

## Iron-induced hydride formation in ZrPd<sub>2</sub>: First-principles calculations

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We show via first-principles calculations that the electronic structure of ZrPd<sub>2</sub>, which does not form a hydride, can be modified by partial substitution of Fe for Pd, leading to a material that forms a hydride. We also show that PdZr<sub>2</sub>, which forms a very stable hydride, can also be modified by Fe addition to lower the enthalpy of hydride formation. These results are explained in terms of electronic structure, specifically electronegativity, charge transfer, and *s-d* bonding, and clearly have implications in the search of new materials for hydrogen storage.

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Materials containing hydrogen have been the subject of much recent interest both for their fundamental interest and for practical reasons for hydrogen storage.<sup>1</sup> Hydrogen storage applications require materials with a combination of several difficult to achieve properties, including high volumetric and mass densities of hydrogen, low enthalpy of formation for the hydride compatible with room-temperature desorption of H<sub>2</sub> (i.e.,  $\sim 0.35$  eV/H<sub>2</sub>), and low cost. In particular, finding materials with appropriate thermodynamics for reversible desorption of H<sub>2</sub> and ambient temperature has proved to be particularly challenging. As such, ways of modifying the thermodynamic properties of hydrogen containing materials are needed, especially for the enthalpies of formation of existing phases.

Here we focus on intermetallic hydrides, which are one of the promising classes of materials for applications, and the question of whether the thermodynamics of the hydrogen uptake can be chemically modified. For this purpose we use the ZrPd phases, PdZr<sub>2</sub> and ZrPd<sub>2</sub>, as model systems. Both of these compounds form in the MoSi<sub>2</sub>-type (*I4/mmm*) structure<sup>2</sup> with one formula per primitive cell. In this structure, there is a body-centered stacking of layers, which alternate  $\cdots\text{Si-Mo-Si-Si-Mo-Si-Si-Mo-Si}\cdots$ . The compound PdZr<sub>2</sub> readily forms a hydride of nominal composition PdZr<sub>2</sub>H<sub>2</sub> but this material is not suitable for applications both because of the modest hydrogen content and because of its very high enthalpy of formation. In the hydride the H atoms occupy tetrahedral sites in the center of the Zr bilayer. Surprisingly, ZrPd<sub>2</sub> does not form a hydride under normal conditions although both Zr and Pd are good hydride forming metals. The different behaviors of the two intermetallics, PdZr<sub>2</sub> and ZrPd<sub>2</sub>, were understood in terms of their electronic structure<sup>3</sup> and can be related to the charge balance between Zr, Pd, and H, related to their electronegativity differences. In particular, in the presence of Zr there is a transfer of charge from Zr to Pd *d* bands which move below the Fermi energy,  $E_F$ . This prevents the formation of bonds between H and Pd. In PdZr<sub>2</sub> the Fermi level of the hydride falls in Zr states and is lower by  $\sim 0.5$  eV relative to the intermetallic. This downward shift in the Fermi level is an important factor that favors the formation of the hydride. In ZrPd<sub>2</sub>, on the other hand, the Fermi level shifts upward by  $\sim 1.5$  eV relative to the intermetallic since Pd *d* bands were already

filled, and no new states are lowered down to lower the Fermi energy. As a result the Pd rich phase ZrPd<sub>2</sub> does not take H. In pure Pd, in contrast, there are holes in the Pd *d* band, and hence the bond formation between Pd and H can occur. Here we show that these electronic structure differences between PdZr<sub>2</sub> and ZrPd<sub>2</sub>, which underlie their different hydriding behaviors, can be used as a guide for modifications of these materials. In particular, we show by first-principles calculations that partial substitution of Pd by Fe in ZrPd<sub>2</sub> leads to the formation of a stable hydride while a similar substitution at the Zr site in PdZr<sub>2</sub> leads to a substantial lowering of the enthalpy of hydride formation. Thus depending upon the intermetallic in question, such substitutions can have both a stabilizing and a destabilizing effect on hydride formation. We note that apart from Fe, other 3*d* elements, such as Ni and Co, are also good candidates for improving the hydrogen absorption characteristics of these intermetallics. While a ZrFePd phase with 1-1-1 stoichiometry has not been reported, intermetallic compounds of Zr and Pd generally show a high solubility limit for Fe,<sup>4</sup> up to 5 at. % for ZrPd<sub>2</sub> and PdZr<sub>2</sub>, 6 at. % for ZrPd, and higher for some other compositions.

The present calculations were performed within the density-functional theory (DFT) as implemented in the Vienna *Ab initio* Simulation Package (VASP) (Refs. 5 and 6) using projector-augmented wave (PAW) pseudopotentials<sup>7</sup> and the full potential linearized augmented plane-wave (FP-LAPW) method<sup>8</sup> in the WIEN2K (Ref. 9) code. We employed the generalized gradient approximation (GGA) (Ref. 10) which is generally more reliable in calculations of formation energies of hydrides<sup>11</sup> than the local-density approximation (LDA). The structures were fully relaxed, including all atomic positions and the lattice parameters, with 2 f.u./cell. We started with the actual structures of ZrPd<sub>2</sub> and PdZr<sub>2</sub> and replaced one Pd by Fe in the former and one Zr by Fe in the latter. This leads to two distinct supercells of the same composition but with different layer stackings. In both cases Fe layers are sandwiched between Zr and Pd layers. However, in ZrPd<sub>2</sub> they are separated by Pd-Zr-Pd blocks while in PdZr<sub>2</sub> by Zr-Pd-Zr blocks. In the following, we denote these as ZrPdFe and PdZrFe structures, respectively. The optimized crystal structures are given in Table I. The heats of formations of these intermetallics calculated with respect to

TABLE I. DFT optimized lattice parameters ( $\text{\AA}$ )  $a$  and  $c$  and the atomic parameter  $z$  in the tetragonal space group  $P4/mmm$  (No. 123) obtained in the ferromagnetic state for the Fe substituted intermetallics and their hydrides. For ZrPdFe and its hydride, Zr is in the  $1a$  and  $1d$ , Pd in  $2g$ , Fe in  $2h$ , and H in  $4i$  positions. The Zr and Pd positions are exchanged in PdZrFe and its hydride.

Parameter	ZrPdFe	ZrPdFeH <sub>2</sub>	PdZrFe	PdZrFeH <sub>2</sub>
$a$	3.3598	3.4649	3.2822	3.3723
$c$	8.6407	8.7709	9.2192	9.5792
$z$ (Pd)	0.3286	0.3405		
$z$ (Zr)			0.3087	0.3207
$z$ (Fe)	0.1540	0.1663	0.1463	0.1301
$z$ (H)		0.1426		0.2029

the constituting metals, with Fe in the ferromagnetic state, are given in Table II. In the paramagnetic state we find that the energy of the relaxed ZrPdFe structure is higher than that of the PdZrFe structure. However, we found that the density of states (DOS) at the Fermi level was high suggesting possible magnetic instabilities. Accordingly, ferromagnetic calculations were performed for both structures including full structural relaxations, and both of these structures were found to be ferromagnetic. The magnetic energy contribution in ZrPdFe is found to be much larger than that in PdZrFe and is sufficiently large to change the ordering of the phases, so that the ZrPdFe structure became more stable by  $0.16 \text{ eV/f.u.}$  The magnetization per f.u. for this structure is  $2.38\mu_B$ , while for the PdZrFe structure it was slightly lower where we obtain  $2.05\mu_B$ .

Similarly, the full structural relaxations were performed for the hydrides of the two structures: ZrPdFeH<sub>2</sub> and PdZrFeH<sub>2</sub>. Without magnetism, ZrPdFeH<sub>2</sub> was found to be the lower energy structure, and the heat of hydride formation is found to be lower by  $\sim 0.62 \text{ eV/f.u.}$  In fact, both of these structures were also found to be ferromagnetic, but the ordering was not changed from the paramagnetic case since the magnetic contributions are nearly the same in the two hydrides so that ZrPdFeH<sub>2</sub> remained lower in energy. The op-

TABLE II. Formation energies (eV/f.u.) of the intermetallics and the hydrides in the paramagnetic (PM) and the ferromagnetic (FM) states. The magnetic contribution (MC) to the formation energy is also shown for clarity. The formation energies of the hydrides in the PM and FM states are calculated with respect to the corresponding PM and FM states of the intermetallics as reference. Note that the sum of the second and third columns is the formation energy with respect to the PM phase. For the hydrides in the FM phase with respect to the intermetallic in the FM phase, the MC contribution of the intermetallic has to be subtracted.

Compound	PM	MC	FM
ZrPdFe	-0.30	-0.54	-0.84
PdZrFe	-0.60	-0.08	-0.68
ZrPdFeH <sub>2</sub>	-1.02	-0.16	-0.64
PdZrFeH <sub>2</sub>	-0.40	-0.16	-0.48

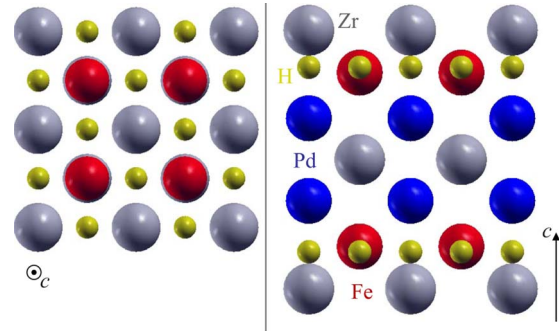


FIG. 1. (Color online) Relaxed crystal structure of ZrPdFeH<sub>2</sub>. The left panel shows a view along (001), while the right panel is along a (100) direction. Note the Pd-Zr-Pd blocks along  $c$ . The structure denoted PdZrFe is similar but has Zr-Pd-Zr blocks.

timized lattice parameters and atomic coordinates obtained in the ferromagnetic states in the tetragonal space group  $P4/mmm$  (No. 123) are given in Table I. In Table II we have given the energies of formation. The relaxed structure of the tetragonal cell of ZrPdFeH<sub>2</sub> is shown in Fig. 1. As may be seen, the H is closely associated with Fe. Each H is coordinated by two Fe atoms at  $1.74 \text{ \AA}$  and two Zr atoms at  $2.14 \text{ \AA}$ . The shortest distance between Pd and H is  $2.45 \text{ \AA}$ , which is the same as the H-H separation. This is reminiscent of the situation in TiFeH<sub>2-x</sub>, where H is closely associated with Fe in the presence of a less electronegative element Ti.<sup>12</sup>

The magnetizations of the hydrides were  $2.20\mu_B$  for PdZrFeH<sub>2</sub> and  $1.30\mu_B$  for the more stable ZrPdFeH<sub>2</sub> compound. The calculated GGA enthalpy of hydride formation, including magnetism, for this hydride, ZrPdFeH<sub>2</sub>, is  $-0.64 \text{ eV/H}_2$ , as compared to  $-0.07 \text{ eV/H}_2$  for ZrPd<sub>2</sub>H<sub>2</sub>, and thus demonstrates the beneficial effect of Fe substitution on hydride formation by a nonhydride forming intermetallic. The large reduction in the value of the heat of formation in ZrPdFeH<sub>2</sub> in the ferromagnetic state relative to its value in the paramagnetic state arises from a much larger magnetic contribution in the intermetallic compared to the hydride. While, as noted above, PdZrFe and PdZrFeH<sub>2</sub> are not the low energy structures, it is nevertheless interesting to note that the enthalpy of formation of this hydride would be  $-0.48 \text{ eV/H}_2$  if that metal ordering actually occurred. This has to be compared to the value of  $-1.39 \text{ eV}$  for PdZr<sub>2</sub>H<sub>2</sub> and emphasizes again the beneficial effect of Fe substitution at the Zr site on the destabilization of a very stable hydride and thus improving its hydrogenation properties.

In our previous work,<sup>3</sup> it was shown that the very different hydriding behaviors of ZrPd<sub>2</sub> and PdZr<sub>2</sub> can be understood in terms of the electronic structure. Specifically, in ZrPd<sub>2</sub> the Pd  $d$  bands are filled due to charge transfer from the less electronegative Zr. These filled  $d$  bands are then unable to participate in bonding with H. On the other hand, in PdZr<sub>2</sub>, where the H site is between the Zr layers, there is a ready bond formation involving H  $s$  orbitals and partially filled Zr  $d$  orbitals. This suggests that chemical modification of ZrPd<sub>2</sub> to produce partially filled  $d$  bands may lead to hydride formation. In order to test this, we have considered Fe, which has a Pauling electronegativity<sup>13</sup> of 1.83, i.e., interme-

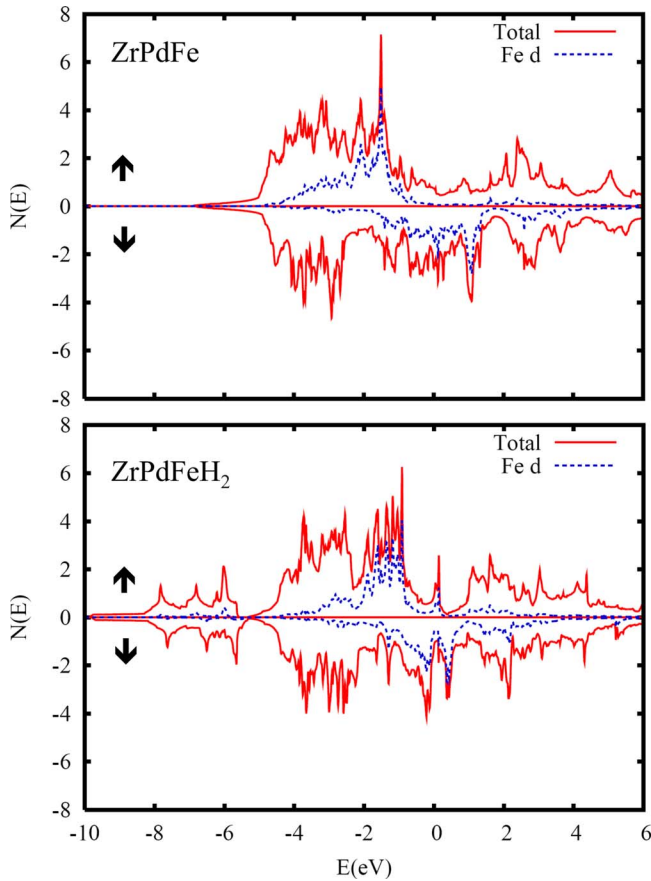


FIG. 2. (Color online) Calculated electronic DOS of ferromagnetic ZrPdFe (top) and ZrPdFeH<sub>2</sub> (bottom), showing the total DOS on a per f.u. basis and the projections onto the Fe linearized augmented plane-wave (LAPW) spheres.

mediate between Zr (1.33) and Pd (2.20) but closer to Pd. The Pauling electronegativity of H is 2.20. The preference of Fe to occur in a Pd site seen in the stabilities of the cells considered in this work can be qualitatively rationalized on this basis since the electronegativity of Fe is closer to that of Pd than to that of Zr.

Figures 2 and 3 show the electronic DOS and its projections for the lower energy ZrPdFe cell before and after hydriding. As may be seen, the Fe *d* states are fully spin polarized, with occupied majority-spin bands and partially filled minority bands. The Pd *d* states for both ZrPdFe and ZrPdFeH<sub>2</sub> are entirely below  $E_F$  and are filled, while the Zr *d* states are largely above  $E_F$ , apparently due to hybridization with Fe states. The hydride shows a split-off part of the DOS between  $\sim -10$  and  $-6$  eV, relative to  $E_F$ . These states with total one band (two electrons) per H are of mixed H *s* Fe *d* character and therefore may be described as a bonding band between Fe and H, similar to the description of PdH, except that in the present case these states are more strongly H derived, i.e., these bonds are polar with charge transfer from the metal to H. The hybridization can be seen both in the Fe *d* component of the DOS for the split-off bands, which is small but noticeable, and in the exchange splitting of  $\sim 0.3$  eV. Since the Fe *d* band filling increases upon hydriding and since the split-off bands are polar, indicating charge

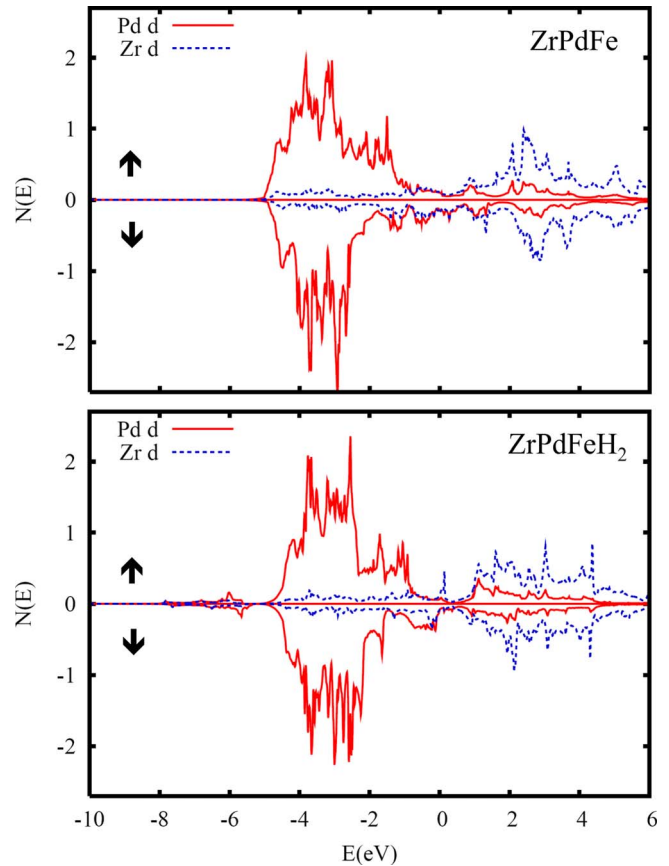


FIG. 3. (Color online) Calculated projections of the DOS of ferromagnetic ZrPdFe (top) and ZrPdFeH<sub>2</sub> (bottom) onto the Zr and Pd LAPW spheres.

transfer to H, it is evident that the charge balance is maintained by transfer from either Zr or Pd. Examination of the DOS shows some Zr character at  $E_F$ , indicating that this charge comes from Zr, which is also what would be anticipated based on the low electronegativity of Zr as compared to Pd or H. In any case, the fact that the Fe *d* band occupancy increases even though Fe-H bonds are polar in the direction of H indicates a stabilization of the electronic states associated with Fe-H part of the unit cell.

Returning to the structure of the cell of ZrPdFe (Fig. 1) there are two inequivalent Zr sites, Zr1 which is coordinated by eight Fe atoms at a distance of 2.68 Å and Zr2 which is between the Pd layers and is coordinated by eight Pd atoms at a distance of 2.80 Å. It is convenient to discuss charge transfer in terms of core-level shifts, which are measurable quantities. The 1*s* core level of Zr2 is at 1.17 eV higher binding energy than that of Zr1, indicating that the main charge transfer from Zr to Pd comes from Zr2. The effects of hydriding to ZrPdFeH<sub>2</sub> on the 1*s* core levels, measured with respect to the Fe 1*s* position, are a shift to higher binding energy of the Zr1 by 0.94 eV, a shift to higher binding energy of the Zr2 by a much more modest 0.19 eV, and a shift to a lower binding energy by 0.07 eV for the Pd. Thus while in the nonhydrided compound charge transfer comes from Zr2 to Pd, in the hydride, on the contrary, the charge needed to fill the split-off H *s*-Fe *d* bonding states is provided mainly

by Zr1. This is in contrast to what was found previously for ZrPd<sub>2</sub>, where all Zr atoms are coordinated by Pd.

In fact, while we obtain a negative heat of formation of  $-0.84$  eV for our ZrPdFe supercell relative to the elements, the phase diagram does not show such a phase as mentioned previously. Therefore, we also investigated a cell in which only one of the four Pd atoms is substituted by Fe and found again the stabilization of the hydride. Again both the intermetallic Zr<sub>2</sub>Pd<sub>3</sub>Fe and the hydride Zr<sub>2</sub>Pd<sub>3</sub>FeH<sub>4</sub> were found to be ferromagnetic with moments of  $2.6\mu_B$  and  $1.1\mu_B$ , respectively, per cell. These values are quite close to the ones obtained above. The heat of hydride formation is also negative,  $-0.28$  eV/H<sub>2</sub>, which is in line with the value expected from the calculations presented above.

Thus we have shown that the electronic structure of the intermetallic can be effectively used to identify chemical

means of modifying their hydrogen storage properties. The substitution of Fe at the Pd site in ZrPd<sub>2</sub> has been taken as an example, and we have shown that while ZrPd<sub>2</sub> does not form a hydride, the substitution of Fe at the Pd site in this intermetallic results in a hydride forming compound. We have shown also that the hydrogenation properties of PdZr<sub>2</sub>, which forms a very stable hydride, can be improved by the substitution of Fe at the Zr site which reduces its enthalpy of formation. These are all intimately related to the electronic structure of the intermetallics in question and the interaction of hydrogen with the elements constituting the intermetallic.

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