EFFECT OF Sc ON THE HYDROGEN-STORAGE PERFORMANCE OF Mg_2Ni: A FIRST-PRINCIPLES STUDY

VPLIV Sc NA UČINKOVITOST ZLITINE MG_2Ni ZA SHRANJEVANJA VODIKA: ŠTUDIJA TEMELJEČA NA PRVEM NAČELU

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The effect of metal scandium (Sc) on the hydrogen-storage properties of the magnesium-nickel (Mg_2Ni) alloy has been explored using the ultrasoft pseudopotential approach, rooted in the principles of Density Functional Theory (DFT). The binding energy, lattice constant, enthalpy of formation, standard enthalpy of reaction, charge density, density of states and bond order for the $Mg_{2-x}Sc_xNi$ ($x = 0, 0.25, 0.5, 1$) alloys and their hydrides were calculated. Furthermore, the analysis of the atomic bonding and the structural stability of $Mg_{2-x}Sc_xNi$ and hydrides were also facilitated. The results show that the preference site of the Sc atom in $Mg_{2-x}Sc_xNi$ ($x = 0, 0.25, 0.5, 1$) alloys is Mg (6i) under the condition of a Sc doping concentration of 0.25. This causes a decrease in the stability of the $Mg_{1.75}Sc_{0.25}Ni$ alloy. Moreover, the addition of Sc to $Mg_{2-x}Sc_xNiH_4$ weakens the interaction of H-Ni and H-Mg, thereby facilitating the hydrogen-release reaction and effectively enhancing the hydrogen-release capability of $Mg_{2-x}Sc_xNiH_4$.

Keywords: Mg_2Ni alloy, first principles, electronic structure, hydrogen storage

Avtorji so študirali vpliv dodatka skandija (Sc) Mg_2Ni zlitini na njeno učinkovitost oziroma sposobnost za shranjevanje vodika. Uporabili so »ultramehki« psevdo-potencialni pristop, temelječ na osnovah funkcionalne teorije gostote (DFT; angl.: Density Functional Theory). Izračunali so vezavno energijo, mrežno konstanto, tvorbeno entalpijo, standardno entalpijo reakcije, gostoto naboja, gostoto stanja in stanje (red) vzave za zlitine vrste $Mg_{2-x}Sc_xNi$ ($x = 0, 0.25, 0.5, 1$) in njene hidrides. Nadalje v članku opisujejo analizo atomske vezave in strukturno stabilnost $Mg_{2-x}Sc_xNi$ in njenih hidridov. Rezultati analiz in izračunov so pokazali da so prednostni položaji atomov Sc v zlitinah $Mg_{2-x}Sc_xNi$ ($x = 0, 0.25, 0.5, 1$) pri položajih Mg (6i) in koncentraciji Sc je 0,25. To povzroča pomembno zmanjšanje stabilnosti zlitine $Mg_{1.75}Sc_{0.25}Ni$ alloy. Nadalje dodatek Sc k hidridu vrste $Mg_{2-x}Sc_xNiH_4$ slabi interakcijo med H-Ni in H-Mg vezmi, kar omogoča sprostitev vodika in tako učinkovito pospešuje sposobnost za sproščanje vodika pri povišani temperaturi iz $Mg_{2-x}Sc_xNiH_4$.

Ključne besede: Mg_2Ni zlitina, študija prvega načela, elektronska struktura, shranjevanje vodika

1 INTRODUCTION

Due to the high theoretical hydrogen-storage capacity, large electrochemical discharge capacity, and the ability to release hydrogen at 253 °C and 0.1 MPa, Mg_2Ni was considered one of the ideal candidates for the negative electrode materials in hydrogen-storage batteries. Among the A_2B-type alloys, Mg_2Ni has garnered extensive recognition as a preeminent contender among hydrogen-storage materials due to its considerable potential.[1] However, as a medium-temperature hydrogen-storage alloy, Mg_2Ni still faces several challenges, such as poor kinetic performance at room temperature and relatively high hydrogen-absorption/desorption temperatures, which somewhat restrict its practical application.

Recently, scholars have endeavored to improve the hydrogen-storage capacity of the Mg_2Ni alloy by modification using doping techniques.[2] Cui et al. implemented a comprehensive inquiry into the intricate hydrogen-diffusion mechanism entrenched within electrodes forged from hydrogen-storage alloys of the Mg_2Ni type.[3] Through a concerted amalgamation of the potentiostatic polarization method based on the spherical diffusion model, electrochemical impedance spectroscopy (EIS) and an array of advanced methodologies, they ascertained that the deliberate substitution of Magnesium (Mg) and Nickel (Ni) within the Mg_2Ni matrix with vanadium (V) and aluminum (Al) engendered a notable augmentation in the alloy's capacity to facilitate hydrogen diffusion. This heightened modification thereby culminates in a substantial amplification of the electrode's discharge capacity, further corroborating the proposition that the introduction of dopant elements can improve the hydrogen absorption and desorption properties of Mg_2Ni. Gao et al. also conducted an extensive exploration of the myriad modes of hydrogen absorption and desorption transpiring along the crystalline plane at the interface of Mg_2Ni doped with rare-earth elements, most notably yttrium, cerium, lanthanum, and scandium, along the designated orientation (010).[4] An insightful revelation underscores that the incorporation of the rare-earth element

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scandium exerts a marked reduction in the cohesive strength at the interface between hydrogen and the Mg$_2$Ni lattice. This profound transformation, in turn, contributes to the amelioration of the intrinsic energy barriers governing hydrogen diffusion and desorption, thereby substantially enhancing the efficiency of the hydrogen storage in Mg$_2$Ni. Nonetheless, there remains a dearth of comprehensive research elucidating the intricate mechanisms through which the rare-earth element Sc influences the hydrogen absorption and dehydrogenation properties of Mg$_2$Ni alloys. Therefore, there is a compelling need for more profound and extensive inquiries, specifically focused on delineating the optimal doping concentration and unraveling the underlying influential mechanisms. Such efforts are imperative to not only enhance the hydrogen-absorption and dehydrogenation properties, but also to pave the way for its seamless integration into diverse realms of practical production and daily existence.

The purpose of this study is to explore the effect of Sc doping on both the crystal structure and electronic configuration of the Mg$_2$Ni alloys. Calculations are executed for a range of Mg$_{2-x}$Sc$_x$Ni (x = 0, 0.25, 0.5, 1) alloys and their corresponding hydrides. The comprehensive evaluation encompasses critical factors such as binding energy, lattice constant, formation enthalpy, hydrogen-absorption enthalpy, density of states, charge density, bond order, as well as an in-depth analysis of the atomic bonding and structural stability. A detailed investigation is carried out to reveal the consequences of Sc replacement for the structural characteristics and hydrogen-storage capabilities of both the Mg$_2$Ni alloy and its affiliated hydrides. These findings unveil intricate traits that often prove elusive in experimental measurements. By illuminating the effect of Sc on strengthening the stability of the hydride structure, along with its cascading influence on the hydrogen-storage capabilities of Mg$_2$Ni, this effort is expected to offer theoretical insights that contributes to the refinement of the hydrogen-storage alloy's design and application strategies.

2 COMPUTATIONAL DETAILS

Utilizing the Quantum-ESPRESSO package,[5] which is firmly grounded in Density Functional Theory (DFT), the computations for this study were conducted.[6] The electronic exchange correlation potential energy was accurately determined using the Generalized Gradient Approximation (GGA) of the Perde/Wang (PW91) version.[7] The pseudo potentials used in this study were classified as ultrasoft type, characterized by their reciprocal space properties. The designated kinetic cutoff energy for plane-wave calculations was established at 410 eV.[8] For Mg$_2$Ni, Mg$_2$NiH$_4$, and Mg$_{2-x}$Sc$_x$NiH$_4$, the k-point grid numbers were 6×6×2, 2×4 ×4 and 2×4×4, respectively. The wave functions of pseudopotentials for the elements Sc, Mg, Ni and H were denoted as follows: H (1s^1), Sc (3s^{2}3p^{6}3d^{1}4s^2), Mg (2p^{6}3s^2), and Ni (3d^{8}4s^2).[9] To attain the stable structures, the geometric optimization of the crystal cells was executed through the utilization of the BFGS (Broyden-Fletcher-Goldfarb-Shanno) methodology.[10] The total energy of the alloy system is calculated using self-consistent iteration techniques, where the convergence threshold of the total energy is set to 1.0×10^{-5} eV/atom, stress error value less than 0.05 GPa, atomic force less than 0.03 eV/Å.[11] The calculation of the H$_2$ molecular energy adopts a simple cubic model with a size of 1 nm.

The Mg$_2$Ni cell model was shown in **Figure 1a** with a space group of P6222 (No. 180). The model consists of 12 Mg atoms and 6 Ni atoms, with lattice constants a = 0.5205 nm and c = 1.3236 nm. To investigate the variation of Sc occupancy in Mg$_2$Ni crystal cells, a Sc atom was used to replace the Mg (6i) and Mg (6f) occupancies in Mg$_2$Ni crystal cells. The corresponding cell models were shown in **Figure 1b** and **1c** respectively. Through geometric optimization calculation and analysis, it was found that the optimal site for Sc in Mg$_2$Ni crystal cells was Mg (6i). Therefore, four Sc-doped Mg$_{2-x}$Sc$_x$Ni (x = 0, 0.25, 0.5, 1) models were constructed and the cell models were displayed in **Figures 1a**, **1d**, **1e** and **1f**. To explore the influence of scandium alloying on the hydrogen-desorption characteristics of the hydride Mg$_2$NiH$_4$, a model of Mg$_{2-x}$Sc$_x$NiH$_4$ (where x = 0, 0.25, 0.5, 1) was built for analysis, as shown in **Figures 1g**, **1h**, **1i** and **1j**. At standard temperature and pressure, Mg$_2$NiH$_4$ has a monoclinic crystalline structure, characterized by a C2/c
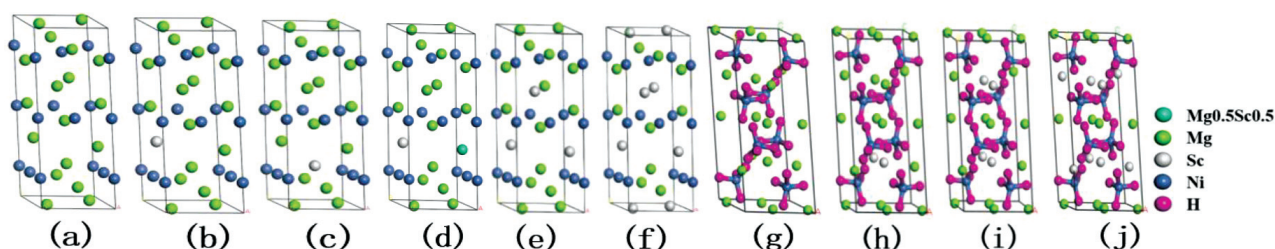

Figure 1: Crystal structure of a) Mg$_2$Ni, b) Mg$_{11}$Sc$_{Mg(6i)}$Ni$_6$, c) Mg$_{12}$Sc$_{Ni(3d)}$Ni$_5$, d) Mg$_{1.75}$Sc$_{Mg(6i)0.25}$Ni, e) Mg$_{1.5}$Sc$_{Mg(6i)0.5}$Ni, f) MgSc$_{Mg(6i)}$Ni, g) Mg$_2$NiH$_4$, h) Mg$_{1.75}$Sc$_{0.25}$NiH$_4$, i) Mg$_{1.5}$Sc$_{0.5}$NiH$_4$, j) MgScNiH$_4$

(No. 15) space group. The lattice constants are defined as follows: $a = 1.4363$ nm, $b = 0.64038$ nm, $c = 0.6483$ nm, and $\beta = 113.52°$.

3 RESULTS AND DISCUSSION

3.1 Structural properties

To validate the reasonableness of the used variables and circumstances, a comparison is made between the lattice constant of the calculated and the measured value, as shown in **Table 1**. The data presented in **Table 1** reveals a remarkable proximity between the computed lattice constant of the Mg₂Ni alloy and the empirical measurement, displaying a maximum deviation of 0.11 %. This observation strongly suggests that the calculated parameters and conditions used in this study were indeed reasonable and well-suited. Moreover, Table 1 also reveals that after Sc replaces a portion of the atoms in the Mg₂Ni alloy, significant changes occur in the lattice constant of Mg₂Ni. With the increase of Sc concentration, the a, b lattice constants and the volume of the Mg₂Ni models gradually expand, resulting in a volume expansion. This phenomenon can be attributed to the atomic radii of Sc and Mg, which were 0.162 nm and 0.160 nm, respectively. As Sc has a larger radius than Mg, its substitution in the Mg₂Ni cell leads to expansion. This was consistent with the principle that the substitution of small atoms by larger ones causes the lattice to expand.

3.2 Enthalpy of formation

The enthalpy of formation was a crucial parameter for evaluating the stability of alloys. Typically, a negative value of the enthalpy of formation indicates a more stable alloy. When investigating the stability of Sc-doped Mg₂Ni alloy structure, the enthalpies of formation for both Mg₂Ni and $Mg_{2-x}Sc_xNi$ ($x = 0, 0.25, 0.5, 1$) were calculated according to the following expressions:[15]

$$\Delta H_{form} = \frac{1}{x+y+z}\left(E_{tot} - xE_{solid}^{Mg} - yE_{solid}^{Ni} - zE_{solid}^{Sc}\right) \quad (1)$$

where E_{tot} represents the total energy in equilibrium lattice per unit; E_{solid}^{Mg}, E_{solid}^{Ni} and E_{solid}^{Sc} are the total energy of hcp Mg, fcc Ni and bcc Sc in their stable state per unit cell, respectively; x, y and z refer to the numbers of Mg, Ni and Sc atoms in the unit cell of $Mg_{2-x}Sc_xNi$, respectively. The calculation of single atom solid-state energy is implemented using the same method as the sum of cell energy in intermetallic compounds. The total energy of elemental Mg, Ni, and Sc crystal cells was calculated to be –974.5887 eV, –1356.74886 eV, and –1277.89783 eV, respectively. By using Eq. (1), the enthalpy of formation for each crystal cell was computed, and the results are also listed in **Table 1**. The enthalpy of formation of Mg₂Ni was –15.47 kJ/mol, exhibiting a notable approximation to the experimental value of –13 kJ/mol.[6] However, it is important to note that the calculations in this work were performed in an ideal 0 K environment. The difference between the calculated and experimental values may be attributed to temperature variations. It is clearly indicated from **Table 1** that the enthalpy of formation for $Mg_{12}Sc_{Ni(3b)}Ni_5$ and $Mg_{12}Sc_{Ni(3d)}Ni_5$ alloys is lower than that of Mg₂Ni, suggesting successful replacement of Ni (3b) and Ni (3d) atoms in the Mg₂Ni crystal lattice with Sc, thereby enhancing the stability of the alloy system. Similarly, the substitution of Mg (6f) and Mg (6i) sites in the Mg₂Ni crystal cells with Sc improves the stability of alloy structures. Especially, Sc preferentially occupies the Mg (6i) site upon addition to the Mg₂Ni alloy. A thorough analysis and comparison of the enthalpy of formation for Mg₂Ni, $Mg_{1.75}Sc_{Mg(6i)0.25}Ni$, $Mg_{1.5}Sc_{Mg(6i)0.5}Ni$, and $MgSc_{Mg(6i)}Ni$ indicate a decreasing order of alloy phase structure stability as follows : $MgSc_{Mg(6i)}Ni > Mg_{1.5}Sc_{Mg(6i)0.5}Ni > Mg_{1.75}Sc_{Mg(6i)0.25}Ni > Mg_2Ni$. It can be concluded that the optimal concentration of Sc-doped Mg₂Ni alloy system is $x = 0.25$.

Table 1: The cell parameters, total energy and enthalpy of formation of Mg₂Ni alloys and their hydrides.

Models	Lattice constants /nm			Cell volume /nm⁻³	Total energy /eV	ΔH_{form} / kJ·mol⁻¹
	a	b	c			
Mg₂Ni	0.5216	–	1.3227	311.7	–19839.4716	–15.47
Mg₂Ni $^{Exp.12}$	0.5205	–	1.3236	313.6	–	–13.00[13]
Mg₂Ni $^{Cal.14}$	0.5218	–	1.3212	–	–	–
$Mg_{11}Sc_{Mg(6f)}Ni_6$	0.5219	–	1.3220	313.7	–20143.3562	–16.83
$Mg_{11}Sc_{Mg(6f)}Ni_6$	0.5182	–	1.3411	313.1	–20143.2269	–16.73
$Mg_{12}Sc_{Ni(3b)}Ni_5$	0.5270	–	1.4700	336.5	–19759.2643	–16.33
$Mg_{12}Sc_{Ni(3d)}Ni_5$	0.4934	–	1.4916	332.7	–19759.4255	–16.33
$Mg_{1.75}Sc_{Mg(6i)0.25}Ni$	0.5220	–	1.3243	314.0	–20465.4659	–17.25
$Mg_{1.5}Sc_{Mg(6i)0.5}Ni$	0.5282	–	1.3120	318.8	–20750.6378	–17.62
$MgSc_{Mg(6i)}Ni$	0.5368	–	1.3048	325.4	–21661.0790	–18.81
Mg_2NiH_4	1.4422	0.6421	0.6513	554.1	–26971.8466	–64.02
$Mg_{1.75}Sc_{0.25}NiH_4$	1.4343	0.6404	0.6483	546.0	–27579.2132	–49.81
$Mg_{1.5}Sc_{0.5}NiH_4$	1.4343	0.6404	0.6483	546.0	–28186.7942	–64.01
$MgScNiH_4$	1.4343	0.6404	0.6483	546.0	–29402.2551	–64.12

The standard enthalpy of the reaction for the transformation of Mg$_2$Ni to hydride Mg$_2$NiH$_4$, denoted as ΔH, can be calculated using Equation (2),

$$\Delta H = \frac{1}{16} E(\mathrm{Mg}_{16}\mathrm{Ni}_8\mathrm{H}_{32}) - \frac{1}{12} E(\mathrm{Mg}_{12}\mathrm{Ni}_6) - E(\mathrm{H}_2) \quad (2)$$

Upon computation using Equation (2), the enthalpy of hydrogen absorption for Mg$_2$Ni is determined to be –64.02 kJ/(mol · H$_2$). Importantly, this value closely agrees with the experimental measurement of –65.5 kJ/(mol · H$_2$),[16] indicating a slight discrepancy between theoretical calculations and the experimental measurement. This provides a method for the evaluation of the reaction enthalpy in the context of Mg$_{2-x}$Sc$_x$Ni ($x = 0$, 0.25, 0.5, 1) hydrides. This computational endeavour draws upon the energy associated with an individual metal atom. The hydrogen absorption reaction can be concisely expressed as follows:

$$\frac{1}{12}\mathrm{Mg}_{2-x}\mathrm{Sc}_x\mathrm{Ni} + \mathrm{H}_2 = \frac{1}{16}\mathrm{Mg}_{2-x}\mathrm{Sc}_x\mathrm{NiH}_4 \quad (3)$$
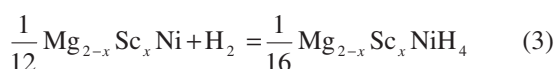
The standard enthalpy of hydrogen absorption reaction can be calculated using Equation (4),

$$\Delta H_{\mathrm{Sc}} = \frac{1}{16} E(\mathrm{Mg}_{2-x}\mathrm{Sc}_x\mathrm{NiH}_4) - \\ - \frac{1}{12} E(\mathrm{Mg}_{2-x}\mathrm{Sc}_x\mathrm{Ni}) - E(\mathrm{H}_2) \quad (4)$$

The total energy of the H$_2$ molecule was calculated by employing the Barth-Hedin exchange-correlation potential function, resulting in a value of –31.565 eV. The standard enthalpy of reaction for the hydrogen absorption of Mg$_{2-x}$Sc$_x$NiH$_4$ (x = 0, 0.25, 0.5, 1) calculated from Equation (4) is presented in **Table 1**. The standard enthalpy of reaction for hydrogen absorption in the four hydrides follows a decreasing order: Mg$_{1.75}$Sc$_{0.25}$NiH$_4$ > Mg$_{1.5}$Sc$_{0.5}$NiH$_4$ > Mg$_2$NiH$_4$ > MgScNiH$_4$. This result indicates that during the hydrogen-release process, the Mg$_{1.75}$Sc$_{0.25}$Ni alloy exhibits the lowest stability, suggest-

ing that under the same conditions, the hydrogen release reaction in this cell is more favourable. This result provides further evidence, from an energy perspective, that doping 25 % Sc significantly enhances the hydrogen-release capability of the Mg$_2$Ni alloy.

3.3 Density of States

In order to attain an insight into the influence of Sc on the structural stability of the Mg$_2$Ni alloy and its hydride from an electronic structure perspective, **Figure 2** illustrates the total densities of states (TDOS) and partial densities of states (PDOS) for Mg$_{2-x}$Sc$_x$Ni ($x = 0$, 0.25, 0.5, 1) alloys, employing the Fermi energy level E_F as the reference point for energy. **Figure 2** reveals a visible bonding peak in the energy range of –7.5 eV to 4 eV for the total density of states of Mg$_2$Ni, with the Ni (3d) electronic orbitals significantly influencing the bonding within Mg$_2$Ni crystals. Nevertheless, the bonding effect between Mg and Ni atoms appears relatively modest. To probe the effect of Sc alloying, **Figures 2b** to **2d** show the total density of states and partial density of states for Mg$_{1.75}$Sc$_{0.25}$Ni, Mg$_{1.5}$Sc$_{0.5}$Ni, and MgScNi, respectively. A comparative analysis with **Figure 2a** reveals two notable distinctions. (1) The height of bonding peak of Ni (3d) in TDOS and PDOS of Mg$_{2-x}$Sc$_x$Ni decreases, showing the beneficial influence of Sc alloying on the hydrogen release reaction of Mg$_2$NiH$_4$, leading to an enhancement in its hydrogen release property. (2) To discern the intricacies of the crystal cell interactions, the addition of Sc promotes orbital hybridization between Sc (3s4s), Sc (3p), and Sc (3d) electron orbitals with Mg (3s) and Ni (3d) within the interval spanning from –4.5 eV to 0 eV. This observation suggests a weakening of the interaction among the Mg (3s), Mg (2p), and Ni (3d) electron orbitals. Ultimately, it leads to a decrease in the stability of the crystal cells. The primary contribution to the density of states in Mg$_2$Ni crystal cells originates from the Ni (3d) orbital electrons. Within the energy span extend-
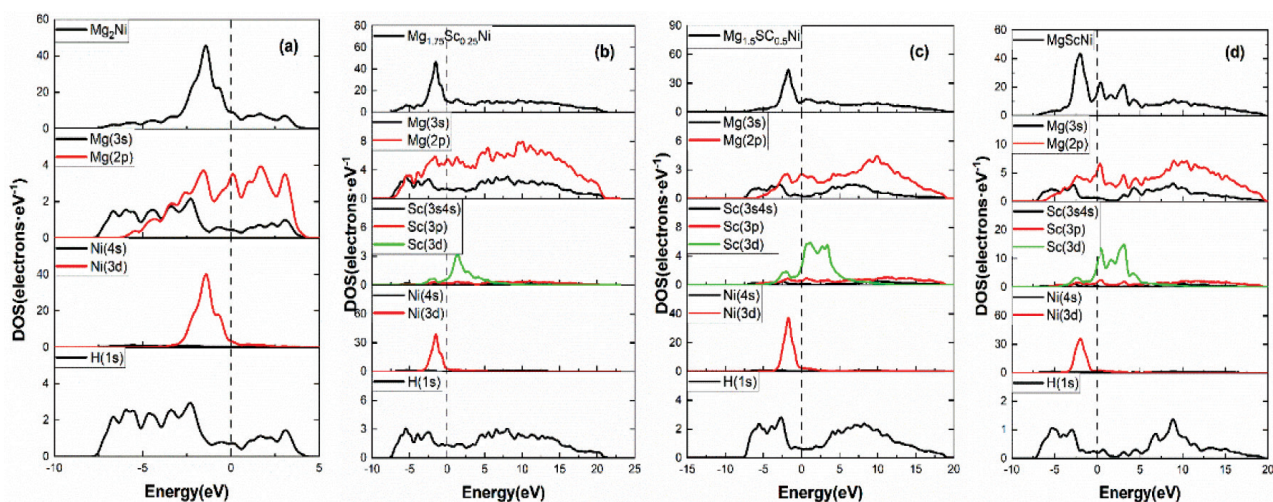

Figure 2: a) The DOS and PDOS of Mg$_2$Ni and b), c), d) Mg$_{2-x}$Sc$_x$Ni ($x = 0.25$, 0.5, 1)

ing from –10 eV to 0 eV for the $Mg_{2-x}Sc_xNi$ unit cell, the number of electrons participating in the bonding within the Ni (3d) orbital is correspondingly quantified as 40.1 electrons ($x = 0$), 38.7 electrons ($x = 0.25$), 37.1 electrons ($x = 0.5$), and 35.9 electrons ($x = 1$). The reduction in the number of bonding electrons weakens the bonding effect in the unit cell, consequently diminishing the stability of the phase structure. These findings agree harmoniously with the results of the enthalpy of formation.[17]

To comprehensively analyse the impact of Sc alloying on the hydrogen-release ability of Mg_2Ni hydrides, TDOS and PDOS of the hydrides $Mg_{2-x}Sc_xNi_4$ were shown in **Figure 3**. In **Figure 3a**, the TDOS of Mg_2NiH_4 exhibits the main bonding peak in the energy spectrum from –8.5 eV to 0 eV, and exhibits strong orbital hybridization between Ni (3d) and H (1s). This hybridization improves the structural stability of Mg_2NiH_4, and therefore make hydrogen-gas release difficult under ambient temperature and pressure conditions. This characteristic contributes to the enhanced hydrogen-absorption performance of Mg_2Ni alloys. Furthermore, it can be seen from **Figure 3a** that Mg_2NiH_4 possesses a band gap of 1.35 eV between its valence and conduction bands, indicative of its non-metallic attributes. In the energy range of the valence band, a distinct convergence is present between the 3d orbitals of Ni atoms and the 1s orbitals of H atoms. Conversely, the overlap between the 1s orbitals of H atoms and the 3s orbitals of Mg atoms is relatively minimal. This observation implies that the interaction between Mg and H is substantially weaker in comparison to that between Ni and H. Consequently, the interplay among Ni and H atoms for Mg_2NiH_4 assumes a pivotal significance in upholding the stability of the hydrides.

As shown in **Figure 3b**, the density of states for $Mg_{1.75}Sc_{0.25}NiH_4$ reveals that there is a reduction in PDOS associated with Ni and H atoms in the region located below the Fermi level. The reduction of orbital hybridization between Ni and H atoms, a result of the Sc doping, precipitates a reduction in the intensity of the Ni-H bond. Consequently, the dehydrogenation reaction

of $Mg_{1.75}Sc_{0.25}NiH_4$ becomes convenient. It is indicated that Sc alloying enhances the hydrogen release for Mg_2NiH_4. Moreover, the orbital hybridization between Ni and H atoms in $Mg_{2-x}Sc_xNiH_4$ hydrides is significantly reduced. In **Figures 3b** to **3d**, it is evident that the bonding peak of TDOS shifts towards a lower energy region due to the substitution of Sc, leading to a similar shift in the PDOS of Ni, Mg, and H atoms towards lower energy levels. The 1s orbitals of the H atom in the valence band converge more extensively with the 3d orbitals of the Sc atom than with the 3s orbitals of the Mg atom. This observation implies that the interaction of the Sc atom with the H atom demonstrates greater potency compared to that of the Mg atom with the H atom for $Mg_{2-x}Sc_xNiH_4$. Moreover, the overlap between the 3d orbitals of Ni and the 1s orbitals of H in $Mg_{2-x}Sc_xNiH_4$ is much smaller than that between the 3d orbitals of Ni and the 1s orbitals of H in Mg_2NiH_4.[18] This effect is particularly noticeable when doped with 25 % Sc. The doping of Sc accelerates the weakening of the interaction between Ni and H, which helps to improve the hydrogen desorption efficiency of the hydrides. This conclusion agrees with the results obtained from the analysis of the standard enthalpy of reaction of hydrogen absorption. It further confirms that Sc alloying positively affects the hydrogen desorption reaction of the Mg_2Ni hydride system and improves its hydrogen desorption property.

3.4 Differential Charge Density

As shown in **Figure 4**, a differential charge density plot of $Mg_{2-x}Sc_xNi$ ($x = 0, 0.25, 1$) is provided to explain the interactions between different atoms in Mg_2NiH_4, $Mg_{1.75}Sc_{0.25}NiH_4$, and $MgScNiH_4$ crystal cells. The interaction between H-Ni is stronger than that between H-Mg in the Mg_2NiH_4 (**Figure 4a**). It is indicated that the addition of Ni in Mg based alloys weakens the interaction between H and Mg atoms. The calculation results are identical to results based on density functional theory by Paula et al.[19,20] In the $Mg_{2-x}Sc_xNiH_4$ crystal cell of Sc alloying (**Figures 4b** and **4c**), it becomes evident that the
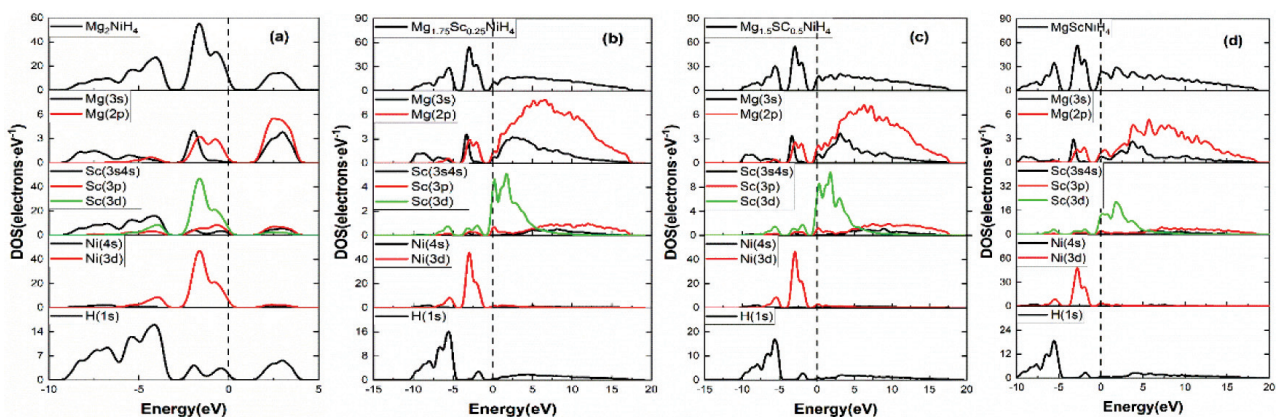

Figure 3: The DOS and PDOS of Mg_2NiH_4 and $Mg_{2-x}Sc_xNi$ ($x = 0.25, 0.5, 1$), a) Mg_2NiH_4, (b) $Mg_{1.75}Sc_{0.25}NiH_4$, c) $Mg_{1.5}Sc_{0.5}NiH_4$, d) $MgScNiH_4$
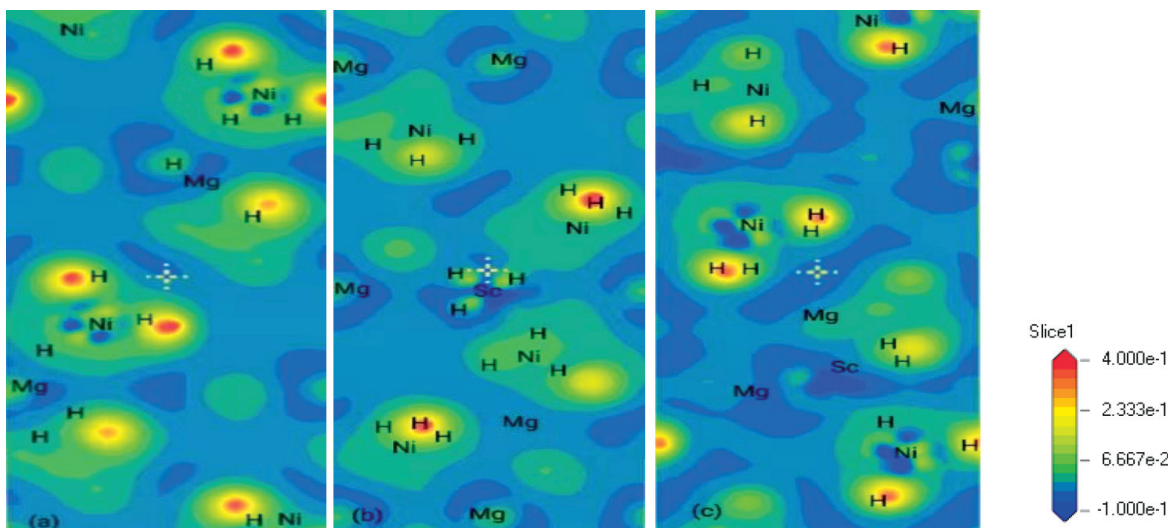
Figure 4: Differential Charge Density of: a) Mg$_2$NiH$_4$, b) Mg$_{1.75}$Sc$_{0.25}$NiH$_4$ and c) MgScNiH$_4$

interaction between H-Sc is greater than that of H-Mg. It coincides with the results of the DOS. Comparing the differential charge density of Mg$_{2-x}$Sc$_x$NiH$_4$ cells with those of Mg$_2$NiH$_4$ cells (**Figure 4a**), it is found that the Sc-H interaction generated by the addition of Sc weakens the interaction between H-Mg and H-Ni, which is particularly significant in the Mg$_{1.75}$Sc$_{0.25}$NiH$_4$ cells. It is beneficial for the hydrogen-absorption and desorption process of Mg$_2$Ni alloy. This is because the addition of Sc reduces the binding energy between H atoms and Mg atoms, as well as between H atoms and Ni atoms, which is beneficial for promoting the progress of hydrogen release reaction and hydrogen desorption reaction.[21]

3.5 Charge Population Analysis

To quantitatively analyse the bonding characteristics of each atom in Mg$_{2-x}$Sc$_x$NiH$_4$, we examined the bond order of hydrides. The strength of the interaction between the atoms can be determined by the bond order value (BO^S), calculated as BO^S = BO/BL, where BO represents the bond length, and BL represents the charge population between the atoms. A positive value of BO^S with a larger bond order indicates a strong covalent bond and a more robust interaction between the two atoms. Conversely, a negative value of BO^S with a smaller bond order indicates stronger repulsion between the atoms.[22] **Table 2** presents the calculated values of BO, BL and BO^S of H-Mg, H-Ni, and H-Sc in Mg$_{2-x}$Sc$_x$NiH$_4$ hydride.[23] The data reveals that in Mg$_2$NiH$_4$, the average bond length of

Ni-H was 0.155546 nm, and the average bond order was 0.69 nm, showing a strong covalent bonds between Ni and H, and there is a strong interaction between Ni and H atoms. To release hydrogen from Mg$_2$NiH$_4$, it is necessary to have conditions of high temperature or high pressure, which explains the difficulty of Mg$_2$NiH$_4$ releasing hydrogen under low-temperature conditions. In Mg$_{2-x}$Sc$_x$NiH$_4$ (x = 0, 0.25, 1) the interaction between Mg-H and Sc-H was weaker than that of Ni-H. Therefore, to improve the hydrogen-release performance of the hydrides, it is necessary to reduce the interaction between Ni and H. A comparison of the H-Ni bond order values in **Table 2** demonstrates that the Ni-H interaction is weakest in the Mg$_{1.75}$Sc$_{0.25}$NiH$_4$ hydride. The addition of Sc can improve the hydrogen-release kinetic property of Mg$_2$Ni. This result is consistent with the previous conclusions on differential charge density, density of states, and enthalpy of the hydrogen-absorption reaction, further verifying that Sc alloying has a positive impact on the hydrogen-release performance of Mg$_2$Ni hydrides.

4 CONCLUSIONS

The crystal structure, thermodynamic stability, and electronic structure of the Mg$_{2-x}$Sc$_x$Ni (x = 0,0.25,0.5,1) alloy and its hydride Mg$_{2-x}$Sc$_x$NiH$_4$ (x = 0,0.25,0.5,1) were studied using a density-functional-theory-based, ultrasoft-pseudopotential method. The results indicate that with the increase of Sc content, the structure stabil-

Table 2: Bond length (BL, nm), average bond order (BO) and unit bond order per unit length (BO^S, nm) between atoms in Mg$_{2-x}$Sc$_x$NiH$_4$ (x = 0, 0.25, 1)

Hydrides	H-Mg			H-Ni			H-Sc		
	BO	BL	BO^S	BO	BL	BO^S	BO	BL	BO^S
Mg$_2$NiH$_4$	−0.008	0.214840	−0.04	0.108	0.155546	0.69	−	−	−
Mg$_{1.75}$Sc$_{0.25}$NiH$_4$	−0.023	0.210030	−0.11	0.054	0.158793	0.34	0.018	0.214279	0.08
MgScNiH$_4$	−0.013	0.207878	−0.06	0.074	0.160386	0.46	0.014	0.218836	0.06

ity of the $Mg_{2-x}Sc_xNi$ (x = 0, 0.25, 0.5, 1) alloy gradually increases, and Sc occupies the Mg (6i) position. The calculation results of electronic density of states indicate that the addition of Sc leads to a decrease in the bonding peak height of Ni (3d) electron orbitals in $Mg_{2-x}Sc_xNi$ alloys, greatly reducing the structural stability of $Mg_{2-x}Sc_xNi$ alloys and facilitating the occurrence of hydrogen-release reactions. In Mg_2NiH_4, there is a strong interaction between H and Ni, while the interaction between H and Mg and Ni and Mg is weak. The charge density between H and Ni and H and Mg in $Mg_{2-x}Sc_xNiH_4$ decreases. This is due to the addition of Sc weakening the interaction between H and Ni and H and Mg, resulting in a decrease in the binding energy between H atoms and Ni atoms, as well as between H atoms and Mg atoms. This helps to promote the hydrogen-release reaction and improve the hydrogen-release ability of $Mg_{2-x}Sc_xNiH_4$. The calculation results of differential charge density, hydride bond order, and enthalpy of hydrogen absorption reaction show that the interaction between Ni-H in $Mg_{1.75}Sc_{0.25}NiH_4$ is the weakest and the structural stability is the lowest when the Sc content is x = 0.25, which is helpful to the occurrence of the hydrogen-release reaction. These results reveal the beneficial effect of Sc alloying on the hydrogen-desorption ability of Mg_2Ni hydrides. They emphasize the enormous potential for significantly improving the practicality of these materials in the field of hydrogen-storage technology.

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