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STRUCTURAL, ELECTRONIC AND DEHYDROGENATION PROPERTIES OF THE MAGNESIUM HYDRIDE-A DFT STUDY

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ABSTRACT: *This paper focuses primarily on the study of the structural, electronic and dehydrogenation properties of the six considered polymorphs of magnesium hydride (α - rutile TiO2, P42/mnm, β - cubic modified CaF_2, $Pa\bar{3}$, γ - orthorhombic PbO_2, Pbcn, δ' -orthorhombic, Pbca, ε - orthorhombic, Pnma and cubic - $Fm\bar{3}$ m).The aim of this study is to find out the polymorph with the most potential for hydrogen storage. For this the total energy calculations are performed in the frame work of the density functional theory using the generalized gradient approximation (GGA-PBE).Furthermore, the energy band structure, the density of states (DOS), bulk modulus , bulk modulus derivative and the dehydrogenation properties are calculated for all the six possible structures. It has been found that the dehydrogenation enthalpy (ΔH) is lower for cubic-MgH_2(-47.02kJ/mol.H_2) which is 18.14% lower than the α -MgH_2 having the highest ΔH value(-57.63kJ/mol.H_2) causing greater destabilization, resulting in larger reduction of its dehydrogenation temperature. It is also seen that cubic-MgH_2 with the hydrogen removal energy of $\Delta E = 0.48eV$ which differ only by 0.01eVof that of ε-MgH_2 which has a lower value of $\Delta E = 0.47eV$ shows improved dehydrogenation kinetics for enhancing its hydrogen storage properties.*

Keywords: *Magnesium hydride polymorphs, Density functional theory, electronic, structural and dehydrogenation properties.*

I. INTRODUCTION

Worldwide demand for green energy to replace fossil fuels has risen drastically in the last few decades. Hydrogen is regarded as a promising candidate of energy carrier owing to its high energy density per unit mass, availability and minimum environmental impact when hydrogen can be produced from renewable resources such as photo electrochemical, biological process, and wind energy [1]. Opportunities and challenges in the realization of a hydrogen economy have been identified, and possible strategies to overcome these challenges are proposed [2]. One of the challenges is the safety of efficient storage and transport of hydrogen. Compared with gaseous and liquid state hydrogen storage, solid state hydrogen storage is favored because of safety consideration and high volumetric capacity. Among the solid state hydrogen storage materials, MgH2 has been considered as a promising hydrogen storage material based on its advantages such as large hydrogen storage capacity (7.6 wt %), good reversibility, low cost and abundant resources. However, the high thermodynamic stability of the magnesium hydride prevents dehydrogenation under mild conditions. Furthermore, its slow hydriding and dehydriding kinetics and high dissociation temperature currently limit its practical applications for hydrogen storage. In order to improve the hydrogen storage properties of Mg-rich alloys, understanding of the structural stability and bonding nature of MgH2 is considered as essential.

By various experimental and theoretical investigations several polymorphs of magnesium hydride were identified as thermodynamically stable forms of MgH_2 under different pressure and temperature conditions. Under ambient conditions the magnesium hydride crystallizes as α -MgH_2 phase, with a rutile-type structure (space groupP42/mnm) [3,4]. Vajeeston et al[5,6] reported that a phase transition occurs from α-MgH2 to γ-MgH_2at 0.39 GPa by Density Functional Theory (DFT) calculations. Moriwaki et al. reported the transition from α→γ, at a higher pressure of 9 GPa by the X-ray diffraction (XRD) measurements at room temperature [7]. Bastide et al. reported that α-MgH_2 structure is transformed into β-MgH_2 (with a modified fluorite-type CaF_2 structure, space group $Pa\bar{3}$) and γ-MgH_2(with an orthorhombic structure of α-PbO_2-type, space group Pbcn) under high pressure and temperature conditions, and by decreasing the pressure the β-MgH_2 is transformed into γ-MgH_2[8]. At pressure above 10 GPa the experimentally established α, γ and β-phase mixture transforms into δ'- MgH_2, an AuSn2-type orthorhombic structure with space group Pbca[6].At a pressure above 10.26GPa transformation from δ' to ε-MgH_2 with space group(Pnma) is predicted but this is not verified experimentally[6]. The cubic structure of fluorite-type, with the space-group $Fm\bar{3}m$ was theoretically considered as a possible structure of the magnesium hydride [5,9], but it has not been experimentally identified. The DFT based studies predict it as a relevant structure for the magnesium hydride alloyed with transition metals MgxTM1−x H_2,x≤0.75 (TM as Sc, Ti, V, Cr and Zr)[10,11]and for multi film MgH_2/TMH_2 systems[12].

Several other magnesium hydride phases are identified at high pressure by theoretical and experimental studies: $Pbc2_1$[6,7], Pbca[6,7], Pnnm[5,13], $Fm\bar{3}$ m [5,9]. The successive phase transitions α(P42/mnm)→γ(Pbcn)→β($Pa\bar{3}$)→δ($Pbc2_1$)→ε(Pnma) were predicted by several DFT studies[5,6,9]. Cui et al. reported a similar sequence of transitions by

DFT-based enthalpy calculations, but found that δ is unstable [14]. Lonie et al. predicted several stable magnesium poly hydrides (MgH_n, $n > 2$) for $T = 0$ K, at much higher pressures by DFT-based thermodynamic calculations [15]. Although the stability of the magnesium hydride polymorphs has been the subject of many experimental and computing investigations it is always a central task to design new materials or adopt efficient strategies for achieving lower desorption temperatures and good dehydrogenation performances. . In the present study we report the results of the comprehensive electronic, structural and the dehydrogenation properties of the six magnesium hydride structures: α- MgH_2,β- MgH_2, γ- MgH_2,δ'- MgH_2, ε - MgH_2 and cubic- MgH_2. The obtained results at ambient condition for the equilibrium lattice constants, bulk modulus and the pressure derivative of bulk modulus have been tabulated and discussed. The plots of the band structure, density of states, dehydrogenation enthalpy, the hydrogen removal energy are shown in graphical form and their obtained trends are interpreted.

II. COMPUTATIONAL DETAILS

To determine the structural and electronic stability of MgH_2, we have used density functional theory (DFT) [16] using the Quantum Espresso[17] software package according to which the many-body problem of interacting electrons and nuclei can be mapped onto a system of one-electron equations called Kohn Sham equations. The exchange and correlation potential were calculated using the generalized gradient approximation (GGA) of Perdew Burke Ernzerhof (PBE-GGA) [18] pseudization method with non-linear core correction. Kinetic energy cutoffs of the wave functions, 60.0 Ry, and of the charge density and potential, 600.0 Ry, were used. The Brillouin Zone (BZ) sampling for the structural optimization converged at a (4×4×4) Monk horst–Pack [19] grid. The iteration process was repeated until the calculated total energy and the charge of the crystal converge to less than 0.0001Ry and $0.001e^-$ respectively. The convergence threshold for force on each atom was set to 1 mRy/a.u. In order to obtain equilibrium parameters, total energy corresponding to different unit cell volumes is optimized. The calculated set of total energy and corresponding unit cell volume are used to make a fit to Murnaghan's equation of states [20] to obtain the equilibrium unit cell volumeV_0, the bulk modulus B_0 and the pressure derivative of bulk modulus B_0'of the studied system . Rest of the calculations has been performed at the optimized unit cell parameters The other software programs used in this work to obtain atomic positions, images of the primitive cells were CIF2Cell,Vesta and XCrysDen.

III. RESULTS AND DISCUSSIONS

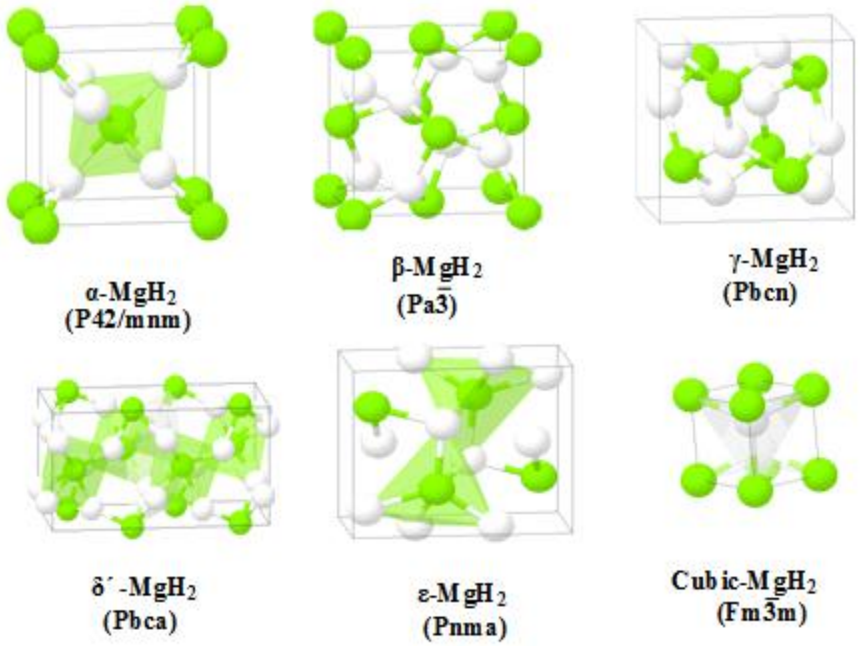
A. STRUCTURAL PROPERTIES

The structural properties of magnesium hydride MgH_2 was investigated by considering the six experimentally or theoretically determined possible structures. The Wyckoff positions of the atoms and their fractional coordinates for the six considered polymorphs of MgH_2, which are optimized, were given in ***Table 1*** and the primitive cells of all the investigated compounds in the present study are presented in ***Fig 1.***

Table 1. Structural parameters of the studied MgH_2 polymorphs.

Structure(Space Group)	Atom	Wyckoff position	x	y	z	Reference
α- MgH_2 (P42/mnm)	Mg	2a	0.0000	0.0000	0.0000	DFT:PBE this work
	H	4f	0.3043	0.3043	0.0000	
	Mg	2a	0.0000	0.0000	0.0000	Exp[3]
	H	4f	0.3060	0.3060	0.0000	
	Mg	2a	0.0000	0.0000	0.0000	DFT:PBE [21]
	H	4f	0.3047	0.3047	0.0000	
	Mg	2a	0.0000	0.0000	0.0000	DFT:PBE[22]
	H	4f	0.3040	0.3040	0.0000	
β- $MgH_2Pa\bar{3}$)	Mg	4a	0.0000	0.0000	0.0000	DFT:PBE this work
	H	8c	0.3469	0.3469	0.3469	
	Mg	4a	0.0000	0.0000	0.0000	Exp[6]
	H	8c	0.3429	0.3429	0.3429	
	Mg	4a	0.0000	0.0000	0.0000	DFT:PBE[22]
	H	8c	0.3471	0.3471	0.3471	
	Mg	4a	0.0000	0.0000	0.0000	DFT:PW91[23]
	H	8c	0.3464	0.3464	0.3464	
γ- MgH_2 (Pbcn)	Mg	4c	0.0000	0.3284	0.2500	DFT:PBE this work
	H	8d	0.2730	0.1090	0.0800	

	Mg	4c	0.0000	0.3313	0.2500	Exp[24]
	H	8d	0.2727	0.1089	0.0794	
	Mg	4c	0.0000	0.3314	0.2500	Exp[6]
	H	8d	0.2717	0.1085	0.0801	
	Mg	4c	0.0000	0.3284	0.2500	DFT:PBE[21]
	H	8d	0.2722	0.1099	0.0806	
δ' - MgH_2 (Pbca)	Mg	8c	0.8830	0.0310	0.2732	DFT:PBE this work
	H	8c	0.7990	0.3830	0.1660	
	H	8c	0.9735	0.7410	0.5105	
	Mg	8c	0.8823	0.0271	0.2790	Exp[6]
	H	8c	0.7970	0.3765	0.1615	
	H	8c	0.9730	0.7433	0.5207	
	Mg	8c	0.8831	0.0308	0.2732	DFT:PBE[22]
	H	8c	0.7982	0.3823	0.1664	
	H	8c	0.9735	0.7413	0.5105	
ε- MgH_2 (Pnma)	Mg	4c	0.2480	0.7500	0.6030	DFT:PBE this work
	H	4c	0.3610	0.2500	0.4250	
	H	4c	0.4770	0.2500	0.8330	
	Mg	4c	0.2519	0.2519	0.2519	DFT:PBE[22]
	H	4c	0.3610	0.3610	0.3610	
	H	4c	0.4786	0.2500	0.8341	
	Mg	4c	0.2500	0.7500	0.6033	DFT:PBE[5]
	H	4c	0.3610	0.2500	0.4250	
	H	4c	0.4794	0.2500	0.8345	
Cubic- MgH_2 (Fm$\bar{3}$m)	Mg	4a	0.0000	0.0000	0.0000	DFT:PBE this work
	H	8c	0.2500	0.2500	0.2500	
	Mg	4a	0.0000	0.0000	0.0000	DFT:PBE[22]
	H	8c	0.2500	0.2500	0.2500	
	Mg	4a	0.0000	0.0000	0.0000	DFT:PBE[5]
	H	8c	0.2500	0.2500	0.2500	



α-MgH_2 (P42/mnm)

β-MgH_2 (Pa$\bar{3}$)

γ-MgH_2 (Pbcn)

δ´-MgH_2 (Pbca)

ε-MgH_2 (Pnma)

Cubic-MgH_2 (Fm$\bar{3}$m)

Figure 1. The primitive cell for the different polymorphs of MgH_2

B. EQUATION OF STATES

We started the calculations by fully relaxing all free internal atomic positions and lattice parameters consistent with the crystal symmetry for each phase of the material. The equilibrium cell volume and equilibrium lattice parameters for all the six polymorphs of MgH2 were determined by energy minimization procedure. For this, we carried out optimization of the total energy with respect to the different values of the unit cell volume and used Murnaghan's equation of state [20] to obtain the optimization curves (Figure 2). It is evident from Figure2 that the ground state structure (the most stable structure) of MgH2 is the α- MgH2 with the tetragonal TiO2-rutiletype structure, for which the primitive unit cell contains two Mg and four H atoms and each Mg atom is octahedrally coordinated to six H atoms, whereas each H atom is coordinated to three Mg atoms in the same plane. The Wyckoff position for Mg, H atoms are 2a, 4f respectively and the calculated (optimized) lattice parameters are a = b = 4.4840 Å and c = 2.9970 Å which are in good agreement with the previously reported results [25].

The optimization curves gives the information about minimal energy (E) corresponding to the equilibrium unit cell volume (V0) of the structure, the bulk modulus (B0) and the first derivative of the bulk modulus (B_0'). The calculated results are given in Table2. In general, the theoretical B0 values are slightly overestimated compared with those of experimental data which is due to the under estimation of the equilibrium volume in the total energy calculations.

Table 2. The lattice parameters a, b and c(Å), the equilibrium volume V_0 (Å^3), bulk modulus (B_0) and its derivative (B_0').

Crystalline Structure	a(Å)	b(Å)	c(Å)	Bulk Modulus (B_0)	B_0'	Equilibrium volume (V_0) (Å^3)
α - MgH_2	4.4840 4.5168^a 4.4853^d 4.5176^b	4.4840 4.5168^a 4.4853^d 4.5176^b	2.9970 3.0205^a 2.9993^d 3.0206^b	52.47 45 ± 2^b 51^d 50.2^d	3.71 3.35 ± 0.3^b 3.45^d 3.57^e	30.42
β - MgH_2	4.8050 4.8055^f 4.6655^b 4.7960^g	4.8050 4.8055^f 4.6655^b 4.7960^g	4.8050 4.8055^f 4.6655^b 4.7960^g	57.10 47.41 ± 4^b 57.2^e	3.08 3.49 ± 0.4^b 1.66^e	26.46
γ - MgH_2	4.5015 4.5045^f 4.5213^c 4.5246^b	5.4186 5.4298^f 5.4382^c 5.4442^b	4.8993 4.9191^f 4.9337^c 4.9285^b	52.23 44.03 ± 2^b 51.6^e	3.28 3.17 ± 0.4^b 3.69^e	29.63
δ' - MgH_2	9.2954 9.3821^e 9.3738^d 8.8069^b	4.8880 4.9362^e 4.8259^d 4.6838^b	4.7210 4.7879^e 4.7798^d 4.3699^b	59.34 59.1^e 58^d 49.83 ± 2^b	3.49 3.99^e 3.45^d 3.49 ± 0.6^b	24.87
ε - MgH_2	5.2360 5.2804^d 5.3454^e	3.0817 3.0928^d 3.1281^e	5.9578 5.9903^d 6.0647^e	64.76 65^d 67.1^e	3.75 3.75^d 2.8^e	21.95
cubic-MgH_2	4.656 4.7296^d 4.7979^e	4.656 4.7296^d 4.7979^e	4.656 4.7296^d 4.7979^e	57.26 59^d 57.4^e	3.54 3.52^d 2.76^e	20.39

[a] Experimental Reference[3] [d]Theoretical Reference[5] [f] Theoretical Reference[21]
[b] Experimental Reference[6] [e]Theoretical Reference[22] [g] Theoretical Reference[23]
[c] Experimental Reference[24]

It is also evident from the ***Table2*** that the bulk modulus for the several MgH_2 polymorphs exceed that of Mg metal (35.4GPa) indicating that the rigidity increases for all the polymorphs with the addition of hydrogen compared to Mg.TheB_0 values for the studied polymorphs are in the increasing order of γ< α< β< δ'< cubic< ε MgH_2 implying that the polymorphs resistance to uniform compression increases in the same order and also as the system with low bulk modulus has higher compressibility(volume change) which in turn reduces the system stability, destabilization occurs more easily for (α and γ) -MgH_2 than the other polymorphs, as they have a low B_0 value of(~52eV). A comparison of equilibrium volume V_0 values suggests that for cubic-MgH_2 with low V_0 value of 20.39 Å^3, the formation of cubic-MgH_2 phase would lead to a volume reduction of 32.97% relative to the most stable α phase(30.42Å^3) which in turn would lead to enhance its volumetric hydrogen storage density. However this volumetric advantage may be reduced due to the simultaneous increase in B_0 value of 9.1% of cubic-MgH_2 which would deteriorate its compressibility.

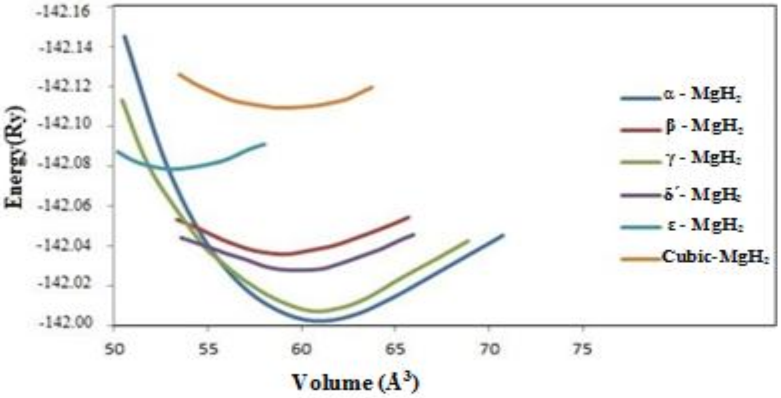


***Figure2**. The Optimization curves for the considered polymorphs of MgH_2*

C. ELECTRONIC STRUCTURE

The band structures for the six polymorphs of MgH_2 are shown in ***Figure 4***. It is seen from the ***Figure 4,*** that the band structures are different for all the investigated systems. For α -MgH2, it is clear that the conduction band minimum (CBM) is situated at G point of the Brillouin zone (BZ), while the valence band maximum (VBM) is located between G and X points of the BZ, resulting in a wide indirect band gap of 3.71eV indicating covalent behavior. This result is very close to the theoretical value of 3.78 eV [26] and are in better agreement than the earlier theoretical findings 3.60 eV [27] and 3.4 eV.[27,28] and is very close to the experimental value 5.16 eV as shown in [29] . For β -MgH2, the conduction band minimum (CBM) is situated between G and X point of the Brillouin zone (BZ), while the valence band maximum (VBM) is located at G point of the BZ with an indirect band gap of 2.93eV which is in good agreement with the earlier reported theoretical result of 2.6 and 2.7eV by Moyses and Araujo et al. [30].For γ - MgH_2 the conduction band minimum (CBM) is situated between G and X point of the Brillouin zone (BZ), while the valence band maximum (VBM) is located at G point of the BZ with band gap of 3.64eV which is in good agreement with the earlier reported theoretical result of 3.8eV [30] . For δ' -MgH2, the conduction band minimum (CBM) is situated at G point of the Brillouin zone (BZ), while the valence band maximum (VBM) is located at G point of the BZ with a band gap of 2.67eV. For ε -MgH2, the conduction band minimum (CBM) is situated between S and Y point of the Brillouin zone (BZ), while the valence band maximum (VBM) is located between Y and G point of the BZ with a band gap of 1.96eV. For cubic-MgH_2, the conduction band minimum (CBM) at the X point is lower than the valence band maximum (VBM) at the G point of the BZ with a small overlap between the bottom of the conduction band and the top of the valence band causing the band gaps to become zero indicating a semi-metallic character for the cubic polymorph of $MgH_{2.}$

The band gaps, valence band width, the Mg and H charges of the different polymorphs of MgH_2 are given in ***Table 3***. As is seen from the ***Table3*** the calculated band gaps for the six structures are different and are smaller than those experimentally measured, of 5.6 ± 0.1 eV [31]. This problem is due to the fact that within the GGA, interaction energies between Mg and H are overestimated which leads to a larger band width and a smaller band gap. Thus all the polymorphs except cubic- MgH_2 are predicted to behave as insulators as they have a wider band gap and the following order of band gap exists: cubic < ε < δ'< β< γ< α. As the calculated band gap is zero for cubic- MgH_2 there will be easy mobility of the valence electrons into the conduction band as a result of which the Mg-H bond in the cubic-MgH_2 is more susceptible to dissociation than other polymorphs leading to a reduction (less negative value) in the formation energy and hence requires less energy for H_2 removal.

The total and partial DOS of the studied polymorphs of MgH_2 are shown in ***Figure 3,*** considering spin polarization. The positive part of the vertical axis corresponds to spin-up states, while the negative part of the vertical axis corresponds to spin-down states. It can be seen that the spin-up and the spin-down states are in perfect symmetry, indicating no spin magnetism. In all the studied polymorphs the valence band is dominated by the s states of the H atom and the conduction band is mostly occupied by the combination of the s states of the Mg atom and the s states of the H atom. We can see the stronger hybridization between H and Mg atoms near the Fermi level, which represents the strong interaction between H and Mg atoms indicating the possibility of covalent characteristics.

Table 3. The electronic structure data for the investigated polymorphs of MgH_2

Crystalline Structure	Band gap (eV)	Valence Band Width (eV)	Charges (e^-)					Distance between Mg and H (Å)	
			Mg (Total)	Mg (s)	Mg (p)	H^1 (Total)	H^2 (Total)	Mg-H^1	Mg-H^2
α - MgH_2	3.71	5.72	8.637	2.612	6.025	1.611	-	1.947	1.956
β - MgH_2	2.93	6.88	8.640	2.628	6.020	1.607	-	1.970	1.970
γ - MgH_2	3.64	5.43	8.635	2.619	6.016	1.609	-	1.912	2.012
δ' - MgH_2	2.67	7.29	8.628	2.616	6.012	1.603	1.609	1.901	2.000
ε - MgH_2	1.96	8.41	8.642	2.633	6.009	1.600	1.594	1.970	2.020
cubic-MgH_2	0.00	9.67	8.617	2.617	6.000	1.616	-	2.060	2.060

Where H^1 represents the two hydrogen atoms that lie along [110] plane and H^2represents the four hydrogen atoms that lie on the (110) plane of the octahedrally coordinated Mg atom.

From the table it is seen that α - MgH_2 has a shorter bond length(1.947and1.956Å) which is in good agreement with other experimental value(1.944and 1.961 Å)[6] and theoretical value(1.948 and1.952 Å)[32] and cubic -MgH_2 has longer bond length (2.060Å) than other polymorphs and as the longer bond will be weaker, cubic -MgH_2 has weaker bonding between Mg and H requiring less energy for the bond dissociation lowering the decomposition temperature leading to reduced hydrogen removal energy.

The total charge transfer from Mg to H in all the MgH_2 polymorphs implies that the magnesium atoms with about 0.6 $|e^-|$ transfers about 0.5 $|e^-|$ from the 3s orbital to the 1s orbital of each nearest-neighbor hydrogen atoms and about one electron to its own 3p states and become positively charged indicating the ionic nature of the MgH_2 which is in agreement with the experimental findings [33].

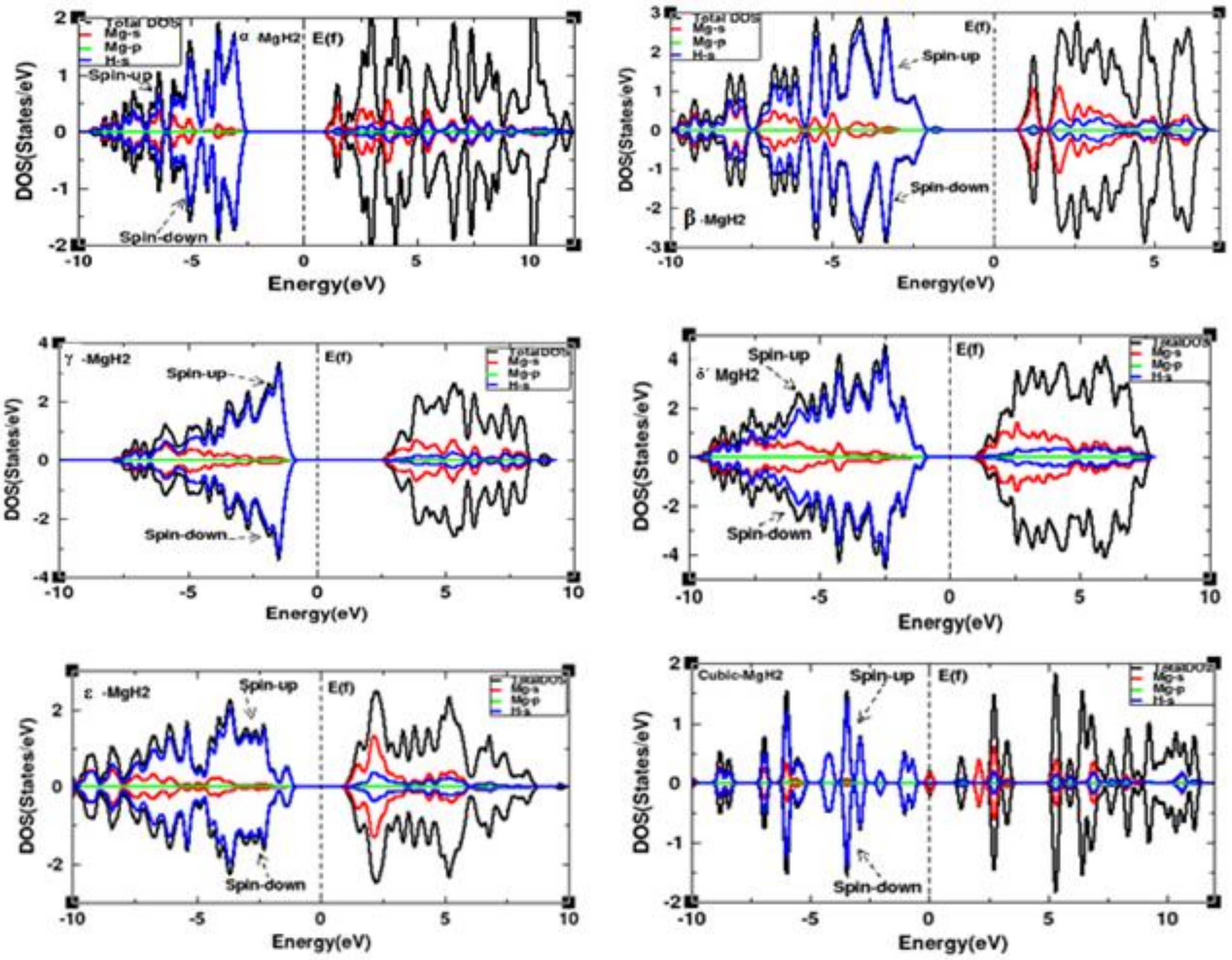


Figure 3. The total and partial DOS for the studied polymorphs of MgH_2.

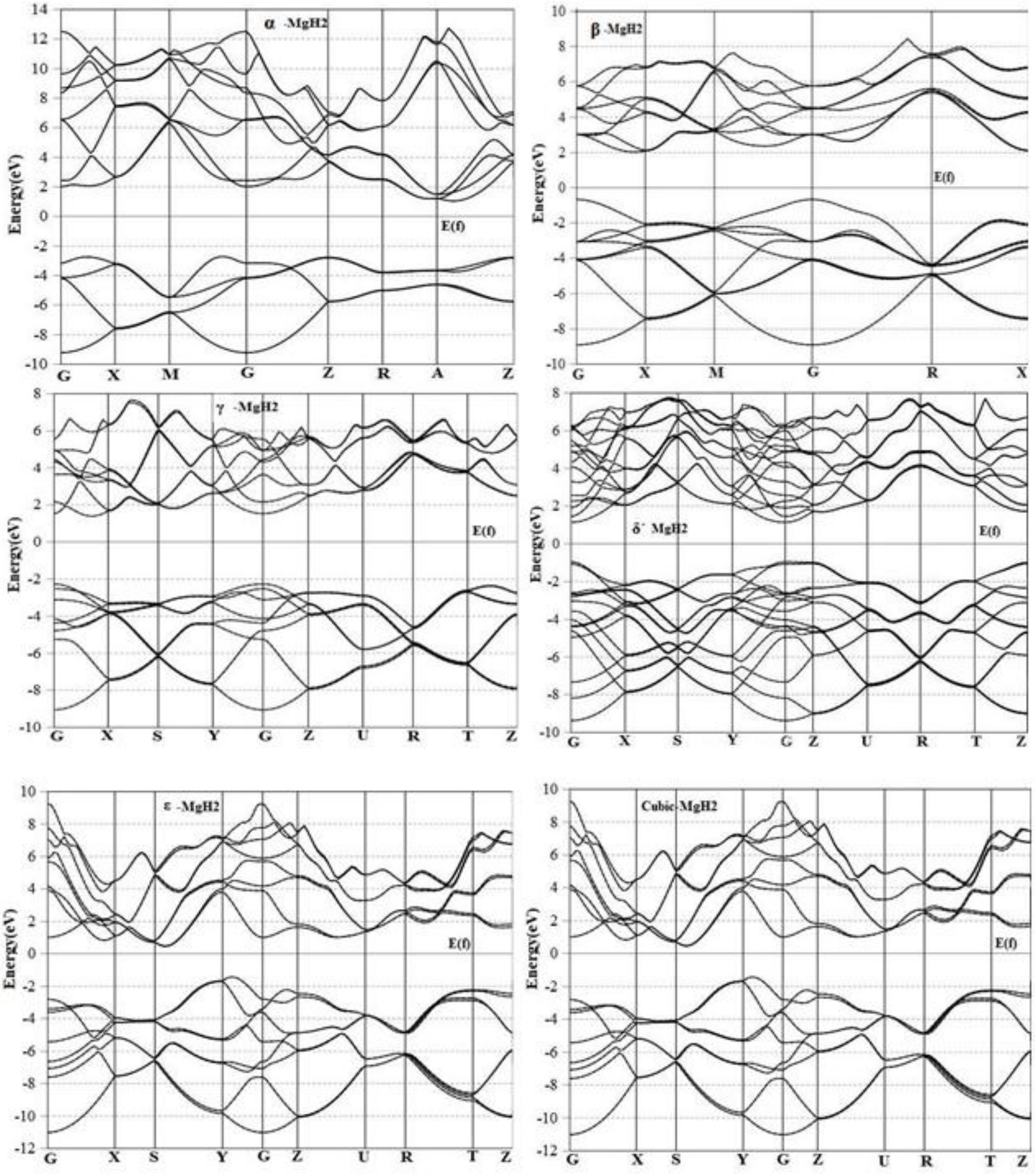


Figure.4 **The** *band structures for the different polymorphs of MgH*$_2$

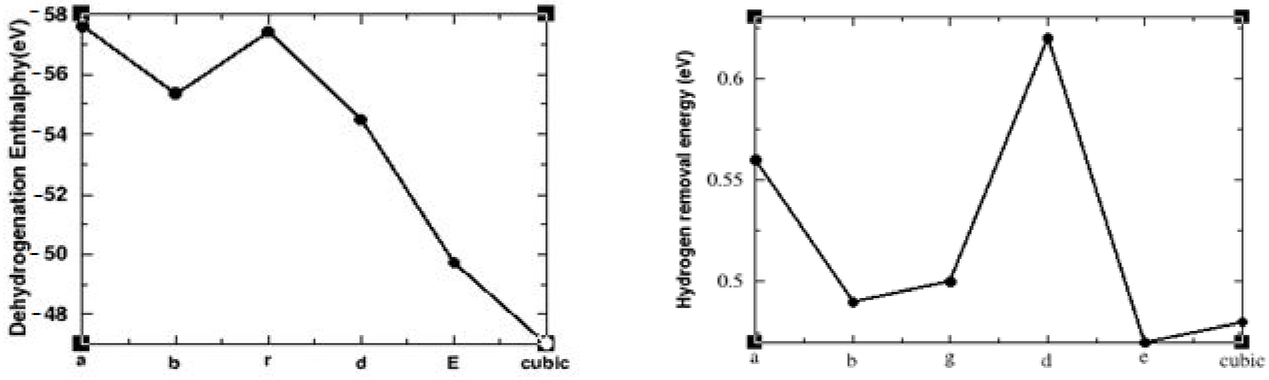
D. DEHYDROGENATION KINETICS

The dehydrogenation enthalpy (ΔH) and the hydrogen removal energy(ΔE) are the two important thermodynamic parameters which are used to identify and classify hydrogen storage materials as they determine the heat of the dehydrogenation reaction (ΔH < 0 hydride is stable and vice versa) and deduce the temperature of desorption of hydrogen in the studied system. The dehydrogenation enthalpy (ΔH) and the hydrogen removal energy(ΔE) have been calculated for all the six polymorphs of MgH$_2$ in order to predict the most potential hydrogen storage material. To calculate the dehydrogenation enthalpy (ΔH) and the hydrogen removal energy(ΔE) we used the following formula:

$$\Delta H\,(MgH_2) = E_{tot}\,(MgH_2) - E_{tot}\,(Mg) - E_{tot}\,(H_2) \qquad (1)$$

$$\Delta E\,(MgH_2) = E_{tot}\,(Mg\,H) + 0.5\,E_{tot}\,(H_2) - E_{tot}\,(MgH_2) \qquad (2)$$

We used the total energies obtained with the optimized structure of MgH_2 and Mg. The value of the total energy of the H_2 molecule $E_{tot}(H_2) = -2{\cdot}320$ Ry has been taken from Shang et al(2004) and Nakamura et al(1998)[34,35] and E_{tot} (Mg H) refers to the total energy of $MgH_2$with one hydrogen atom removed. The dehydrogenation enthalpy (ΔH), the hydrogen removal energy or the hydrogen dissociation energy(ΔE), the decomposition temperature(T) for all the six polymorphs of MgH_2 are given in ***Table4*** **.**The calculated dehydrogenation enthalpy and the hydrogen removal energy are plotted for the studied systems as shown in ***Figure5***



(a) **(b)**

Figure5. The calculated dehydrogenation enthalpy and the hydrogen removal energy for the investigated systems.

Table 4.Dehydrogenation properties of the studied polymorphs of MgH_2

Crystalline Structure	Dehydrogenation enthalpy (ΔH) (KJ/mol.H_2)	Decomposition temperature T(K)	Hydrogen Dissociation energy(ΔE) (eV)
α - MgH_2	-57.63	441	0.56
β - MgH_2	-55.36	424	0.49
γ - MgH_2	-57.43	440	0.50
δ' - MgH_2	-54.48	417	0.62
ε - MgH_2	-49.72	380	0.47
cubic-MgH_2	-47.02	360	0.48

As is seen from the ***Table4*** that the dehydrogenation enthalpy (ΔH) for α - MgH_2 (-57.63kJ/mol.H_2) is in good agreement with the theoretical values of ΔH = -55.648to -65.196kJ/mol.H_2[36], ΔH = -59.9913 kJ/mol. H_2[37] but is slightly underestimated relative to the experimental value of 76 kJ/mol.H_2[38]as the temperature effect on the crystal structure has not been considered in the present work as in the case of the experimental calculations. It is seen that the dehydrogenation enthalpy (ΔH) is lower for cubic-MgH_2 which is 18.14% lower than the α -MgH_2 having the highest ΔH value and hence cubic-MgH_2 is less stable than α -MgH_2 causing greater destabilization, resulting in larger reduction of its dehydrogenation temperature. The order of the calculated ΔH for the studied polymorphs is: cubic < ε < δ' < β < γ ~ α - MgH_2.

The decomposition temperature is directly proportional to the formation enthalpy as per Gibbs free energy relation and can be calculated according to the relation,

$$T = \Delta H/\Delta S$$

where ΔH and ΔS (ΔS ~ ΔS(H_2) = 130.7 J/mol K)[39] are the heat of formation and the entropy change of the dehydrogenation reaction respectively. The calculated decomposition temperature for α - MgH_2 is 441K which is close to the other values of T = 460.12[40], T = 573-673K[39], T = 420K [41].From the **Table4** it is clear that the decomposition temperature decreases with decrease in the dehydrogenation enthalpy (ΔH),thus follows the same trend as that of the dehydrogenation enthalpy (ΔH).

The hydrogen removal energy or the hydrogen dissociation energy (ΔE) for α - MgH_2 (0.56eV) is in good agreement with the theoretical values of 0.5eV [42,44],0.4eV[42,43] and also with the experimental findings of 0.75 ± 0.15[44].The more positive ΔE is, the stronger the hydrogen is bound. Thus ε -MgH_2 with the lowest energy(ΔE =0.47eV) which is 24.2% less than that of δ' - MgH_2 with the highest energy(0.62eV) and 16.1% less than that of α - MgH_2(0.56eV) has weaker hydrogen bonding, lowering the energy required for dissociation of Mg-H bonding consequently reducing the dehydrogenation temperature compared to other polymorphs. The order of the calculated ΔE for the studied polymorphs is: $\varepsilon < \text{cubic} < \beta < \gamma < \alpha < \delta'$ - MgH_2. It is also seen from the ***Table 4*** that cubic-MgH_2 with ΔE = 0.48eV which differ only by 0.01eVof that of ε-MgH_2 also shows improved dehydrogenation kinetics for enhancing its hydrogen storage properties.

IV. CONCLUSIONS

We have performed the first principles calculation under the frame work of the density functional theory using the generalized gradient approximation and investigated the band structure, density of states, bulk modulus, dehydrogenation enthalpy, decomposition temperature and hydrogen removal energy of the six polymorphs of MgH_2. It is seen that the ground-state structure of MgH_2 is α- MgH_2 whose structural parameters are in good agreement with the experimental reported results. In all the phases except cubic- MgH_2, MgH_2 shows the behavior of an insulator whereas cubic – MgH_2 shows semi- metallic behavior .Of all the studied polymorphs of MgH_2, cubic – MgH_2 with longer bond length, lower dehydrogenation enthalpy, decomposition temperature, hydrogen removal energy along with the smaller equilibrium volume has the most potential for enhancing the hydrogen storage properties.

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