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First-principles investigation of Mg_2CoH_5 complex hydride

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Abstract: Within the framework of density functional theory, crystal structure parameters, physical properties, electronic structures and thermal stability of Mg_2CoH_5 complex hydride are comprehensively investigated. The optimized structural parameters including lattice constants, atomic positions and bond lengths are well close to the experimental data determined from X-ray and neutron powder diffraction. A detailed study on the energy band, density of states (DOS) and charge density distribution shows the orbital hybridization and bonding characteristics of the complex hydride. It is found that Mg_2CoH_5 is a semiconductor with a pseudo-gap of about 1.638 1 eV, and there is a mixed ionic-covalent bonding between Co and H in CoH_5 complexes embedded in the matrix Mg^{2+} cations. The calculated formation enthalpy of Mg_2CoH_5 is in good agreement with the experimentally determined value.

Key words: Mg_2CoH_5; density functional theory; electronic structure; formation enthalpy

1 Introduction

Among hydrogen storage materials explored and studied, Mg-based ones are always attractive because of their great abundance, light density, and high hydrogen capacity. However, the slow kinetics and high dissociation temperature make them still not satisfy the requirement of engineering applications[1]. In the practical applications, the key is to find a suitable material that absorbs hydrogen close to room temperature and desorbs hydrogen at a temperature low enough to use the waste heat of exhaust gas[2]. Complex hydrides like Mg_2TH_y (T=Fe, Co, Ni) are assumed as the renewable fuel used in both cells and combustion engines because they have a mixed ionic-covalent bonding between metal and hydrogen complex which may be adjustable and facilitate the hydrogenation/dehydrogenation process[3]. Recently, Mg_2CoH_5 hydride, as an intermediate member of Mg_2TH_y family, has attracted considerable interest because of its higher storage capacity (4.5%, mass fraction) and hydrogen volumetric density (about 100 kg/m^3) than Mg_2NiH_4, as well as a better hydrogen absorption/desorption kinetics than MgH_2. However, this hydride has the peculiarity that Mg_2Co intermetallic compound has not been observed in a stable form, which makes Mg_2CoH_5 production difficult[4−6]. Several previous studies associated with Mg_2CoH_5 have been mainly focused on the synthesis methods to enhance the hydride yield. For example, ZOLLIKER et al[4] first produced Mg_2CoH_5 and its deuteride through sintering at 620−770 K, and the structures and thermodynamic properties of the hydride were determined from neutron powder diffraction and pressure-composition isotherms, respectively. HUAIYU et al[5] successfully synthesized the nanostructured Mg_2CoH_5 and Mg_2Co from Mg and Co nanoparticles by hydrogen plasma-metal reaction method, and they found that the nanometer-scale effect plays an important role in synthesis. GONZÁLEZ et al[6] obtained Mg_2CoH_5 by a procedure of milling a 2Mg-Co mixture under argon followed by reactive mechanical alloying (RMA) under hydrogen at room temperature. It is found that the improvement in the yield and the formation could be associated with both refinement of microstructure and enhancement of intermixing of Mg-Co during pre-milling stage.

In order to synthesize much efficiently, it is essential

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to identify the physical and thermodynamic properties of this hydride which are commonly dependent on the complex atomic bonding interactions as well as its thermal stability. Although theoretical studies using the first-principles calculations are so common for complex metal hydrides[7−9], scarce studies on Mg_2CoH_5 as a potential hydrogen storage material have been reported. In the present work, first-principles calculations based on density functional theory are employed to conduct a comprehensive study on the structural, electronic and stability properties of Mg_2CoH_5 complex hydride. The results are expected to provide the theoretical guidance for designing and improving the advanced fuel cell materials.

2 Models and calculation method

Mg_2CoH_5 has a tetragonally distorted CaF_2-type atom structure, as shown in Fig.1(a)[4]. Its unit cell has space group of *P*4/*nmm* (NO.129), and 16 atoms with lattice parameters of a=4.480 Å and c=6.619 Å. Fig.1(b) shows the cluster model of Mg_2CoH_5, from which it can be seen that Co atom is surrounded by two types of symmetry-independent H atoms (H1 and H2) in an ordered square-pyramidal configuration bonded to eight nearest Mg atom (Mg1 and Mg2) neighbors. The atomic coordinates in the unit cell are

Mg1 (2*a*): (0.75, 0.25, 0)
Mg2 (2*b*): (0.75, 0.25, 0.5)
Co (2*c*): (0.25, 0.25, 0.2561)
H1 (2*c*): (0.25, 0.25, 0.4972)
H2 (8*j*): (0.4879, 0.4879, 0.2257)

In the present work, the structural optimization and the corresponding total energy calculations are performed by the $DMol^3$ package[10] based on the density functional theory (DFT)[11−12], and Perdew-Burke-Eruzerhof (PBE) exchange-correlation functional [13] is adopted for generalized gradient approximation (GGA) correction. All-electron Kohn-Sham wave functions are expanded in a Double Numerical basis with Polarized orbital (DNP). The positions of all atoms in the structure are relaxed to get the final structure with the minimum total energy. The convergences criteria of optimization are 2.72×10^{-4} eV, 0.0544 eV/Å and 0.005 Å for energy, gradient and atomic displacement, respectively.

3 Results and discussion

3.1 Crystal structure parameters and physical properties

To examine the accuracy of the computation parameters selected in this work, some testing calculations on crystal structure parameters as well as physical properties have been performed on the related solid (hcp-Mg, hcp-Co) and H_2 molecule included in the phase of Mg_2CoH_5. The corresponding results are listed in Table 1. It is found that the equilibrium lattice constants

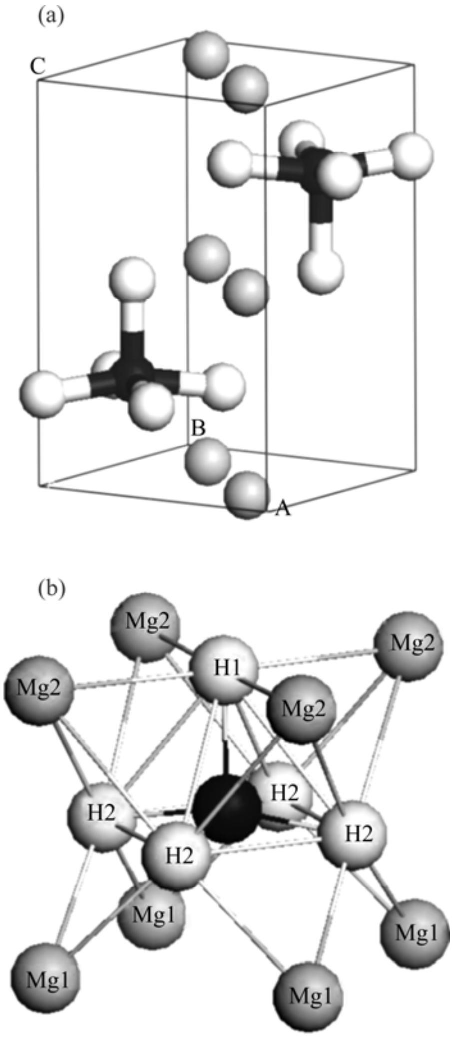

Fig.1 Model of crystal cell (a) and cluster (b) of Mg_2CoH_5

Table 1 Equilibrium lattice constants a and c, cohesive energy E_{coh}, and bulk modulus B_0 for hcp-Mg, hcp-Co, H_2 molecule in Mg_2CoH_5

Material	Property	This work	Experimental value
hcp-Mg	a/Å	3.175 1	3.21 [14]
	c/Å	5.150 4	5.21
	E_{coh}/(eV·atom^{-1})	1.494 2	1.51
	B_0/GPa	32.457 9	35.4
hcp-Co	a/Å	2.493 3	2.51 [14]
	c/Å	4.019 2	4.07
	E_{coh}/(eV·atom^{-1})	6.223 4	4.39
	B_0/GPa	229.395 3	191.4
H_2	d(H—H)/Å	0.749 0	0.741 [15]
	E_{coh}/(eV·atom^{-1})	4.550 2	4.74

and cohesive energies of them are in good agreement with the experimental data. For example, the present lattice constants *a*, *c* and *c*/*a* ratio of hcp-Mg are 3.171 5 Å, 5.150 4 Å, 1.624 0, respectively, which are close to the experimental values[14] of *a*=3.21 Å, *c*=5.21 Å and *c*/*a*=1.623, and the error of *c*/*a* ratio calculated here relative to the experimental result is about 0.06%. The calculated cohesive energy E_{coh}=1.494 2 eV/atom of hcp-Mg is close to the experimental value[14] of E_{coh}=1.51 eV/atom, and the error of cohesive energy calculated here relative to the experimental result is about 1.05%. The present lattice constants *a*，*c* and *c*/*a* ratio of hcp-Co are 2.493 3 Å, 4.019 2 Å and 1.612 0, respectively, which are close to the experimental values[14] of *a*=2.51 Å, *c*=4.07 Å and *c*/*a*=1.622, and the error of *c*/*a* ratio calculated here relative to the experimental result is about 0.62%. The present bond length of free H_2 molecule is 0.749 0 Å, which is close to the experimental value[15] of $d_{\mathrm{H-H}}$= 0.741 Å, and the error of bond length calculated here relative to the experimental result is about 1.08%. Evidently, a good agreement between present calculations and experimental values can be seen. Although the calculated bulk modulus values (B_0) of the solid such as Co have larger error relative to the experimental results[14], they can be acceptable in testing calculation.

Then, the lattice constants, atomic positions as well as bond lengths of Mg_2CoH_5 unit cell are estimated from the minimized total energy with breaking its symmetry. The final results are listed in Tables 2-4. It is found that the optimized structure of Mg_2CoH_5 unit cell keeps *P*4/*nmm* symmetry, which is in good agreement with the experimental structure extracted from X-ray and neutron powder diffraction data[4]. The present lattice constants *a*, *c* and *c*/*a* ratio of Mg_2CoH_5 are 4.464 6 Å, 6.602 4 Å and 1.478 8, respectively, which are close to the experimental values[4] of *a*=4.480 Å, *c*=6.619 Å and *c*/*a*=1.477, and the error of *c*/*a* ratio calculated here relative to the experimental result is about 0.12%. The present positions of Mg, Co, H atoms as well as bond lengths in Mg_2CoH_5 unit cell are also in good agreement with the experimental results[4]. Meanwhile, we also present the cohesive energy E_{coh} and bulk modulus B_0 of Mg_2CoH_5, and they are 22.783 4 eV/atom and 54.330 1 GPa, respectively. Due to the absence of experimental E_{coh} and B_0, both of the calculated values in this work cannot be compared with the experimental data, but these new results are expected to have some referenced values for further investigation of this complex hydride.

Table 2 Equilibrium lattice constants *a* and *c*, cohesive energy E_{coh} and bulk modulus B_0 for Mg_2CoH_5

Property	This work	Experimental value[4]
a/Å	4.464 6	4.480
c/Å	6.602 4	6.619
E_{coh}/(eV·atom^{-1})	22.783 4	−
B_0/GPa	54.330 1	−

3.2 Electronic structure

Figs.2 and 3 show the energy band structure and

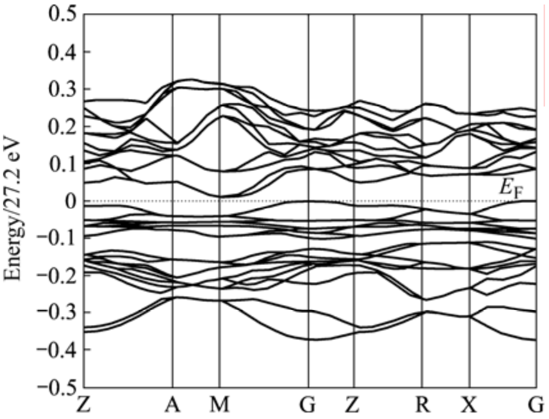

Fig.2 Energy band structure of Mg_2CoH_5

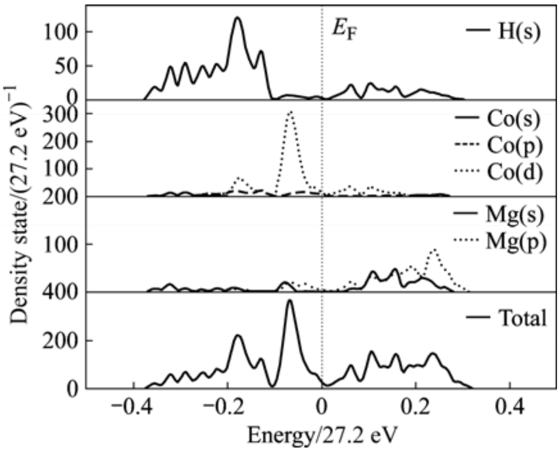

Fig.3 Total and partial density of states of Mg_2CoH_5

Table 3 Atomic positions for Mg_2CoH_5

Atomic position	*x*		*y*		*z*	
	This work	Experimental value	This work	Experimental value	This work	Experimental value
Mg1(2*a*)	0.750 0	0.750 0	0.250 0	0.250 0	0	0
Mg2(2*b*)	0.750 0	0.750 0	0.250 0	0.250 0	0.500 0	0.500 0
Co(2*c*)	0.250 0	0.250 0	0.250 0	0.250 0	0256 7	0.256 1
H1(2*c*)	0.250 0	0.250 0	0.250 0	0.250 0	0495 7	0.497 2
H2(8*j*)	0.493 1	0.487 9	0.493 1	0.487 9	0.226 9	0.225 7

Table 4 Bond lengths for Mg_2CoH_5 (Å)

Bond	This work	Experimental value
Mg1—H2	2.176 8	2.170
Mg1—Co	2.802 9	2.798
Mg2—H1	2.232 5	2.232
Mg2—H2	2.396 6	2.402
Mg2—Co	2.750 0	2.751
Co—H1	1.577 7	1.590
Co—H2	1.547 3	1.515
$(H1—H2)_{intra}$	2.345 9	2.337
$(H1—H2)_{inter}$	2.446 6	2.465
$(H2—H2)_{intra}$	2.170 5	2.124
$(H1—H2)_{inter}$	2.294 2	2.340

electronic density of states (DOS) of Mg_2CoH_5, respectively. Both of two figures exhibit a pseudo-gap of about 1.638 1 eV, and the region around the Fermi level has a very low density of states. The sixteen valence bands in Fig.2 have a width of about 10.336 eV and are split into three disjointed groups consisting of two, eight and six bands, respectively. It can be seen that two valence bands in the low energy range between −10.336 and −7.344 eV mainly originate from the contribution of H(s), a few Mg(s) and a few Co(s) orbitals. The eight valence bands in the energy range between −7.344 eV and −2.992 eV are mainly derived from H(s), Co(d) and a few Co(p) orbitals. The next six valence bands in the higher-energy range between −2.992 eV and 0 eV are mainly from H(s), Co(d) as well as a few Mg(p) states. Apparently, there is a strong hybridization between H and Co orbitals at the energy range from −7.344 eV to Fermi level, whereas, there is a weak one between H and Mg orbitals. The conduction bands are mainly from Mg empty states. Mg has hardly any projection in the occupied states as shown in Fig.3, indicating that each Mg donates two electrons to the CoH_5 complex[16]. Significant charge transfer leads to Mg^{2+} ions and negatively charged CoH_5 complex, which constitutes the ionic bonding between them. Meanwhile, there exits a strong covalent bonding interaction between hydrogen and cobalt within CoH_5 complex. Comparatively, the latter plays a dominant role in this complex hydride.

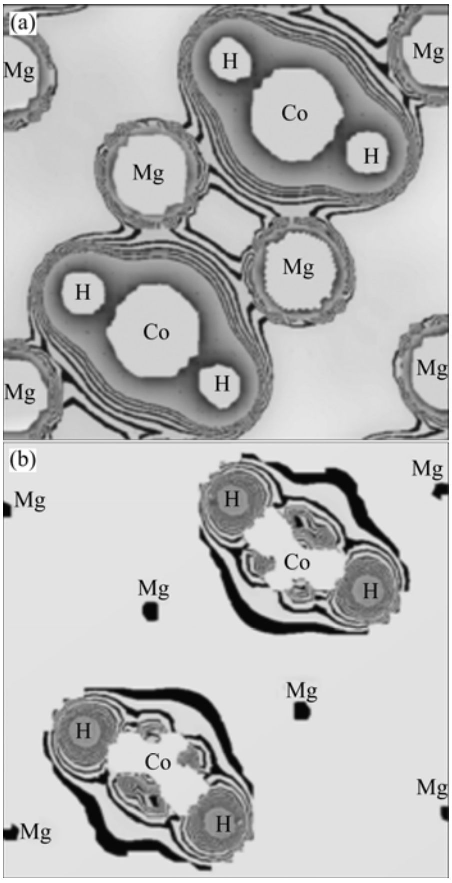

Fig.4 Total and difference charge density plots of Mg_2CoH_5 on $(\bar{1}\bar{1}1)$ plane: (a) Total charge density; (b) Charge density difference

Further analysis of the charge distribution of Mg_2CoH_5 and charge transfer in CoH_5 complexes is performed. The total charge density $\rho(r)$ and the charge density difference $\Delta\rho(r)$ in the plane containing Mg, Co, H atoms are shown in Fig.4. The charge density difference $\Delta\rho(r)$[17] is defined as the difference between the total charge density of the solid and a superposition of atomic charge density with the same spatial coordinates as those in the solid. In Fig.4(a), the total charge density plot shows that there is a strong bonding between Co and H in CoH_5 complexes, while there is a weak bonding interactions between Mg and CoH_5 complexes, and the electron density is mainly around the positions of the CoH_5 complexes, which are consistent with the analytical results based on electronic density of states (DOS) shown in Fig.3. From the density difference plot shown in Fig.4(b), it can be seen that there are significant charge transfer leading to Mg positively and CoH_5 complexes negatively charged. For CoH_5 complexes, it is found that there exists partial charge transfer from Co to H, indicating that besides the covalent bonding, there is also an ionic bonding interaction between Co and H in CoH_5 complexes. These features support well a mixed ionic-covalent bonding between Co and H in CoH_5 complexes embedded in the matrix of Mg^{2+} cations.

3.3 Heat of formation

The heat of formation is the most fundamental and important parameter for hydrogen storage materials, which is often used for evaluating the dehydrogenating properties of hydrides. Commonly, the smaller the heat of formation is, the lower the structural stability of the corresponding hydride[18]. Thus, in order to investigate the dehydrogenating properties of Mg_2CoH_5 complex hydride, it is necessary to calculate its heat of formation (ΔH). The heat of formation for Mg_2CoH_5 is calculated according to the following equation[19]:

$$\Delta H = \frac{2}{5}[E_{\text{tot}}(\text{Mg}_2\text{CoH}_5) - 2E_{\text{tot}}(\text{Mg}_{\text{hcp}}) - E_{\text{tot}}(\text{Co}_{\text{hcp}}) - \frac{5}{2}E_{\text{tot}}(\text{H}_2)] \quad (1)$$

where $E_{\text{tot}}(Mg_2CoH_5)$ refers to the total energy of Mg_2CoH_5 unit cell at the equilibrium lattice constant; $E_{\text{tot}}(Mg_{\text{hcp}})$, $E_{\text{tot}}(Co_{\text{hcp}})$ are the single atomic energies of hcp-Mg, hcp-Co in the solid states, respectively; and $E_{\text{tot}}(H_2)$ refers to the total energy of gaseous H_2 molecule. In this work, the energy of a pure metal crystal in the solid states is calculated, then the energy is divided by the number of atoms involved in the crystal, and the result from the above calculation is just the energy of a single atom in the pure metal. The calculated values of $E_{\text{tot}}(Mg_2CoH_5)$, $E_{\text{tot}}(Mg_{\text{hcp}})$, $E_{\text{tot}}(Co_{\text{ hcp}})$ and $E_{\text{tot}}(H_2)$ are −1 785.718 4 Ha, −200.008 9 Ha, −1 382.701 2 Ha and −1.1642 Ha (1 Ha≈27.2 eV), respectively. From Eq.(1), the heat of formation for Mg_2CoH_5 is estimated to be −0.968 7 eV per H_2 molecule (i.e. −93.460 2 kJ/mol per H_2) without the zero-point energy contributions. If the thermodynamic effect on crystal structure is considered, the present calculation should be in good agreement with the experimental results evaluated by VAN HOFF plots (−86 kJ/mol per H_2)[4]. With respect to the heat of formation, Mg_2CoH_5 appears in a higher thermal stability than Mg_2NiH_4 (ΔH=64 kJ/mol per H_2)[20], but a lower one than Mg_2FeH_6 (ΔH=98 kJ/mol per H_2)[21].

4 Conclusions

1) The calculated structural parameters and physical properties of Mg_2CoH_5 hydride are in good agreement with the experimental results determined from X-ray and neutron powder diffraction.

2) Detailed calculations of electronic band structure suggest that the complex Mg_2CoH_5 has a pseudo-gap of about 1.638 1 eV.

3) The total and partial density of states (DOS) as well as the charge density plots indicate that significant charge transfer leads to Mg positively charged and CoH_5 complex negatively charged. The bonding within the CoH_5 complex mainly involves the hybridization between Co(p), Co(d) and H(s) orbitals, but exhibits a little ionic characteristic for partial charge transfer from Co to H.

4) Total energy calculations are used to estimate the heat of formation. The calculated value (−93.4602 kJ/mol per H_2) is very close to the experimental value evaluated by VAN HOFF plots.

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