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Hydrogen solid storage: First-principles study of $ZrNiH_3$

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ABSTRACT

The $ZrNiH_3$ compound is a good candidate for hydrogen storage. In this work we used the first-principles calculation to study this compound. The crystal structures, the electronic properties and the optimization of the internal parameters are treated by the FP-LAPW method implanted in the WIEN2K code. The enthalpies of the dehydrogenation of the $ZrNiH_3$ compound are calculated. We found that the enthalpy is about −42.89 kJ/mol H, greater but similar to the experimental value of −34.3 kJ/mol H. Potential reasons for this discrepancy are discussed.

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1. Introduction

The crucial problem in extending the application of hydrogen as a clean source of energy, resides in the choice of the storability and portability. Hydrogen is often stored in gaseous or liquid forms. However, these techniques are expensive, unable to give greater safety, and may be accompanied by energy losses in charge–discharge cycle. Consequently, many authors try to find alternatives to such techniques by taking into account the aspects cost, environment, reliability and efficiency. The metal hydrides appear to be the promising devices of hydrogen storage. The choice of the hydrides is based on their storage capacities, their good reversibility and their large reactivity.

Intensive research has been recently conducted on the metal hydrides for improving the adsorption/desorption properties based on hydrogen-storage capacity, kinetics, thermal properties, toxicity, cycling behaviour and cost [1–3]. Sakintuna et al. [4] and Bououdina et al. [5] reviewed many metal hydride materials that have been studied and can be good candidates for hydrogen storage.

In addition to experimental studies, computational science can provide reliable and in-depth information about the system under consideration. First principle calculations based

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on density functional theory have successfully been used to predict the physical properties of hydrides [6,7]. The hydride ZrNi is of convenient stability for the storage of hydrogen. The application of ZrNi hydrides for mobile and stationary hydrogen storage and purification is rather advanced.

It is known that ZrNi absorbs a large number of hydrogen atoms per metal and forms $ZrNiH_3$ [8–13].

In this work, we make use of an accurate full-potential density–functional method to study the electronic properties $ZrNiH_3$ and its decomposition to the ZrNiH compound by using a hybrid full-potential (linear) augmented plane-wave plus local orbitals (L/APW + lo) method.

2. Computational method

We apply the most recently developed Vienna package WIEN2k [14,15] for the full-potential augmented plane-waves plus local orbitals (FP-APW + lo) method within the density functional theory (DFT) [16,17], for which the electron exchange correlation energy, is described in the generalized gradient approximation (GGA) using the Perdew–Burke–Enzerhof functional parameterization [18]. The APW + lo method expands the Kohn–Sham orbitals in atomic like orbitals inside the atomic muffin-tin (MT) spheres and plane waves in the interstitial region. The details of the method have been described in the literature [19–21]. Basis functions, electron densities and potentials were expanded inside the muffin-tin spheres in combination with spherical harmonic functions with a cut off $l_{max} = 10$, and in Fourier series in the interstitial region. We use a parameter RMT $K_{max} = 3.5$, which determine the matrix size, where RMT denotes the smallest atomic sphere radius and K_{max} gives the magnitude of the largest K vector in the plane-wave expansion. All of the calculations were carried out at the theoretical equilibrium lattice constants. We choose the muffin-tin radii of H, Ni and Zr to be 0.7, 1.8, and 2.0 a.u. respectively. The K integration over the Brillouin zone is performed using the Monkhorst–Pack scheme [22] with 1000 K points in the whole Brillouin zone. The self-consistent calculations are considered to be converged only when the calculated total energy of the crystal is converged to less than 0.1 mRyd.

3. Crystal structure of ZrNiH and $ZrNiH_3$

Experimentally, Kost et al. [10] have conferred to ZrNiH an orthorhombic structure. Using X ray diffraction, Westlake et al. [8] have shown that this compound crystallises in the triclinic structure:

$a = 3.367\text{Å}, b = 10.313\text{Å}, b = 10.313\text{Å}, c = 4.063\text{Å}$ and
$\alpha = 89.18^\circ, \beta = 89.60^\circ, \gamma = 89.43^\circ$

This structure can be considered as an orthorhombic structure slightly distorted [23,24]. However, it is found that $ZrNiH_3$ has an orthorhombic structure [8,25]. The hydrogen atoms occupy two kinds of interstitials sites: H1 atoms in pyramidal sites (4c), whereas H2 atoms occupy tetrahedral sites (8f).

Table 1 – Experimental data available and used in our calculations.

Hydride and space group	Wyckoff positions	Parameters structure
ZrNiH (63*Cmcm*)	Zr(0,0.860,0.25) Ni(0,0.570,0.25) H(0,0.2152,0.25)	$a = 3.367$Å $b = 10.313$Å $c = 4.063$Å
$ZrNiH_3$ (63*Cmcm*)	Zr(0,0.140,0.25) Ni(0,0.430,0.25) H1(0,0.956,0.25) H2(0,0.298,0.507)	$a = 3.53$Å $b = 10.48$Å $c = 4.30$Å

We summarized in Table 1 the proposed crystallographic parameters and the atomic positions used in our calculations.

4. Results and discussion

4.1. *The electronic structure of ZrNiH and $ZrNiH_3$*

In Fig. 1, we represent the total and the partial electronic densities of states (DOS) for $ZrNiH_3$ as function of energy (eV). The Fermi level is set at zero energy (dotted line). We can see, between −9 eV and −4.5 eV (curves $ZrNiH_3$ total), the appearance of the metal–hydrogen bands. The contribution of the transition atoms Zr and Ni to the metal–hydrogen bonding can be observed. The projection around the different atomic sites (H_{tot}, Zr_{tot} and Ni_{tot}), confirms that the contribution of Zr and Ni atoms to the hydrogen metal interaction is equivalent. The density of states at the Fermi level is essentially dominated by the Ni-d states (curves Zr-d and Ni-d). While, beyond the Fermi level the contribution to the total DOS is dominantly by the Zr-d states.

The calculations of the total and the partial electronic densities of states (DOS) for ZrNiH are plotted in Fig. 2. The curves reveal a formation of a new structure (between −8.6 and −5.5 eV) induced by the presence of hydrogen in the ZrNi compound. The attractive potential of the proton H will lower some occupied states of metal. Consequently, a strong hybridization occurs between this state and H-s states which provide the formation of the metal-hydrogen bands.

The decomposition of total density in partial wave on the atomic sites of Ni, Zr and H indicates a difference in the contribution of the d states of the Ni atoms and Zr atoms to the metal-hydrogen bands. This is a good agreement with a previous work [24]. This work shows that the greatest contribution to the interaction metal-hydrogen in the monohydrid ZrNiH, with Zr4 (4c) interstitial sites occupied by hydrogen, is assured by the d states of zirconium atoms.

In the Fig. 3, we report the curves of total and partial densities of states (DOS) of ZrNi. From this figure we can see that ZrNi has a metallic character. We can distinguish two areas:

a. One, situated between −6 and 3 eV in which the contribution of nickel d states to the DOS is more important
b. Another area between 3 and 6 eV, dominated by the zirconium d states.

The Fermi level is located in the part where the nickel contribution is very strong. By comparing the curve of total

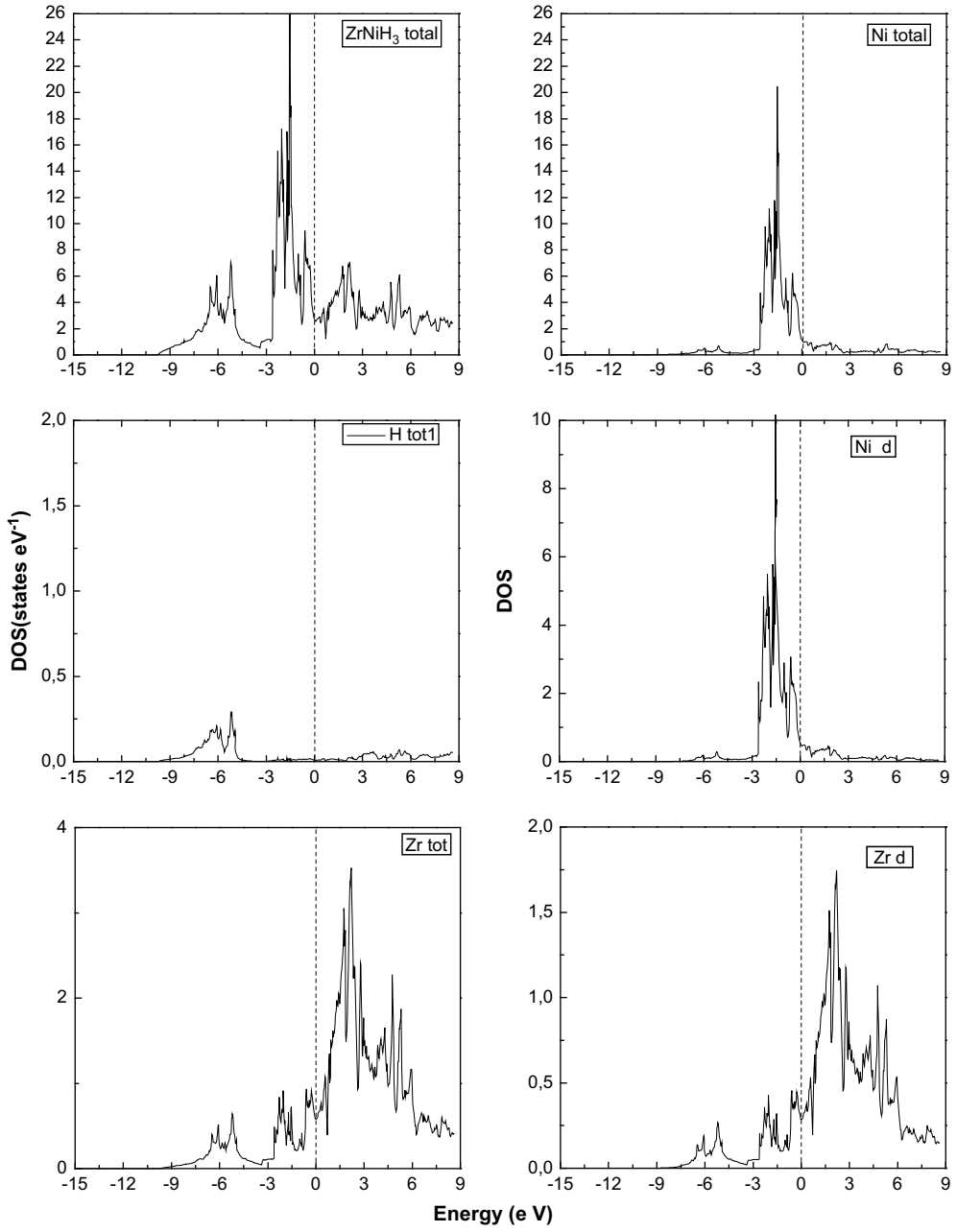

Fig. 1 – Calculated DOS for $ZrNiH_3$. The Fermi level is set at zero energy and marked by vertical lines.

energy of ZrNi to that of ZrNiH we note a decrease in the width of valence band of the hydride. Below the Fermi energy, we notice that electronic structure is due mainly to Ni-d states whereas beyond the Fermi level the structure is dominated by Zr-d states. Finally, the Fermi level moves towards the higher energies and the contribution is almost divided between the two atoms.

4.2. *Optimized structure and bulk properties*

To obtain the ground state properties, the total energies are calculated at several volumes around the equilibrium and are fitted to the Murnaghan's equation of state [26]. As a prototype the results obtained for $ZrNiH_3$ and ZrNiH are shown in Figs. 4 and 5respectively. In this way, we obtained the equilibrium lattice constant (equilibrium volume V_0), ground state energy E_0, bulk modulus B_0 and its pressure derivative B'_0. The calculated equilibrium parameters are given in Table 2.

The deviations of the optimized parameters compared to the experimental ones are 1.79%, 1.75% and 1.72% for ZrNiH and of 2.54%, 2.57% and 2.58% for $ZrNiH_3$. These deviations are acceptable. The obtained bulk modulus B_0 for ZrNiH and $ZrNiH_3$ is 124.8426 GPa and 128.2632 GPa respectively. $ZrNiH_3$ appears to be more fragile than ZrNiH (fragility by hydrogen).

4.3. *Enthalpy of formation*

The reaction related to the decomposition of the hydride $ZrNiH_3$ and the release of hydrogen is:

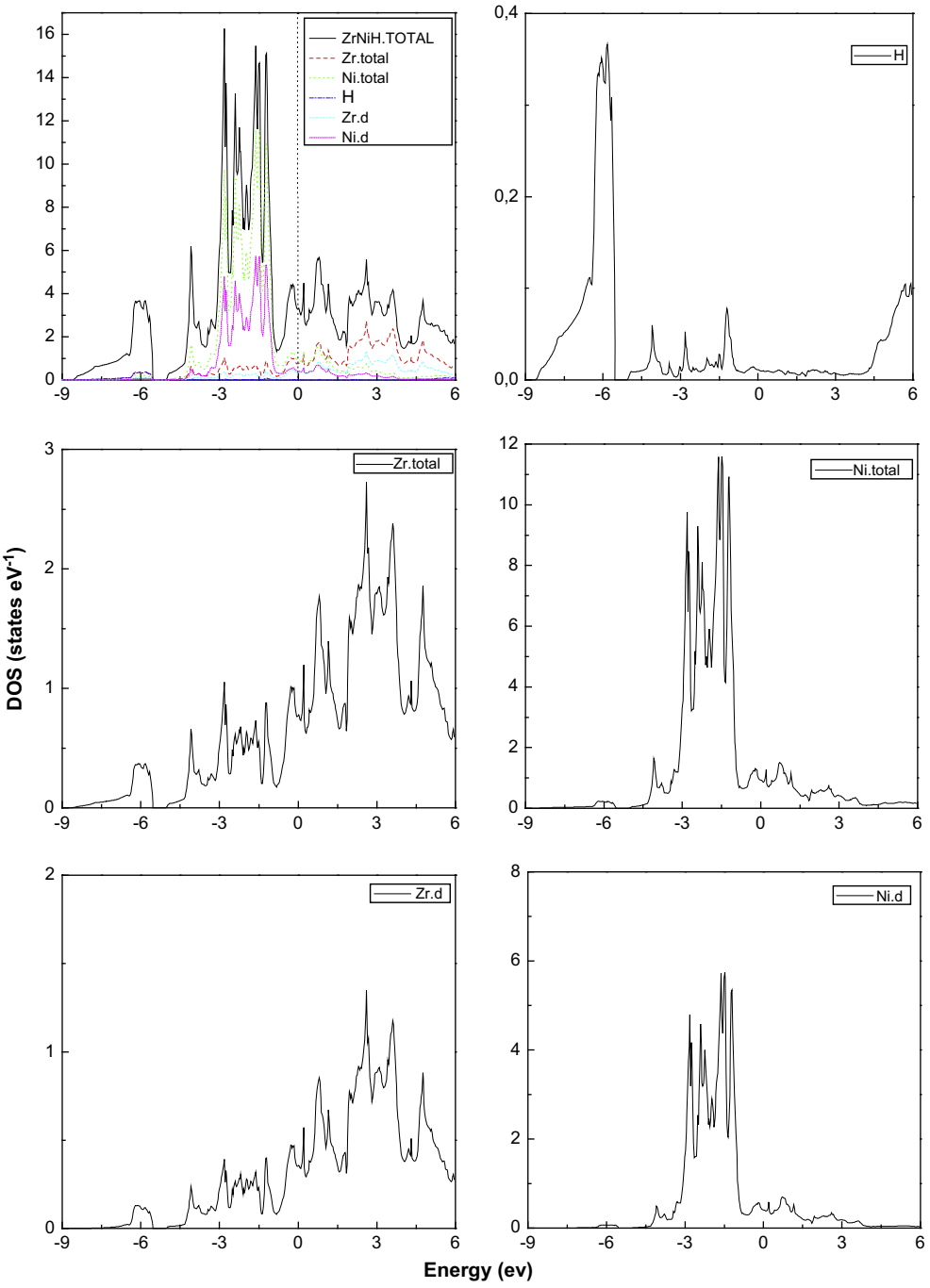

Fig. 2 – Calculated DOS for ZrNiH. The Fermi level is set at zero energy and marked by vertical lines.

$$ZrNiH_3 \rightarrow ZrNiH + H_2 \quad (1)$$

So the enthalpy of formation is calculated by the subtraction of the total energies of ZrNiH, and of the hydrogen molecule from the hydride $ZrNiH_3$:

$$\Delta H(ZrNiH_3) = E_{tot}(ZrNiH_3) - E_{tot}(ZrNiH) - E_{tot}(H_2) \quad (2)$$

The total energies of $ZrNiH_3$ and ZrNiH used in the calculation are those obtained with the optimized structures (Figs. 4 and 5) while the energy of H_2 has been calculated for an isolate molecule in the same conditions (Table 3). According to the theoretical approximations (GGA [18]), the agreement with the experiment is appreciable.

This value is appreciable taking into account the following points:

- This data can be ameliorated with the use of the local density approximation LDA by 1 KJ/mol H.
- The discrepancy can be explained by the zero-point energy due to the vibration motion [29]. We neglect the contribution of zero-point energy in our calculation of the

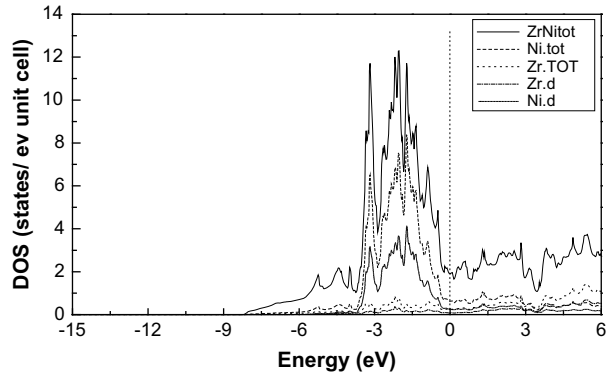

Fig. 3 – Calculated DOS for ZrNi. The Fermi level is set at zero energy and marked by vertical line.

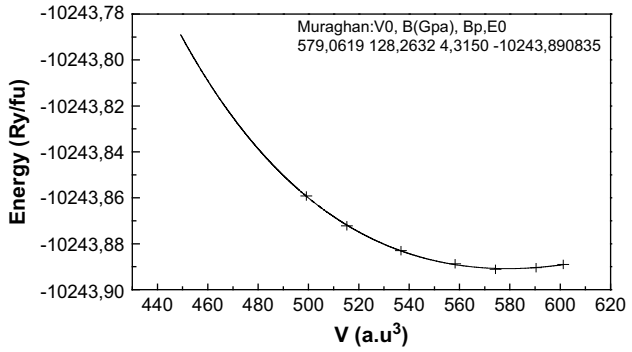

Fig. 4 – Total energy (Ry/f.u.) vs unit-cell volume for $ZrNiH_3$.

heat of formation. Such contributions are negligible for heavy elements (Zirconium and nickel) whereas they may be significant for hydrogen [29].

- But the most important cause is in our approach of the calculation of the H_2 total energy. The WIEN2K like several codes based on DFT, is used to calculate the periodical and solid system but not for gas like H_2. However, we can use it for binary gas if we consider the binary gas in a big box and we keep the bond length between the two atoms of binary gas. Technically, it is to build a molecule in a big unit cell (with lots of vacuum), and increase the amount of vacuum until the total energy no longer changes as a function of the vacuum.

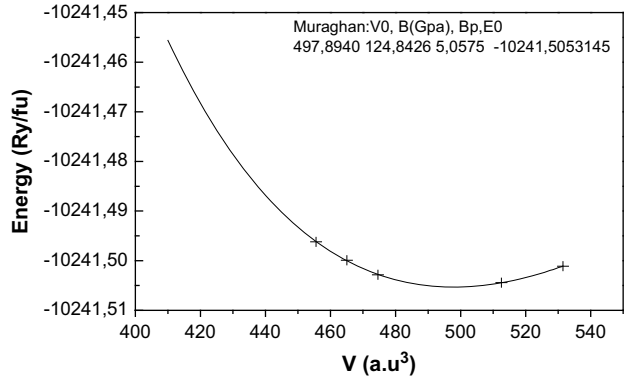

Fig. 5 – Total energy (Ry/f.u.) vs unit-cell volume for ZrNiH.

Table 2 – Experimental and calculate structural parameters of ZrNiH and $ZrNiH_3$.

Hydride	Present	Experiment [8, 23–25]
ZrNiH	$a = 3.42$ A° $b = 10.49$ A° $c = 4.13$ A°	$a = 3.36$ A° $b = 10.31$ A° $c = 4.06$ A°
$ZrNiH_3$	$a = 3.63$ A° $b = 10.76$ A° $c = 4.42$ A°	$a = 3.53$ A° $b = 10.49$ A° $c = 4.30$ A°

Table 3 – Totals energies and enthalpy of formation calculated by FP-LAPW.

compound	Total energies (Ry)	The calculate heat of formation (kJ/mol H)	The experimental heat of formation (kJ/mol H)
ZrNiH	−10241.5053	42.89	34.3 [27,28]
H_2	−2.320060		
$ZrNiH_3$	−10243.8908		

For the calculation on H_2, the molecule was isolated in a repeating cube and only the H–H bond length was allowed to relax.

With the cube of 6 Å of edge length the calculated energy is 2.32006 Ry so the calculated heat of formation is 42.89 KJ/mol H.

With the cube of 10 Å edge length the calculated energy is 2.33 Ry so the calculated heat of formation is 36.37 KJ/mol H, and this value is more accurate than the first one. But the last calculation is very expensive in terms of time and memory due to the use of all-electron full-potential linearized augmented plane-wave (FP-LAPW) method in the WIEN2K code [15]. The FP-LAPW is a very accurate method and reproduces with great precision the physical proprieties of hydrides. However, it is very expensive in time of calculations (several days and sometimes weeks) and not flexible in some cases of complex hydrides, as some DFT based codes [7,30,31].

5. Conclusions and perspectives

In this work we try to show the utility of ab-intio calculation in the choice of the hydrides suitable to the storage of hydrogen. The electronic structure has been predicted for $ZrNiH_3$, ZrNiH and ZrNi and it is in good agreement with the experiment one. The contribution of the transition atoms Zr and Ni to the metal-hydrogen bonding can be observed. Also the calculated parameters for the ZrNi hydrides are in good agreement with the experimental values. The enthalpy of formation can be theoretically given with an acceptable deviation from the experimental data.

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