



Nickel induced iono-covalent character of hydrogen in RbMgH₃ from first principles

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ABSTRACT

The large ionic character in hexagonal perovskite RbMgH₃ is reduced by selective substitutions by Ni followed by full geometry optimization within DFT leading to preserve the structure and symmetry of the pristine hydride. From the Bader charge analysis, an increasingly iono-covalent character is introduced with larger amounts of Ni substituting to Mg. For the Ni rich composition RbMg_{1/3}Ni_{2/3}H₃, found most stable from cohesive energies, the charge on H decreases down to −0.2. This peculiar behavior should enable enhancing the kinetics of H release for potential applications.

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1. Introduction

Metallic magnesium is a good candidate for the hydrogen storage. It can be assigned one of the largest gravimetric densities (7.6 wt.%) owing to its light molecular weight of 24.3 g/mol. The reaction of Mg with hydrogen giving MgH₂ is strongly exothermic and very slow, whence the stability of the hydride resulting in a strong Mg–H chemical bond. This makes difficult the direct use of MgH₂ in devices. Introducing nickel within leads to materials with reversible hydrogen adsorption ability such as in Mg₂NiH₄ [1,2].

Beside archetype MgH₂ [3], there are several experimental reports on ionic hydrides [4–7]. Among ternary hydrides with Mg, the ionic hydride RbMgH₃ was synthesized and characterized by X-ray diffraction leading to a hexagonal 6H-type perovskite structure, like the fluoride RbMgF₃ [7] (Table 1 and Figure 1). Then similarly to MgH₂, it becomes relevant to investigate the role played by nickel in RbMgH₃ on the change of ionic behavior of hydrogen as to its charge. The pristine ionic compound has a gravimetric density of 2.66 wt.%. The proposed compound after replacing Mg by Ni has this value decreasing slightly down to 2.21 wt.%. Then the “cost” of the proposed improvement due to this substitution is not large. Such compounds cannot be envisaged for energy storage in mobile devices, etc. However issues in materials science fundamentals can justify their study.

The purpose of this work is to examine substitution effects from *ab initio* using computations within the well established quantum theoretical density functional DFT framework [8,9].

2. Computation methods

A pseudo-potential approach within DFT built VASP code [10] is performed to optimize the geometry of atomic positions and lattice

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parameters. We use ultra soft pseudo potentials US PP which potentials are built within the generalized gradient approximation (GGA) for an account of the effects of exchange and correlation [11]. The calculations are converged at an energy cut-off of 349.4 eV which defines the separation of valence and core states. The *k*-point integration is carried out with a starting mesh of 4 × 4 × 4 up to 8 × 8 × 8 for best convergence and relaxation to zero strains. The Brillouin-zone integrals are approximated using a special *k*-point sampling following Blöchl [12].

Further an analysis of the charge density is done with the approach of ‘atoms in molecules and crystals’ (AIM) introduced by Bader [13] who developed an intuitive way of dividing molecules into atoms as based purely on the electronic charge density. We use this criterion to evaluate the charge on H in the hydrogenated compound.

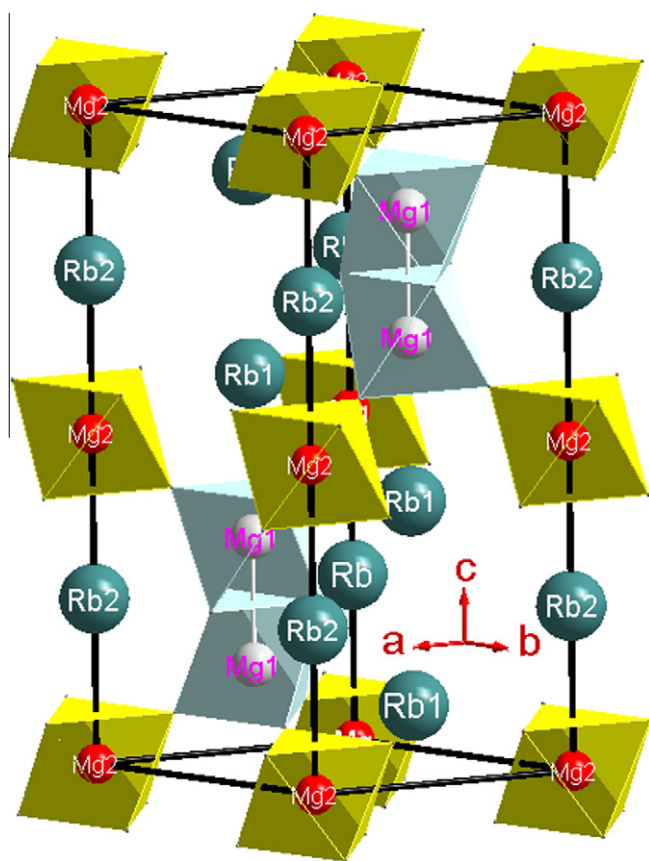
3. Calculations and results

3.1. Crystal structure and geometry optimizations

6H-type perovskite RbMgH₃ crystallizes in the hexagonal symmetry with *P6₃/mmc* space group and six formula units (fu) per cell (Table 1, first column). Its structure, shown in Figure 1, characterizes Mg₁H₆ like octahedral chains along the *c* axis. These octahedra are face sharing with three H₂ atoms within the *a,b* plane. Further, the Mg₁H₆ chains are connected to each other with Mg₂H₆ like octahedra through H₁ atoms. Note that the Mg–H distances are systematically smaller than Rb–H ones for the two sites of Mg (Mg1/Mg2) and of Rb (Rb1/Rb2). Starting from the internal lattice coordinates of literature [2] we carried out a full geometry optimization for the ternary hydride RbMgH₃. The optimized lattice parameters, shown in Table 1, are in good agreement with experimental data. This validates *a posteriori* the use of US PP potentials within GGA approximation.

Table 1Experimental and calculated crystal characteristics of RbMgH₃, and calculated ones of RbMg_{2/3}Ni_{1/3}H₃ and RbMg_{1/3}Ni_{2/3}H₃.

P6 ₃ /mmc	Rb ₆ Mg ₆ H ₁₈ (RbMgH ₃ Exp. [2])	Calculated	Rb ₆ Mg ₄ Ni ₂ H ₁₈ (RbMg _{2/3} Ni _{1/3} H ₃)	Rb ₆ Mg ₂ Ni ₄ H ₁₈ (RbMg _{1/3} Ni _{2/3} H ₃)
<i>a</i> (Å)	5.903	5.908	5.754	5.706
<i>c/a</i>	2.425	2.422	2.434	2.363
Volume (Å ³)/6 fu	432	432.6	401.6	380.1
Rb1 (4f)	1/3, 2/3, 0.0949	1/3, 2/3, 0.096	1/3, 2/3, 0.095	1/3, 2/3, 0.096
Rb2 (2b)	0, 0, 1/4	0, 0, 1/4	0, 0, 1/4	0, 0, 1/4
Mg1 (4f)/Ni	1/3, 2/3, 0.6532	1/3, 2/3, 0.6545	1/3, 2/3, 0.6525	1/3, 2/3, 0.657
Mg2 (2a)/Ni	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0
H1 (12k)	0.1651, 2x, 0.5797	0.1661, 2x, 0.5797	0.1429, 2x, 0.5673	0.183, 2x, 0.590
H2 (6h)	0.5247, 2x, 1/4	0.5240, 2x, 1/4	0.5231, 2x, 1/4	0.557, 2x, 1/4
Distances (Å)				
Rb1–H1/H2	2.96–3.035/2.96	2.94–3.04/2.94	2.91–2.96/2.88	2.86–2.92/3.03
Rb2–H1/H2	2.965/2.962	2.97/2.96	2.93/2.89	2.82/2.91
Mg1–H1/H2	2.016/2.007	2.02/2.00	2.73/1.98	–
Mg2–H1	2.038	2.05	–	2.18
Ni–H1/H2	–	–	1.706/1.709	1.73/1.66

**Figure 1.** Crystal structure of hexagonal perovskite RbMgH₃, Showing the stacking of MgH₆ octahedra belonging to the two Mg different sites.

The hypothesis of replacing Mg by Ni can be done with two compositions:

RbMg_{2/3}Ni_{1/3}H₃ when Ni substitutes for Mg2 and RbMg_{1/3}Ni_{2/3}H₃ when Ni substitutes for Mg1.

Also other substitution schemes involving mixing both Mg1 and Mg2 sublattices led to the breaking down of the lattice symmetry with non converged calculations. In as far as our purpose is to reduce the ionic behavior of RbMgH₃ through introducing nickel we consider both mechanisms of substitution in order to evaluate the effect of Ni on the change of the ionic-covalent character of hydrogen. The 3rd and 4th columns of Table 1 show the results of full geometry optimization in both hypotheses. The hexagonal structure is kept as well as the symmetry of pristine structure in both hypotheses. The change brought by increasing amounts of Ni is

the decrease of the cell volume. This is expected from the smaller atomic size of Ni (1.62 Å) with respect to Mg (1.72 Å). Further the Ni–H distance is particularly smaller than Mg–H. The smallest Ni–H distance of 1.66 Å is closer to the one found in Mg₂NiH₄ of 1.55 Å with similar calculations. The larger separation between Rb and H observed from RbMg_{2/3}Ni_{1/3}H₃ to RbMg_{1/3}Ni_{2/3}H₃ is indicative of a larger lattice internal anisotropy in the latter.

3.2. Cohesive energies and charge analysis

Considering the compounds as formed from the hydrides: RbH, MgH₂ and NiH₂, the calculations of such reactants total energies were undertaken with the same US PP GGA potentials assuming rocksalt RbH, rutile MgH₂ and NiH₂ [14]:

$$E_{\text{tot}}(\text{RbH}) = -4.6 \text{ eV}(1 \text{ fu})$$

$$E_{\text{tot}}(\text{MgH}_2) = -17.95 \text{ eV}(2 \text{ fu})$$

$$E_{\text{tot}}(\text{NiH}_2) = -24.25 \text{ eV}(2 \text{ fu})$$

Then the cohesive energy within each system can be obtained:

$$\begin{aligned} E_{\text{bind}}(\text{Rb}_6\text{Mg}_6\text{H}_{18}) &= E_{\text{tot}}(\text{Rb}_6\text{Mg}_6\text{H}_{18}) - 6 \times E_{\text{tot}}(\text{RbH}) \\ &\quad - 3 \times E_{\text{tot}}(\text{MgH}_2) = -83.87 + 81.99 \\ &= -1.88 \text{ eV}; \text{ i.e. } -0.313 \text{ eV/fu} \end{aligned}$$

$$\begin{aligned} E_{\text{bind}}(\text{Rb}_6\text{Mg}_4\text{Ni}_2\text{H}_{18}) &= E_{\text{tot}}(\text{Rb}_6\text{Mg}_4\text{Ni}_2\text{H}_{18}) - 6 \times E_{\text{tot}}(\text{RbH}) - 2 \\ &\quad \times E_{\text{tot}}(\text{MgH}_2) - E_{\text{tot}}(\text{NiH}_2) \\ &= -87.84 + 88.29 \\ &= +0.45 \text{ eV}; \text{ i.e. } 0.075 \text{ eV/fu} \end{aligned}$$

and

$$\begin{aligned} E_{\text{bind}}(\text{Rb}_6\text{Mg}_2\text{Ni}_4\text{H}_{18}) &= E_{\text{bind}}(\text{Rb}_6\text{Mg}_2\text{Ni}_4\text{H}_{18}) - 6 \times E_{\text{tot}}(\text{RbH}) \\ &\quad - E_{\text{tot}}(\text{MgH}_2) - 2 \times E_{\text{tot}}(\text{NiH}_2) \\ &= -96.11 + 94.59 \\ &= -1.52 \text{ eV}; \text{ i.e. } -0.253 \text{ eV/fu} \end{aligned}$$

These results show that the compound with the larger Ni content is most stable. Furthermore the energy difference suggests an easier hydrogen release with respect to the pristine hydride. This can be further assessed using a charge analysis within Bader atom in molecule AIM theory [13].

In RbMgH₃, hydrogen at both lattice sites carries a charge of –1 indicative of a fully ionic character, as expected. This is followed for the H2 site within RbMg_{2/3}Ni_{1/3}H₃ while H1 shows an ionic-covalent behavior with a charge ranging from –0.62 to –0.73.

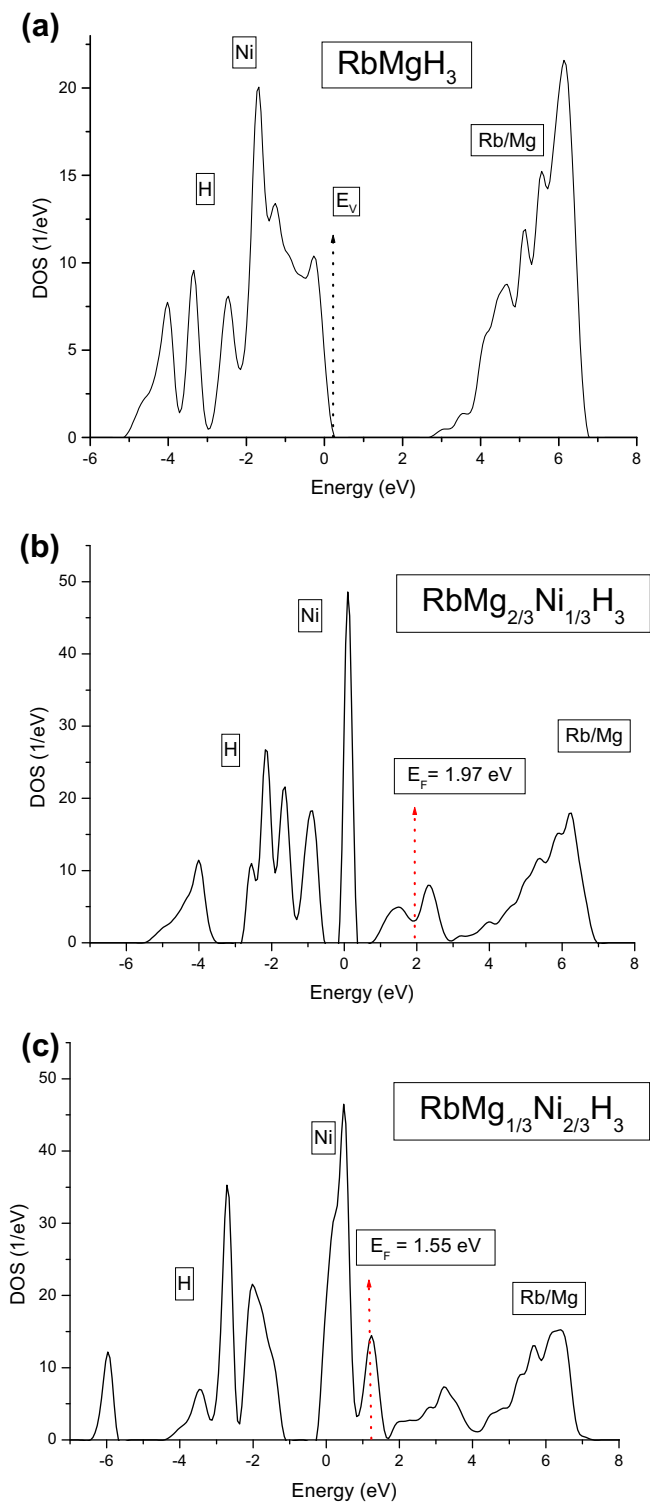


Figure 2. Density of states of pristine RbMgH_3 (a), $\text{RbMg}_{2/3}\text{Ni}_{1/3}\text{H}_3$ (b) and $\text{RbMg}_{1/3}\text{Ni}_{2/3}\text{H}_3$ (c).

The H2 ionic behavior is due to its close neighborhood to Mg of 1.98 Å (Table 1). This value is close to the magnitude of 2 Å found in RbMgH_3 and MgH_2 . The decrease of the charge magnitude on H1 can be commented with respect to its interatomic separation with Ni of 1.71 Å as compared to Ni–H distance of 1.55 Å found within (metastable) NiH_2 , calculated for the purpose of this work using the same methods.

Turning to $\text{RbMg}_{1/3}\text{Ni}_{2/3}\text{H}_3$, H1 atoms carry charges ranging from -0.68 to -0.8 while H2 atoms exhibit a strong covalent

character with charges ranging from -0.4 down to -0.21 . The latter result, related to their close distance to Ni, can be compared with NiH_2 where hydrogen carries a charge of -0.29 . It is important to mention, that $\text{RbMg}_{1/3}\text{Ni}_{2/3}\text{H}_3$ exhibits less covalence for the H1 sublattice and strong covalence for the H2 one. The latter is expected to enable an easier release of hydrogen leading to better kinetics with respect to Ni-poor compounds. Further, the substitution of large amounts of Ni to Mg within RbMgH_3 is related to the overall larger electropositive nature of pristine hydride ($\chi_{\text{Rb}} = 0.8$, and $\chi_{\text{Mg}} = 1.3$) than MgH_2 , mainly due to Rb.

3.3. Density of states

The density of states (DOS) are shown in Figure 2 for RbMgH_3 and for the two Ni substituted hydrides. The former (Figure 2a) is found insulating with a band gap of ~ 2.5 eV. E_V indicates the top of the valence band (VB) which is mainly constituted of H s like states DOS while the conduction band (CB) contains Rb and Mg s,p empty states. This features the ionic character of the compound with fully ionized species. Turning to $\text{RbMg}_{2/3}\text{Ni}_{1/3}\text{H}_3$ DOS (Figure 2b), a weakly metallic character is featured by a crossing of the Fermi level (E_F) at low magnitude. DOS due to Ni d states. A large part of the Ni states is found localized at ~ 0 eV. The major part of the VB is dominated by H states below -1 eV. When a larger amount of Ni is introduced (Figure 2c), the density of states at E_F increases and the compound is identified as metallic. Concomitantly the overall covalence is increased. This is resembled by the broadening of the CB as well as the VB. In particular, both Ni and H DOS blocks are less localized, i.e. more spread. Further, H s states are found down at -6.5 eV.

4. Conclusion

We have shown that the chemical modification of an ionic hydride by modeling selective substitutions of Mg by Ni leads to an ionic-covalent behavior featured by the change of hydrogen ionization from -1 (fully anionic) to covalent -0.2 . The latter charge which is expected to enable an easier release of hydrogen with better kinetics is obtained for the largest amount of Ni substituting for Mg with $\text{RbMg}_{1/3}\text{Ni}_{2/3}\text{H}_3$ composition due to the large electropositive character of Rb in RbMgH_3 . In view of these results synthesis routes of such ionic-covalent hydride compositions are underway mainly through mechanochemistry (energetic ball milling) [15]. Such a technique might not lead to a well-defined stoichiometry such as the finite compositions discussed in this work but it will allow isolating new compounds in which the adjoining of nickel will permit further characterizations relevant to new candidates for the storage of hydrogen with potential applications.

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