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Ab initio investigation of $ScMn_2$-H system

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In this study, a first-principles search for the possible hydrides with the prepreerence sites of hydrogen in AB_2 C14-type Laves structure was carried out for the Sc-Mn-H system. The obtained structural parameters were close to the available experimental results. Total energy was calculated by ab initio pseudopotential method within the generalized gradient approximation (GGA) to density functional theory (DFT). Formation energies of $ScMn_2H_x$ (x =0.75-3) hydrides are systematically investigated to analyze the influence of the hydrogen content and hydrogen sites in the alloy on the site preference of hydrogen in the hydrides on the basis of crystal and electronic structures and structural stability. The calculated results show that $ScMn_2H_{0.75}$ with the *P3* space group has the highest stability for all hydrides. The density of states, the charge density distribution were investigated in order to get insight into the underlying mechanism for structural stability, electronic bonding nature of $ScMn_2H_x$ and the preference of hydrogen entering into C14-type Laves structure. The results show that the prepreerence site of H atom in C14-type Laves structures is 3*d*(x 2x z) site in *P*3 (No.143) space group.

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1. Introduction

In AB_2 Laves phase structure (hexagonal C14 and cubic C15 structures), all interstices are formed by tetrahedrons. There are three types of tetrahedral interstices in each formula unit of Laves phase, i.e. 12 A_2B_2-type, 4 AB_3-type and 1 B_4-type [1,2]. In previous studies of the hydrogen site of the alloys [3,4], hydrogen atoms go into two different tetrahedral A_2B_2 and AB_3 sites in the AB_2 alloys such as ZrV_2 [3] and $Zr_{0.9}Ti_{0.1}MnCr$ [4]. Recently, The Sc-based Laves phase alloys ($ScMn_2$, ScMnCr, $ScFe_2$, $ScCo_2$, $ScNi_2$, etc.) have attracted extensive attention on hydrogen storage properties due to their fast kinetics, high storage capacity and good structural stability. Li et al. have reported the experimental results of the crystal structures and hydrogen storage properties for ScMnCr [5,6] and $ScMn_2$ [7] alloys. They pointed out that Sc-based alloys with Cr-Mn as common component exhibit extraordinary catalytic effect on hydrogen dissociation and absorption [6]. Yoshida et al. [8] studied the hydrogen absorbing properties of ScM_2 (M = Fe, Co and Ni) Laves phase alloys and estimated the enthalpies of the hydride formation. In spite of this interest, the $ScMn_2$-H_2 systems seem not to have been extensively studied from various points of view. For example, the influence of the hydrogen content and hydrogen sites in the alloy on the stability and the structural transition of the hydride have not been reported so far to our knowledge.

In the studies described in this paper, the crystal structures, the influence of the hydrogen content and hydrogen sites in the alloy on the stability and the site preference of hydrogen in the hydrides with different space group and electronic properties of the hydrides are investigated by using the pseudopotential plane-wave method based on density functional theory. The enthalpies of formation are estimated, and the bonding nature of hydrogen atoms and alloying elements in the hydrides is described.

2. Models and methods

2.1 Computational details

In this work, the Laves phase structures of the hydrides $ScMn_2H_x$ (x=0.75, 1.5 and 3) were investigated computationally using density functional theory (DFT) and plane-wave pseudopotential technique implemented in the Quantum-ESPRESSO package [9]. The ion–electron interaction was modeled by ultrasoft pseudopotentials [10]. Generalized gradient approximation (GGA) with the PBE exchange-correlation functional [11] was used. For the hydrides $ScMn_2H_x$, we used a 5×5×4 Monkhorst–Pack [12] *k*-point mesh for sampling Brillouin zone. A Gamma centered 18×18×12 mesh was used for hexagonal close-packed metal Sc, and an 18×18×18 Monkhorst–Pack *k*-point mesh was used for body-centered cubic metal Mn. Convergence with respect to the *k*-point sampling for the Brillouin zone (BZ) integration was tested independently on these compounds using regular meshes of increasing density. Tests indicated that the total energy converges to 1 meV/atom. The valence electronic configurations were taken to be $3s^23p^6 3d^1 4s^2$ for Sc, $3s^23p^63d^54s^24p^0$ for Mn and $1s^1$ for H. The cut-off energy of atomic wave functions (PWs) was set at 400 eV for all the calculations. The other values of the cut-off energy of atomic wave functions have been tested, such as 310 eV, 360 eV and 450 eV etc. Tests indicated that the total energies of the crystals have been not obviously changed. The structural optimization was first performed using a conjugate gradient algorithm until the Hellman–Feynman force on each of the unconstrained atoms was less than 0.01eV/⊕. The self-consistent calculations were considered to be converged when the difference in the total energy of the crystal did not exceed 10^{-6} eV at consecutive steps. After the structures are optimized, the total energies are recalculated self-consistently with the tetrahedron method [13]. The latter technique is also used to calculate the electronic density of states (DOS).

2.2 Crystal structure

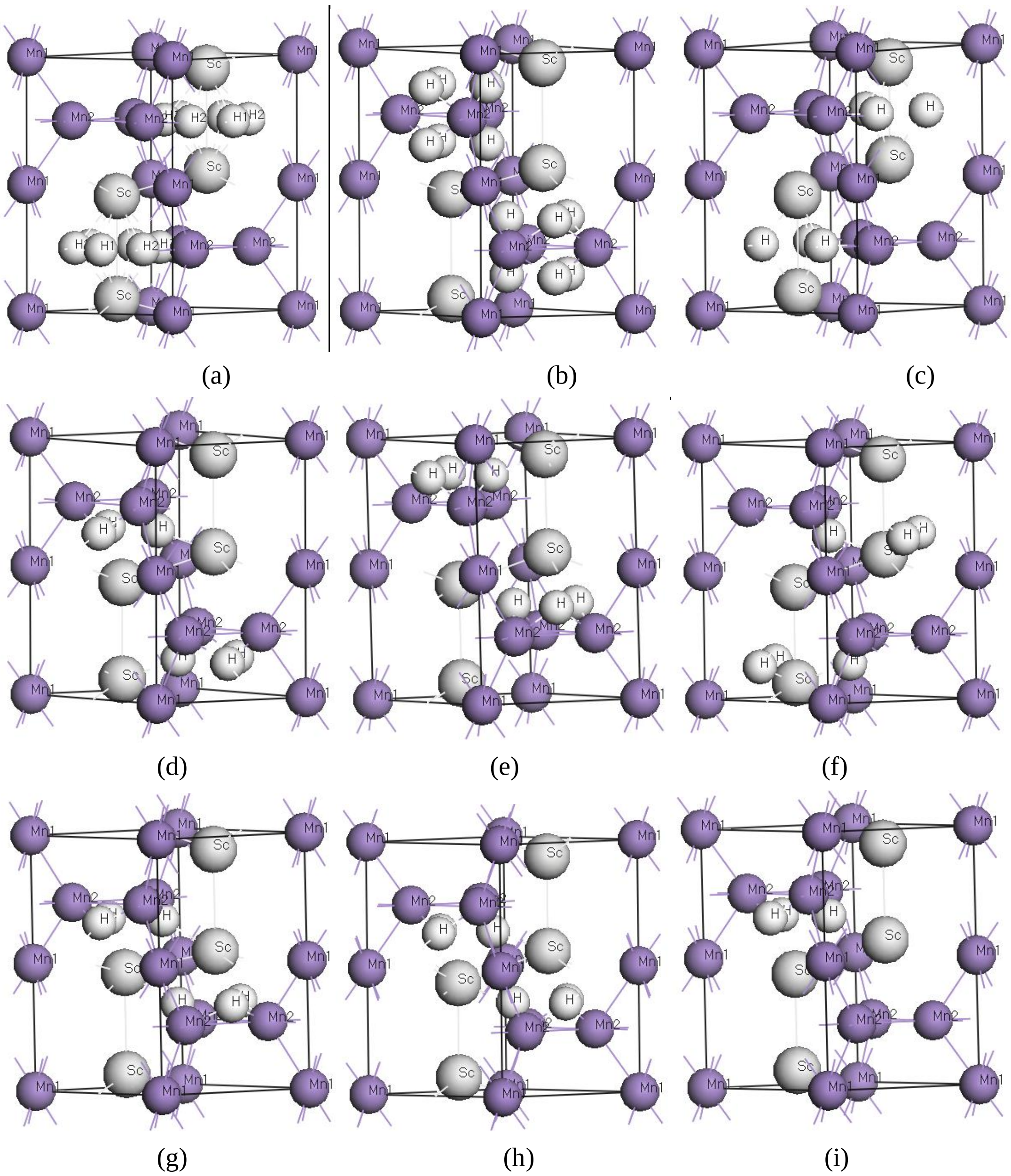
Li et al. [7] charged the $ScMn_2$ alloy sample with hydrogen gas, the composition of the formed hydride was found to correspond to ~3.5 atoms of H per formula unit (f.u.). Furthermore, this hydride was referred to as $ScMn_2H_{3.5}$. And the hydrogen storage capacity of 2.1 wt.% can be achieved [7]. Hydrogen atoms in Laves phase compound usually occupy interstitial sites and induce an increase in the lattice parameters often accompanied with change of its structure. The interstitials available for hydrogen in the AB_2 compounds are tetrahedral sites that are formed by two B and two A atoms (A_2B_2) or by three B atoms and one A atom (AB_3) or by four B atoms (B_4). However, the occupancy criterion of hydrogen atoms must be obeyed in order to stabilize the hydrides when hydrogen atoms enter into Laves phase [14,15]. Those studies showed that hydrogen atoms in ternary hydrides, based on the C14-type, only occupy interstitial tetrahedral-like A_2B_2 interstitial hole in sites such as: $6h_1$, $6h_2$, 12k and 24l [16,17]. Therefore, it was found that the maximum of hydrogen capacity for AB_2 alloys can store six hydrogen atoms per formula. The XRD investigation results of $ScMn_2D_{3.5}$ indicated that the hydrogenation of the $ScMn_2$ alloy did not alter the matrix lattice structure [7]. The derived structural parameters of the hydride $ScMn_2H_{3.5}$ were very similar to that of the alloy, with nearly ideal values for the close-packed C14 structure.

The choices for hydrogen insertion sites were done based on the neutron diffraction studies of Sun et al. on the deuterated C14 compound $Zr_{0.9}Ti_{0.1}MnCr$ [4,18]. For the saturated deuteride $Zr_{0.9}Ti_{0.1}MnCrD_{3.5}$, the occupancies of D atoms in the $6h_1$ and 12k sites are higher in comparison with that of the $6h_2$ and 24l sites. In the present work, a series of calculations were done with the assumption that there are three hydrides with different hydrogen content, $ScMn_2H_3$, $ScMn_2H_{1.5}$ and $ScMn_2H_{0.75}$, to investigate the occupancy preference of hydrogen atom in these interstitial sites. When crystal structure of these hydrides was investigated, it was understood that hydrogen atoms does not fill Wyckoff sites exactly. Therefore, there are different crystal structures which have different space groups because of the different sites of hydrogen atoms. The unit cells of nine structures investigated in this study were constructed using the symmetry and atomic sites as given in Table 1. For example, there are three structures having the $P6_3/mmc$ (No.194) space group, giving two different sites. In all these structures Sc, Mn1 and Mn2 atoms are occupying the $4f$, $2a$ and $6h$ Wyckoff sites, respectively. In the first and second structures (the sample-1 and sample-2 in Table 1), hydrogen atoms occupy the $6h_1$+$6h_2$ and $12k$ sites in which the obtained the number of hydrogen atoms in formula unit is 3. In the third structure, hydrogen atoms occupy the $6h_2$ site in which the obtained the number of hydrogen atoms in formula unit is 1.5. For the five structures having the $P6_3mc$ (No.186) and $P\text{-}3m1$ (No.164) space groups, hydrogen atoms occupy the $6c$ and $6i$ sites, respectively, yielding the same the number of hydrogen atoms, which is 1.5. For structure having the $P3$ (No.143) space group, hydrogen atom only occupy the $3d$ site, yielding 0.75 hydrogen atoms. The nine structural models of the hydrides $ScMn_2H_x$ are shown in Fig. 1 (a)-(i).

Table 1. The definition of the structures used in this study, giving the space groups and Wyckoff sites of the atoms within the unit cells.

Models	Compounds	Lattice parameters (⊕)^d		Space group	Sc	Mn1	Mn2	H		
		a	*c*					0.75	1.5	3
Sample-1	$ScMn_2H_3$	5.463	8.863	$P6_3/mmc$	$4f$	$2a$	$6h$			$6h_1+6h_2$
Sample-2	$ScMn_2H_3$	5.463	8.863	$P6_3/mmc$	$4f$	$2a$	$6h$			$12k$
Sample-3	$ScMn_2H_{1.5}$	5.426	8.762	$P6_3/mmc$	$4f$	$2a$	$6h$		$6h_2$	
Sample-4	$ScMn_2H_{1.5}$	5.426	8.762	$P6_3mc$	$2b$	$2a$	$6c$		$6c$ $(x, 2x, z)$	
Sample-5	$ScMn_2H_{1.5}$	5.426	8.762	$P6_3mc$	$2b$	$2a$	$6c$		$6c$ $(-x, -2x,- z)$	
Sample-6	$ScMn_2H_{1.5}$	5.426	8.762	$P6_3mc$	$2b$	$2a$	$6c$		$6c$ $(-x, -2x, z+1/2)$	
Sample-7	$ScMn_2H_{1.5}$	5.426	8.762	$P\text{-}3m1$	$2d$	$1a$	$6i$		$6i$ $(x, 2x, z)$	
Sample-8	$ScMn_2H_{1.5}$	5.426	8.762	$P\text{-}3m1$	$2d$	$1a$	$6i$		$6i$ $(-x, -2x,- z)$	
Sample-9	$ScMn_2H_{0.75}$	5.421	8.753	$P3$	$1b$	$1a$	$6i$	$3d$ $(x, 2x, z)$		

d is the experimental values of the equilibrium lattice parameters for the hydrides $ScMn_2H_x$.



(a) (b) (c)

(d) (e) (f)

(g) (h) (i)

Fig. 1. Crystal structures of $ScMn_2H_x$ (a). Sample-1, (b) Sample-2, (c) Sample-3, (d) Sample-4, (e) Sample-5, (f) Sample-6, (g) Sample-7, (h) Sample-8, (i) Sample-9.

3. Results and discussion

3.1 Structural stability

Starting from the above the crystal structures, the geometry optimization was performed by relaxing both atomic sites and lattice parameters simultaneously. The lattice constants of $ScMn_2H_x$ obtained are given in Tables 2. It is found the present lattice constants *a* and *c* of $ScMn_2H_x$ both deviate appreciably the experimental values shown in Table 1 and the maximum deviation of the lattice constants calculated here relative to the experimental results is about 5.7 % for *a* and 12.2 % for *c*, respectively. The deviations possibly attribute to the difference of hydrogen occupancy between the assumptive models here and the unit cell obtained experimentally. The neutron and X-ray diffraction results of $Zr_{0.9}Ti_{0.1}MnCr$ alloy shown that the D atoms randomly occupy four tetrahedral interstices of $6h_1$, $6h_2$, 12k and 24l formed by two A atoms and two B atoms in C14-type Laves structure with $P6_3/mmc$ [4]. Furthermore, the D atoms in the deuterides with high D concentrations occupy $6h_1$, $6h_2$, 12k and 24l sites. However, the D atoms in the deuterides with low D content remains in the more stable $6h_1$ and 24l sites. In the present work, the H atoms in $ScMn_2H_3$ structures occupy $6h_1$ and $6h_2$ sites or 12k site. And for $ScMn_2H_{1.5}$ structures

$6h_2$ site in *P*6_3*/mmc*, 6c site in *P*6_3*/mc*, 6i site in *P*-3*m*1 were only considered for 6 H atoms occupancy. This may result in the difference of the calculated values and experimental values for the lattice constants.

Table 2. Optimized results for $ScMn_2H_x$ including equilibrium lattice constants, total energy E_{tot}, formation enthalpy ΔH and interatomic distances.

Compounds	Lattice parameters (⊕)		E_{tot}	ΔH	Atomic distances (⊕)		
	a	c	(eV)	(kJ/mol)	H-Mn2	H-Sc	H-H
Sample-1	5.554	7.782	-10532.5415	-62.78	H1: 1.631	2.253	2.749
					H2: 1.634	2.200	2.618
Sample-2	5.301	8.324	-10532.1015	-55.71	1.750	1.974	2.384
Sample-3	5.118	8.210	-10435.2675	-42.67	1.669	2.015	2.048
Sample-4	5.182	8.087	-10435.9727	-65.34	1.685	1.934	2.10
Sample-5	5.442	8.079	-10434.6438	-22.62	1.704	1.965	2.475
Sample-6	5.180	8.085	-10435.9733	-65.36	1.685	1.933	2.097
Sample-7	5.205	8.011	-10435.6155	-53.86	1.683	1.922	3.132
Sample-8	5.195	7.959	-10435.5745	-52.54	1.70	1.902	2.062
Sample-9	5.066	8.086	-10387.9473	-87.12	1.679	1.931	2.274

To estimate the stability of $ScMn_2H_x$ phases the formation enthalpies of the unit cells were calculated. The formation enthalpies (Δ*H*) of per atom of $ScMn_2H_x$ phases were calculated [19,20]:

$$\Delta H(\mathrm{ScMn_2H}_x)=\frac{1}{n}[E_{\mathrm{tot}}(\mathrm{ScMn_2H}_x)-8E_{\mathrm{tot}}(\mathrm{Mn})_{\mathrm{solid}}-4E_{\mathrm{tot}}(\mathrm{Sc})_{\mathrm{solid}}-\frac{n}{2}E_{\mathrm{tot}}(\mathrm{H_2(g)})] \tag{1}$$

where $E_{\mathrm{tot}}(\mathrm{ScMn_2H}_x)$ are the total energy of $ScMn_2H_x$ cell unit with *n* hydrogen atoms, as shown in Table 2. $E_{\mathrm{tot}}(\mathrm{Sc})_{\mathrm{solid}}$ and $E_{\mathrm{tot}}(\mathrm{Mn})_{\mathrm{solid}}$ are the single atomic energy in pure solid states Sc and Mn, respectively. $E_{\mathrm{tot}}(\mathrm{H_2(g)})$ is the total energy of hydrogen molecule, which was calculated as 31.5652 eV using the GGA/PBE exchange correlation potential. In the present work, we calculate the single atomic energy by the following method: at first, the energy of a pure metal crystal in the solid state was calculated, then the energy was divided by the number of atoms involved in the crystal, and this result is the energy of a single atom in the pure metal. The calculated energies of Sc and Mn atoms for our considered systems were -1277.8963 eV and –653.4574 eV, respectively. The calculated formation enthalpies of $ScMn_2H_x$ phases are listed in Table 2. Generally, the lower the formation enthalpy is, the more stable the crystal structure is. It was found that the formation enthalpies of $ScMn_2H_x$ phases with different hydrogen sites vary greatly.

For C14-type Laves structures with *P*6_3*/mmc* space group, the formation enthalpies of $ScMn_2H_x$ phases decreases from sample-3 to sample-2 to sample-1. This shows clearly the preference of the tetrahedral sites (A_2B_2) occupancy with hydrogen ($6h_1$>12k>$6h_2$). This result was consistent with the results reported early for hydride $Zr_{0.9}Ti_{0.1}MnCrD_{3.5}$ [4]. The H occupancy of different tetrahedron sites is mainly determined by atom affinity and interstitial size. According to Magee et al. [17], the interstitial hole radius of A_2B_2, AB_3 and B_4 tetrahedron site is a function of the lattice constant *a*, and the stability increases as the hole size increase. Moreover, "A" atom affinity for H atom is larger than that of "B" atom, so the H atoms will preferably occupy the A_2B_2 site rather than the AB_3 and B_4 sites. In the present work, only A_2B_2 sites are occupied. The differences in interstitial size for A_2B_2 sites in the $ScMn_2H_x$ may be indicated by the summation of the minimum distances between the H atom in the interstices and "A" atom and "B" atom forming the tetrahedron which are listed in Table 2. The minimum distance at $6h_1$ (and $6h_2$), 12k, and $6h_2$ sites is 3.884 (3.834)Å, 3.724Å, and 3.684Å, respectively. This shows that the H atoms entering $6h_1$ and 12k sites can form more stable deuteride than entering $6h_2$ sites.

As can be seen in Table 2, $ScMn_2H_{0.75}$ phase with the *P3* space group has the highest stability for all hydrides in this work. The present formation enthalpy of $ScMn_2H_3$ phases is -62.78 kJ·mol^{-1} and -55.71 kJ·mol^{-1} for sample-1 and sample-2, respectively, which is close to the values of the formation enthalpy obtained experimentally by Shilov et al. [21], Griessen et al. [22] and Li et al. [7] was -63.0 kJ·mol^{-1}, -40.2 kJ·mol^{-1} and -45.2 kJ·mol^{-1}, respectively. Hence, the value of the calculated formation enthalpy of $ScMn_2H_3$ phase in this work is close to the result obtained by Shilov et al. [21].

3.2 Electronic structure

In order to investigate intrinsic influence of hydrogen sites on structural stability and electronic bonding nature, the density of states (DOS) and the charge density distribution for $ScMn_2H_x$ phases were calculated. Fig. 2, Fig. 3 and Fig. 4 show the total densities of states (TDOS) and partial densities of states (PDOS) for $ScMn_2H_3$, $ScMn_2H_{1.5}$ and $ScMn_2H_{0.5}$ phases with different hydrogen sites, respectively, in which Fermi level was set to zero. The values of the total DOS at Fermi level was larger than zero for all $ScMn_2H_x$ phases, which indicated the metallic property.

The DOSs of $ScMn_2H_3$ with the different hydrogen sites (sample-1 and sample-2) are shown in Fig. 2. Comparing the DOSs of sample-1 and sample-2, it is found that there were the following characteristics: (i) the positions and height of the bonding peaks located at the energy range from -2.0 eV to 1 eV on TDOS plot for sample-1 were the same as sample-2. Those bonding peaks of the two samples were formed by the overlap of the Sc-3d and Mn2-3d orbit electrons. A small amount of contribution of Sc-3p, Sc-4s, Mn2-3p and Mn2-4s orbital electrons to those peaks was also observed in Fig.2. (ii) The positions and height of the bonding peaks which resulted from the contribution of the bonding electron numbers of Sc-3d, Mn2-3d and H-1s orbits located at the energy range from -3.0 eV to -10 eV on TDOS plot for sample-1 were different from sample-2. The height of the bonding peaks for sample-2 is markedly larger than that of sample-1 and those bonding peaks shifted to the Fermi level for sample-2. It is indicated that the electron delocalization is stronger for sample-1 than that of sample-2. That is, the bonding interactions between Sc, Mn2 atom and H atom are stronger for sample-1.

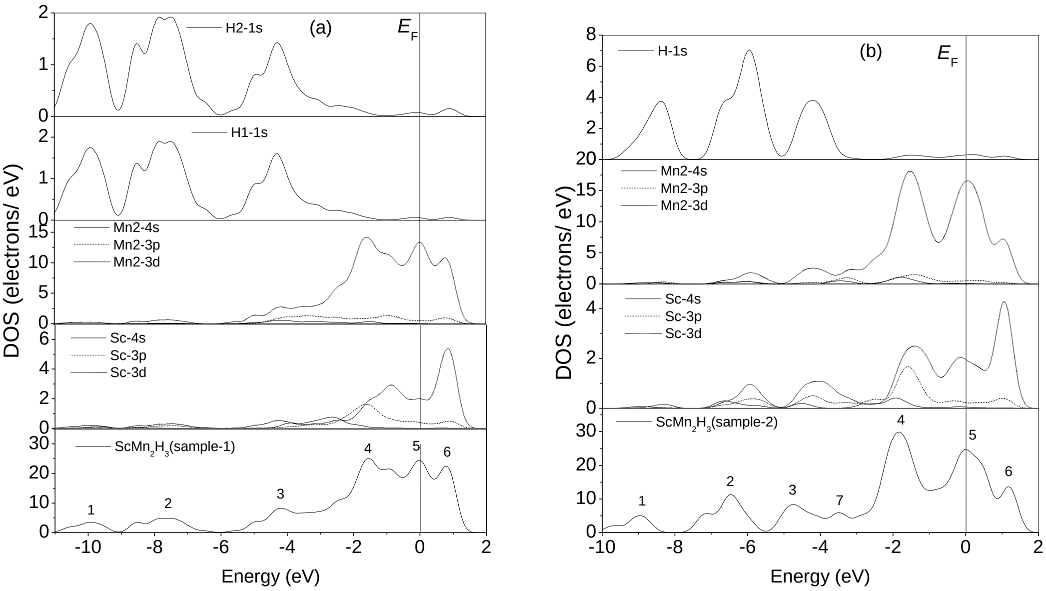


Fig. 2. Total and partial density of states of sample-1 (a) and sample-2 (b), and Fermi level was set at zero energy and marked by the vertical dot line.

The DOSs of $ScMn_2H_{1.5}$ with the hydrogen sites 6*c*(x 2x z) and 6*i*(x 2x z) corresponding to sample-4 and sample-7, respectively, are shown in Fig. 3. It was seen that there are no obvious difference on TDOS plots for the two hydrides, although they have different space group and hydrogen sites in hydrides (also see Table 1). The bonding peaks appeared in the energy range from -8.5 to -4.0 eV, which were formed by the overlap of the H-1s orbit and the Sc-3d, Mn2-3d orbit. For $ScMn_2H_{0.75}$ with the hydrogen sites 3*d*(x 2x z) (sample-9), the bonding peaks formed between H and Sc, Mn2 atoms appeared in the energy range from -8.0 to -4.0 eV, as shown in Fig. 4. The positions of the bonding peaks are similar to $ScMn_2H_{1.5}$.

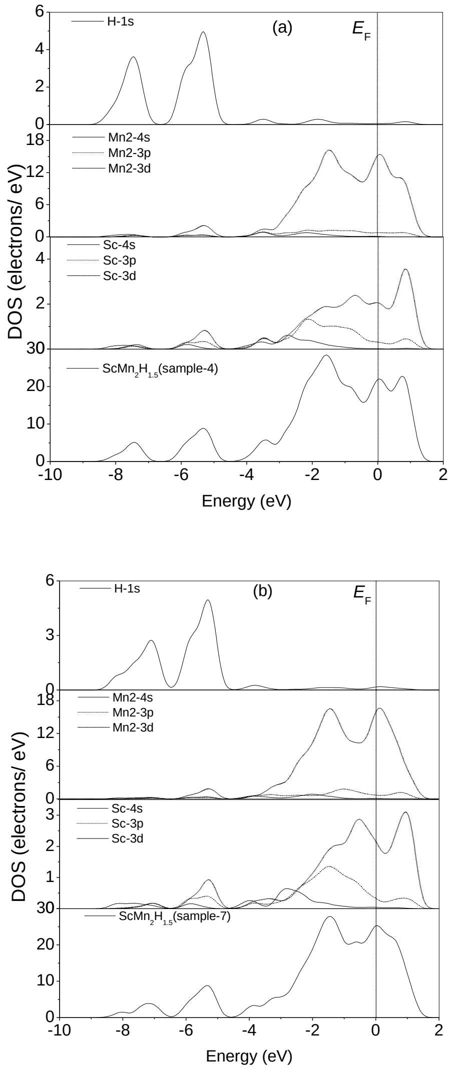


Fig. 3. Total and partial density of states of sample-4 (a) and sample-7 (b), and Fermi level was set at zero energy and marked by the vertical dot line.

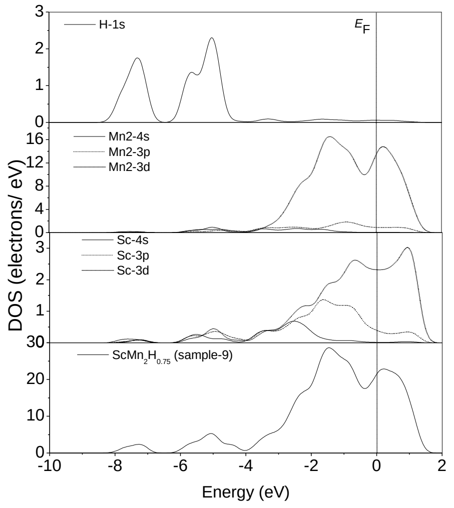
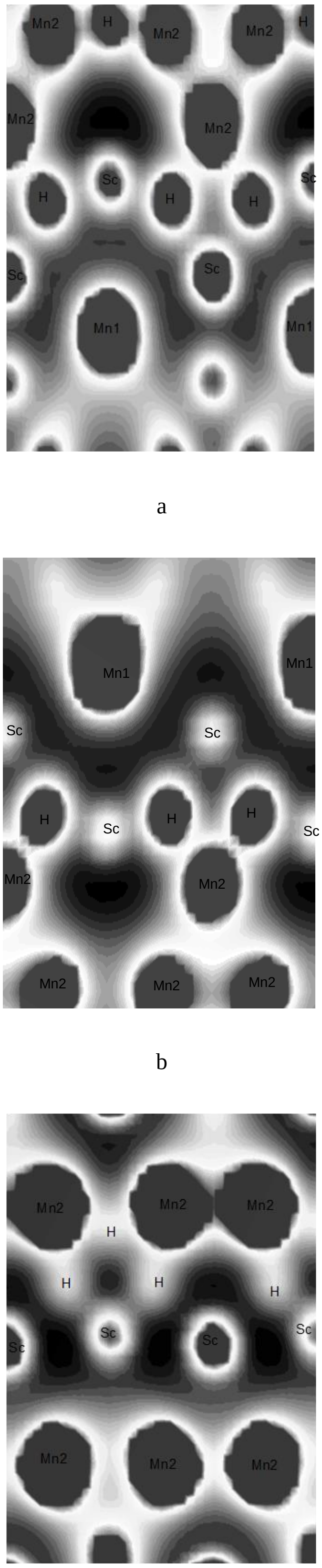


Fig. 4. Total and partial density of states of sample-9.

By comparing Fig. 2, Fig. 3 and Fig. 4, it was found that with the decrease of the hydrogen content in the hydrides, the energy ranges of bonding between H and metal atoms reduced. The bonding interactions between H-1s orbit electron and Sc-4s electrons increase as space group symmetry of the crystal structures of the hydrides decreases. This shows that the most stable site of H atom in C14-type Laves structures is 3*d*(x 2x z). The conclusion can be also supported by the bonding electron numbers at the Fermi level, $N(E_F)$ for the hydrides. $N(E_F)$ is 24.5, 24.7, 21.8, 25.2 and 21.6 for sample-1, sample-2, sample-4, sample-7 and sample-9, respectively. In general, $N(E_F)$ on DOS plot can be used to characterize the activity of valance electrons of the atoms in crystal. Namely, the smaller $N(E_F)$, the less is change probability of the electronic structures of the crystal when external conditions change, thus the crystal has the higher stability [23]. It is shown that the stability of sample-9 is highest in nine hydrides.

To visualize the nature of the bond character and to explain the charge transfer and the bonding properties of the $ScMn_2H_x$ compounds, we have investigated change of the charge density distribution for hydrides with different hydrogen site in C14-type Laves structures. Fig. 5 shows the charge-density contours in the (013) plane for sample-2, sample-4 and sample-9. It is found that the interactions between H and Mn2 atom are stronger than that between H and Sc atom. Form the view of the formation enthalpy of the hydrides formed by the elements, hydrogen absorbing alloys are consist of the hydride-generation metals A (Ti, Sc, Zr, Mg and La etc.) with endothermic reaction property during hydrogenation and the non-hydride-generation metals B (Cr, Mn, Fe, Co and Ni etc.) with exothermic reaction property during hydrogenation, such as $ScMn_2$, $ZrMn_2$, Mg_2Ni. In general, the A metals form easily hydrides (TiH_2, ScH_2, ZrH_2, and MgH_2 etc.), whereas the B metals are helpful to accelerating hydrogenation process. This trend also were observed in some hydrogen absorbing alloys, such as $LaNi_5$ [24], Mg_2Ni [25] and TiFe [26]. Moreover, the interactions between H and Mn2 atom increase with decrease of hydrogen content in hydrides, as also shown in Fig. 5. It is indicated that the stability of the hydrides decreases as hydrogen content in hydrides increases. This conclusion was consistent with aforementioned energetic results.



a

b

c

Fig. 5. Total charge density distribution on the (0 1 3) plane of sample-2 (a), sample-4 (b) and sample-9 (c).

4. Conclusions

We have investigated $ScMn_2$ hydride systems up to H/M=1 i.e. $ScMn_2H_3$ from the view point of first principles DFT in GGA, by considering possible occupation of interstitial tetrahedral sites of the C14-type Laves structures. Ab initio results show that the optimized cell parameters are close to the existing experimental results. The obtained enthalpies of formation revealed that the stability of the hydrides decreases with increase of hydrogen content in hydrides and increasing space group symmetry of the crystal structures of the hydrides. For the same space group, the stability of the hydrides with different hydrogen site did not demonstrate obvious change trend whether hydrogen content changes or not.

The analysis of the density of states, charge density indicates that bonding in hydrides is dominated by H-1s and Sc-3d, Mn2-3d states, and the interactions between H and Mn2 atom are stronger than that between H and Sc atom for all hydrides. With the decrease of the hydrogen content, the energy ranges of bonding between H and metal atoms reduce and the bonding interactions between H-1s orbit electron and Sc-4s electrons increase as space group symmetry of the crystal structures of the hydrides decreases. The most stable site of H atom in C14-type Laves structures is 3*d*(x 2x z). The results can provide helpful guidance for improving hydrogen storage properties of the Sc-based Laves phase alloys. We also propose that these results should apply to other C14 Laves phases hydrides.

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