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Density functional theory studies of the hydrogenation properties of Mg and Ti

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Absorption energies of hydrogen in Mg and Ti as a function of the hydrogen concentration were calculated using density functional theory. We investigated hydrogen absorbed in metal hosts with different structures (fcc, hcp, and bct for Mg; hcp and fcc for Ti). The most stable configurations were determined for different hydrogen concentrations. Rutile and fluorite structures are found to be the most stable for Mg and Ti hydrides, respectively. Preference of hydrogen filling up the interstices of the metal hosts, and crystal lattice transformations and distortions were also investigated. Hydrogen atoms prefer to pair up and form clusters in Mg; but hydrogen atoms like to occupy sites which are apart as far as possible in Ti. The differences in the hydrogenation behavior of Mg and Ti were compared and analyzed using the electron density. The hydrogenation behaviors can be related to bonding characteristic of Mg and Ti hydrides. Mg hydride is more ionic than Ti hydride.

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I. INTRODUCTION

Mg is considered to be one of the most promising materials for hydrogen storage. It is light and abundant. In spite of the fact that MgH2 satisfies the requirement set by the U.S. Department of Energy, with a theoretical capacity of 7.6 wt. % hydrogen, its high thermodynamic stability, resulting in a low partial hydrogen pressure at ambient temperatures, prevents it from being adopted as hydrogen storage material. Moreover, MgH2 suffers from slow hydrogenation kinetics.1 Recently, promising new hydrogen storage alloys were reported of Mg and Ti.2–5 Electrochemical measurements showed that adding Ti positively affects the kinetics of hydride formation which is related to structure transformation from rutile to fluorite of the hydride. This was confirmed by our previous experimental and theoretical work.6,7 Furthermore, in recent experimental work of Vermeulen et al.,8 substitution of Mg and Ti by Al or Si shifts the plateau pressure of the isotherms to higher pressures. It has been shown that, by controlling the chemistry of the metal alloy, the thermodynamic properties of Mg-based hydrides can be regulated over a wide range. The favorable storage capacity and kinetic and thermodynamic properties of the Mg-Ti hydride system make this alloy a good starting point for the development of new advanced hydrogen storage materials. The main focus of this paper is the hydride of pure Mg and Ti and their comparison.

There is abundant experimental data on hydrogen storage in pure Mg and Ti and alloys in which Mg is the major component. It has been established experimentally that Mg dihydride (MgH2) possesses a rutile-type structure at standard conditions, although a fluorite-type structure can be formed under extreme conditions.9 Vajeeston et al.10 have demonstrated by theoretical methods that the structural stability of MgH2 depends highly on pressure. Rutile type MgH2 transforms into four other modifications upon application of pressure. All polymorphs of MgH2 have a dominant ionic character.

II. COMPUTATIONAL METHODS

All calculations were performed using density functional theory as implemented in the Vienna Ab Initio Simulation Package (VASP).20,21 The Kohn-Sham equations were solved using a basis of projector augmented wave functions with a plane-wave energy cutoff of 300 eV,22 and using pseudopotentials23 to describe the core electrons. The
Perdew-Wang 1991 generalized gradient approximation was used for the electron-exchange correlation potential. A total of $13 \times 13 \times 13$ $k$ points were used to model the Brillouin zone for all investigated structures (see Fig. 1 for the unit cell).\textsuperscript{24} With this number of $k$ points, the influence of the distribution of the $k$ points on the calculated total energies became less than 0.02% and therefore this number of $k$ points was deemed sufficiently large. Energy cutoff of 300 and 400 eV shows a difference in formation energies only about 0.02%. Therefore 300 eV is sufficient.

For all structures the lattice parameters, volume and atom positions were allowed to relax, but initially symmetry restriction were imposed. When, after structure optimization with symmetry constraints, frequency calculations showed imaginary frequencies, indicating that the resulting structure was not the most stable one, the symmetry constraints were discarded and the structure reoptimized. Mg is nonmagnetic and therefore does not require spin-polarized calculations. On the other hand, we have performed spin-polarized calculations for Ti and its hydrides in the fluorite structures to estimate the importance of spin polarization on the hydride formation energies. It turned out that the inclusion of spin polarization has no effect on the hydride formation energies. Electron densities were calculated to understand the bonding properties of the metal-hydrogen and hydrogen-hydrogen bonds. A unit cell containing four metal atoms was used in all calculations.

The formation energy of the hydride in this work was defined as

$$\Delta E_{H_2} = \left( E_{M,H_2} - 4E_{M,hcp} - \frac{y}{2}E_{H_2} \right) / 2,$$

where $\Delta E_{H_2}$ is formation energy of metal hydride normalized to number of $H_2$ molecules in the hydride, and it is always used to compare formation energies of different hydrogen concentrations. $E_{H_2}$, $E_{M,H_2}$ and $E_{M,hcp}$ are the energy of the $H_2$ molecule, the metal hydride (per unit cell with four metal atoms), and the hcp metal (per metal atom) as obtained from their respective calculations.

For validation purposes, the structural parameters of the metals were calculated and compared with the literature values. The calculated cell parameters for Mg, Ti, and their hydrides are listed in Table I. The agreement between the

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice type</th>
<th>Cell parameters (Å)</th>
<th>Energy (eV)</th>
</tr>
</thead>
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<td>-6.754</td>
</tr>
<tr>
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<tr>
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<td>-7.789</td>
</tr>
<tr>
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<td>fcc</td>
<td>$a=4.10$</td>
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<tr>
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<td>hcp</td>
<td>$a=2.98$ $c=5.42$</td>
<td>-15.497</td>
</tr>
</tbody>
</table>

TABLE I. Structural parameters and energies of the elements and binary hydrides. Experimental literature values (Ref. 9) and literature values from DFT calculations for bct MgH$_2$ (Ref. 10) are in parentheses. Energies are total energies taken from VASP calculations. For the solids they are per metal atom. For the hydrides the lattice type of the metal atoms is specified. The hydrogen atoms are at tetrahedral sites so fcc corresponds to a fluorite structure, bct to a rutile structure, and hcp to a hypothetical hcp type hydride with hydrogen atoms at tetrahedral sites.

III. RESULTS AND DISCUSSION

A. Hydrogenation of Mg hydride

The hydride formation energy as a function of hydrogen loading for the metal with different structures (hcp, fcc, bct) was calculated. Various distributions of the hydrogen atoms over the interstitial sites were considered.

1. Hydrogen atom absorption in fcc Mg

Within the fcc Mg crystal there are two sets of minima which the hydrogen atom may occupy; tetrahedral sites where the hydrogen atom is fourfold coordinated and octahedral sites where the hydrogen atom is sixfold coordinated (see Fig. 1). To determine the hydrogen site preference and the influence of the hydrogen positions on the total energy, all 26 possible permutations with respect to the distribution of the hydrogen atoms over only tetrahedral sites were calculated. All four possible permutations with respect to the distribution of the hydrogen atoms over only octahedral sites were calculated as well. In addition 16 permutations with hydrogen atoms distributed over tetrahedral and octahedral sites were calculated. Tetrahedral sites are always favored
over the octahedral sites. Hydrogen in octahedral sites is 248
and 510 meV/hydrogen atom less stable than those in tetra-
hedral sites when H/M = 0.25 and H/M = 1, respectively.

When filling the fcc Mg host with two hydrogen atoms in
tetrahedral sites in the unit cell in Fig. 1 (MgH$_{0.5}$), the con-
figuration in which the hydrogen atoms are placed next to
each other (position e and f in Fig. 1) is the most stable one.
The differences in energy with respect to the structure with a
pair of hydrogen atoms in a larger (e, k) and the largest (e, l)
distance are 198 and 128 meV/hydrogen atom, respectively.
For MgH$_{0.75}$ (three hydrogen atoms in the unit cell), the most
stable distribution is that in which the hydrogen atoms are
closest to each other. Placing one hydrogen further away
results in an energy increase of 32 meV/hydrogen atom, and
placing all hydrogen atoms at distances of a/$\sqrt{2}$ results in an
even more unstable structure with an energy increment of
393 meV/hydrogen atom. For higher loadings the hydrogen
atoms always maximize the number of hydrogen-hydrogen
pairs the results with the fcc unit cell, we double the unit cell
in the direction of the a axis to form a four metal atoms cell
and 510 meV/hydrogen atom less stable than those in tetra-
hedral sites. The crystallographic c axis is in the vertical direction.

2. Hydrogen atoms absorption in hcp Mg

Within the hcp unit cell there are two Mg atoms. To com-
pare the results with the fcc unit cell, we double the unit cell
in the direction of the a axis to form a four metal atoms cell
(see Fig. 2). In the four metal atoms hcp cell there are also
eight octahedral and eight tetrahedral sites (see Fig. 2). As for
fcc Mg, 46 permutations with respect to the distribution of the
hydrogen atoms over tetrahedral and octahedral sites were
calculated. Octahedral sites are not favorable in hcp Mg
either but the difference is less than for fcc Mg. For MgH$_{0.5}$
a tetrahedral site is 30 meV/hydrogen atom more stable than
an octahedral site. At H/M = 1, the combination of four oc-
tahedral sites is 127 meV/hydrogen atom less stable than that
of four tetrahedral sites. The most stable hydrogen distribu-
tions are obtained by filling the sites in the order e, f, g, h, i,
j, k, and l. We found that in the high loading (when 1 < H/M < 2) hydrogen atoms moved away from their ideal
tetrahedral sites and the c/a ratio is increased from the origi-
nal 1.63 to 1.89 (with full hydrogen loading).

3. Hydrogen atoms absorption in bct Mg

It is experimentally found that Mg hydride has a rutile
structure below approximately 2 GPa and 1100 K. In rutile
MgH$_2$ (see Fig. 3), the hydrogen atoms are arranged approxi-
mately octahedrally around the Mg ions, which in turn are
arranged trigonally around the hydrogen atoms. When we
add a second hydrogen atom to the cell, it prefers to sit close
to the first hydrogen atom (a) at site (c). A third hydrogen
does not like to sit close to the sites a and c but rather goes to
position g. Four hydrogen atoms cluster in sites (a, b, c, d),
but a fifth hydrogen goes to position h. Hydrogen atoms in
rutile hydride refer to pair up as long as there is an even
number of hydrogen atoms. If there is an odd number of
hydrogen atoms, one always prefers to sit far away from the
cluster of the other hydrogen atoms. We found that the com-
binations (a), (a, c), (a, c, g), (a, b, c, d), (a, b, c, d, h), (a, b,
c, d, e, g), (a, b, c, d, e, g, f), and (a, b, c, d, e, f, g, h) are the
most favorable.

4. Comparison of hydrogenation in different Mg structures

Comparisons of the formation energy and volume expansion
are made in Figs. 4(a) and 4(b). Upon loading with
hydrogen, the metallic Mg atoms trade their hexagonal envi-
ronment of the hcp structure for a bct sublattice in the rutile
structure. The structure also becomes partly ionic, and the
radius of Mg shrinks upon becoming partly cationlike. This
creates room for the hydrogen atoms to be inserted. From
Fig. 4(a), at very low loading, we see that the fluorite is a
little more favorable than rutile. The reason may be geom-
metric as will be discussed in Sec. III. However when H/M
> 0.25, rutile is always the most stable. In fluorite and rutile
Mg hydride, an odd number of hydrogen atom always corre-
sponds to an increase in the energy, and coupling of two
hydrogen atom is necessary to make the hydride stable.

B. Hydrogenation of Ti hydride

The same calculations as for Mg hydride were done for Ti
hydride with the hcp and fcc metal lattice.
1. Hydrogen atoms in fcc Ti

The same distributions of hydrogen atoms over tetrahedral and octahedral sites as for fcc Mg within a unit cell at concentration from 0 to 2 were calculated. The occupancy of hydrogen atoms in the tetrahedral sites is different from that in fcc Mg. In Mg hydrogen atoms prefer to pair up and cluster together, but in Ti the hydrogen atoms stay as far apart as possible. For example, for two hydrogen atoms in fcc Ti the configuration is the most favorable one. It is 136 and 126 meV/hydrogen atom more stable than hydrogen atoms located in and , respectively. Similar behavior is found when there are more hydrogen atoms. They are located apart as far as they can within the eight tetrahedral sites. The most stable combinations in different hydrogen loadings are , , , , , , , and . The formation energy and the volume expansion are shown in Fig. 5.

We can also fill the octahedral sites first. All combinations with the same number of hydrogen atoms are equivalent. After filling four tetrahedral sites subsequent hydrogen atoms must be put in tetrahedral sites. All the possible hydrogen positions were again calculated, and the preferred order is e, f, g, and h. This means that the four tetrahedral hydrogen atoms prefer to be in a planar arrangement. As can be seen in Fig. 5(a), when H/M < 1 the formation energy decreases with the increasing hydrogen loading. When H/M > 1, the formation energy increases and becomes less negative (−1.25 eV) compared to that of all hydrogen atoms in tetrahedral sites (−1.55 eV). It can be seen that at the very low loading (H/M < 0.25), the hydrogen atoms preferentially fill the octahedral sites. Beyond H/M=0.25, the converse is true. The reason for the preference of hydrogen in octahedral site in fcc Ti at low loading will be explained in Sec. III C.

2. Hydrogen atoms in hcp Ti

A 2x1x1 hcp unit cell as for Mg has been adopted for Ti hydride (Fig. 2). The preferred order of hydrogen atoms filling the tetrahedral sites in hcp Ti is e, f, g, h, i, j, k, and l. This is the same as in Mg, but the difference is that at high hydrogen loading, the hydrogen atoms in Mg are displaced more from the exact positions of the tetrahedral sites. The original c/a ratio without hydrogen atom was 1.58, and it increases up to 1.82 with full hydrogen loading. In the case of hydrogen in octahedral sites, the occupancy occurs in the order of a, b, c, d, e, f, g, and h. Formation energies and volume expansion information with respect to hydrogen occupancy in octahedral and tetrahedral sites are shown in Fig. 5. In both cases, for hydrogen concentration H/M < 1 the formation energy decreases. Beyond H/M=1 the energy increases, which is related to the strong hydrogen-hydrogen repulsion in the octahedral and tetrahedral sites. When H/M < 0.5 hydrogen in octahedral sites is more stable than to hydrogen in tetrahedral sites, which is as for fcc Ti.

FIG. 4. Hydride formation energy (a) and volume (b) of Mg hydride (four metal unit cell) as a function of hydrogen concentration. The volume is in Å³.

FIG. 5. Formation energy (a) and volume (b) of Ti hydride (four metal unit cell) as a function of hydrogen concentration. The “O” and “T” indicate that hydrogen atoms absorb first in octahedral and tetrahedral sites, respectively. The volume is in Å³.
using geometry effects and energy contributions. With respect to the differences and the shape of the most stable formation energy curves, an explanation is given below using geometry effects and energy contributions.

1. Geometry effects

Various distances between the interstices and the radii of the interstitial sites in different structures of Mg and Ti are shown in Table II. Data listed in Table II are calculated from unhydrided metal lattice parameters. The metallic radii of Mg and Ti atom are 1.60 and 1.47 Å, respectively. Radii of the sites are calculated by subtracting the metal radii from the metal-site distances. The distances in the metals are calculated from the parameters of the unit cell. In case of fcc Mg, the first hydrogen atom prefers to absorb in a tetrahedral site. The site has a radius of 0.44 Å and the distance between the sites is 2.26 Å. When there is more than one hydrogen atom present, hydrogen atoms pair up in trigonal sites between the sites is 2.26 Å. When there is more than one hydrogen atom present, hydrogen atoms pair up in trigonal sites with a distance of 2.10 Å. When we talk about the size of the hydrogen, and a minimum hydrogen-hydrogen distance of 0.65 Å.

C. Comparison between Mg and Ti and their hydrides

Figures 4 and 5 show some important differences between Mg and Ti hydride. The most stable structures for Ti and Mg hydride are fluorite and rutile, respectively. The formation energy of the Ti hydride is much higher than that of Mg hydride. In Mg the octahedral sites are never favored. In Ti the octahedral sites are preferred at very low loading, not only in fcc but also in hcp Ti. In fcc and bct Mg the hydrogen atoms like to pair up, but in fcc Ti the hydrogen atoms prefer to stay apart. The shape of the most stable formation energy curves for Mg and Ti is different. For Mg the formation energies always decrease with increasing hydrogen concentration; for Ti, the formation energy decrease dramatically when H/M < 1, while for H/M > 1, the energy stays more or less constant. With respect to the differences and the shape of the formation energy curves, an explanation is given below using geometry effects and energy contributions.

3. Comparison of hydrogenation in different Ti structures

According to our calculations, during the hydrogenation the crystal structure changes from hcp to fcc to tetragonally distorted fcc and back to fcc. We did not find a stable hcp type hydride. With increasing hydrogen concentration the metal lattice structure rearranges from hcp to fcc. The metal keeps the fcc symmetry during hydrogen atoms filling the first octahedral site, and the two farthest tetrahedral sites. Then the third to fifth hydrogen atom causes lattice distortion from the fcc to tetragonally distorted fcc. The c/a ratios are 1.04, 1.10, and 1.08 when the third, fourth and fifth hydrogen atom are introduced, respectively. After that the structure reverts back to fcc symmetry. The volume expands 22% from 69.25 to 84.36 Å³. The formation energy decreases with increasing hydrogen concentration for H/M ≈ 1, but after that the formation energy stops decreasing and increases a bit instead. The formation energy of fluorite TiH₂ is −1.55 eV.
in the hydride. (2) Expansion of the unit cell to fit the lattice parameter of the hydride. (3) Introduction of hydrogen atoms into the interstices of the lattice so as to form the hydride.

The energy change during the first step (either the hcp converting to fcc or to bct) is very small, which we can see from Table I. The energy differences between hcp, bct, and fcc Mg are less than 0.03 eV/metal atom. Thus, two major contributions to the hydride formation energy are the chemical effect due to the hydrogen insertion and the elastic effect due to the expansion of the lattice. Here fluorite TiH2 and MgH2 are taken as an example. Four different configurations were calculated according to the hypothetical consecutive reactions. The formation energies are shown in Table III. The expansion energy is positive, but the insertion energy is much more negative, resulting in a negative formation energy for both TiH2 and MgH2.

The process of hydrogenation may be related to three different bond effects upon insertion of hydrogen. When inserting hydrogen atoms into the metal host, metal-hydrogen and hydrogen-hydrogen interactions form, while metal-metal interactions are weakened. Bonds with metallic, ionic, and covalent character may be all involved in this process. To understand the metal-hydrogen, metal-metal, and hydrogen-hydrogen interactions, electron-density calculations were performed. Figure 6 shows the valence electron-density contours of MgH2 and TiH2. Planes with only hydrogen atoms and only metal atoms parallel to (100) are shown. The valence electron density of MgH2 shows ionic character, in which the valence electrons are all localized around hydrogen sites and hardly any valence electrons around Mg sites. This agrees with the results of Vajeeston.27 In the TiH2 electron localization around both hydrogen sites and Ti sites is observed, which indicate that TiH2 is more covalent compared to MgH2.

To explain the different clustering behavior of hydrogen atoms in Mg and Ti, fcc type M4H2 is taken as example. (e, f), (e, k), and (e, l) (see Fig. 1) are three different combinations of tetrahedral sites in fcc metal. (e, f) is the one with the smallest distance, and (e, l) is with the largest one. Because Mg hydride is ionic, one might expect the hydrogen atoms to stay as far apart as possible. Ti hydride is less ionic, so hydrogen atoms might prefer to be closer there. In fact, the opposite is observed. It indicates that there must be other effect which is more important. In both Mg and Ti, the pair of hydrogen atoms absorbing in (e, f) sites has the smallest volume expansion but the biggest distortion (in fcc Mg, the volume is 96.36 Å³; lattice parameters are a=4.46 Å, b=4.64 Å, and c=4.64 Å), whereas the pair of hydrogen atoms absorbing in (e, l) has the biggest volume expansion but keeps the fcc symmetry (in fcc Mg, the volume is 98.09 Å³; lattice parameters are all 4.61 Å. In fcc Mg, hydrogen atoms absorbing in (e, f) are more favorable because the smallest volume expansion costs the least expansion energy. Once the hydrogen atom is inserted in Mg metal it becomes ionic, and the lattice distortion does not affect the nondirectional metallic-hydrogen bonding. Also Mg-Mg metal bonding is mainly nondirectional and only slightly affected by the distortion, so (e, f) is prefered because it causes the smallest volume expansion. In covalent dominated Ti-hydrogen system, the molecular geometry around each atom is determined by directional covalent bonds. The lattice distortion cost is the dominating contribution to the total energy of Ti hydride, so (e, l) is preferred.

### IV. CONCLUSIONS

We have calculated the formation energies of the Mg and Ti hydride as a function of the hydrogen concentration using DFT theory. The rutile structure is found to be the most stable for Mg hydride. Hydrogen atoms always prefer to sit in the tetrahedral sites in fcc Mg and hydrogen atoms pair up and form cluster in both bct and fcc Mg. The rutile structure is found to be the most stable for Ti hydride. At low loading hydrogen atoms prefer octahedral sites in Ti. When H/M > 0.25, hydrogen atoms start filling up tetrahedral sites. Hydrogen atoms like to occupy sites which are as far apart as possible in Ti hydride. The different site preference of hydrogen in Mg and Ti was explained as a geometry effect. The reason is probably that Ti has a smaller crystal lattice than Mg. Tetrahedral sites in Ti are too small and the distance between tetrahedral sites is too short for hydrogen atoms at low hydrogen loading. On the other hand, the lattice structure will be altered by increasing loading of hydrogen, so that tetrahedral sites are enlarged enough and the interstitial distance is extended enough to form the hydride. Another
possible reason is that the valence $d$ electrons in Ti give an electron hybridization bonding in the octahedral sites which is missing in Mg. Different bonding characteristics of Ti-hydrogen and Mg-hydrogen were found to be the reason for the different hydrogen clustering behaviors. Mg-hydrogen bond is more ionic than Ti-hydrogen. Consequently in Mg the lattice expansion is the dominating contribution to the energy difference, but in Ti lattice distortion is the dominating contribution. Future work will be the study of hydrogen absorption in MgTi alloys.

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