Hydrogen storage of $Mg_{1-x}M_xH_2$ (M=Ti, V, Fe) studied using first-principles calculations

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In this work, the hydrogen storage properties of the Mg-based hydrides, i.e., $Mg_{1-x}M_xH_2$ (M=Ti, V, Fe, $0 \leq x \leq 0.1$), are studied using the Korringa–Kohn–Rostoker (KKR) calculation with the coherent potential approximation (CPA) approximation. In particular, the nature and the concentrations of the alloying elements and their effects are studied. Moreover, the material's stability and hydrogen storage thermodynamic properties are discussed. In particular, we find that the stability and the temperature of desorption decrease without significantly affecting the storage capacities.

Keywords: first-principles calculation, formation energy, electronic structure, hydrogen storage

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1. Introduction

Up to date, the magnesium is one of the most attractive materials for hydrogen storage applications due to its high gravimetric and volumetric capacities (7.65 wt.% and 110 gH2/l, respectively) in the form of stoichiometric binary MgH_2.[1] However, its slow hydrogen absorption and desorption kinetics as well as the high dissociation temperature of 573–673 K, essentially limit its application for hydrogen storage.[2] Numerous attempts have been made to improve the magnesium hydrogen absorbing-desorbing characteristics. Experimentally, it has been reported that the mixing magnesium or the magnesium hydride with small amounts of transition metals (TM) or their oxides drastically accelerates the hydrogen kinetics, and a slight decrease of the desorption temperature was observed.[3–9]

Electronic structure studies of Mg-based alloy hydrides are performed to predict further modifications that destabilize the corresponding hydrides by lowering the desorption temperature and enhance the hydrogen kinetics characteristics. Several theoretical studies have been carried out to clarify the mechanisms of the alloying effects on the thermodynamic properties of the magnesium-based hydrides.[10–16] On the other hand, the observed catalytic mechanism is still not adequately explained.

The aim of this work is to study the electronic structures of Mg-based hydrides $Mg_{1-x}M_xH_2$ (M=Ti, V, Fe) with $0 \leq x \leq 1$ by using the Machikaniyama2000 KKR (Korringa-Kohn-Rostoker) code package from Akai of Osaka University.[17,18] The code package is based on the coherent potential approximation (CPA), and provides an intuitive yet accurate approach when combined with the generalized gradient approximation (GGA) methods, and it gives very good results for alloying systems. The obtained results are used to discuss the hydrogen storage thermodynamic properties. In particular, we find that the stability and the temperature of desorption decreases without significantly affecting the storage capacities.

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2. Computational methods

To solve the density functional theory (DFT) one-particle equations, we use the multiple-scattering theory, i.e. the KKR Green's function (KKR-GF) method and the KKR-CPA for low impurity concentrations. The coherent potential approximation is employed to describe the random disordered distribution of impurities. The relativistic effects are taken into account by using the scalar relativistic approximation. The crystal potential is approximated by a muffin-tin potential, and the wave functions in the respective muffin-tin spheres are expanded in real harmonics up to $l = 3$, where l is the angular momentum quantum number defined at each site. In our calculations, 1000 k-points in the irreducible part of the first Brillouin zone are used. For the present KKR-CPA calculations, the package MACHIKANEYAMA2000 coded by Akai[18] is used. In this study, the KKR method within the GGA and the GGA91 for parameterization of the exchange energy[19] is applied. Table 2 shows that the calculated values are in good agreement with those obtained by the Wien2K code.[14,20−22]

The hydride MgH_2 crystallized in the rutile-type structure ($P4_2/mnm$, space group N°136) at ambient conditions.[23] The Wyckoff positions of Mg and H are 2a (0, 0, 0) and 4f (0.304, 0.304, 0), respectively (Fig. 1). The lattice constants used as the input for our calculation are the experimental values, $a = 4.501$Å and $c = 3.01$Å.[23] The lattice constants of Mg, Ti, V, and Fe (Table 1) are taken as reference.[24]

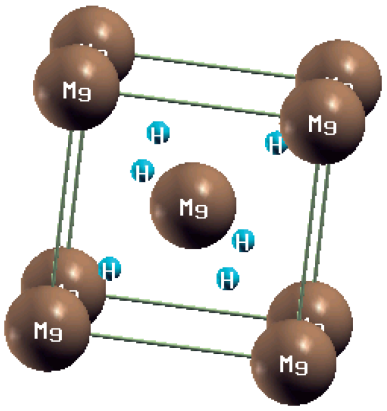


Fig. 1. (colour online) Crystal structure of MgH_2 in the primitive cell.

Table 1. Lattice parameters of simple elements.

Element	Space group	Crystalline structure	a/Å	c/Å
Mg	194–$P6_3/mmc$	Hcp	3.21	5.21
Ti	194–P_3/mmc	Hcp	2.95	4.68
V	227–$Im3m$	Bcc	3.03	3.03
Fe	227–$Im3m$	Bcc	2.87	2.87

3. Results and discussion

3.1. Structural relaxation

We first study the effect of doping on the structure relaxation. The total energy of the system computed by the DFT method depends on the nucleon positions, hence we can minimize the energy functional with respect to the positions. The total energy of MgH_2 as a function of lattice parameter a before and after doping with a certain element (Ti, V, and Fe), has been calculated using the Hellmann–Feynman method[25] in the KKR-CPA method with the GGA91 parameterization.[19] Our results are given in Fig. 2. The equilibrium positions corresponding to the minimal energies for both cases (MgH_2 and MgH_2:TM) are determined by $a_{eq} = 4.585$ Å and the ratio $c/a = 0.6572$. These values are comparable to those obtained experimentally ($a = 4.501$ Å and $c/a = 0.6687$)[22]

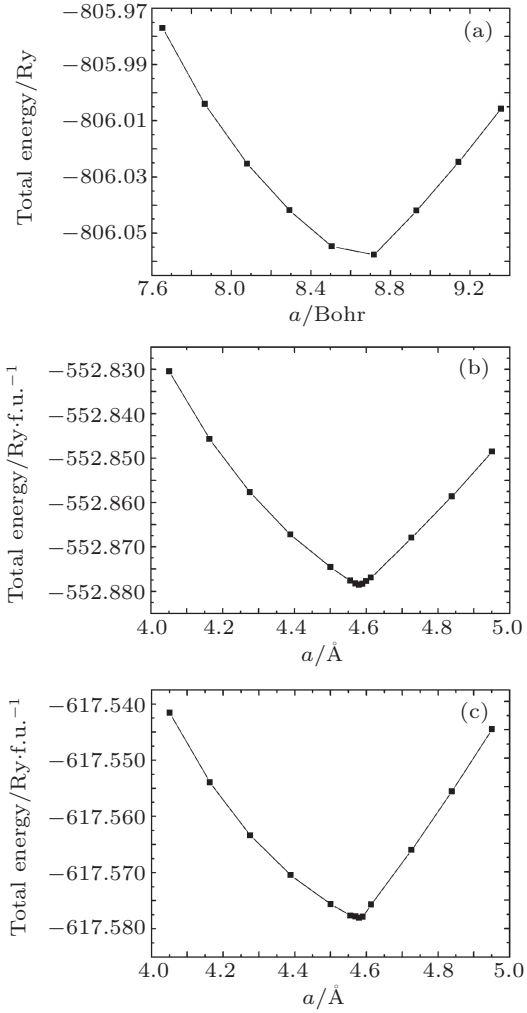


Fig. 2. Total energies of (a) MgH_2, (b) $Mg_{0.9}V_{0.1}H_2$, and (c) $Mg_{0.9}Fe_{0.1}H_2$ each as a function of parameter a of the primitive cell.

and ($a = 4.515$ Å and $c/a = 0.6686$).[26] This means that the volumetric capacity is the same for MgH_2 and MgH_2:TM. This good agreement allows validating our modeling approximations based on the KKR-CPA method with the GGA91 parameterization.

3.2. Hydrides stability: heat of formation

We now evaluate the heat of formation (ΔH) of hydride MgH_2 before and after doping with certain transition metals to study the stability of these hydrides. The heat of formation ΔH is the most important thermodynamic parameter used to identify and classify hydrogen storage materials. This is due to the fact that it can be used to determine the heat of the hydrogenation reaction ($\Delta H < 0$ hydride is stable and vice versa) and deduce the temperature of desorption of hydrogen from the system. The ΔH of hydride can be defined as the difference between the sums of total energies of products and reactants[10]

$$\Delta H_{\rm HF} = \sum E_{\rm tot}(\text{products}) - \sum E_{\rm tot}(\text{reactants}). \quad (1)$$

The reaction related to the formation of hydride MgH_2 reads

$$\text{Mg} + \text{H}_2 \rightarrow \text{MgH}_2. \quad (2)$$

To calculate the heat of formation of reaction (2), we subtract the total energies of the pure element Mg and the hydrogen molecule from that of hydride MgH_2

$$\Delta H = E_{\rm tot}(\text{MgH}_2) - E_{\rm tot}(\text{Mg}) - E_{\rm tot}(\text{H}_2). \quad (3)$$

The value of the total energy of the H_2 molecule, $E_{\rm tot}(\text{H}_2) = -2.320$ Ry, has been taken from Refs. [6] and [27], and that of Mg is calculated and is equal to -400.6670692 Ry, which is comparable to that obtained in Ref. [28].

The calculated enthalpy of formation based on the KKR-CPA method for the magnesium hydride with the optimized and the experimental structure parameters are -85.709 kJ/mol|*cdot*H_2 and -79.577 kJ/mol·H_2, respectively (see Table 2). These values are comparable to those obtained experimentally, -74.3 ± 0.5 kJ/mol·H_2,[29] -81.2 kJ/mol·H_2,[30] and -76.15 ± 9.2kJ/mol·H_2.[22] This good agreement allows validating our modeling approximations based on the KKR-CPA method with the GGA91 parameterization.

Table 2. Total energies and heats of formation obtained with experimental and optimized parameters of MgH_2.

Element	Total energy/Ry·f.u.$^{-1}$		Formation heat/kJ·mol^{-1}·H_2	
	Our cal.	Literature	Our cal.	Literature
Mg	–400.6670692	–400.6675[33]	–	–
H_2	–	–2.320[5,26]	–	–
MgH_2[a)]	–403.0477706	–403.042937[13]	–79.577	–74.3 ± 0.5[27]
MgH_2[b)]	–403.0524479		–85.709	

[a)]with experimental parameters, [b)]with optimised parameters

In order to destabilize the MgH_2 systems, transition elements have been introduced, which are known for their role in the destabilization of magnesium hydride[6,28] following the reaction

$$\text{MgH}_2 + xM \rightarrow \text{Mg}_{1-x}M_x\text{H}_2 + x\text{Mg}. \quad (4)$$

Based on this reaction, we can calculate the enthalpies of formation of doped Mg-based hydrides according to the following formula:

$$\Delta E_{\rm HF} = E_{\rm tot}(\text{Mg}_{1-x}M_x\text{H}_2) + x(E_{\rm tot}(\text{Mg}) - E_{\rm tot}(M)) - E_{\rm tot}(\text{MgH}_2), \quad (5)$$

where the total energies per atom for the pure elements are calculated and listed in Table 3. The total energies as well as the resulting heats of formation of the studied hydrides are listed in Table 4. It is shown that the addition of the transition metal to MgH_2 generally reduces the stability of MgH_2, which can lead to an improvement of the dehydrogenation kinetics. This agrees well with the trend observed experimentally[6] and theoretically.[6,28] This destabilization effects on MgH_2 obtained in this work increase in the order of Fe, Ti, and V according to the values of heat of formation of the mixtures. It follows from Eq. (5) that we can control the value of the heat of formation in $Mg_{1-x}M_xH_2$ (M=V, Ti, and Fe, $0 < x < 1$) by varying the concentrations of the doped elements. In fact,

it is shown in Fig. 3 that when we increase the concentration, the heat of formation decreases linearly with a specific slope for each dopant. Consequently, for each doped element, the stability increases until it reaches the one associated with MgH_2 according to its specific concentration C_S in the following order: $C_S(MgH_2{:}Fe)<C_S(MgH_2{:}V)<C_S(MgH_2{:}Ti)$, see Table 5.

Table 3. Total energy per atom for pure elements.

Element	Total energy/Ry·f.u.$^{-1}$
Mg	–400.6670692
Ti	–1707.629854
V	–1898.637153
Fe	–2545.544327

Table 4. Total energy and heat of formation of $Mg_{1-x}M_xH_2$ (M=Ti, V, and Fe) with $x = 0.01$, 0.05, and 0.1.

System	Total energy/Ry	Heat of formation/kJ·mol^{-1}·H_2
MgH_2	–806.104896	–85.709
$Mg_{0.95}Ti_{0.05}H_2$	–936.82869	–18.05273336
$Mg_{0.95}V_{0.05}H_2$	–955.932961	–20.37647298
$Mg_{0.95}Fe_{0.05}H_2$	–1020.63547	–28.11172472

Table 5. Concentration limits (C_S) and gravimetric hydrogen capacities of $Mg_{1-x}M_xH_2$ (M=Ti, V, and Fe).

C_S		31.01%	26.7%	18.57%
Gravimetric hydrogen capacities wt.%	$Mg_{1-C_S}M_{C_S}H_2$	5.994	5.208	6.264
	$Mg_{0.95}M_{0.05}H_2$	7.330	7.289	7.225
	MgH_2		7.658	

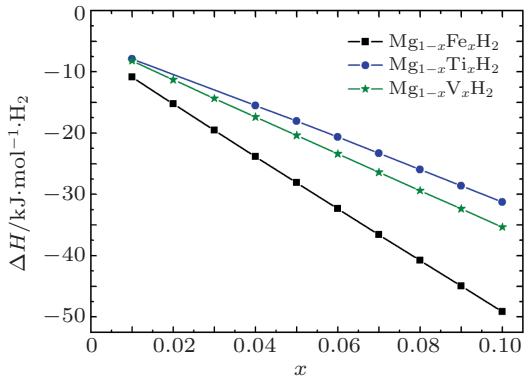


Fig. 3. (colour online) Heat of formation as a function of concentration for MgH_2 doped with Ti, V, and Fe.

3.3. Desorption temperature

The thermodynamic properties of the hydrides are described with the standard Gibbs energy $\Delta G = \Delta H - T\Delta S$, where ΔH and ΔS are enthalpy and entropy change of the dehydrogenation reaction, respectively. For a complex hydride, when the material is heated, the entropy factor slowly overcomes the enthalpy contribution. At the decomposition temperature and under a constant pressure, the standard Gibbs energy is zero. So the temperature of dehydrogenation can be estimated by $\Delta H = T\Delta S$. During heating, the entropy change of the solid is very small compared to that of the gas, so the entropy change during the decomposition reaction is primarily due to the H_2 evolution. At the standard pressure and temperature, for most simple metal hydrides, the entropy is taken to be $\Delta S \approx \Delta S$ (H_2)=130.7 J/mol·K, corresponding to the entropy change due to a mole of gas transforming into the solid.[32] For most of the dehydrogenation reactions, it is estimated that ΔS is in the range of 95 J/mol·K< ΔS < 140 J/mol·K.[33] Therefore ΔH is, to some extent, a reliable predictor of the dehydrogenation temperatures for various metal hydrides.[34]

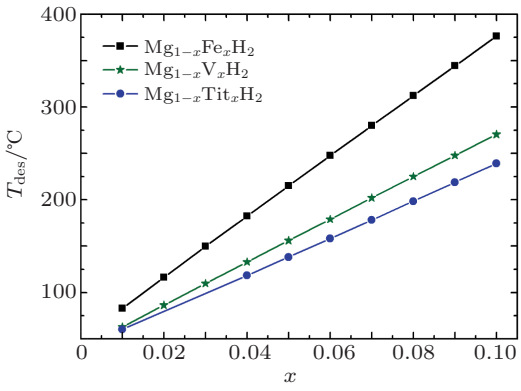


Fig. 4. (colour online) Desorption temperature as a function of concentration for MgH_2 doped with Ti, V, and Fe.

The calculation results of this study show that for the pure MgH_2, the decomposition temperature is

equal to 655.76 K, which is close to values 573–673 K in the other works.[2,6] On the other hand, alloying MgH_2 with small amounts of transition metals can have large effect on destabilizing the parent compound MgH_2 by lowering the decomposition temperature (see Fig. 4) without reducing significantly its high hydrogen capacity (listed in Table 5).

We can show that with the increasing concentration, the temperature also increases until it reaches that of MgH_2, the specific concentrations are C_{Ss} = 31.01%, 26.7%, and 18.57% for MgH_2:Ti, MgH_2:V, and MgH_2:Fe, respectively. Therefore, iron is the best doping element, because it reduces the desorption temperature at a concentration smaller than that in the other doping elements without excessively reducing the storage capacity, see Table 5.

3.4. Electronic structure

The density of state has been used to understand and explain the effect of the nature and the concentration of the transition metal on both the stability and the kinetics of the hydrogen absorption-desorption in $Mg_{1-x}M_xH_2$. For this purpose, the total (DOS) and the partial (PDOS) densities of electronic states of MgH_2 with and without transition metals (M=Ti, V, and Fe) have been calculated.

Figure 5 shows the total density of states of MgH_2 as well as the partial DOS related to Mg-s, Mg-p, and H-s. We find that there are two parts in the valence band (VB). In the first part, the band in the energy range from −0.062 eV to −0.31 eV is called the high VB and composed mainly of strongly hybridized H-s and Mg-3p states. The second part is the band with the energy ranging from −0.31 eV to −0.57 eV, which is called the lower VB and originated mainly from Mg-s and H-s states. While the contribution to the lowest conduction band (CB) are from Mg-p, Mg-s and few H-s states. We can see that the interactions of p (Mg) and s (H) lead the top of the VB to move to a higher energy and make the bottom of the VB move to a lower energy, which increase the width of the VB and consequently decrease the band gap, providing a perfect argument for the discrepancy between our calculation result of 2.745 eV and the experimental results of 5.16 eV in Ref. [35] and 5.6 eV in Ref. [36]. This is related with the result obtained using the GGA approximation, which overestimates the interaction energies between states of Mg and H. So it leads to a large band width and a smaller band gap, and it is well known that the first-principles calculation based on the density functional theory suffers from the errors in the calculated band gap.

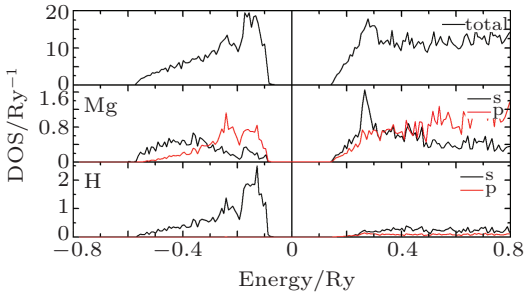


Fig. 5. (colour online) Total and partial DOS of MgH_2 system.

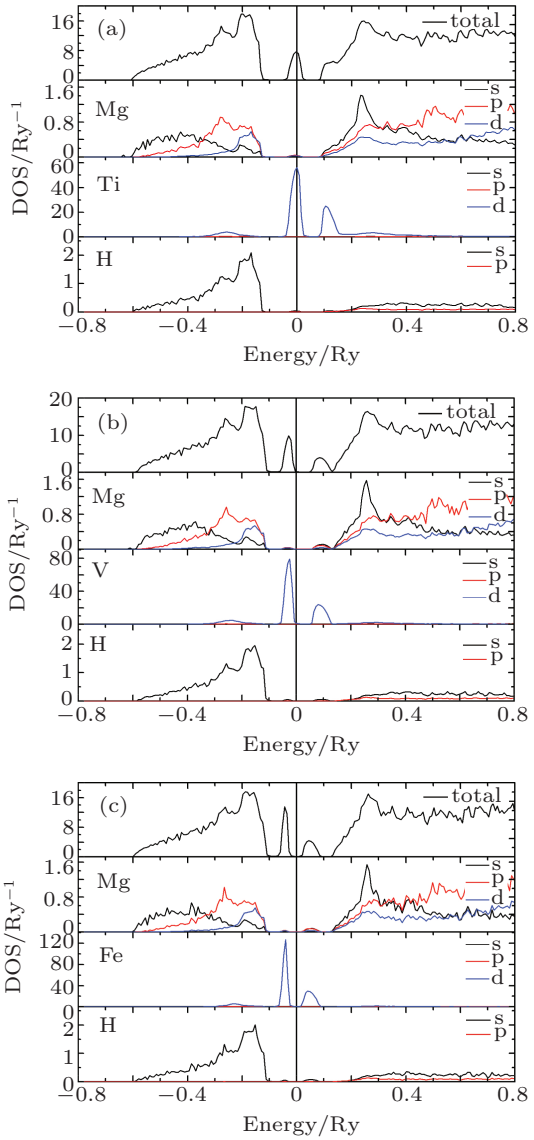


Fig. 6. (colour online) Total and partial DOS of (a) $Mg_{0.95}Ti_{0.05}H_2$, (b) $Mg_{0.95}V_{0.05}H_2$ and (c) $Mg_{0.95}Fe_{0.05}H_2$.

For MgH_2 doped with transition metals (M=Ti, V, and Fe) with concentrations varying from 1% to 10%, we find the same behavior. For this reason, we

plot in Figs. 6 and 7 only the total and the partial DOSs of MgH_2 doped with 5% of M. These figures show that the five orbits of the d state are divided into two energy levels, called t_{2g} and e_{2g}. The t_{2g} energy level is below that of e_{2g}. The appearance of these levels is accord with the crystal field theory in the case of transition metals inserted in the octahedral symmetry,[37] which is the case in our compound. The t_{2g} and e_{2g} states are localized in the band gap. This indicates that there is a weak hybridization between M-d and H-s unlike the case of pure MgH_2, where there is a strong hybridization between H and Mg. Moreover, there is no hybridization between M and Mg, which is consistent with the consideration that no binary MgM exists after releasing the hydrogen.[30]

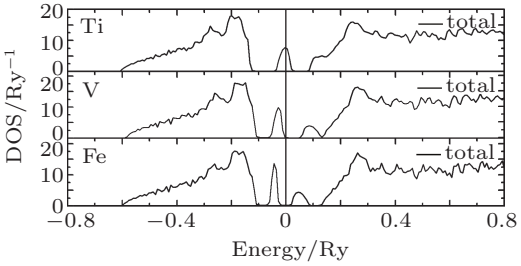


Fig. 7. Total DOS of $Mg_{0.95}M_{0.05}H_2$ (M=Ti, V, and Fe).

Figure 8 shows that the positions of the two levels (t_{2g} and e_{2g}) of the impurity shift to the valence band, and consequently the offset between the energy level t_{2g} and the VB decreases in the order of Ti, V, and Fe. This observation accords with the results of our calculations of heat formation, which increases in the same order. This shows that for all concentrations, the mixture MgH_2:Fe is most stable (MgH_2:Fe>MgH_2:V>MgH_2:Ti) (see Fig. 4).

In order to explain the increases of both the stability and the hydrogen desorption temperature with the increasing concentration of the transition metal in hydrides based on Mg ($Mg_{1-x}M_xH_2$, M=Ti, V, and Fe, $0 \leq x \leq 0,1$), we plot the d states of these transition metals with different concentrations on the same figures (Figs. 8(a)–8(c)). For all systems, we observe that the more the concentration increases, the more the d state of the transition metal shifts to the valance band, which indicates that stability increases with the increasing concentration. This is accord with our calculation of heats of formation for different concentrations.

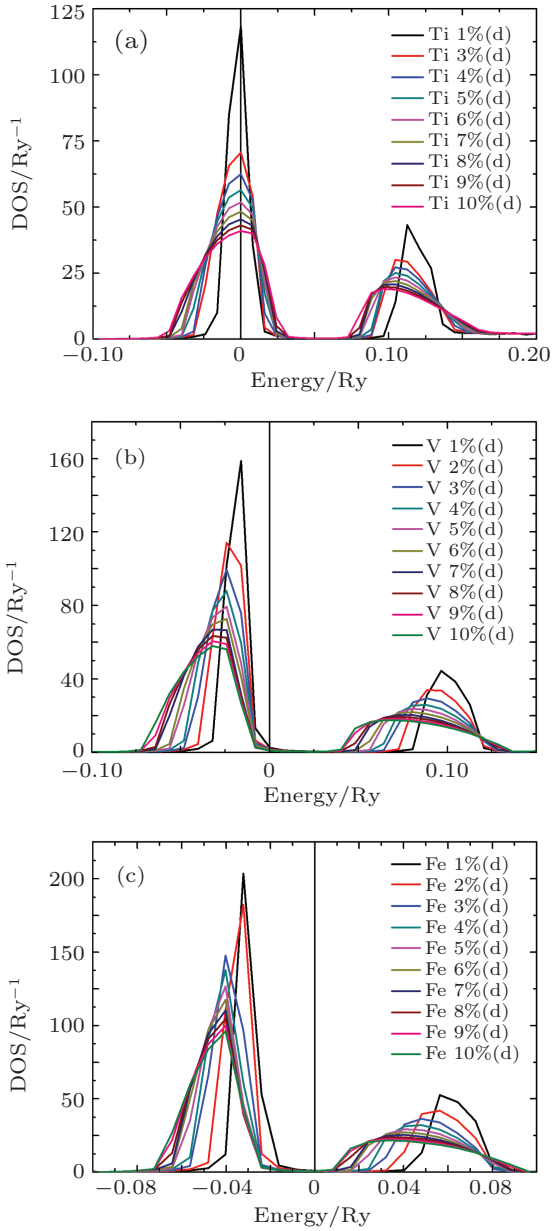


Fig. 8. (colour online) Partial DOSs of d states for the transition metals (a) Ti , (b) V, and (c) Fe in $Mg_{1-x}M_xH_2$ with $0 < x \leq 0.1$.

4. Conclusion

In order to improve the hydrogen storage properties of the Mg-based hydrides, such as $Mg_{1-x}M_xH_2$, (M=Ti, V, and Fe), we have perfomed the first-principles theoretical studies based on the KKR-CPA method. The calculations results of heats of formation for MgH_2 and MgH_2:TM as well as their electronic structures confirm that alloying TM (Ti, V and Fe) can lower the stability of MgH_2. It is favorable for the improvement of the dehydrogenating properties of MgH_2. As a consequence, it can be concluded that alloying MgH_2 with small amounts of transition metals

can drastically lower the decomposition temperature without reducing much its high hydrogen capacity (between 7.225 wt.% and 7.369 wt.% at concentration $x = 5\%$).

References

[1] Cabo M, Garrroni S, Pellicer E, Milanese C, Girella A, Marini A, Rossinyol E, Surinach S and Dolors Baro M 2011 *International Journal of Hydrogen Energy* **36** 5400

[2] Kurko S, Matovic L, Novakovic N, Matovic B, Jovanovic Z, Paskas Mamula B and Novakovic J 2011 *International Journal of Hydrogen Energy* **36** 1184

[3] Liang G, Huot J, Boily S, Van Neste A and Schulz R 1999 *J. Alloys Comp.* **292** 247

[4] Rivoirard S, de Rango P, Fruchart D, Charbonnier J and Vempaire D 2003 *J. Alloys Comp.* **622** 356

[5] Charbonnier J, De Rango P, Fruchart D, Miraglia S, Pontonnier L, Rivoirard S, Skryabina N and Vulliet P 2004 *J. Alloys Comp.* **383** 205

[6] Shang X, Bououdina M, Song Y and Guo Z X 2004 *International Journal of Hydrogen Energy* **29** 73

[7] Song M Y, Bobet J L and Darriet B 2002 *J. Alloys Comp.* **340** 256

[8] Spassov T, Rangelova V, Solsona P, BaróM D, Zander D and Köster U 2005 *J. Alloys Comp.* **398** 139

[9] Shao H, Asano K, Enoki H and Akiba E 2009 *J. Alloys Comp.* **477** 301

[10] Xiao X B, Zhang W B, Yu W Y, Wang N and Tang B Y 2009 *Physica* B **404** 2234

[11] Gremaud R, Broedersz C P, Borsa D M, Schreuders H, Rector J H, B Dam B and Griessen R 2007 *Adv. Mater.* **19** 2813

[12] Araùjo C M and Ahuja R 2005 *J. Alloys Comp.* **404** 220

[13] Hou Z F 2006 *Journal of Power Sources* **159** 111

[14] Bouhadda Y, Rabehi A and Bezzari-Tahar-Chaouche S 2007 *Revue des Energies Renouvelables* **10** 545

[15] Alapati S V, Johnson J K and Sholl D S 2007 *J. Alloys Comp.* **446** 23

[16] Velikokhatnyi O I and Kumta P N 2007 *Materials Science and Engineering* B **140** 114

[17] Akai H 1989 *J. Phys.*: *Condens. Matter* **1** 8045

[18] Akai H 2002 *MACHIKANEYAMA*2002v08

[19] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 *Phys. Rev.* B **46** 6671

[20] Friedlmeier G M and Bolcich J C 1988 *International Journal of Hydrogen Energy* **13** 467

[21] Klose W and Stuke V 1995 *International Journal of Hydrogen Energy* **20** 309

[22] Vajeeston P, Ravindran P, Kjekshus A and Fjellvåbg H 2002 *Phys. Rev. Lett.* **89** 175506

[23] Bortz M, Bertheville B, Bottger G and Yvon K 1999 *J. Alloys Comp.* **287** L4

[24] Kittel C 1986 *Introduction to Solid State Physics* (New York: Wiley)

[25] Fenman R P 1939 *Phys. Rev.* **56** 340

[26] Moriwaki T, Akahama Y and Kawamura H 2006 *J. Phys. Soc. Jpn.* **75** 074603

[27] Nakamura H, Nguyen-Manh D and Pettifor D G 1998 *J. Alloys Comp.* **281** 81

[28] Novaković N, Novaković J G, Matović L, Manasijević M, Radisavljević I, Mamula B P and Ivanović N 2010 *International Journal of Hydrogen Energy* **35** 598

[29] Friedlmeier G M and Bolcich J C 1988 *International Journal of Hydrogen Energy* **13** 467

[30] Klose W and Stuke V 1995 *International Journal of Hydrogen Energy* **20** 309

[31] Gremaud R, Broedersz C P, Borsa D M, Schreuders I H, Rector I J H and Dam B 2007 *Adv. Mater.* **19** 2813

[32] Zeng Q, Su K, Zhang L, Xu Y, Cheng L and Yan X 2006 *J. Phys. Chem.* **35** 1385

[33] Alapati S V, Johnson J K and Sholl D S 2006 *J. Phys. Chem.* B **110** 8769

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

[35] Yu R and Lam P K 1988 *Phys. Rev.* B **37** 8730

[36] Westerwaal R, Broedersz C, Gremaud R, Slaman M, Borgschulte A, Lohstroh W, Tschersich K, Fleischhauer H, Dam B and Griessen R 2008 *Thin Solid Films* **516** 4351

[37] Cotton F A 1963 *Chemical Applications of Group Theory* (New York: Interscience)