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Alloying effects on the energy and electronic structures of vanadium hydrides

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A first-principles plane-wave pseudopotential method based on the density functional theory is used to investigate the energy, electronic structure and stability of VH and VH_2 alloyed by a 3d transition metal. It is found that the stability of VH and VH_2 decreases after alloying, which originates from a small number of bonding electrons at the Fermi level. In the case of VH_2, the ionic interaction is dominant between alloying atoms and H atoms, while the ionic bond interaction between the later 3d alloying atoms and H atoms is important in VH.

Key words: *plane-wave pseudopotential theory; vanadium hydride; electronic structure*

1. Introduction

Magnesium-based hydrogen storage alloys have been extensively studied due to their high hydrogen storage capacity, low density and low cost. However, slow hydriding and dehydrogenating kinetics and high dissociation temperatures caused by their relatively high stability limit their practical application for hydrogen storage. Liang et al [1] have found that mechanical milling of MgH_2 with 5 at. % of V produces a nanocomposite structure of β-MgH_2 + γ-MgH_2 + $VH_{0.81}$, and this nanocomposite solves the problem of slow kinetics of MgH_2 below 473 K in vacuum. They suggest that nucleation of α-Mg at the VH/MgH_2 interface might be easy but there has been little effort to prove the view. Recently, in our group, $VH_{0.81}$ crystal structure is considered as VH phase, and a VH/MgH_2 interfacial model is designed and constituted

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to investigate the structural stability and hydriding and dehydrogenating kinetics of MgH_2–V system [2]. The results show that the catalytict effect of V on dehydrogenating kinetics of MgH_2 phase can be attributed to the effects of VH/MgH_2 interfaces with a low structural stability [2]. But H atoms in MgH_2 slab are adsorbed by V atoms due to strong interactions between V and H, and a very stable hydride, VH, can be formed. Hence, H atom is not easy to release through the reaction: $VH \rightarrow V+H$, which is not benefit for the hydriding and dehydrogenating kinetics of the MgH_2–5 at. % V system. Moreover, as the hydriding proceeds further, another reaction, $VH+H \rightarrow VH_2$, takes place and a new hydride, VH_2, is formed [3]. To understand the intrinsic mechanisms of alloying effects on the structural stability of vanadium hydrides, Matumura et al. [4] calculated the electronic structure of V_2H and VH_2 compounds with alloying elements X (X = Ti, V, Cr, Fe, Co, Ni, Zr, Nb, Mo, W) by adopting the DV-X_a cluster method. It was shown that the alloying elements considered destabilized vanadium hydrides and the interaction between alloying atoms and H atoms is important for improving the structural stability and the dehydrogenation properties. However, despite such great efforts, alloying effects of various metals, such as 3d transition metals, have not as yet been elucidated for the structural stability and dehydrogenation properties of VH and VH_2. Based on the previous work [2], in this paper, at first, the stability of VH and VH_2 is analyzed and discussed, and then, the energy, electronic structure and stability of VH and VH_2 alloyed by 3d transition metal are investigated by using first-principles plane-wave pseudopotentials methods based on density functional theory. Some new results will be expected to be of benefit for designing the advanced magnesium-based hydrogen storage materials.

2. Method of computation

Cambridge Serial Total Energy Package (CASTEP) [5], a first-principles plane-wave pseudopotentials method based on the density functional theory, is used in this work. CASTEP uses a plane-wave basis set for the expansion of the single-particle Kohn-Sham wave-functions, and pseudopotentials to describe the computationally expensive electron-iron interaction, in which the exchange-correlation energy by the generalized gradient approximation (GGA) of Perdew is adopted for all elements in our models by adopting the Perdew–Burke–Ernzerhof parameters [6]. Ultrasoft pseudopotentials represented in reciprocal space are used [7]. The atomic orbitals used in the present calculations are: H $1s^1$,Sc $3s^2$, $3p^6$, $3d^1$, $4s^2$, Ti $3s^2$, $3p^6$, $3d^2$, $4s^2$, V $3s^2$, $3p^6$, $3d^3$, $4s^2$, Cr $3s^2$, $3p^6$, $3d^5$, $4s^1$, Mn $3d^5$, $4s^2$, Fe $3d^6$, $4s^2$, Co $3d^7$, $4s^2$, Ni $3d^8$, $4s^2$, Cu $3d^10$, $4s^1$, Zn $3d^10$, $4s^2$. For cluster and crystal models, the cutoff energy of atomic wave functions (PWs), E_{cut}, is set at 220 eV, 310 eV, respectively. Sampling of the irreducible wedge of the Brillouin zone is performed with a regular Monkhorst–Pack grid ($12 \times 12 \times 12$) of special k-points, which is 0.5 nm^{-1}. A finite basis set correction and the Pulay scheme of density mixing [8–10] are applied for the evaluation of energy and stress. All atomic positions in our model have been relaxed according to the total energy and force using the Broyden–Flecher–Goldfarb–Shanno (BFGS) scheme [12] based on the cell optimization criterion (RMs force of 0.05e V/Å, stress of 0.1 GPa, and displacement of 0.002 Å). The calculation of total energy and electronic structure are followed by the cell optimization with the self-consistent -field (SCF) tolerance of 2.0×10^{-6} eV.

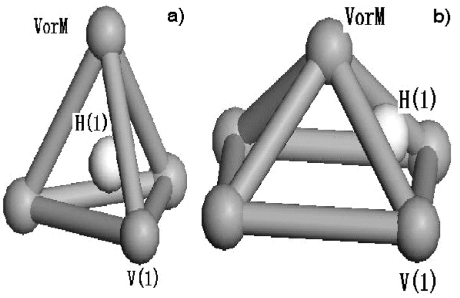

Fig. 1. Cluster model employed in the VH_2 (a) and VH calculations (b), where alloying elements M (M = Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn) are substituted for one V atom

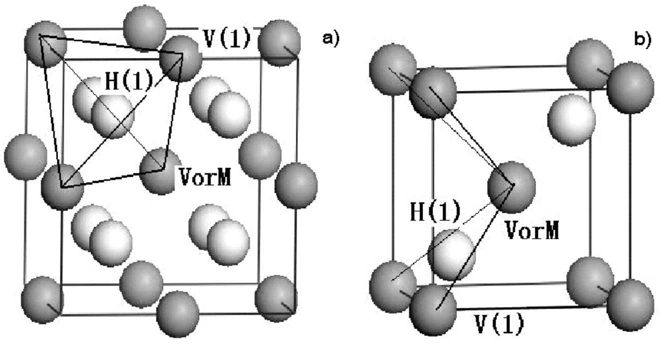

Fig. 2. Crystal models of VH_2 (a) and VH (b)

The cluster model shown in Fig. 1a is constructed based on the CaF_2 type crystal structure of VH_2 (*Fm*3*m*, group No. 225, Fig. 2a) [11]. As far as VH_2 crystal is concerned, the lattice parameters are $a = b = c = 4.271$ Å, and four V atoms occupy (0,0,0) sites and eight H atoms locate in (0.25,0.25,0.25) sites. Another cluster model shown in Fig. 1b is constructed on the basis of a hypothetical structure of VH. For the VH crystal structure (Fig. 2b), we consider that VH crystal cell is similar to the *bcc* V(H) solid solutions and the site occupied by H atoms in this cell is similar to that in MgH_2 crystal [2]. In order to compare the stability of VH and VH_2, the crystal model is used, shown in Figs. 2a, b. In order to examine alloying effects on the energy and electronic structure of vanadium hydrides, one V atom in the cluster shown in Fig. 1a for VH_2, or Fig. 1b for VH are substituted for various alloying elements, M (M = Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn). Hence, the corresponding VH_2 and VH cluster models are expressed as V_3MH and V_4MH, respectively.

3. Results and discussion

3.1 Stability of VH and VH_2

In this paper, the stability of VH and VH_2 is discussed by the following [12]

$$\Delta H_1 = E_{\mathrm{tot}}(\mathrm{VH}) - \mathrm{E}_{\mathrm{tot}}(\mathrm{V}) - \frac{1}{2}E_{\mathrm{tot}}(\mathrm{H}_2) \tag{1}$$

$$\Delta H_2 = E_{\mathrm{tot}}(\mathrm{VH}_2) - E_{\mathrm{tot}}(\mathrm{VH}) - \frac{1}{2}E_{\mathrm{tot}}(\mathrm{H}_2) \tag{2}$$

where $E_{\mathrm{tot}}(VH_2)$ and $E_{\mathrm{tot}}(VH)$ are the energies of primitive cells of VH_2 and VH, respectively. $E_{\mathrm{tot}}(V)$ and $E_{\mathrm{tot}}(H_2)$ are the energies of a V atom and a hydrogen molecule, respectively. The value of ΔH_1 calculated from Eq. (1) is 3.5465 eV/atom, which means the heat absorbed during the reaction $V + H \rightarrow VH$ but the value of ΔH_2 calculated from Eq. (2), is –1.94095 eV/atom, which means that upon further hydriding, another reaction, $VH + H \rightarrow VH_2$, proceeds and a new hydride, VH_2 is formed.

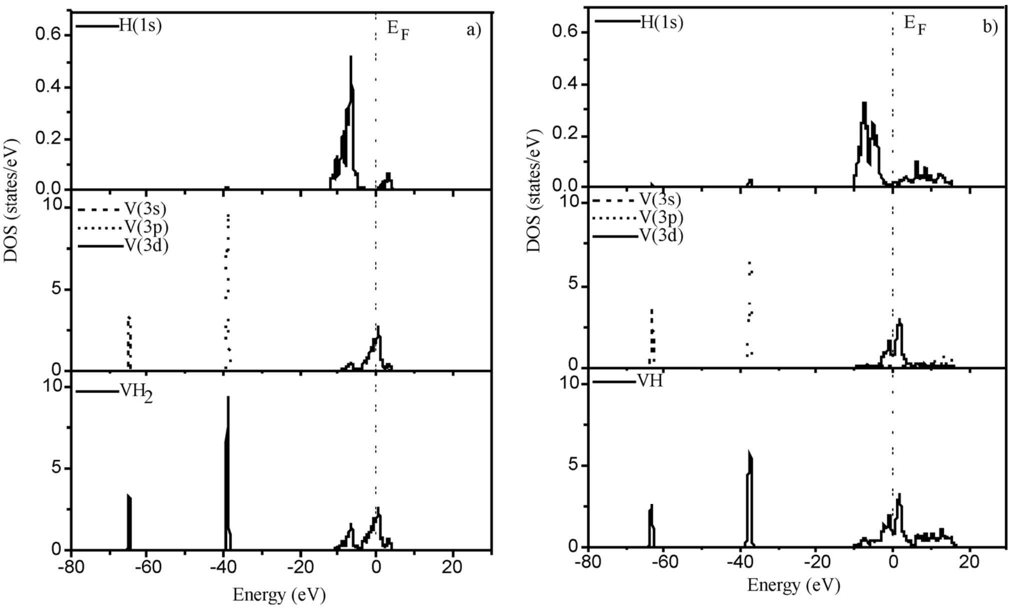

Fig. 3. Total and partial density of states of (a) VH_2 (b) VH crystal structure

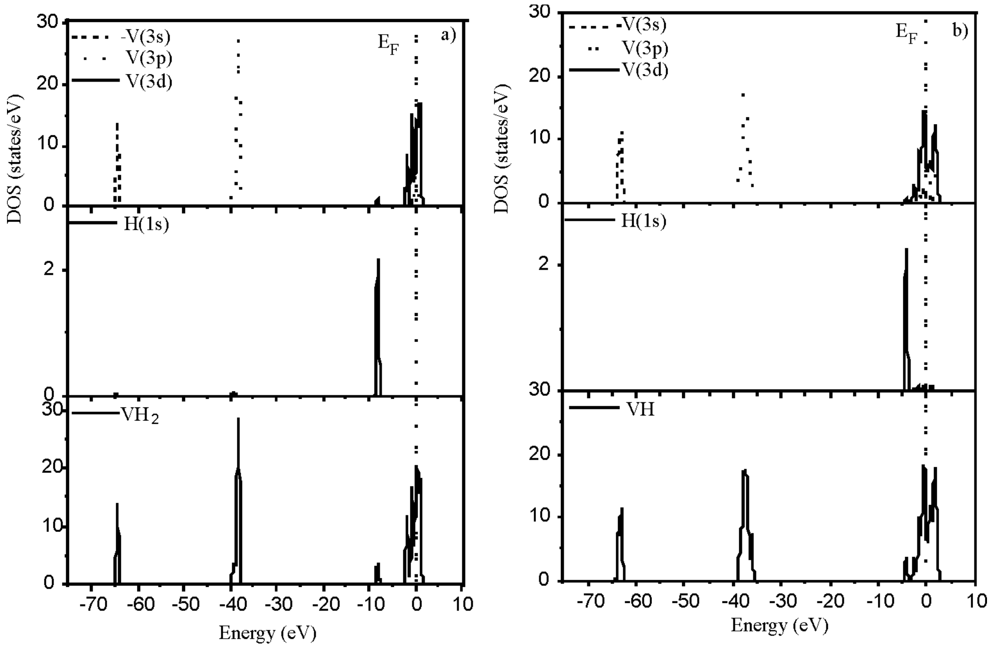

Fig. 4. Total and partial density of states of (a) VH_2 (b) VH cluster structure

Further analysis of total and partial densities of states (DOS, PDOS) of the crystal model for VH_2 and VH has been performed. As shown in Figs. 3a and 3b, for VH_2 and VH, the states located around –65 eV and –40 eV originated from V(3s) and V(3p) electrons, respectively. These electrons are usually considered as inner-core electrons and do not contribute to the bonding between atoms. Here, it must be pointed out that for VH_2, the main bonding peaks at E_F are dominated by the V(3d) electrons, while for VH the bonding peaks at E_F are the result of the bonding between H(1s) and V(3d) electrons. Therefore, this leads to a relatively high formation energy of VH [13–15]. The same analysis get the similar results for VH_2 and VH cluster models, shown in Figs. 4a and 4b, respectively. Since H atom is not easy to release for VH, it is necessary that the stability of VH and VH_2 is reduced by 3d transition metal alloying in order to improve the hydriding and dehydrogenating kinetics of MgH_2-5at%V systems.

3.2. Influence of alloying elements on the stability of VH and VH_2

Heat of formation. In order to study the influence of alloying elements on the stability of VH and VH_2, the heat of formation of the cluster model for VH_1 and VH_2 based on the above analysis of DOS shown in Figs. 3 and is calculated from [16]:

$$H_1 = E_{\text{tot}}\left(\text{V}_3\text{MH}\right) - 3E_{\text{tot}}\left(\text{V}\right) - E_{\text{tot}}\left(\text{M}\right) - \frac{1}{2}E_{\text{tot}}\left(\text{H}_2\right) \qquad (3)$$

$$H_2 = E_{\text{tot}}\left(\text{V}_4\text{MH}\right) - 4E_{\text{tot}}\left(\text{V}\right) - E_{\text{tot}}\left(\text{M}\right) - \frac{1}{2}E_{\text{tot}}\left(\text{H}_2\right) \qquad (4)$$

where $E_{\text{tot}}(\text{V}_3\text{MH})$ and $E_{\text{tot}}(\text{V}_4\text{MH})$ are total energies of the cluster model for VH_2 and VH, respectively. $E_{\text{tot}}(\text{M})$ is the energy of M atoms. Heats of formation for VH_2 and VH calculated from Eqs. (3) and(4) are shown in Figs. 5a, b, respectively. The results show that heat of formation decreases after alloying. Hence, the stabilities of VH_2 and VH are reduced compared with those without alloying.

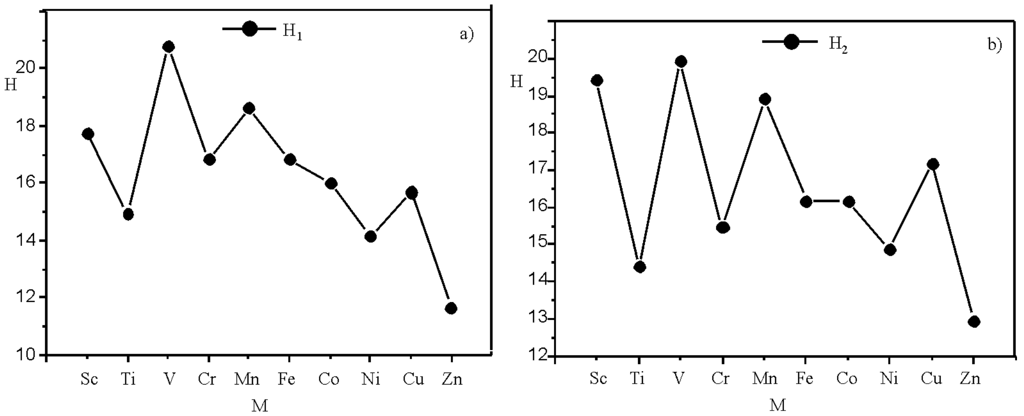

Fig. 5. Heats of formation of VH_2 (a) and VH (b) with alloying elements addition. H_1 and H_2 denote the heat of formation of the cluster model for VH_1, VH_2 (Eqs. (3) and (4), respectively

Density of states. Further analysis of total and partial densities of states (DOS, PDOS) of VH_2 and VH was performed to understand the electronic structure mechanism on the change of the stability. As far as VH_2 is concerned, the main bonding peaks at E_F are dominated by the V(3d) electrons, while for VH the bonding peaks at E_F are the result of the bonding between H(1s) and V(3d) electrons (cf. Sect. 3.1). Calculations of total and partial densities of states (DOS, PDOS) of the cluster model with alloying elements addition have been performed. The results show that the energy range and the contribution of valence electron of VH_2 or VH are almost the same as those without alloying element added. As far as the crystal with the same constituent and various types of structure is concerned, a conclusion about relative stability of phase is often derived from comparison of the values of their densities of states at the Fermi level $N(E_F)$, that is, the lower is $N(E_F)$, the more stable is the corresponding phase [17–19]. To verify if the criterion is valid in the case of VH and VH_2, the calculated values of $N(E_F)$ of VH_2 and VH have been analysed (Figs. 6a, b). As shown in Fig. 6a, $N(E_F)$ value of pure VH_2 is 9.3750 electrons/eV, but for Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn alloying systems, the $N(E_F)$ value of VH_2 are (in electrons/eV) 10.3676, 10.2206, 10.5147, 9.6547, 13.4449, 12.9596, 9.9265, 11.9485, respectively. As shown in Fig. 6b, the $N(E_F)$ value of pure VH is 6.9118electrons/eV, but for the alloying systems, the $N(E_F)$ value of VH are (in electrons/eV) 7.3529, 8.2353, 6.1765, 7.9044, 8.7500, 12.6471, 10.4412, 8.6765, 7.7206, respectively. Based on the above analysis, as far as VH and VH_2 is concerned, there are less bonding electrons at the Fermi level compared with those without alloying.

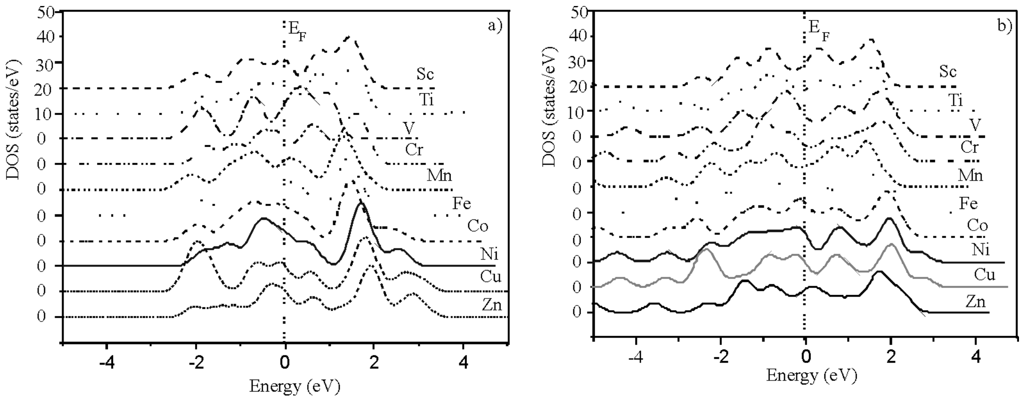

Fig. 6. Density of states of (a) VH_2 (b) VH at Feimi level with alloying elements addition

Bond order between atoms and ionicities. As explained earlier, the bond order is the overlap population of electrons between atoms, and this is a measure of the strength of the covalent bond between atoms. In order to discuss the change in calculated properties (see Fig. 5) when the alloying atom changes from Sc to Zn, the bond order between atoms changing with alloying elements is calculated (Fig. 7). Every bond order shown in this figure is the value per atomic bond in the cluster. M = V means pure VH_2. As shown in Fig. 7, the V(1)–V(2) bond orders are always positive, and there are no obvious changes. The H(1)–V(1) bond orders are also positive, not including Cr and V, indicating that there is a strong interaction between them. On the other hand, the H–M bond orders are negative, not including Cu and Cr. But for the sum of these metal–hydrogen bond orders, a big change can be found. Sc–V, Cu–V and Zn–V bonds cannot be identified, not including Ti, the V–M bond order becomes smaller when the atomic size of alloying elements is larger. This reason is attributable to the atomic size of M being much larger than that of V. The substitution of a large M atom for a small V atom induces the lattice expansion, and the M–V(1) distance becomes longer than the V–V(1) distance. As a result, the strength of the covalent bond between M and V atoms reduces.

Further analysis on the ionicity of each atom in the cluster for VH_2 is also done according to the Mulliken population analysis. The results are shown in Fig. 8. The ionicities of V atoms and M (not including Cr, Cu and Zn) are always positive, whereas the ionicities of hydrogen atoms are always negative. These results indicate that charge transfer takes place mainly from V atoms and alloying elements towards the hydrogen atoms. Such a change transfer induces the ionic interaction between them.

As shown in Fig. 9 (the signs of V atoms are shown as in Figs. 1b and 2b), the V(1)–V(2) bond orders are always positive, and there are not obvious changes. On the other hand, the H(1)–V(1) bond orders are also positive, indicating that there is a strong interaction between them. The H–M bond orders are also positive. But for the sum of these metal–hydrogen bond orders, a big change can be found. The change of V–M bond order is not distinct when atomic sizes of alloying elements are larger.

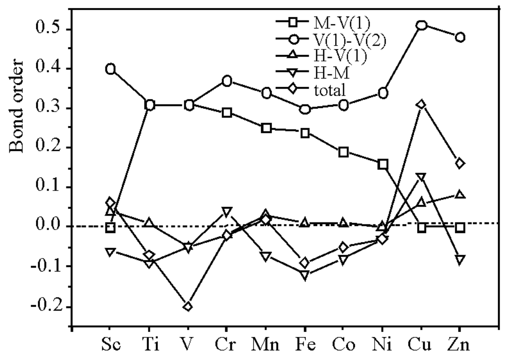

Fig. 7. Bond orders with alloying elements in the VH_2 cluster

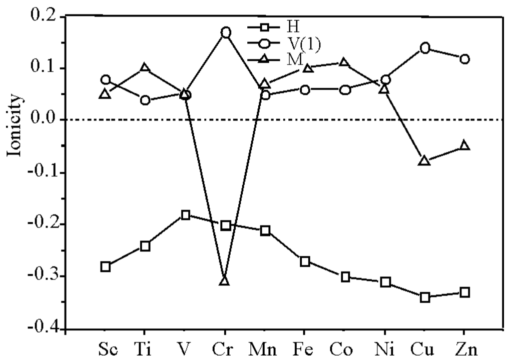

Fig. 8. Ionicities of atoms in the VH_2 cluster with alloying elements

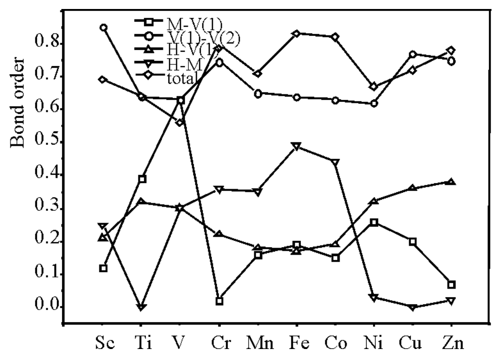

Fig. 9. Bond orders with alloying elements in the VH cluster

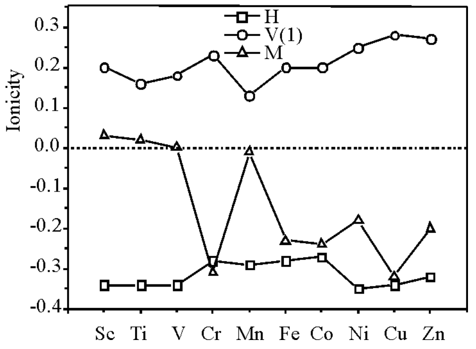

Fig. 10. Ionicities of atoms in the VH cluster with alloying elements

The same analysis is done for the ionicity of each atom in the cluster for VH. The results are shown in Fig. 10. The ionicities of V atoms are always positive, whereas the ionicities of hydrogen atoms are always negative. But the ionicities of M (not including Sc and Cu) are positive. These results indicate that charge transfer takes place mainly from V atoms and alloying elements towards the hydrogen atoms.

The ionicity difference. In the previous section, it was found that there is the ionic bond interaction between alloying atoms and H atoms. Based on this result, in this section, the ionicity difference between H and M atom for VH_2 and VH is calculated and shown in Figs. 11a, b, respectively. As far as VH_2 is concerned, it is apparent that the calculated result from Fig. 11a is similar to heat of formation shown in Fig. 5a, even though there is a certain discrepancy in Cr and Ni. Thus, the ionic interaction between H and M atoms is important in alloyed VH_2. But this does not necessarily mean that the covalent interaction is not dominant. For VH, it is found that the calculated value from Fig. 11b is not similar to heat of formation shown in Fig. 5b, except for later-3d transition metal alloying elements. Therefore, for the change in calculated properties (See Fig. 5) when the alloying atom changes from Sc to Zn, in the case of VH_2, the ionic interaction is dominant between alloying atoms and H atoms [4], while the ionic bond interaction between the later 3d alloying atoms and H atoms is important in VH. Here, an important view must be pointed out that the work is being done on further studying the reason for the correlation between the ionicity difference and calculated properties.

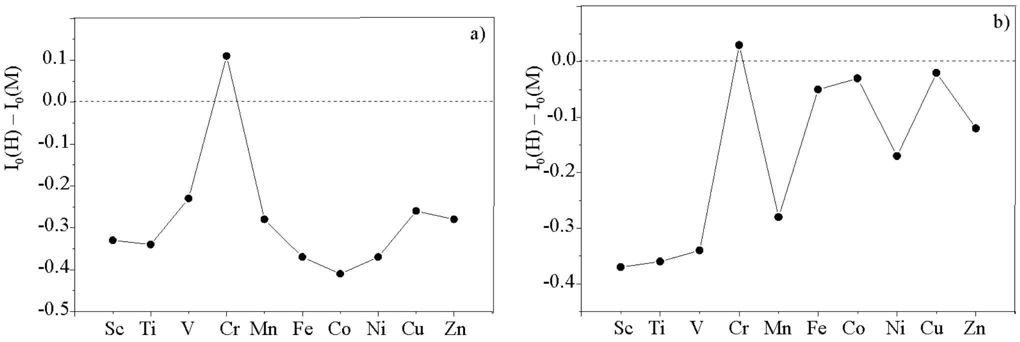

Fig. 11. Comparison between the calculated ionicity differences: a) VH_2, b) VH

4. Conclusions

- The stability of VH and VH_2 decreases after alloying, which originates from small numbers of bonding electrons at the Fermi level.
- In the case of VH_2, the ionic interaction is dominant between alloying atoms and H atoms, while the ionic bond interaction between the later 3d alloying atoms and H atoms is important in VH.

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