Pressure-Induced Structural Transitions in MgH$_2$

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The stability of MgH$_2$ has been studied up to 20 GPa using density-functional total-energy calculations. At ambient pressure α-MgH$_2$ takes a TiO$_2$-rutile-type structure. α-MgH$_2$ is predicted to transform into γ-MgH$_2$ at 0.39 GPa. The calculated structural data for α- and γ-MgH$_2$ are in very good agreement with experimental values. At equilibrium the energy difference between these modifications is very small, and as a result both phases coexist in a certain volume and pressure field. Above 3.84 GPa γ-MgH$_2$ transforms into β-MgH$_2$, consistent with experimental findings. Two further transformations have been identified at still higher pressure: (i) β- to δ-MgH$_2$ at 6.73 GPa and (ii) δ- to ϵ-MgH$_2$ at 10.26 GPa.

The utilization of high-pressure technology, which can reach the range of giga Pascal (GPa), has made considerable progress in experimental studies of hydrogen-storage materials. It has been demonstrated for a number of metal-hydrogen systems that application of high pressure is an effective tool to produce vacancies in the host metallic matrix, which in turn leads to various novel properties [1]. The Mg-based alloys possess many advantageous functional properties, such as heat resistance, vibration absorption, recycling ability, etc. [2]. In recent years, therefore, much attention has been paid to investigations on specific material properties of Mg alloys. Magnesium is an attractive material for hydrogen-storage applications because of its light weight, low manufacture cost, and high hydrogen-storage capacity (7.66 wt. %). On the other hand, owing to its high operation temperature (pressure plateau of 1 bar at 525 K) and slow absorption kinetics, practical applications of magnesium-based alloys have been limited. However, it has recently been established that improved hydrogen absorption kinetics can be achieved by reduced particle size and/or addition of transition metals to magnesium and magnesium hydrides [3]. γ-MgH$_2$ often occurs as a by-product in high-pressure syntheses of technologically important metal hydrides such as Mg$_2$NiH$_4$. Hence, a complete characterization of γ-MgH$_2$, in particular, knowledge about its stability at high pressure is highly desirable. Present theoretical investigation assumes importance as the high-pressure x-ray diffraction and neutron diffraction studies are unable to identify the exact position of hydrogen atoms owing to its very low scattering cross section. This contribution represents the first theoretical report on the high-pressure properties of MgH$_2$ as evident from *ab initio* density-functional calculations.

α-MgH$_2$ crystallizes with TiO$_2$-r-type (r = rutile) structure at ambient pressure and low temperature [4,5]. At higher temperatures and pressures, tetragonal α-MgH$_2$ transforms into orthorhombic γ-MgH$_2$. Recently Bortz *et al.* [6] solved the crystal structure of γ-MgH$_2$ (α-PbO$_2$

type) on the basis of powder neutron diffraction data collected at 2 GPa. The α- to γ-MgH$_2$ transition pressure is not yet known. Owing to the difficulties challenged in establishing hydrogen position in a metal matrix by x-ray diffraction, high-pressure information on MgH$_2$ is scarce. The aim of the present investigation is to remedy this situation by examining MgH$_2$ theoretically at high pressure in 11 closely related structural configurations.

We used the *ab initio* generalized gradient approximation (GGA) [7] to obtain accurate exchange and correlation energies for a particular structural arrangement. The structures are fully relaxed for all the volumes considered in the present calculations using force as well as stress minimization. Experimentally established structural data were used as input for the calculations when available. The full-potential linear muffin-tin orbital (FP-LMTO) [8] and the projected augmented wave (PAW) implementation of Vienna *ab initio* simulation package (VASP) [9] were used for the total-energy calculations to establish phase stability and transition pressures. Both methods yielded nearly the same result; e.g., the transition pressure from α- to γ-MgH$_2$ came out as 0.385 and 0.387 GPa from FP-LMTO and VASP, respectively. Similarly, almost identical values were obtained for ground-state properties such as bulk modulus and equilibrium volume. Hence, for the rest of the calculations we used only the VASP code because of its computational efficiency. In order to avoid ambiguities regarding the free-energy results, we have always used the same energy cutoff and a similar **k**-grid density for convergence. In all calculations 500 **k** points in the whole Brillouin zone were used for α-MgH$_2$ and a similar density of **k** points for the other structural arrangements. The PAW pseudopotentials [10] were used for all our VASP calculations. A criterion of at least 0.01 meV/atom was placed on the self-consistent convergence of the total energy, and the calculations reported here used a plane wave cutoff of 400 eV.

In addition to the experimentally identified α- and γ-modifications of MgH$_2$, we have carried out

calculations for several other possible [11] types of structural arrangements (see Table I and Figs. 1 and 2). The calculated total energy vs volume relation for all these alternatives are shown in Fig. 1. In order to get a clear picture about the structural transition points, in Fig. 2 we have displayed the Gibbs free-energy difference between the pertinent crystallographic structures of MgH_2 with reference to α-MgH_2 as a function of pressure. The equilibrium volumes (30.64 and 30.14 Å^3/f.u. for α- and γ-MgH_2, respectively) are within 1% of the experimental values, indicating that the theoretical calculations are reliable. The calculated positional parameters (Table I) are also in excellent agreement with the experimental data. The calculated values for the bulk modulus (B_0, see Table I) vary between 44 to 65 GPa for the various structural arrangements. Among the 11 possibilities considered, the Ag_2Te type leads to the smallest B_0 value and the $AlAu_2$ type to the highest.

The calculated transition pressure for the α- to γ-MgH_2 conversion is 0.39 GPa (Fig. 3) and as the free energy of the two modifications is nearly the same at the equilibrium volume (Fig. 1), it is only natural that these phases coexist in a certain volume range [6]. Structurally α- and γ-MgH_2 are also closely related, both comprising Mg in an octahedral coordination of 6 H which in turn are linked by edge sharing in one direction and by corner sharing in the two other directions. The chains are linear in tetragonal α-MgH_2 and run along the fourfold axis of its TiO_2-r-type structure, while they are zigzag shaped in γ-MgH_2 and run along a twofold screw axis of its orthorhombic α-PbO_2-type structure. The octahedra in γ-MgH_2 are strongly distorted. The pressure induced α-to-γ transition involves reconstructive (viz. bonds are broken and reestablished) rearrangements of the cation and anion sublattices. The occurrence of a similar phase transition in PbO_2 suggests that thermal activation or enhanced shear is of importance [14].

The subsequent phase transition from γ- to β-MgH_2 occurs at 3.84 GPa. Bortz et al. [6] found no evidence for the formation of such a β modification up to 2 GPa, whereas Bastide et al. [4] found that at higher pressure (4 GPa) and temperature (923 K) there occurs a new phase (viz. β in accordance with our findings). However, the H positions are not yet determined experimentally and, hence, our optimized structural parameters for β-MgH_2 should be of particular interest. The volume shrinkage at the transition point is 1.45 Å^3/f.u. On further increase of the pressure to around 6.7 GPa, β-MgH_2 is predicted to transform into δ-MgH_2 (orthorhombic $Pbc2_1$) with a volume shrinkage of 1.1 Å^3/f.u. In the

TABLE I.   Optimized structural parameters, bulk modulus (B_0), and its pressure derivative (B_0') for MgH_2 in the different structural arrangements considered in the present study.

Structure type	Space group	Unit cell (Å)			Positional parameters	B_0 (GPa)	B_0'
		a	b	c			
TiO_2-r[a]; α-MgH_2[b]	$P4_2/mnm$	4.4853	4.4853	2.9993	Mg (2a): 0, 0, 0	51	3.45
		(4.501	4.501	3.010[c])	H (4f): 0.3043, 0.3043, 0 (0.304, 0.304, 0[c])	55[d]; 50[e]	
Mod. CaF_2; β-MgH_2[b]	$Pa\bar{3}$	4.7902	4.7902	4.7902	Mg (4a): 0, 0, 0; H (8c): 0.3417, 0.3417, 0.3417	56	3.52
At 3.84 GPa[b]					Mg (4a): 0, 0, 0; H (8c): 0.3429, 0.3429, 0.3429		
α-PbO_2; γ-MgH_2[b]	$Pbcn$	4.4860	5.4024	4.8985	Mg (4c): 0, 0.3314, 1/4 (0, 0.3313, 1/4[c])	48	3.07
		(4.501	5.4197	4.9168[c])	H (8d): 0.2717, 0.1085, 0.0801 (0.2727, 0.1089, 0.0794[c])		
At 0.39 GPa[b]					Mg (4c): 0, 0.3307, 1/4; H (8d): 0.2710, 0.1073, 0.0797		
Ortho; δ-MgH_2[b]	$Pbc2_1$	4.8604	4.6354	4.7511	Mg (4a): 0.0294, 0.2650, 3/4;	60	3.68
					H1 (4a): 0.3818, 0.0976, 0.8586; H2 (4a): 0.2614, 0.5584, 0.0298		
At 6.73 GPa[b]					Mg (4a): 0.0294, 0.2665, 3/4;		
					H1 (4a): 0.3933, 0.1090, 0.8475; H2 (4a): 0.2586, 0.5576, 0.0305		
$AlAu_2$; ϵ-MgH_2[b]	$Pnma$	5.2804	3.0928	5.9903	Mg (4c): 1/4, 3/4, 0.6033; H1 (4c): 0.3610, 1/4, 0.4250;	65	3.72
					H2 (4c): 0.4794, 1/4, 0.8345		
At 10.2 GPa[b]					Mg (4c): 1/4, 3/4, 0.6075; H1 (4c): 0.3602, 1/4, 0.4260;		
					H2 (4c): 0.4765, 1/4, 0.8300		
$InNi_2$[b]	$P6_3$	3.2008	3.2008	5.9870	Mg (2b): 1/3, 2/3, 1/4; H1 (2a): 0, 0, 0;	59	3.42
					H2 (2b): 1/3, 2/3, 3/4		
Ag_2Te[b]	$P2_1/c$	4.8825	4.6875	5.0221	Mg (4e): 0.2630, 0.4788, 0.2117;	44	3.31
			(β = 99.25)		H1 (4e): 0.0718, 0.2039, 0.3818; H2 (4e): 0.4309, 0.7430, 0.5021		
CaF_2[b]	$Fm\bar{3}m$	4.7296	4.7296	4.7296	Mg (4a): 0, 0, 0; H (8c): 1/4, 1/4, 1/4	59	3.52
TiO_2-a[b,f]	$I4_1/amd$	3.7780	3.7780	4.7108	Mg (4a): 0, 0, 0; H (8e): 0, 0, 0.2101	45	3.19
$AuSn_2$[b]	$Pbca$	9.3738	4.8259	4.7798	Mg (8c): 0.8823, 0.0271, 0.2790; H1 (8c): 0.7970, 0.3765, 0.1651;	58	3.45
					H2 (8c): 0.9738, 0.7433, 0.5207		
$CaCl_2$[b]	$Pnnm$	4.4810	4.4657	3.0064	Mg (2a): 0, 0, 0; H (4g): 0.3076, 0.2991, 0	58	3.45

[a]r = rutile.
[b]To elucidate variations of atomic positions with pressure, parameter values are given at equilibrium volume as well as at transition pressures.
[c]Experimental value [6].
[d]Theoretical value [12].
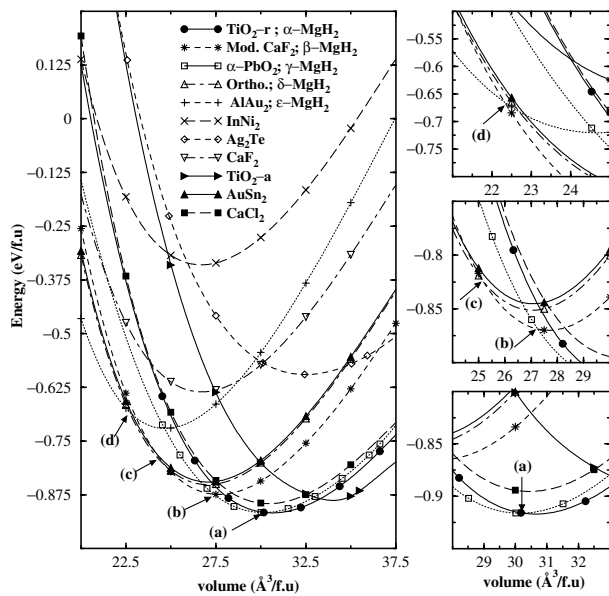[e]Theoretical value [13].
[f]a = anatase.

FIG. 1. Calculated unit-cell volume vs total-energy relations for MgH_2 in actual and possible structural arrangements as obtained from VASP. Magnified versions of the corresponding transition points are shown on right-hand side of the figure.

pressure range 6.7–10.2 GPa, the structural arrangements β-MgH_2, $AuSn_2$, and δ-MgH_2 are seen to lie within a narrow energy range of some 10 meV (Fig. 1). This closeness in energy suggests that the relative appearance of these modifications will be quite sensitive to, and easily
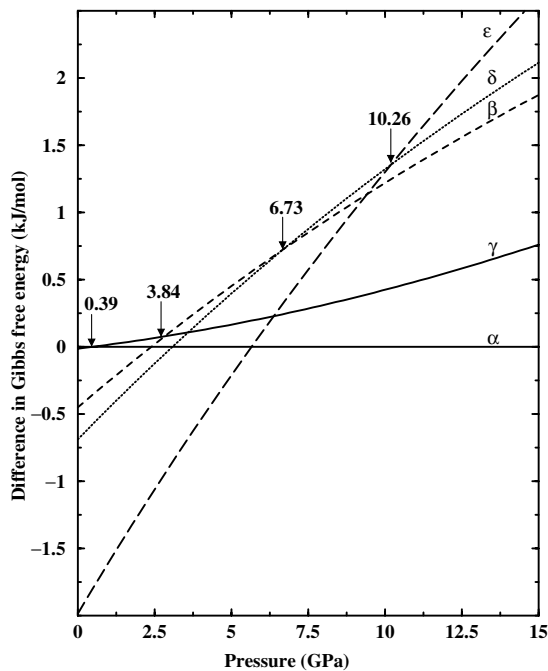
affected by, other external factors such as temperature and remnant lattice stresses. A transformation to ϵ-MgH_2 ($AlAu_2$-type structure also called cotunnite-type) is clearly evident from Fig. 1 with a volume change of 1.7 Å^3/f.u. at the transition point (see also Figs. 2 and 3). It is interesting to note that similar structural transition sequences are reported for transition-metal oxides such as HfO_2 [11]. Recently, the cotunnite-type structure of TiO_2 (synthesized at pressure above 60 GPa and high temperatures) has been shown [15] to exhibit an extremely high bulk modulus (431 GPa) and hardness (38 GPa). The present study predicts that it should be possible to stabilize MgH_2 in the $AlAu_2$-type structure as a soft material ($B_0 = 65$ GPa) above 10.26 GPa, a prediction which should be of considerable interest.

The calculated unit-cell volume difference between the involved phases at their equilibrium volume relative to the α phase is 0.50 (for γ), 2.94 (for β), 3.60 (for δ), and 5.96 (for ϵ) Å^3/f.u., which is approximately 1.6%, 9.5%, 11.8%, and 19.5%, respectively, smaller than the equilibrium volume of the α phase. The energy difference between α phase and the γ, β, δ, and ϵ phases at their equilibrium volume is 0.81, 43, 66, and 197 meV/f.u., respectively, which is considerably smaller than for similar types of phase transitions in transition-metal dioxides [11]. The known stabilization of the high-pressure phase of TiO_2 by using high-pressure–high-temperature synthesis [15] indicates that it may be possible to stabilize the high-pressure phases of MgH_2 due to their small energy differences and (partly) reconstructive phase transitions. Such stabilization of MgH_2 high-pressure phases at room temperature would reduce the volume considerably, and in the extreme case the expected volume reduction would be ca. 19.5% for ϵ-MgH_2 compared with α-MgH_2. This

FIG. 2. The stabilities of various known and hypothetical MgH_2 phases relative to α-MgH_2 as a function of pressure. The transition pressures are marked by arrows at the corresponding transition points.
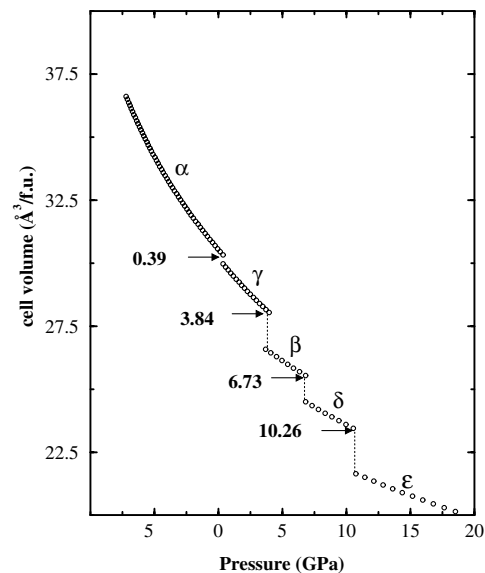

FIG. 3. Pressure vs volume relation for MgH_2. Pressure stability regions for the different modifications (see Table I and text) are indicated.
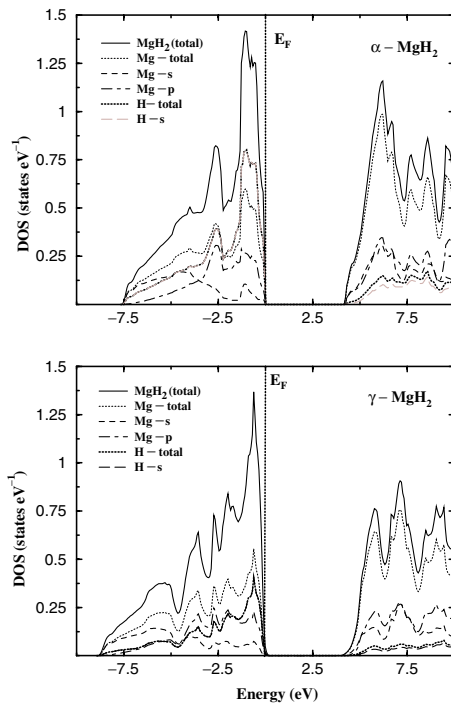
FIG. 4. The electronic total and partial density of states for α- and γ-MgH$_2$.

would imply an increased volumetric storage capacity of hydrogen for MgH$_2$. Of interest would be to explore the possibility of stabilizing the high-pressure phases by chemical means. At the same time, this may possibly open up for improved kinetics with respect to reversible hydrogen absorption/desorption. Hence, the observation of high-pressure phases in MgH$_2$ may have technological significance.

The calculated energy gap [from the top of the valence band (VB) to the bottom of the conduction band] is 4.2 and 4.3 eV for α- and γ-MgH$_2$, respectively. According to Fig. 4, the width of VB is 7.5 and 8.3 eV in α- and γ-MgH$_2$, respectively. The increased width of VB in γ-MgH$_2$ is due to the reduction in the Mg-H separation (1.93 Å in α-MgH$_2$ vs 1.91 Å in γ-MgH$_2$). An experimental UV absorption study [12] of α-MgH$_2$ gave an absorption edge at 5.16 eV, whereas an earlier theoretical electronic structure investigation [12,13] reported a band gap around 3.4 eV. Hence, our calculated energy gap value is in better agreement with the experimentally measured value than the earlier values. In fact, the present underestimation of the band gap by about 17% is typical for the accuracy obtained by first principle methods for semiconductors and insulators. Such distinctions probably originate from the use of GGA-based exchange correlation functionals.

In conclusion, the calculated structural parameters for α- and γ-MgH$_2$ are in excellent agreement with the experimental findings. We found that the ground state of α-MgH$_2$ becomes unstable at higher pressure and the calculated transition pressures for α-to-γ- and

γ-to-β-MgH$_2$ are found to be in very good agreement with the experimental findings. We predict that further compression of β-MgH$_2$ will lead to a phase transition to δ-MgH$_2$ (orthorhombic; $Pbc2_1$) at 6.73 GPa and that the AlAu$_2$-type structure of a hypothetical ϵ modification stabilizes above 10.26 GPa. Our total-energy study suggested that the formation of the high-pressure ϵ phase could also be possible by appropriate preparation methods. This may reduce the volume requirement by ca. 19.5% compared with α-MgH$_2$. In agreement with experiments, α-MgH$_2$ turns out to be an insulator, and the theoretical treatment shows that the high-pressure modifications also should exhibit insulating behavior.

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