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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 MgH_2 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, MgH_2 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 (MgH_2) 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 MgH_2 depends highly on pressure. Rutile type MgH_2 transforms into four other modifications upon application of pressure. All polymorphs of MgH_2 have a dominant ionic character.

Pure Ti hydride forms a dihydride with a structure of the fluorite type. The Ti-H phase diagram exhibits a two-phase region when the ratio of hydrogen to metal atoms is in the range $0.1 < H/M < 0.9$ at temperatures below 573 K. When $H/M > 0.9$, only fluorite-type hydride exists.[11] X-ray and neutron-diffraction results by Sidhu *et al.*[12] indicated that H atoms might occupy octahedral sites. A number of theoretical studies with respect to various properties, such as the electronic structure, formation energies, metal-hydrogen and hydrogen-hydrogen interactions, surface properties have been carried out on Mg based[13–15] and Ti based[16–19] hydrogen storage materials as well.

Although there are many studies on various Mg and Ti metal hydrides, still some fundamental problems are not well understood. These include lattice expansion and phase transformation, and the hydrogen atom preference of the interstitial site occupancies. As far as we know, a theoretical prediction of the heat of formation of hydride as a function of hydrogen concentration is still absent. We aim to get a better understanding of geometric and thermodynamic properties by calculating the total energy as a function of the hydrogen concentration. Furthermore, the most optimal distributions of the hydrogen atoms over the interstitial sites and the hydrogen-hydrogen, metal-hydrogen, and metal-metal interactions are investigated by comparing the electron density. The paper is organized as follows. In Sec. II our theoretical approach is described. Section III presents the results and the discussions of the results. Section IV summarizes the main results of this study.

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 pseudopotentials[23] to describe the core electrons. The

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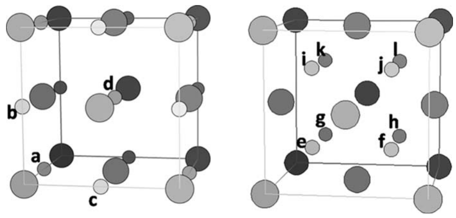

FIG. 1. fcc unit cell for Mg and Ti with four metal atoms. The big spheres represent metal and the small spheres represent hydrogen atoms. Labels a through d are positions of octahedral sites, and e to l are positions of tetrahedral sites.

Perdew-Wang 1991 generalized gradient approximation was used for the electron-exchange correlation potential. A total of $13\times13\times13$ k points were used to model the Brillouin zone for all investigated structures (see Fig. 1 for the unit cell).[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

$$\Delta E_{\mathrm{H}_2} = \left(E_{\mathrm{M}_4\mathrm{H}_y} - 4E_{M,\mathrm{hcp}} - \frac{y}{2}E_{\mathrm{H}_2}\right)/\frac{y}{2},$$

ΔE_{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}, $E_{\mathrm{M}_4\mathrm{H}_y}$ and $E_{M,\mathrm{hcp}}$ 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 literature[9,10] and calculated values is fairly good. The calculation of atomic hydrogen and molecule H_2 has been done using a cubic supercell with size $10\times10\times10$ Å^3. The bond length is predicted as 0.746 Å and the binding energy as 461 kJ/mol H_2. The agreement with the experimental data (0.741 Å and 456 kJ/mol H_2) is satisfactory.

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.

Material	Lattice type	Cell parameters (Å)	Energy (eV)
Hydrogen atom			−1.111
H_2 molecule			−6.754
Mg	hcp	a=3.19(3.21) c=5.20(5.21)	−1.477
Mg	fcc	a=4.52	−1.465
Mg	bct	a=3.72 c=3.26	−1.449
Ti	hcp	a=2.93(2.95) c=4.65(4.69)	−7.789
Ti	fcc	a=4.10	−7.732
MgH_2	bct	a=4.45(4.50) c=2.99(3.01)	−8.887
MgH_2	fcc	a=4.70	−8.559
MgH_2	hcp	a=3.18 c=6.04	−7.634
TiH_2	fcc	a=4.40(4.53)	−16.090
TiH_2	hcp	a=2.98 c=5.42	−15.497

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

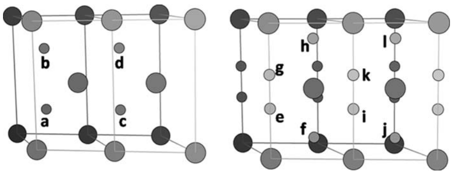

FIG. 2. hcp unit cells for Mg and Ti with four metal atoms as used in the calculations. The crystallographic unit cell is doubled in the direction of the a axis. The big spheres represent metal and the small spheres represent hydrogen atoms. Label a through d are positions of octahedral sites, and e to l are positions of tetrahedral sites. The crystallographic c axis is in the vertical direction.

over the octahedral sites. Hydrogen in octahedral sites is 248 and 510 meV/hydrogen atom less stable than those in tetrahedral 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 configuration 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 at the minimum distance of $a/2$. Hydrogen filling up the fcc Mg lattice occurs in the order of e, f, g, h, i, j, k, and l. Loading fcc Mg from $H/M=0-2$ expands the volume 13% from 92.32 to 104.08 Å^3. The metal lattice changes from fcc to tetragonally distorted fcc at $H/M=0.5$ and back to fcc when $H/M=1.75$. Between $H/M=0.5$ and 1.75, there is another interesting phenomenon. The cell parameters generally increase except when the hydrogen atoms pair up. The cubic phase transforms to a tetragonally distorted fcc structure with compression along one axis and expansion along the other two. The c/a ratios are 1.04, 1.01, 1.01, 1.01, and 1.02 for $H/M=0.5$, 0.75, 1.00, 1.25, and 1.50, respectively.

2. Hydrogen atoms absorption in hcp Mg

Within the hcp unit cell there are two Mg atoms. To compare 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 four 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 octahedral sites is 127 meV/hydrogen atom less stable than that of four tetrahedral sites. The most stable hydrogen distributions 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 original 1.63 to 1.89 (with full hydrogen loading).

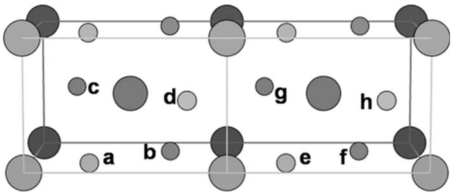

FIG. 3. bct unit cell for Mg with four metal atoms as used in the calculations. The crystallographic unit cell is doubled in the direction of the a axis. The big spheres represent metal and the small spheres represent hydrogen atoms. The crystallographic c axis is in the vertical direction.

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 approximately 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 combinations (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 environment 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 geometric 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 corresponds 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.

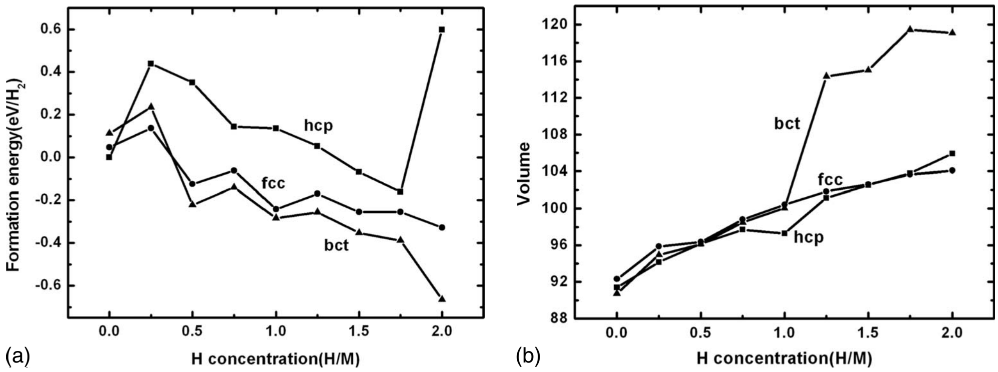

FIG. 4. Hydride formation energy (a) and volume (b) of Mg hydride (four metal unit cell) as a function of hydrogen concentration. The volume is in Å^3.

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 (e, l) configuration is the most favorable one. It is 136 and 126 meV/hydrogen atom more stable than hydrogen atoms located in (e, f) and (e, k), 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 (e), (e, l), (e, f, l), (e, f, k, l), (e, h, k, j, f), (e, f, k, l, h, i), (e, f, k, l, h, i, j), and (e, f, k, l, h, i, j, g). 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 octahedral 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 $2 \times 1 \times 1$ 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.

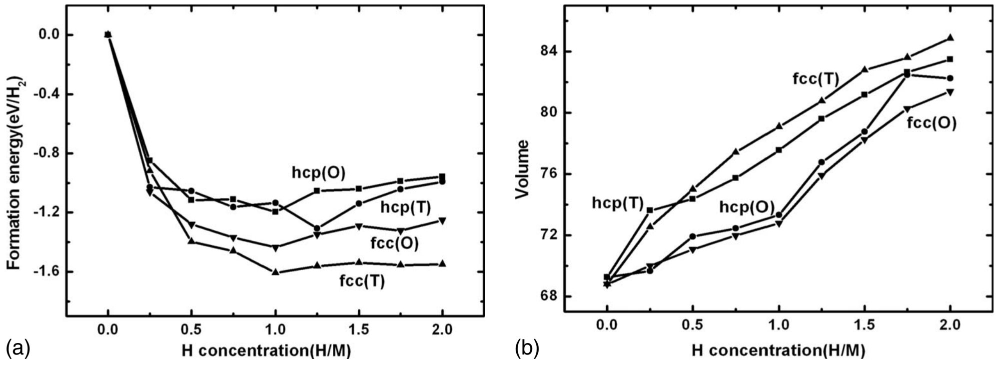

FIG. 5. Formation energy (a) and volume (b) of Ti hydride (four metal unit cell) as a function of hydrogen concentration. The “O” and “T” indicate that hydrogen atoms absorb first in octahedral and tetrahedral sites, respectively. The volume is in Å^3.

TABLE II. Structure information including cell parameters, the interstitial distance and the number and radius of the interstitial sites. Unit are in Å.

Metal	Lattice type	Cell parameters	$N_{\text{interstices}}$	Distance	Radii
Mg	hcp	$a=3.19$	4(octahedral)	2.60 (a, b)	0.65
Mg	hcp	$c=5.20$	8(tetrahedral)	2.71 (e, f)	0.34
Mg	bct	$a=3.72$	4 (trigonal)	2.10 (a, b)	0.31
Mg	bct	$c=3.26$	4 (trigonal)	2.10 (a, c)	0.31
Mg	fcc	$a=4.25$	4(octahedral)	3.20 (a, b)	0.70
Mg	fcc		8(tetrahedral)	2.26 (e, f)	0.44
Ti	hcp	$a=2.93$	4(octahedral)	2.32 (a, b)	0.58
Ti	hcp	$c=4.65$	8(tetrahedral)	2.45 (e, f)	0.27
Ti	fcc	$a=4.10$	4(octahedral)	2.90 (a, b)	0.68
Ti	fcc		8(tetrahedral)	2.05 (e, f)	0.43

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 Å^3. The formation energy decreases with increasing hydrogen concentration for $H/M \leq 1$, but after that the formation energy stops decreasing and increases a bit instead. The formation energy of fluorite TiH_2 is -1.55 eV.

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.

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,[25] 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 in bct Mg. These sites are comparative smaller; 0.31 Å and with a distance of 2.10 Å. When we talk about the size of the site, the expansion of the metal lattice, should be taken into account. The trigonal sites become favorable because their size is increased and they become big enough for hydrogen atoms. This size factor is consistent with the Westlake criterion,[26] which states that the available interstitial sites must have a minimum radius of 0.4 Å to be occupied by hydrogen, and a minimum hydrogen-hydrogen distance of 2.1 Å. It can be used to rationalize the observed site occupancies. When more than one type of site meets the size criterion, the occupancy is apparently such as to yield a densest hydrogen atom packing within the limits of the hydrogen-hydrogen distance criterion. Our results are in agreement with this criterion. In the case of Ti, it is understandable that the tetrahedral sites in both of hcp and fcc lattices are not favorable at the very low loading because of the limited size of the site. The octahedral site in fcc is favorable in low loading. In high loading, with the lattice expansion, tetrahedral sites in fcc become bigger and are available for hydrogen atoms.

2. Electronic effects

Having analyzed the geometric effect, we now explain the shape of the formation energy curves and the pairing of hydrogen atoms by analyzing the electronic energy contributions during hydriding. Miwa[18] and Smithson[19] split the total hydride formation reaction into three hypothetical consecutive reactions, the energy of each of which can be directly related to the electronic structure. The three reactions are the following. (1) Lattice structure conversion of the metal from its equilibrium one to the structure that the metal atoms form

TABLE III. Decomposition of the formation energy (see text) of fluorite MgH_2 and TiH_2 obtained for a unit cell of four metal atoms. The unit of the energy is eV/metal atom.

Metal	Lattice conversion	Lattice expansion	Hydrogen insertion
Ti	0.20	1.07	−6.19
Mg	0.03	0.17	−1.31

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 TiH_2 and MgH_2 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 TiH_2 and MgH_2.

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 MgH_2 and TiH_2. Planes with only hydrogen atoms and only metal atoms parallel to (100) are shown. The valence electron density of MgH_2 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 TiH_2 electron localization around both hydrogen sites and Ti sites is observed, which indicate that TiH_2 is more covalent compared to MgH_2.

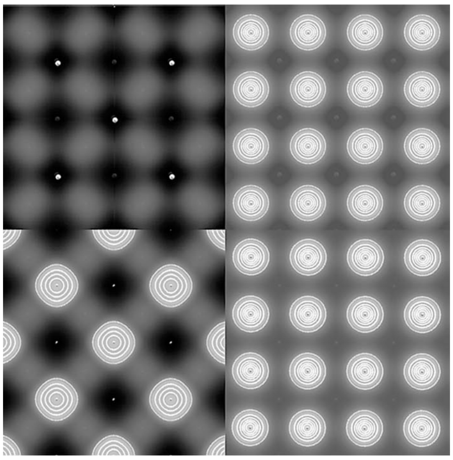

FIG. 6. Valence electron density for Mg (top) and Ti (bottom) fluorite hydride in cross sections parallel to (100). On the left are electron densities in a plane with only metal atoms; on the right are electron densities in a plane with only hydrogen atoms. The contour lines are drawn from 0 to 1.72 (1.74) for Mg (Ti) hydride at 0.22 $e/\text{Å}^3$ intervals.

To explain the different clustering behavior of hydrogen atoms in Mg and Ti, fcc type M_4H_2 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 Å^3; 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 Å^3; 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 metal-hydrogen ionic bonding much. Also Mg-Mg metal bonding is mainly nondirectional and only slightly affected by the distortion, so (e, f) is preferred 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 fluorite 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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[1] K. H. J. Buschow, P. C. P. Bouten, and A. R. Miedema, Rep. Prog. Phys. **45**, 937 (1982).

[2] R. A. H. Niessen and P. H. L. Notten, Electrochem. Solid-State Lett. **8**, A534 (2005).

[3] P. Vermeulen, R. A. H. Niessen, and P. H. L. Notten, Electrochem. Commun. **8**, 27 (2006).

[4] P. Vermeulen, R. A. H. Niessen, D. M. Borsa, B. Dam, R. Griessen, and P. H. L. Notten, Electrochem. Solid-State Lett. **9**, A520 (2006).

[5] D. M. Borsa, A. Baldi, M. Pasturel, P. Vermeulen, P. H. L. Notten, B. Dam, and R. Griessen, Appl. Phys. Lett. **88**, 241910 (2006).

[6] B. R. Pauw, W. P. Kalisvaart, S. X. Tao, M. T. M. Koper, A. P. J. Jansen, and P. H. L. Notten, Acta Mater. **56**, 2948 (2008).

[7] W. P. Kalisvaart, R. A. H. Niessen and P. H. L. Notten, J. Alloys Compd. **417**, 280 (2006).

[8] P. Vermeulen, E. F. M. J. van Thiel, and P. H. L. Notten, Chem.-Eur. J. **13**, 9892 (2007).

[9] P. Villars, *Pearson's Handbook "Crystallographic Data for Intermetallic Phases"* (ASM International, Materials Park, OH, 1997).

[10] P. Vajeeston, P. Ravindran, A. Kjekshus, and H. Fjellvåg, Phys. Rev. Lett. **89**, 175506 (2002).

[11] G. Libowitz, J. Nucl. Mater. **2**, 1 (1960).

[12] S. S. Sidhu, L. Heston, and D. D. Zauberis, Acta Crystallogr. **9**, 607 (1956).

[13] S. Banerjee, C. G. S. Pillai, and C. Majumder, J. Chem. Phys. **129**, 174703 (2008).

[14] A. J. Du, Sean C. Smith, X. D. Yao, and G. Q. Lu, Surf. Sci. **600**, 1854 (2006).

[15] G. N. García, J. P. Abriata, and J. O. Sofo, Phys. Rev. B **59**, 11746 (1999).

[16] R. Yang, Y. M. Wang, Y. Zhao, L. B. Wang, H. Q. Ye, and C. Y. Wang, Acta Mater. **50**, 109 (2002).

[17] W. Wolf and P. Herzig, J. Phys.: Condens. Matter **12**, 4535 (2000).

[18] K. Miwa and A. Fukumoto, Phys. Rev. B **65**, 155114 (2002).

[19] H. Smithson, C. A. Marianetti, D. Morgan, A. Van der Ven, A. Predith, and G. Ceder, Phys. Rev. B **66**, 144107 (2002).

[20] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[21] G. Kresse and J. Furthmüller, Comput. Mat. Sci. **6**, 15 (1996).

[22] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[23] J. P. Perdew, J. Phys.: Condens. Matter **172**, 1 (1991).

[24] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[25] N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements* (Butterworth-Heinemann, Oxford, 1997).

[26] D. G. Westlake, J. Less-Common Met. **75**, 177 (1980); **90**, 251 (1983); **91**, 275 (1983).

[27] P. Vajeeston, P. Ravindran, B. C. Hauback, H. Fjellvåg, A. Kjekshus, S. Furuseth, and M. Hanfland, Phys. Rev. B **73**, 224102 (2006).