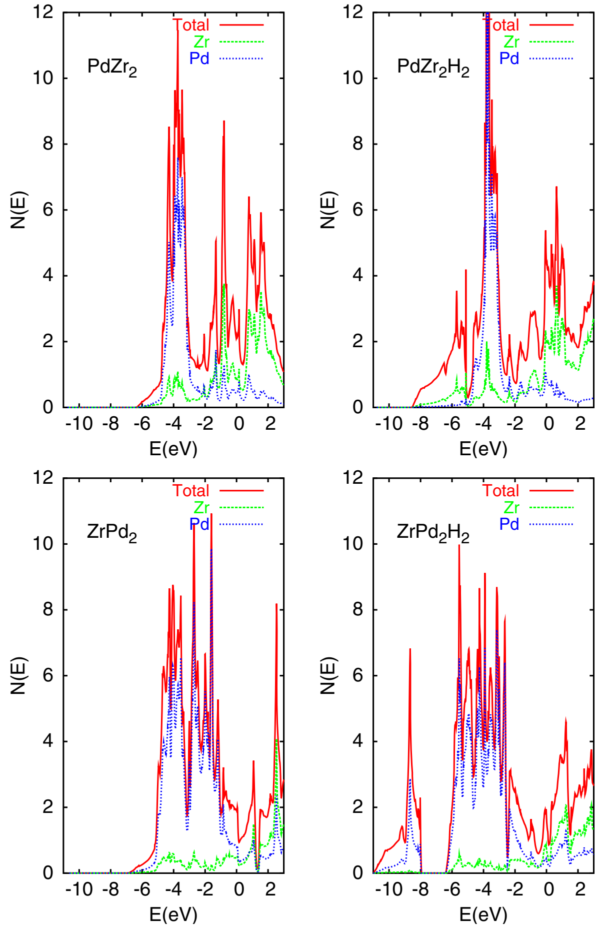

FIG. 1 (color online). DOS and projections for the $PdZr_2$ and $ZrPd_2$ and their hydrides with H in the ideal tetrahedral site (see text). The Fermi level is at 0 eV.

Figure 1 also shows the DOS of the hydrides. On hydrogen absorption, the filled Pd $4d$ bands of $PdZr_2$ become narrower, an effect that can be attributed to the 7% volume expansion. The metal-hydrogen bonding states extending from -8.5 to -5 eV appear below the Pd $4d$ bands. They are mainly derived from the Zr-H interaction; the Pd contribution to this bonding is very weak. This trend in the bonding is consistent with the calculated core level shifts. The $1s$ Zr core level shifts towards higher binding energy by $\sim$0.58 eV from the intermetallic to the hydride, indicating a charge transfer from Zr to H while the Pd $1s$ core level is insensitive to the presence of hydrogen. This is supported by the Bader analysis, which yields an excess Bader charge of $0.69e$ on each H and $1.47e$ on each Pd (cf. $1.36e$ in $PdZr_2$). The Fermi level of the hydride falls in the Zr states at $\sim$2.5 eV above the filled Pd $4d$ bands, and it is thus $\sim$0.5 eV lower relative to the d bands in the pure intermetallic compound $PdZr_2$. This downward shift in the Fermi energy is an important factor that favors the formation of the hydride in this compound, in addition to the stabilizing effect of metal-hydrogen bonding. In this hydride, the Zr-H interaction is strong enough to stabilize below E_F new electronic states that were empty in the pure intermetallic compound. These states are numerous enough to hold the two additional electrons brought by the H atoms and lead to a downward shift of E_F.

In hypothetical $ZrPd_2H_2$ the metal-hydrogen bonding states occur from -11 to -8 eV relative to E_F, i.e., at lower energies than in $PdZr_2H_2$ and thus at first sight favorable for hydride formation. However, as seen in Fig. 1, these states are formed from the interaction of H with the lower lying Pd $4d$ states; the corresponding antibonding states also lie below E_F. This is consistent with the calculated core level shift of Pd $1s$ level which shifts upwards by 1.28 eV, indicating a charge transfer from Pd to H. Since the bonding states were already filled in the pure intermetallic compound and the antibonding states also lie below the Fermi energy, there are no new states brought down at lower energies, and thus there is no net gain in energy to stabilize the hydride. This is in contrast to the case of $PdZr_2H_2$ where empty Zr $4d$ states in the pure intermetallic compound were lowered in energy to form metal-hydrogen bonding states. The formation of metal-hydrogen bonds in $ZrPd_2$ thus does not favor the hydride formation. Indeed, E_F has to shift upwards by a considerable amount relative to the Pd d bands to accommodate the two extra electrons brought by the hydrogen atoms. The Fermi energy again falls in the Zr $4d$ states but at a higher position than in the intermetallic; E_F is at least 1.5 eV higher relative to the Pd d bands in $ZrPd_2$. Such a large upward shift is very unfavorable to the formation of the hydride. This situation is opposite to that discussed above for $PdZr_2H_2$ where there was a downward relative shift in E_F. This difference is reflected in the Bader analysis, which yields an excess charge of $0.70e$ on each Pd (cf. $0.78e$ in nonhydrided $ZrPd_2$) but only a $0.07e$ excess charge per H, indicating an electronic stiffness of $ZrPd_2$ against the charge transfer to H.

To confirm the qualitative analysis presented above, the enthalpies of formation, ΔH_f, of the two hydrides have been calculated from the total energy, E, differences using

$$\Delta H_f(PdZr_2H_2) = E(PdZr_2H_2) - E(PdZr_2) - E(H_2),$$

$$\Delta H_f(ZrPd_2H_2) = E(ZrPd_2H_2) - E(ZrPd_2) - E(H_2).$$

The LDA total energy of the H_2 molecule is an underestimate [20] reflecting large self-interaction errors for this molecule. We have therefore taken the value 2.3489 Ry from the work of Kolos and Roothan [21] for the total energy of the hydrogen molecule. This value does not include the effect of the zero point motion. With this we obtain a strongly exothermic enthalpy of formation of -98 kJ/mol H_2 for $PdZr_2H_2$, while for $ZrPd_2H_2$ an endothermic $+62$ kJ/mol H_2 is obtained. These values do not include the contribution from hydrogen zero point motion, which is significant and needs to be considered. The LDA zero point energy of H_2 is 25.2 kJ/mol molecule. Neglecting the metal modes and considering only the H atoms, LDA calculations were performed in $PdZr_2H_2$ to estimate the average H vibrational frequency, assuming that H behaves in an Einstein-like fashion. One of the H atoms in the unit cell was displaced along the Cartesian directions and the force constants determined. The frequencies along the (x, y) and z directions were 1111 and 1065 cm^{-1}, respectively. These rather isotropic values lead to an average phonon frequency of 1096 cm^{-1}, in excellent agreement with the experimental value of 1089 cm^{-1} (135 meV) obtained from neutron inelastic scattering [13]. This value in conjunction with the zero point energy of the H_2 molecule leads to a zero point correction of $+14$ kJ/mol H_2 for $PdZr_2H_2$, thus reducing the enthalpy of formation somewhat but still maintaining a large exothermic value, -84 kJ/mol H_2. An attempt was made to determine the H vibrational frequency in the hypothetical $ZrPd_2H_2$, but a soft mode was found. Accordingly, we further relaxed the atomic positions without symmetry constraints and found that the H layer undergoes a large buckling with smaller shifts of the metal atoms, lowering the symmetry and leading to a strongly distorted octahedral H environment. This lowers the static energy, but still yields a strongly endothermic result of $+37$ kJ/mol H_2. The average vibrational frequency is then 1040 cm^{-1}, leading to a positive zero point correction and a final value of $+45$ kJ/mol H_2. The DOS for this relaxed structure (Fig. 2) shows the same features discussed above for the ideal tetrahedral site, pointing to the same mechanism. We also calculated the enthalpy of formation of PdH in the same way, including zero point motion, and find -35 kJ/mol H_2, in good accord with the experiment [11] (-40 kJ/mol H_2).

Thus the results clearly show that $ZrPd_2$ cannot be a hydrogen absorbing material. Griessen and Driessen [22] have proposed a model for the heat of formation of hydrides. This model has successfully predicted the trends in the heats of formation for many hydrides, but wrongly predicted an exothermic heat of formation, -52 kJ/mol H_2 for $ZrPd_2$.

The hydride formation capability has been sometimes related to Miedema's empirical rule of reverse stability [23] according to which an intermetallic compound with a higher heat of formation may not form a hydride. In fact, a recent extension of Miedema's rule does correctly indicate that $ZrPd_2$ hydrides will not form [24]. This rule is not truly universal, and the concept of *critical stability limit* has never been established for the hydride formation. Even for the binary hydrides, this rule does not always work properly [25]. We have, nonetheless, investigated the relative stabilities of the pure intermetallic compounds to further understand the origin of the lack of hydride formation in $ZrPd_2$. We calculate ΔH_f from

$$\Delta H_f(ZrPd_2) = E(ZrPd_2) - E(Zr) - 2E(Pd)$$

and

$$\Delta H_f(PdZr_2) = E(PdZr_2) - E(Pd) - 2E(Zr).$$

We obtain $\Delta H_f(ZrPd_2) = -230$ kJ/mol formula unit and $\Delta H_f(PdZr_2) = -145$ kJ/mol f.u., showing that $ZrPd_2$ is indeed much more stable than $PdZr_2$, in agreement with the

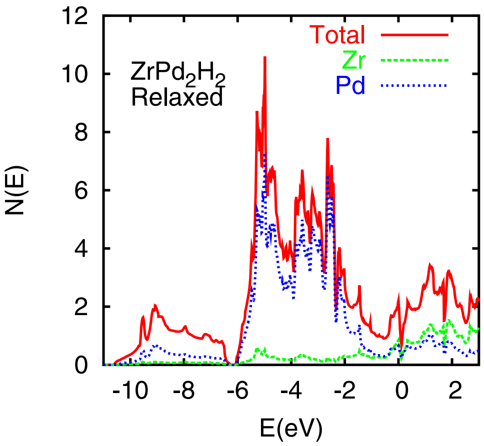

FIG. 2 (color online). DOS and projections for the relaxed structure of hypothetical $ZrPd_2H_2$ as in Fig. 1.

trend observed in the calorimetry data of Selhaoui and Gachon [26] at 1573 K and the values of Stolen *et al.* [27] estimated from Knudsen effusion mass spectroscopy. Selhaoui and Gachon [26] obtained -255 and -144 kJ/mol f.u. for $ZrPd_2$ and $PdZr_2$, respectively, while Stolen *et al.* [27] obtained -232 and -126 kJ/mol f.u. Miedema's original model for binary intermetallics yields -354 and -321 kJ/mol f.u. for $ZrPd_2$ and $PdZr_2$, respectively.

The difference, -85 kJ/mol f.u., in our calculated heats of formation for $ZrPd_2$ and $PdZr_2$, is just enough, within the limits of computational accuracy, to offset the gain in energy, -84 kJ/mol H_2, obtained by hydride formation in $PdZr_2$. The greater stability of $ZrPd_2$ with respect to $PdZr_2$ may thus play a role in the anomalous absence of hydride formation in $ZrPd_2$. Certainly it is important in explaining why $ZrPd_2$ does not separate in the presence of hydrogen to form a mixture of Zr_2PdH_2 and PdH, for example.

In conclusion, we find that the key point in understanding the difference in the H absorption properties of $PdZr_2$ and $ZrPd_2$ is related to the creation of new states below E_F that lead to a lowering of E_F from the intermetallic compound to the hydride. This occurs in $PdZr_2$ and the hydride formation is exothermic, while in $ZrPd_2$ the metal-H interaction does not lead to the creation of new states but solely to a stabilization of states already filled in the intermetallic compound; thus E_F increases and the hydride cannot be formed. Essentially, in the presence of Zr, the Pd d levels are shifted to higher binding energy. This prevents effective bonding between H and Pd. In Pd-rich, $ZrPd_2$ the possible H sites have Pd neighbors, and it is this electronic suppression of bonding that then disfavors hydride formation. The greater relative stability of the intermetallic compound also plays a role in the absence of hydride formation. An effective H storage material must have a high storage capacity combined with a reasonably low, but exothermic, enthalpy of formation. Many of the best materials from a capacity point of view are too stable for use in applications. The results suggest a charge-transfer-based destabilization mechanism to modify the thermodynamics of very stable hydrides, and may help in the search for new hydrogen storage materials.

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