The Electronic Structure of MgY$_2$H$_{6+x}$ High-Pressure Hydride

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The electronic structure of the MgY$_2$H$_{6+x}$ high-pressure hydride has been investigated by means of the full potential linearized augmented plane wave method, and the stability of the octahedral and tetrahedral sites for H atoms has been discussed. The calculation models used were MgY$_2$H$_{6+x}$, corresponding to H/M = 2–3. From the calculation of the density of states for MgY$_2$H$_{3+1}$, it was found that the states originating from H-s and Y-d mainly formed valence and conduction bands, respectively. In the valence band, bonding states originating from H-s of tetrahedral sites, Y-d, Y-p, and Mg-p can be observed in a wide energy range, especially between −3 ~ −5 eV below the Fermi level. In addition, the contour plots of the valence electron charge density revealed that the bonding between Y and H atoms on the tetrahedral sites was predominantly covalent, while the H atom on the octahedral sites showed a weak interaction with Y and H atoms on the tetrahedral sites. The cell volume optimization indicated that the calculated equilibrium volume linearly increased with increasing the number of vacancies on the octahedral sites, while it decreased in the case of introducing the vacancy on the tetrahedral site. From these observations, it can be concluded that the H atoms on the tetrahedral sites seem to be responsible for holding its crystal structure, while ones on the octahedral sites had a certain level of contribution to enhancing the bond strength. These observations support the experimental results that the crystal structure of MgY$_2$H$_{6+x}$ is stable even after the partial desorption of hydrogen, which presumably occupy the octahedral sites, at around 600 K.

Keywords: high-pressure hydride, magnesium-yttrium-based hydride, full potential linearized augmented plane wave method, electronic structure, density of states, charge density

1. Introduction

Mg-based alloys and their hydrides have been extensively studied because of their promising applications as hydrogen storage media. However, it is well known that the Mg-based hydrides need high operating temperatures, especially for dehydrogenation, due to ionic or covalent bonds between Mg and H atoms. To improve the low desorption properties, a number of studies, such as micro- and nanostructural evolution of Mg and Mg-Ni alloys, have been conducted. In addition to this, it is important to keep exploring new Mg-based hydrides. For that purpose, the high-pressure synthesis has been increasingly utilized. As examples, novel hydrides of Mg$_3$MnH$_7$ and REMg$_2$H$_6$ (RE = La, Ce) have been prepared by using either of anvil- or autoclave-type apparatuses. Moreover, Mg$_2$Ni$_3$H$_{14}$, (Ca, Mg)$_2$NiH$_6$, and MgY$_2$H$_{6+x}$ (δ ≈ 1.8; H/M ≈ 2.6) have been synthesized in our previous work. Among them, MgY$_2$H$_{6+x}$ with an FCC-type structure was found to be stable even after partial dehydrogenation, unlike other high-pressure hydrides that immediately decomposed into stable phases by dehydrogenation. From the crystal structural and thermogravimetric analyses, it was suggested that H atoms may occupy two different crystallographic sites in MgY$_2$H$_{6+x}$, i.e. tetrahedral and octahedral sites. Moreover, H atoms occupying the octahedral sites seemed to be preferably desorbed at lower temperatures than those on tetrahedral sites. To clarify differences in the stability of tetrahedral and octahedral sites in MgY$_2$H$_{6+x}$, further information on electronic structures and chemical bonding between metal and H atoms is required. To date, the electronic structures and the nature of chemical bonding in metal hydrides, including high-pressure hydrides of REMg$_2$H$_6$ (Re = La, Ce), have been calculated by means of the local density approximation (LDA) of density-functional theory and the GW approximation (GWA). However, the electronic structure of the MgY$_2$H$_{6+x}$ high-pressure hydride remains unknown.

This paper describes the electronic structure of the MgY$_2$H$_{6+x}$ high-pressure hydride calculated by means of the local density approximation (LDA) of the density-functional theory. The stability of the octahedral and tetrahedral sites for H atoms will be discussed in the context of the density of states, charge density plots, and total energies as a function of the unit cell volume for various structures of MgY$_2$H$_{6+x}$ with hydrogen vacancies.

2. Structure Models and Calculation Methods

The crystal structure of MgY$_2$H$_{6+x}$ was determined by the Rietveld method. The detailed structural data have been described elsewhere MgY$_2$H$_{6+x}$ exhibits an FCC-type structure with a lattice constant of a = 0.51657(2) nm as shown in Fig. 1(a). Since reflections coming from a superstructure were not observed in the X-ray diffraction patterns, Mg and Y seem to randomly occupy the metal atom sites. However, an L1$_2$-type metal-sublattice structure, in which Mg and Y occupy the corner and face-centered positions, respectively, was used as a calculation model in this study. By assuming this ordered crystal structure, it is possible to compute the electronic structure of MgY$_2$H$_{6+x}$ without using a supercell. This assumption was useful to simplify the calculation model for reduction of the computational time. Note that the compositional ratio of Mg and Y (1 : 3) slightly differs from the real one (1 : 2) under this assumption. H atoms were estimated to be able to occupy eight of tetrahedral and four of octahedral sites. Hereafter, the sites will be referred as T- and O-sites, respectively. Figure 1(b) shows the schematic illustration of the (110) plane of MgY$_2$H$_{12}$ (H/M = 3), in which O1-sites are coordinated by

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two of Mg and four of Y atoms, while O2-sites are surrounded by six of Y atoms. Therefore, O1- and O2-sites can be regarded as a different environment. As mentioned above, since the H/M ratio of MgY\(_2\)H\(_6\) is experimentally determined as close to 2.6 (\(\delta \approx 1.8\)), MgY\(_2\)H\(_{11}\) with a vacant O1-, O2-, or T-site (H/M = 2.75) was employed as a calculation model. In addition, the electronic structure of MgY\(_3\)H\(_8\) (H/M = 2) was computed as well.

The electronic structures of the Mg–Y-based high-pressure hydrides were computed by means of the full potential linearized augmented plane wave (FPLAPW) method. The program code used was WIEN2k developed by Blaha et al.\(^{15}\) For the exchange and correlation potentials, the generalized gradient approximation (GGA) was utilized.\(^{16}\) Inside muffin-tin spheres, the wave function was expanded in spherical harmonics with \(l_{\text{max}} = 10\) for the potential and charge density representations, while non-spherical components of the density and potentials are included up to \(l_{\text{max}} = 6\). Muffin-tin radii of 0.116 (2.2), 0.105 (2.0), and 0.085 (1.6) nm (a.u.) for Y, Mg, and H atoms were assumed, respectively, and RK\(_{\text{max}}\) was fixed to 7.0 throughout this study. The total density of states (DOS) and angular-momentum-resolved density of states for each element (PDOS) were calculated. The total energies as a function of cell volumes were also calculated around the equilibrium volumes to clarify the role of H atoms on the chemical bonding in the structure.

3. Results and Discussion

3.1 Density of states

First of all, assuming that one of the four O-sites was vacant, PDOS and DOS for MgY\(_3\)H\(_{11}\), which corresponded to H/M = 2.75, was calculated. Figure 2 shows the PDOS and DOS of MgY\(_3\)H\(_{11}\) with a vacant O1-site. As well as many hydrides, the states originating from H-s and Y-d mainly formed valence and conduction bands, respectively. Precisely speaking, PDOS coming from H-s of O2-sites (third column) tended to increase at near the Fermi level (\(E_F\)) and in the conduction band. This may suggest the O-sites should be more instable than the T-sites. In the valence band, bonding states originating from H-s of T-sites, Y-(p, d), and Mg-(s, p) can be observed in a wide energy range, especially between \(-3 ~ -5\) eV below \(E_F\). Moreover, since a small energy gap of about 0.2 eV was found to exist, this hydride might be a semi-conductor. To clarify the effect of difference in the H vacancy site on the PDOS and DOS, the same calculations were conducted for the other structure models.

Figure 3 shows the PDOS and DOS of MgY\(_3\)H\(_{11}\) with a vacant O2-site. Even though the band gap was slightly increased up to 0.6 eV, PDOS and DOS were similar to those...
of MgY$_3$H$_{11}$ with a vacant O1-site. The valence and conduction bands were predominated by the states originating from H-s and Y-d, respectively. In Fig. 3(c), PDOS coming from H-s of the O-sites (dashed line) tended to show large values at a higher energy region ($\approx 1 \sim 3$ eV), while that of the T-sites (solid line) showed a maximum value at around $0.8$ eV. On the other hand, as shown in Fig. 4, PDOS and DOS for MgY$_3$H$_{11}$ with a vacant T-site exhibited a different behavior. In Fig. 4(c), PDOS of H-s for the O-sites showed a relatively large value at around $0.5$ eV. This difference may suggest that the site of H vacancies affects the chemical bonding between H atoms and cations. Moreover, a finite density of states was observed at $E_F$, implying a metallic state in this calculation model.

Regarding a magnitude of the band gap, $E_g$, a relatively large value ($e.g. E_g \geq 2$ eV) was expected to appear, since the resultant sample showed yellowish color but not metallic after the preparation under high pressures.$^{35}$ However, as mentioned above, a small gap of 0.2–0.6 eV and even a metallic states depending on the vacancy sites were obtained from these calculations. This discrepancy in a magnitude of $E_g$ is also observed in the band structure calculation of YH$_x$, which is well known to exhibit a metal-insulator transition depending on the hydrogen content of $x$. Their band structures have been calculated by LDA and GWA. For the band structure calculation of semi-conductive YH$_3$ phase, there is an argument that LDA without a self-energy correction tends to give a conduction band that is shifted down by 2–3 eV compared to the quasiparticle band structure calculated by GWA with a self-energy correction. As a result, for LDA calculation of YH$_3$, the valence and conduction bands are overlapped with a magnitude of about 0.8 eV, while the band gap of about 2 eV should appear based on optical measurements. This discussion is well documented in Ref. 11). However, it is also pointed out in Ref. 11) that the valence band itself is insensitive to the self-energy correction, and as a result, both of LDA and GWA give a similar valence band structure including a wide bandwidth of H-s. The small value of $E_g$ obtained for MgY$_3$H$_{11}$ seems to originate from the same reason. In fact, the shape of PDOS and DOS calculated for MgY$_3$H$_{12}$ was very similar with those for Y$_4$H$_{12}$ with the same lattice parameters.

Therefore, even though further consideration is required to quantitatively evaluate a magnitude of $E_g$, the following can be pointed out regarding PDOS and DOS for MgY$_3$H$_{11}$ with a vacant H site: 1) the states originating from H-s and Y-d mainly formed valence and conduction bands, respectively; 2) H atoms on the T-sites had an important role on the chemical bonding; and 3) an energy gap was observed for the calculation models with a vacant O-site.

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**Fig. 3** Total, site, and angular-momentum-resolved density of states for MgY$_3$H$_{11}$ with a vacant O2-site. $V_{H(O2)}$ denotes the vacancy on the O2-site.

**Fig. 4** Total, site, and angular-momentum-resolved density of states for MgY$_3$H$_{11}$ with a vacant T-site. $V_{H(T)}$ denotes the vacancy on the T-site.
3.2 Charge density

To clarify the role of H atoms on the chemical bonding in the novel Mg–Y-based high-pressure hydride, charge densities were calculated. Figure 5 shows the valence electron charge density plots of MgY$_3$H$_{11}$ with a various vacant site in the (110) plane, in which the contour line corresponding to the electron density of 200 e/nm$^3$ is indicated as a thicker line. The density plot of MgY$_3$H$_8$ corresponding to H/M = 2 was plotted as well. For MgY$_3$H$_{11}$ with a vacant O1-site (Fig. 5(a)), Mg and Y atoms can be seen on the corner and the middle of the horizontal axis, respectively. Moreover, four of H atoms on T-sites and one H atom on the O2-site (center) can be observed. From this contour plot, it should be noted that the bonding between Y and H atoms on the T-sites is predominantly covalent judging from the existence of a finite charge density between them. On the other hand, the covalent bonding between Mg and H atoms on the T-sites appears to be weaker than that in the Y–H bonding. In addition, the H atom on the O2-site also showed a weak interaction with Y and H atoms on the T-sites, suggesting the instability of this site.

For MgY$_3$H$_{11}$ with a vacant O2- or T-site, and MgY$_3$H$_8$ (Figs. 5(b), (c), and (d), respectively), the same magnitude of covalent interactions between Y and H atoms on the T-sites was observed. In addition to this, the H atom on the O-sites shows a weak bond towards H atoms on the T-sites in Figs. 5(b) and (c). From these contour plots of the valence electron charge density, as expected, it can be said that the covalent bonding between Y and H atoms on the T-sites has an important role on holding its crystal structure, while the H atoms on the O-sites also have a certain level of contribution to the chemical bonding. This observations support the experimental results that the crystal structure of MgY$_3$H$_{6+2}$ is still stable even after the partial desorption of hydrogen, which presumably occupy the O-sites, at around 600 K.

3.3 Volume optimization

The difference in the role of H on the chemical bonding was also investigated in the context of the volume optimization. Figure 6 shows the total energy as a function of the unit cell volume of (a) MgY$_3$H$_{12}$ without H vacancies (H/M = 3), (b) MgY$_3$H$_{11}$ with a vacant O-sites (H/M = 2.75), and (c) MgY$_3$H$_8$ (H/M = 2). The calculated equilibrium volumes, corresponding to minimum points indicated by arrows, showed a relatively good agreement with the observed volume (0.1378 nm$^3$), within a deviation of 2–5%. It should be also noted that the calculated equilibrium volume tends to increase with the number of H vacancies on the O-sites.

The equilibrium volume and bulk modulus that can be also obtained from the volume optimization are then plotted as a function of the number of H vacancies in Figs. 7(a) and (b), respectively. In which, the results of the volume optimization for MgY$_3$H$_{11}$ with a vacant T site are plotted as well. For a series of MgY$_3$H$_{11}$ with O-site vacancies, the calculated equilibrium volume (Fig. 7(a)) linearly increases with increasing the number of vacancy sites. On the other hand,
the volume decreased in the case of introducing the T-site vacancy. Since a small volume expansion of 0.6% was experimentally observed after the partial desorption of hydrogen at around 600 K, hydrogen emitted at the temperature range was considered to originate from the O-sites.

In addition, the bulk modulus (Fig. 7(b)) decreased with increasing the number of hydrogen vacancies regardless of the occupancy sites. In other words, the hydrogenation enhances the bond strength as observed in the other metal hydrides. From these calculations, it can be concluded that, in the novel Mg–Y-based high-pressure hydride, the H atoms on the T-sites, which show the covalent nature, are responsible for holding its crystal structure, while ones on the O-sites, which have a certain level of contribution to enhancing the bond strength, can be released without the corruption of the crystal structure.

4. Conclusions

The electronic structure of the MgY$_2$H$_{6+}$ high-pressure hydride has been investigated by means of the FP-LAPW method, and the stability of the octahedral and tetrahedral sites for H atoms has been discussed. From the calculation of the PDOS and DOS for MgY$_3$H$_{11}$ with a vacant H site, it was found that the states originating from H-s and Y-d mainly formed valence and conduction bands, respectively. In the valence band, bonding states originating from H-s of T-sites, Y-d, Y-p, and Mg-p can be observed in a wide energy range, especially between $-3 \sim -5$ eV below $E_F$, while the PDOS coming from H-s of O-sites tended to increase at near $E_F$ and in the conduction band. In addition, the contour plots of the valence electron charge density revealed that the bonding between Y and H atoms on the T-sites was predominantly covalent, while the H atom on the O-site showed a weak interaction with Y and H atoms on the T-sites. Moreover, the volume optimization indicated that the equilibrium volume showed a good agreement with the observed value within a deviation of 2–5%, and the volume linearly increased with increasing the number of O-site vacancies, while it decreased in the case of introducing the T-site vacancy.

From these observations, it can be concluded that the H atoms on the T-sites, which show the covalent nature, seem to be responsible for holding its crystal structure, while ones on the O-sites had a certain level of contribution to enhancing the bond strength. These observations support the experimental results that the crystal structure of MgY$_2$H$_{6+}$ is stable even after the partial desorption of hydrogen, which presumably occupy the O-sites, at around 600 K.

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