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# First-principles plane-wave pseudopotential method calculations for Cu alloying $Mg_2Ni$ hydride

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Energetics and electronic structures have been calculated based on the first-principles plane-wave pseudopotential method for Cu alloying $Mg_2Ni$ phases and the corresponding hydrides. These calculations show that the $Mg_2Ni(II)''_{1-x}Cu_x$ ($x = 1/3$) phase has the highest structural stability and Cu alloying $Mg_2Ni$ hydride benefits the improvement of the dehydrogenating properties of the system, which is also well explained through the density of states (DOS) and the charge distributions of $Mg_2Ni$ phases and $Mg_2Ni$ hydrides with and without Cu alloying.

Key words: *$Mg_2Ni$ phase; heat of formation; plane-wave pseudopotential theory; dehydrogenating properties; electronic structure*

## 1. Introduction

Magnesium and its alloys have been considered the most promising hydrogen storage materials due to their high hydrogen storage capacity, light weight and low cost. However, a slow hydriding and dehydrogenating kinetics and high dissociation temperature limit their practical application for hydrogen storage. In recent years, $Mg_2Ni$ ($A_2B$)-type hydrogen storage alloys have been extensively researched as potential candidates for Ni/MH cathode materials. To improve the hydriding and dehydrogenating kinetics of $Mg_2Ni$ alloy, partial component substitution has been confirmed to be an efficient method. For example, a partial substitution of Al, V, Ti, Zr for Mg at A positions [1–3] or Cu, V, Fe, Co, Mn, Cr for Ni at B positions [4–7] in $Mg_2Ni$ phase will reduce the structural stability of the hydride ($Mg_2NiH_4$) and decrease its dissociation temperature. Among these substitutions, the corresponding $Mg_2Ni_{1-x}Cu_xH_4$ ($x \leq 0.4$)

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hydride with the partial substitution of Cu for Ni at B positions in $Mg_2Ni$ phase has excellent dehydrogenating properties.

Nowadays, considerable experimental and theoretical investigations have been performed on studying the dehydrogenating properties of Cu alloying $Mg_2Ni$ hydride. Dehouche et al. [5] found that the heat of formation (53.2 kJ/mol) of the $Mg_2Ni$ hydride with Cu alloying is decreased compared to that of the hydride without Cu alloying (64.5 kJ/mol), meanwhile, the dissociation temperature of the system is reduced significantly. Simicic et al. [6] synthesized $Mg_2Ni_{0.75}Cu_{0.25}$ and $Mg_2Ni_{0.6}Cu_{0.4}$ alloys by mechanical milling of $Mg_2Ni$ with different contents of Cu, which remarkably improves hydriding and dehydrogenating kinetics of pure $Mg_2Ni$ at low temperature below 473 K. Yang. et al. [7] fabricated $Mg_2Ni_{0.75}M_{0.25}$ (M = Ti, Cr, Mn, Fe, Co, Ni, Cu and Zn) alloys by milling diffusion method. They found that the structural stability, dissociation enthalpy and dissociation temperature of the corresponding hydrides are all decreased with the increasing unit volume of these alloys, and the effect of Cu on $Mg_2Ni$ hydride is proved to be the most promising. All above experiments have been focused on destabilizing the phase structure of $Mg_2Ni$ hydride by Cu alloying to decrease the dissociation temperature of this system. Whereas, due to the complexity of crystal structure for $Mg_2Ni$ hydride ($Mg_2NiH_4$) and the uncertainty of Cu occupying sites in $Mg_2Ni$ phase, it becomes difficult for the dehydrogenating properties of Cu alloying $Mg_2Ni$ hydride to be further experimentally investigated. Garcia et al. [8] calculated the electronic structure of the $Mg_2Ni$ hydride ($Mg_2NiH_4$) by the *ab initio* method. They determined the occupying sites of H atoms in the structure, and then, the bonding types of different atoms were deduced according to the charge distributions in $Mg_2NiH_4$. They suggested that the $[NiH_4]^{4-}$ anion exists in the form of covalent bonding interaction between H and Ni, while there are electrovalent bonding interaction between $[NiH_4]^{4-}$ anion and $Mg^{2+}$ cation. Therefore, $Mg_2NiH_4$ with the antifluorite structure possesses a relatively stable phase structure. Takahashi et al. [9] calculated the electronic structure of $Mg_2NiH_6$ cluster model alloyed by 3d transition metal elements M (M = V, Cr, Fe, Co, Cu, Zn) by using DV-Xα method. It was found that the bonding interaction between Ni and H is stronger than that between Mg and H, and the stability of the hydride directly lies on the bonding interactions between Ni and Mg, Ni and H. After the partial substitution of different alloying elements M for Ni, it was noted that the reduced structural stability of the $Mg_2Ni$ hydride can be ascribed to the weakened bonding interaction between M and Mg. In addition, the negative heat of formation of the system with the substitution of Cu for Ni is the smallest, which means that the Cu substitution makes the hydride become the most unstable. Recently, Jasen et al. [10] calculated the electronic properties of $Mg_2NiH_4$ monoclinic phase by using a density functional approach. It was concluded that the hydrogen atoms present a bonding much more developed with Ni than with Mg in the hydride from the electronic density and overlap populations analyses. Since $Mg_2NiH_4$ is also a stable compound under normal conditions, it is essential to decrease the stability of the hydride by transition metal (Cu) alloying to produce a suitable material for practical hydrogen storage.

The most stable phase structure of Cu alloying $Mg_2Ni$ has not been detected so far and the electronic structures of the hydrides with and without Cu alloying have not been well studied from the energy point of view to illuminate the electronic mechanism of improved dehydrogenating properties. Grounded on the previous work, first-principles plane-wave pseudopotential method based on density functional theory is used to systematically investigate the energetics and electronic structures of Cu alloying $Mg_2Ni$ phases and their hydrides in the present work, some new results are expected to be the theoretical guidance for designing the advanced Ni/MH battery materials.

## 2. Models and method of computation

The $Mg_2Ni$ phase has the $A_2B$ type structure as shown in Fig. 1a. The lattice parameters of its unit cell are $a$ = 0.5219 nm and $c$ = 1.3293 nm with the space group $P6222$ (NO.180) [6]. The atomic coordinates in the unit cell are: +6Mg(I): (0.5, 0, $z$) $z$ = 1/9, +6Mg(II): ($x$, 2$x$, 0) $x$ = 1/6, +3Ni(I): (0, 0, 1/6), +3Ni(II): (0, 0.5, 1/6).

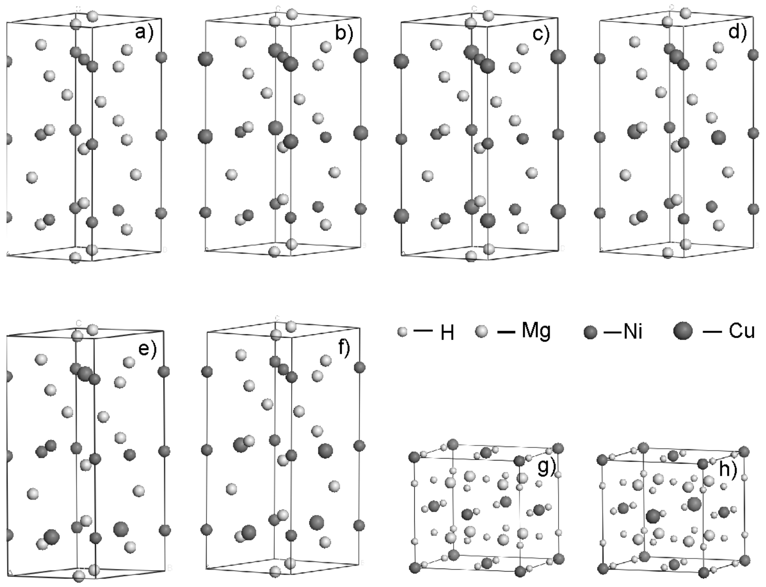

Fig. 1. Models used in calculations: a) crystal structure of $Mg_2Ni$, b) cell of $Mg_2Ni(I)_{1-x}Cu_x$, c) cell of $Mg_2Ni(I)'_{1-x}Cu_x$, d) cell of $Mg_2Ni(II)_{1-x}Cu_x$, e) cell of $Mg_2Ni(II)'_{1-x}Cu_x$, f) cell of $Mg_2Ni(II)''_{1-x}Cu_x$, g) cell structure of $Mg_2NiH_4$, h) cell of $Mg_2Ni_{1-x}Cu_xH_4$

Considering the cell character of $Mg_2Ni$ phase and computational cost, the cell models of $Mg_2Ni_{1-x}Cu_x$ ($x$ = 1/3) have been constituted by substituting two Cu atoms for two Ni atoms. To determine the most stable positions of two Cu atoms in $Mg_2Ni_{1-x}Cu_x$ ($x = 1/3$) cell, five possible models have been designed as shown in Figs. 1b–f. If the two different sites of Ni(I) atoms are occupied by two Cu atoms, there will be two possible cases: $Mg_2Ni(I)_{1-x}Cu_x$ and $Mg_2Ni(I)'_{1-x}Cu_x$ as shown in Fig.1(b) and (c); If the two different sites of Ni(II) atoms are occupied by two Cu atoms, there will be three possible cases: $Mg_2Ni(II)_{1-x}Cu_x$, $Mg_2Ni(II)\ )'_{1-x}Cu_x$ and $Mg_2Ni(II)\ )''_{1-x}Cu_x$ as shown in Figs. 1d–f. To evaluate the dehydrogenating properties of Cu alloying $Mg_2Ni$ hydride, the cell models of $Mg_2NiH_4$ [8] and $Mg_2Ni_{1-x}Cu_xH_4$ ($x = 1/4$) are constituted as shown in Figs. 1g and 1h. The lattice parameters of $Mg_2NiH_4$ are $a = b = c = 0.6507$ nm with the space group $Fm3m$ (NO.225). The positions of atoms are +4Ni (0, 0, 0), +8Mg (0.25, 0.25, 0.25) and +16H $(x, 0, z)$, $(0, x, -z)$, $(-x, 0, z)$, $(0, -x, -z)$, $x = 0.2379$, $z = 0$, respectively.

Cambridge serial total energy package (CASTEP) [11], the first-principles plane-wave pseudopotential 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 pseudopotential 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 [12]. Ultrasoft pseudopotential [13] represented in a reciprocal space is used. In the present calculations, the cutoff energy of atomic wave functions (PWs), $E_{\mathrm{cut}}$, is set at 310 eV. A finite basis set correction and the Pulay scheme of density mixing [14, 15] are applied for the evaluation of the energy and stress. The atomic orbits used are: Mg $2p^63s^2$, Ni $3d^84s^2$, Cu $3d^{10}4s^1$, and H $1s^1$. All atomic positions in Cu alloying $Mg_2Ni$ models and the inner atomic positions in Cu alloying $Mg_2Ni$ hydride model have been relaxed according to the total energy and force by using the Broyden–Flecher–Goldfarb–Shanno (BFGS) scheme [16] and their lattice parameters are well tested as shown in Table 1; the experimental cell structure and lattice constant for $Mg_2NiH_4$ are directly adopted without geometry optimization. The calculations of total energies and electronic structures for all the models are followed by cell optimization with self-consistent-field (SCF) tolerance of $2.0\times10^{-6}$ eV/atom, RMs force of 0.5 eV/nm, stress of 0.1 GPa, and displacement of $2.0\times10^{-4}$ nm.

## 3. Results and discussion

### 3.1. Stable structure of Cu alloying $Mg_2Ni$ phase

Commonly, as an important index, the heat of formation ($\Delta H$) is used for evaluating the structural stability of alloys with the same constituent elements but different types of structures, i.e., the bigger the negative heat of formation, the more stable is the corresponding alloy [17]. Hence, $\Delta H$ of $Mg_2Ni$ and all $Mg_2Ni_{1-x}Cu_x$ cells (Figs. 1a–f) per atom is calculated by using the following formula [18, 19]:

$$\Delta H = \frac{1}{18}\left(E_{\text{tot}} - 12E_{\text{solid}}^{\text{Mg}} - (6-x)E_{\text{solid}}^{\text{Ni}} - xE_{\text{solid}}^{\text{Cu}}\right) \tag{1}$$

where $E_{\text{tot}}$ refers to the total energy of the cell at the equilibrium lattice constant, $E_{\text{solid}}^{\text{Mg}}$, $E_{\text{solid}}^{\text{Ni}}$ and $E_{\text{solid}}^{\text{Cu}}$ are single atomic energies of *hcp*-Mg, *fcc*-Ni, *fcc*-Cu in solid states, respectively, $x$ refers to the numbers of the alloying Cu atoms. In this paper, when the single atomic energies are calculated, the same pseudopotential with $Mg_2Ni_{1-x}Cu_x$ cell models is adopted. We calculate single atomic energies by the following method. First, the energy of a pure metal crystal in the solid state is calculated, then the energy is divided by the number which means the amounts of atoms involved in the crystal, and the result of the calculation is just the energy of a single atom of pure metal. The calculated energies of Mg, Ni and Cu atoms for the considered systems are –977.87 eV, –1356.19 eV, –1352.67 eV, respectively. The calculated heats of formation of $Mg_2Ni$, $Mg_2Ni(I)_{1-x}Cu_x$, $Mg_2Ni(I)'_{1-x}Cu_x$, $Mg_2Ni(II)_{1-x}Cu_x$, $Mg_2Ni(II)'_{1-x}Cu_x$, $Mg_2Ni(II)''_{1-x}Cu_x$ are listed in Table 1.

Table 1. Equilibrium lattice constants, cell volume, total energies and formation heat of crystal models

| Model | Lattice parameter [nm] | | | Cell volume [$nm^3$] | Total energy [ eV] | | $\Delta H$ [$kJ \cdot mol^{-1}$] |
|---|---|---|---|---|---|---|---|
| | *a* | *b* | *c* | | Crystal cell | Primitive cell | |
| $Mg_2Ni$ | 0.5202 | 0.5202 | 1.3254 | 0.3133 | −19876.9837 | −3312.8306 | –28.97 |
| $Mg_2Ni$ [6] | 0.5219 | 0.5219 | 1.2930 | 0.3136 | – | – | –13 [20] |
| $Mg_2Ni(I)_{1-x}Cu_x$ | 0.5160 | 0.5224 | 1.3456 | 0.3176 | −19869.4309 | −3311.5718 | –26.26 |
| $Mg_2Ni(I)'_{1-x}Cu_x$ | 0.5220 | 0.5153 | 1.3463 | 0.3173 | −19869.4709 | −3311.5785 | –26.47 |
| $Mg_2Ni(II)_{1-x}Cu_x$ | 0.5168 | 0.5238 | 1.3416 | 0.3183 | −19869.3637 | −3311.5606 | –25.90 |
| $Mg_2Ni(II)'_{1-x}Cu_x$ | 0.5231 | 0.5167 | 1.3431 | 0.3184 | −19869.3643 | −3311.5607 | –25.90 |
| $Mg_2Ni(II)''_{1-x}Cu_x$ | 0.5183 | 0.5183 | 1.3425 | 0.3185 | −19869.4908 | −3311.5818 | –26.58 |
| $Mg_2NiH_4$ | 0.6507 | 0.6507 | 0.6507 | 0.2755 | −13506.5860 | −3376.6465 | – |
| $Mg_2Ni_{1-x}Cu_xH_4$ | 0.6507 | 0.6507 | 0.6507 | 0.2755 | −13501.5611 | −3375.3903 | – |

In the present work, the calculated heat of formation of $Mg_2Ni$ is –28.97 kJ/mol, being a little different from the experimental value (–13 kJ/mol) [20]. If the thermodynamic effect on crystal structure is considered, the present calculation should be in good agreement with the experimental result. Further analysis was done, and it was found that the heat of formation of Cu alloying $Mg_2Ni$ phase is all negative, which means that the structures of these phases can exist and be stable [17]. Since the negative heat of formation for $Mg_2Ni(II)''_{1-x}Cu_x$ ($x = 1/3$) system is the biggest among the five substitutions when two Cu atoms occupying the two sites at (0, 0.5, 0.16667) and (0.5, 0, 0.5) of Ni (II) atoms as shown in Fig. 1f, it can be concluded that this kind of structure has the highest structural stability. Due to the limitation of actual experimental conditions, it is difficult to detect the precise sites occupied by Cu atoms in Cu alloying $Mg_2Ni$ systems. The results calculated in this paper cannot be compared with the experimental data but these new results are expected to be a theoretical guidance for designing the advanced Ni/MH battery materials.

### 3.2. Dehydrogenating properties of Cu alloying $Mg_2Ni$ hydride phase

Dehouche et al. [5] found experimentally that the heat of formation of Cu alloying $Mg_2Ni$ hydride and its phase structural stability are both decreased compared with that of pure $Mg_2Ni$ hydride system, which benefits improving the dehydrogenating properties of this system. Simicic et al. [6] solved the problem of slow kinetics of pure $Mg_2Ni$ at low temperature by substituting Cu for Ni which remarkably destabilizes the phase structure of the $Mg_2Ni$ hydride ($Mg_2NiH_4$). To further understand the experimental phenomenon, the dehydrogenating reaction heat ($Q$) of the $Mg_2Ni$ hydride systems with and without Cu alloying is calculated from the chemical reaction view, respectively, in addition, the Cu alloying effect on dehydrogenating properties of the $Mg_2Ni$ hydride will also be well investigated.

The equation of hydriding/dehydrogenating reaction of $Mg_2Ni$ system with and without Cu alloying can be written as:

$$\mathrm{Mg_2Ni_{1-\mathit{x}}Cu_{\mathit{x}}+2H_2} \longleftrightarrow \mathrm{Mg_2Ni_{1-\mathit{x}}Cu_{\mathit{x}}H_4} \qquad (2)$$

The energy of this system itself will be changed during the hydriding/dehydrogenating: commonly, the hydriding is exothermic, while the dehydrogenating is endothermic. Hence, as far as the Cu alloying $Mg_2Ni$ system is concerned, the change of the energy before and after hydriding/dehydrogenating reaction can be expressed as:

$$E_{\mathrm{tot}}(\mathrm{Mg_2Ni_{1-\mathit{x}}Cu_{\mathit{x}}}) + 2E_{\mathrm{tot}}(\mathrm{H_2}) = E_{\mathrm{tot}}(\mathrm{Mg_2Ni_{1-\mathit{x}}Cu_{\mathit{x}}H_4}) + Q \qquad (3)$$

where $E_{\mathrm{tot}}(\mathrm{Mg_2Ni_{1-\mathit{x}}Cu_{\mathit{x}}})$, $E_{\mathrm{tot}}(\mathrm{Mg_2Ni_{1-\mathit{x}}Cu_{\mathit{x}}H_4})$ refer to the total energy of the $\mathrm{Mg_2Ni_{1-\mathit{x}}Cu_{\mathit{x}}}$ system before and after hydriding, respectively, $E_{\mathrm{tot}}(\mathrm{H_2})$ is the energy of a gaseous hydrogen molecule, and $Q$ refers to the heat absorbed for dehydrogenating (or released for hydriding). From Eq. (3), it can be seen that whether the dehydrogenating reaction is easy, mainly depends on the value of $Q$, i.e., the smaller the value of $Q$, the less the heat to absorb for dehydrogenating is, and then, the easier the dehydrogenating reaction of this hydride system becomes.

Based on the above analysis, the heat of dehydrogenating reaction of $Mg_2Ni$ hydrides with and without Cu alloying is calculated by using the following equations:

$$Q_{\mathrm{Ni}} = -[E_{\mathrm{tot}}(\mathrm{Mg_2NiH_4}) - E_{\mathrm{tot}}(\mathrm{Mg_2Ni}) - 2\mathrm{E}_{\mathrm{tot}}(\mathrm{H_2})] \qquad (4)$$

$$Q_{\mathrm{Cu}} = -[E_{\mathrm{tot}}(\mathrm{Mg_2Ni_{1-\mathit{x}}Cu_{\mathit{x}}H_4}) - E_{\mathrm{tot}}(\mathrm{Mg_2Ni_{1-\mathit{x}}Cu_{\mathit{x}}}) - 2\mathrm{E}_{\mathrm{tot}}(\mathrm{H_2})] \qquad (5)$$

where $Q_{\mathrm{Ni}}$, $Q_{\mathrm{Cu}}$ refer to the heat of dehydrogenating reaction of $Mg_2Ni$ hydrides with and without Cu alloying, respectively. The calculated values of $E_{\mathrm{tot}}(\mathrm{Mg_2NiH_4})$, $E_{\mathrm{tot}}(\mathrm{Mg_2Ni_{1-\mathit{x}}Cu_{\mathit{x}}H_4})$, $E_{\mathrm{tot}}(\mathrm{Mg_2Ni})$ and $E_{\mathrm{tot}}(\mathrm{Mg_2Ni_{1-\mathit{x}}Cu_{\mathit{x}}})$ are –3376.65 eV, –3375.39 eV, –3312.8306 eV, –3311.5818 eV, respectively. The total energy of $H_2$ ($E_{\mathrm{tot}}(\mathrm{H_2})$ takes | –2.320Ry (≈ –31.5652196848 eV) [21]. Hence, from Eqs. (4) and (5), it can be found that the calculated values of $Q_{\mathrm{Ni}}$ and $Q_{\mathrm{Cu}}$ are 33.07kJ/(mol $H_2$) and 13.56 kJ/(mol $H_2$), respectively. The dehydrogenating reaction heat to be absorbed for the Cu alloying $Mg_2Ni$ hydride system is significantly decreased compared with that before Cu alloying, which means that the $Mg_2Ni$ hydride becomes unstable after Cu alloying, and the dehydrogenating properties of this system are improved markedly. Based on this, the experimental phenomenon reported by Dehouche [5] and Simicic [6] can also be well interpreted based on the present calculated results.

### 3.3. Density of states

An analysis of total and partial density of states (DOS) of $Mg_2Ni_{1-x}Cu_x$ cell models with five various structures is performed to understand the electronic structure mechanism of the most stable phase structure for Cu alloying $Mg_2Ni$ systems. It is found that there is little difference in the bonding peaks at various energy ranges of valence electrons in these structures. As far as the crystals with the same constituent Cu at. % but different types of structures are concerned, a conclusion about relative stability is often derived from comparison of the values of their density of states at the Fermi level $N(E_F)$, i.e., the lower the $N(E_F)$, the more stable is the corresponding phase structure [22]. To verify the criterion in the case of $Mg_2Ni_{1-x}Cu_x$ compounds, the calculated values of $N(E_F)$ of $Mg_2Ni_{1-x}Cu_x$ with five different types of structures are presented in Fig. 2.

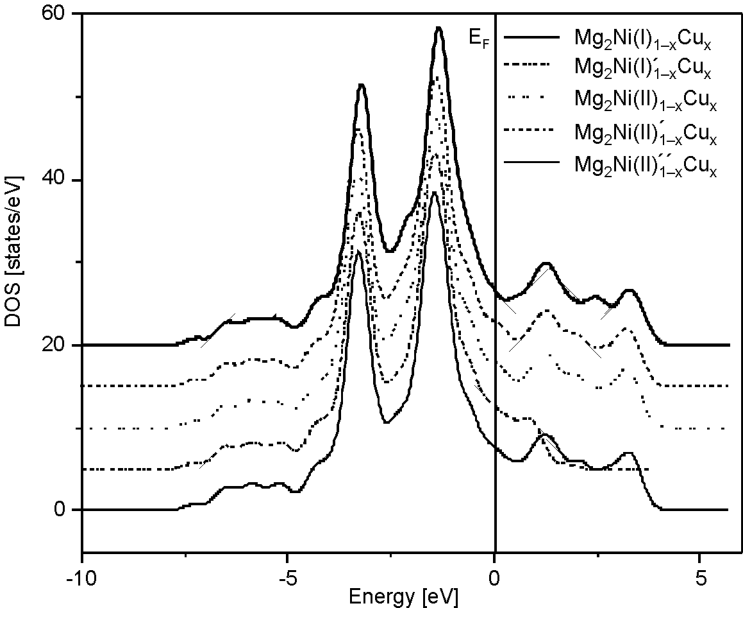

Fig. 2. Total DOS of Cu alloying $Mg_2Ni$ phase around $E_F$. The curves have been vertically displaced

The $N(E_F)$ values of five computational models in the order of Fig. 1d, 1e, 1b, 1c and 1f are 8.04702 electrons/eV, 7.94366 electrons/eV, 7.67374 electrons/eV, 7.65078 electrons/eV, 6.65797 electrons/eV, respectively. It is found that the decreasing order of the $N(E_F)$ values is in good agreement with the increasing order of the negative heat of formation of the computational models as shown in Fig. 3, which means that the $N(E_F)$ value of the $Mg_2Ni(II)''_{1-x}Cu_x$ ($x = 1/3$) phase structure is the lowest in Cu alloying $Mg_2Ni$ systems and this structure is the most stable.

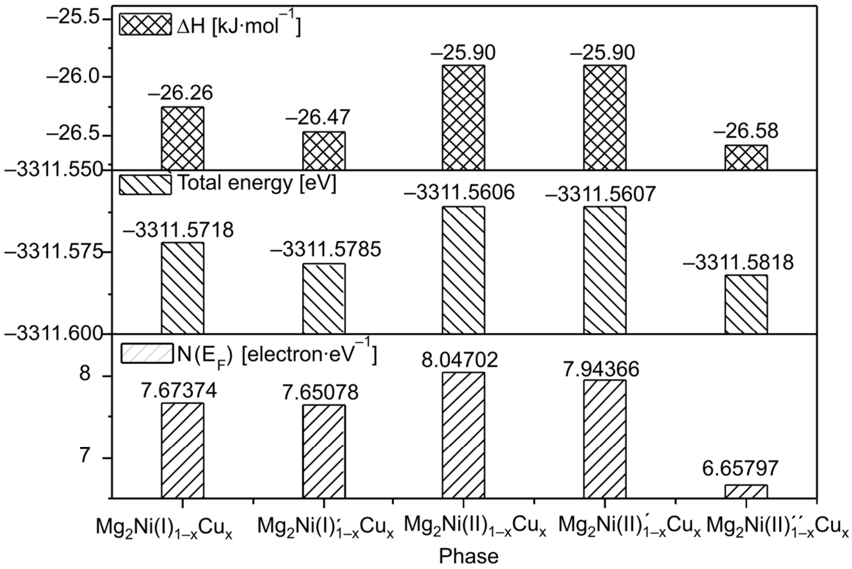

Fig. 3. $N(E_F)$, total energy and heat of formation in Cu alloying $Mg_2Ni$ phase

A further analysis of total and partial density of states (DOS) of $Mg_2Ni$ hydride with and without Cu alloying is also done to understand the Cu alloying effect on dehydrogenating properties of $Mg_2Ni$ hydride. The total and partial DOSs of $Mg_2NiH_4$ and $Mg_2Ni_{1-x}Cu_xH_4$ ($x = 1/4$) cell are plotted in Figs. 4a and b. It is found that the main bonding peaks of $Mg_2NiH_4$ are located at the energy range from the Fermi energy ($E_F$) to –11 eV (Fig. 4a). The bonding peak between $E_F$ and –2 eV mainly originates from the contribution of valence electrons of Mg(s) and Mg(p) as well as a few Ni(d) and H(s) orbits. The bonding peak between –4 eV and –2 eV results from the bonding of valence electrons of Mg(s), Mg(p), Ni(d) and a few H(s). The bonding peak between –7 eV and –4 eV is the interaction of Ni (d) and H(s) as well as a few Mg(s) and Mg (p) electrons. The bonding peak between –11 eV and –7 eV is caused by Mg(s), H(s) and a few Ni(s). After Cu alloying, the energy range of the main bonding peaks is not markedly changed (Fig. 4b), which is still from $E_F$ to –11 eV, but there is a new bonding peak appearing at the energy range between –5 eV and –4 eV. The heights of the main bonding peaks originating from the contribution of valence electrons of Mg, Ni and H orbits are all decreased compared with that before Cu alloying. For example, the height of the peak between –4 eV and –2 eV is decreased from 29.16 electronic states/eV before Cu alloying to 22.30 electronic states/eV after Cu alloying.

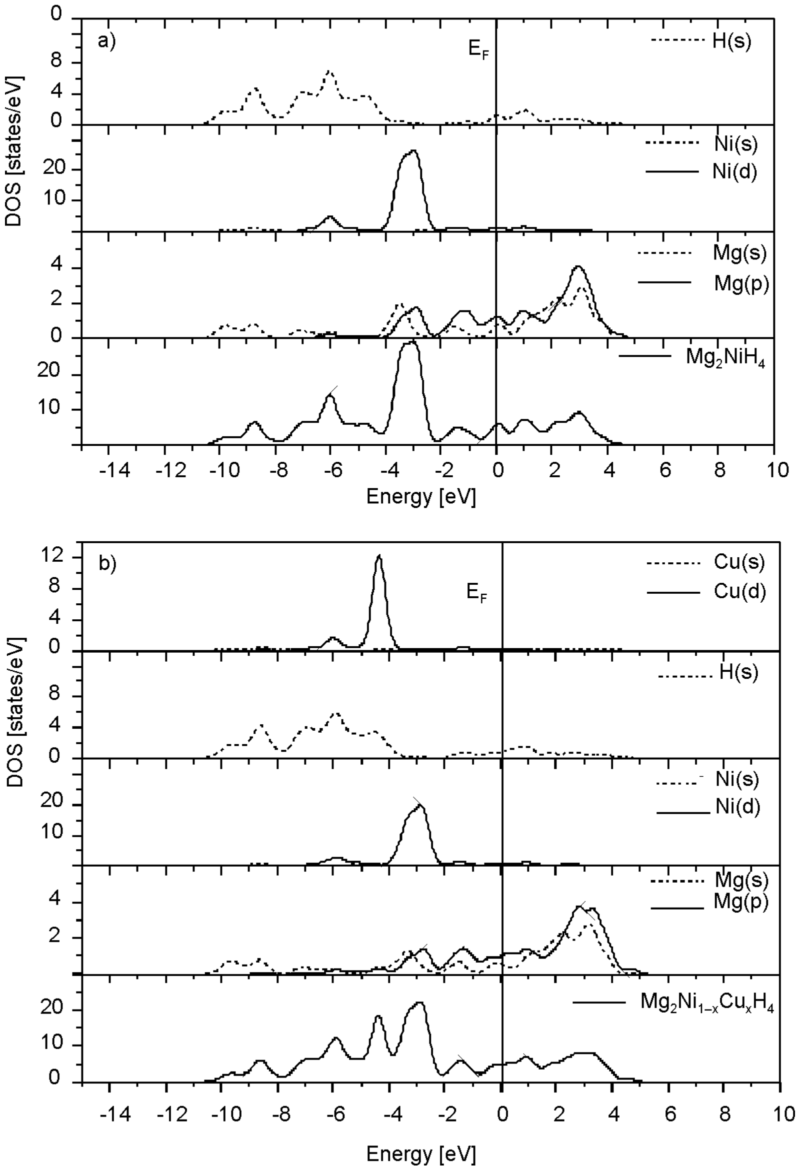

Fig. 4. Total and partial DOS of alloying $Mg_2NiH_4$ (a) and $Mg_2Ni_{1-x}Cu_xH_4$ (b)

The height of the peak between –7 eV and –5 eV is decreased from 14.13 electronic states/eV before Cu alloying to 12.22 electronic states/eV after Cu alloying. The height of the peak between –11 eV and –8 eV is decreased from 6.57 electronic states/eV before Cu alloying to 2.37 electronic states/eV after Cu alloying. Based on the analysis above, it is found that there are fewer bonding electrons in Cu alloying $Mg_2Ni$ hydride than in pure $Mg_2NiH_4$. The fewer the bonding electron numbers, the weaker are the charge interactions, and fewer electrons in low energy range far below the Fermi level will lead to reduce the structural stability of the corresponding system [23, 24]. Hence, when Ni atoms are partially substituted by Cu atoms in $Mg_2NiH_4$, the structural stability of the hydride will be reduced and the dehydrogenating reaction will become easier, which benefits in improving the dehydrogenating properties of the $Mg_2Ni$ hydride system.

### 3.4. Electron density

The total valence electron density contour plots of $(1\bar{1}0)$ planes of $Mg_2Ni$ hydrides before and after Cu alloying are presented in Figs. 5a, b, respectively.

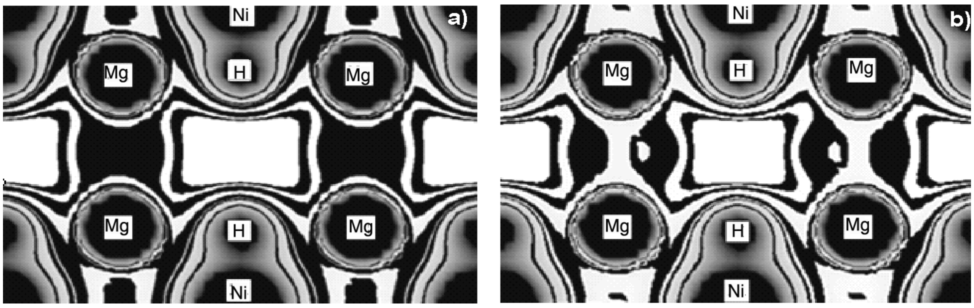

Fig. 5. Charge distribution on $(1\bar{1}0)$ planes of $Mg_2NiH_4$ (a) and $Mg_2Ni_{1-x}Cu_xH_4$ (b)

It can be seen that there is a strong bonding between Ni and H in $Mg_2NiH_4$ cell, while there are weakened bonding interactions between Mg and H, Ni and Mg (Fig. 5a). Takahashi [9] and Jasen [10] found that the bonding interaction between Ni and H atoms is stronger than that between Mg and H, which is in good agreement with our results. After Cu alloying, due to the addition of Cu, the bonding interactions between Ni and Mg, Ni and H are both slightly reduced (Fig. 5b) which will benefit in reducing the structural stability, decreasing the heat of dehydrogenating and markedly improving the dehydrogenating properties of $Mg_2Ni$ hydride system.

## 4. Conclusions

Based on calculations of negative heat of formation of Cu alloying $Mg_2Ni$ phases, it can be seen that the $Mg_2Ni(II)''_{1-x}Cu_x$ ($x = 1/3$) phase structure is the most stable among the five substitutions when two Cu atoms occupy two sites at (0, 0.5, 0.16667) and (0.5, 0, 0.5) of Ni(II) atoms.

From the calculated results of the dehydrogenating reaction heat of Cu alloying $Mg_2Ni$ hydride, it results that the heat of dehydrogenating reaction is remarkably decreased compared with that without Cu alloying, which benefits in improving its dehydrogenating properties.

After comparing the density of states (DOS) and the charge distributions of $Mg_2Ni$ and $Mg_2NiH_4$ with and without Cu alloying, it is found that the main reason for the $Mg_2Ni$ $(II)''_{1-x}Cu_x$ ($x = 1/3$) with the most stable phase structure should be ascribed to the lowest $N(E_F)$ value at the Fermi level in this system compared with that of other substitutions. The improved dehydrogenating properties of $Mg_2Ni$ hydride system with Cu alloying mainly originates from the weakened bonding between Mg and Ni, Ni and H as well as the decreasing of bonding electron numbers in low energy range below the Fermi level.

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