Hydrogen Release from Pristine and Ti-doped $KMgH_3$

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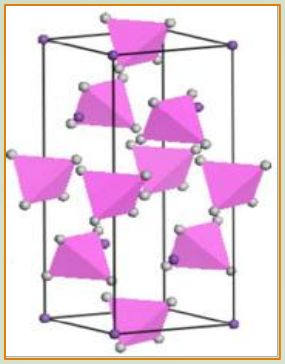
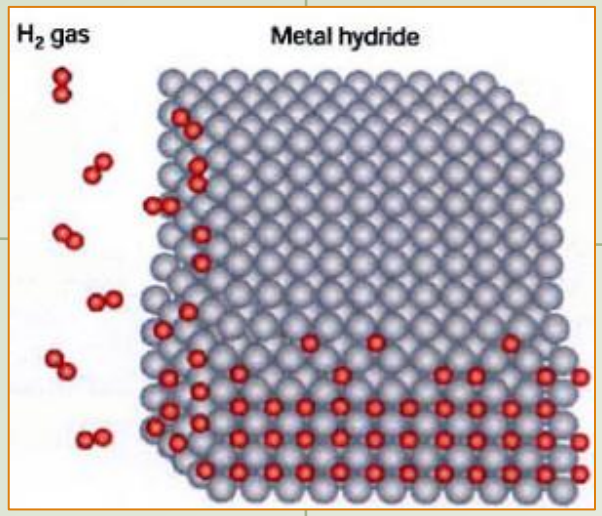
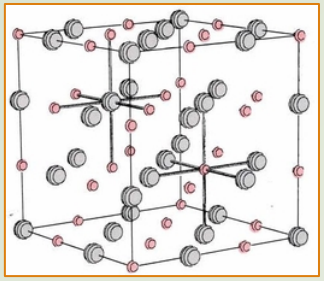
Advisor: Dr. Daniela Mainardi

H can be stored in metal hydrides

Alanates



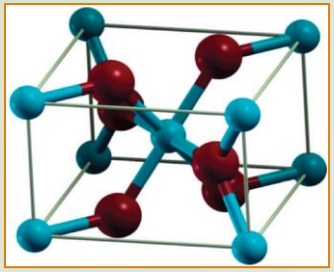


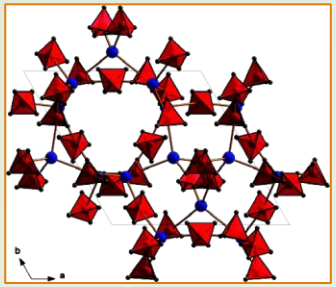


Perovskite-type

- group 1 cation
- XH_6 group

MgH_2

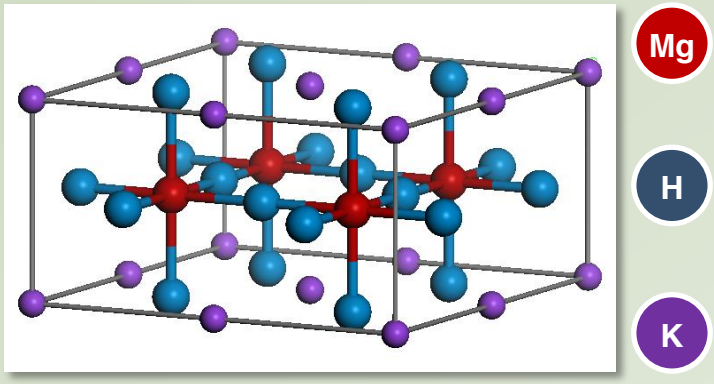




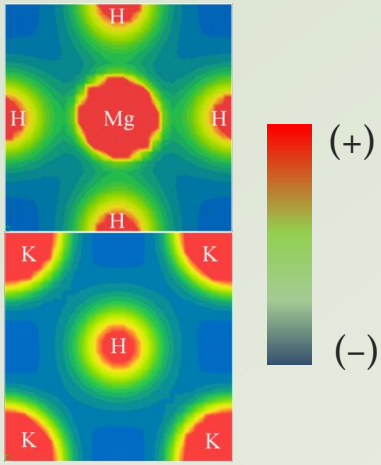
Borohydrates

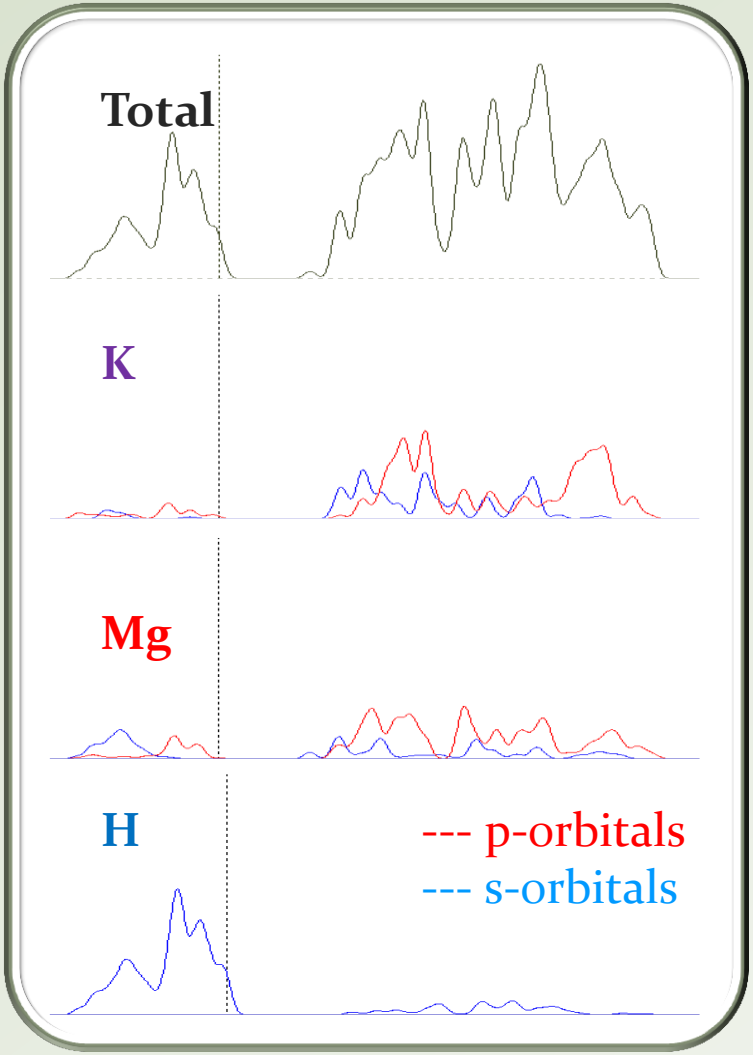
Perovskite $KMgH_3$

$KMgH_3$



- Light
- Dense in H
- Stable
- Slow hydrogen release



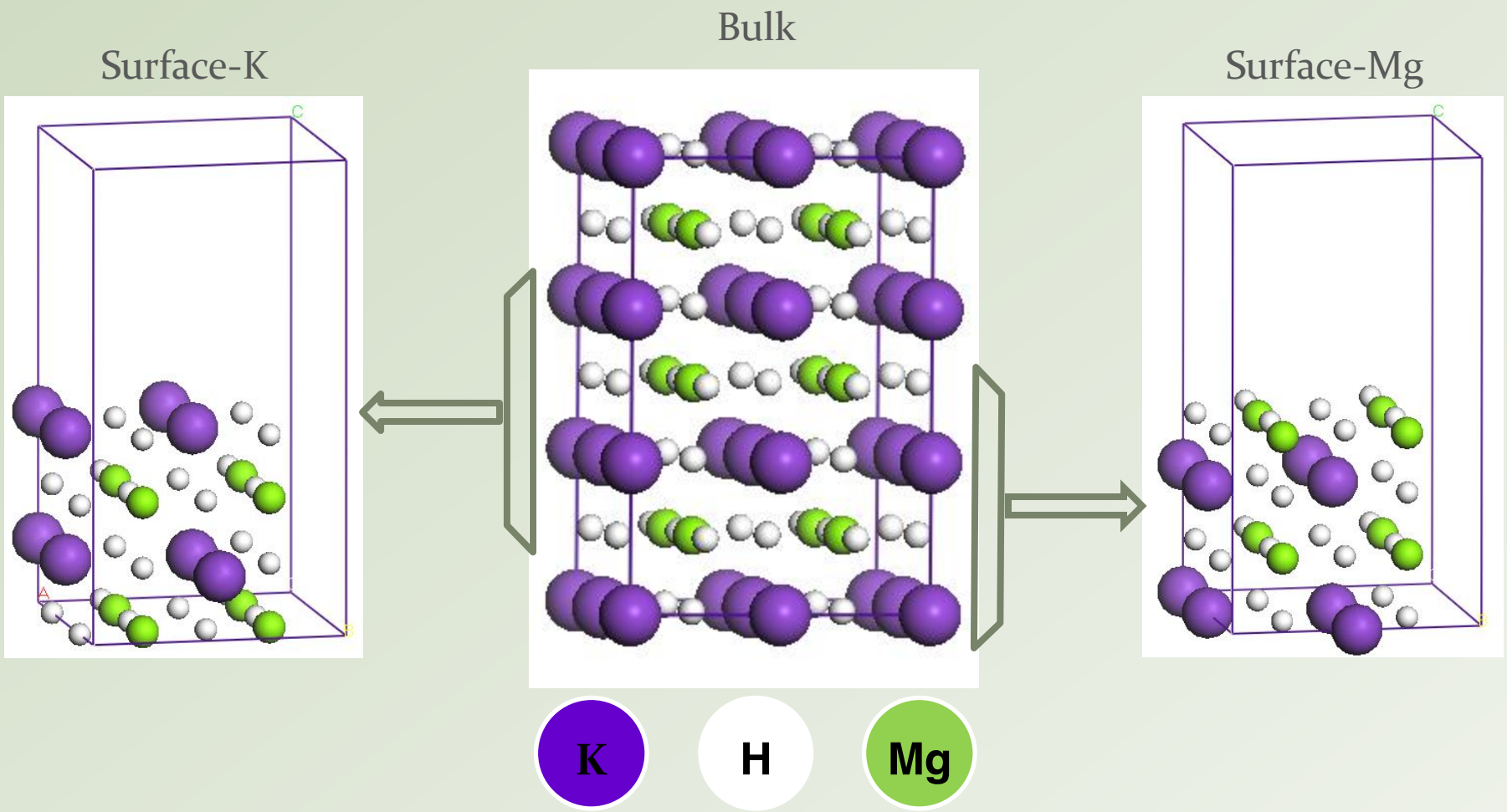


Method

- Materials Studio
- DFT (implemented by the CASTEP module)
  - GGA (Generalized Gradient Approach)
    - PBE functional
  - Basis set: ultasoft psudopotentials
  - Geometry optimization
    - True configuration after modifying
  - Transition state search
  - 0 Kelvin

- Procedure
  - Removing H atoms
  - Removing H_2
  - Adding Ti atoms
  - Modifying the original structure without removing

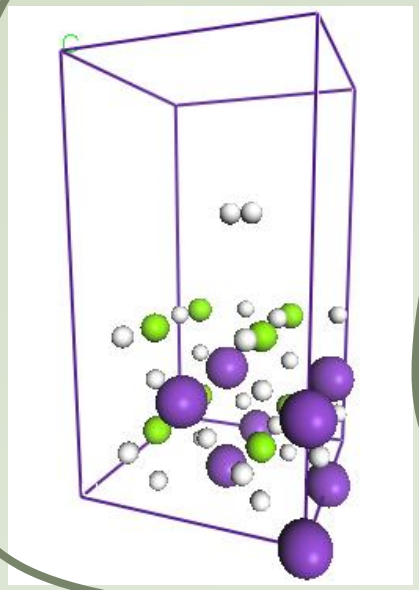
Surface modeling



Dehydrogenation

$$\Delta E_{dehyd} = E_T(\text{surface}) - [\, E_T(\text{surface} - H) + \frac{1}{2} E_T(H_2)\,]$$

- Lower ΔE_{dehyd} – smaller attraction of H to surface



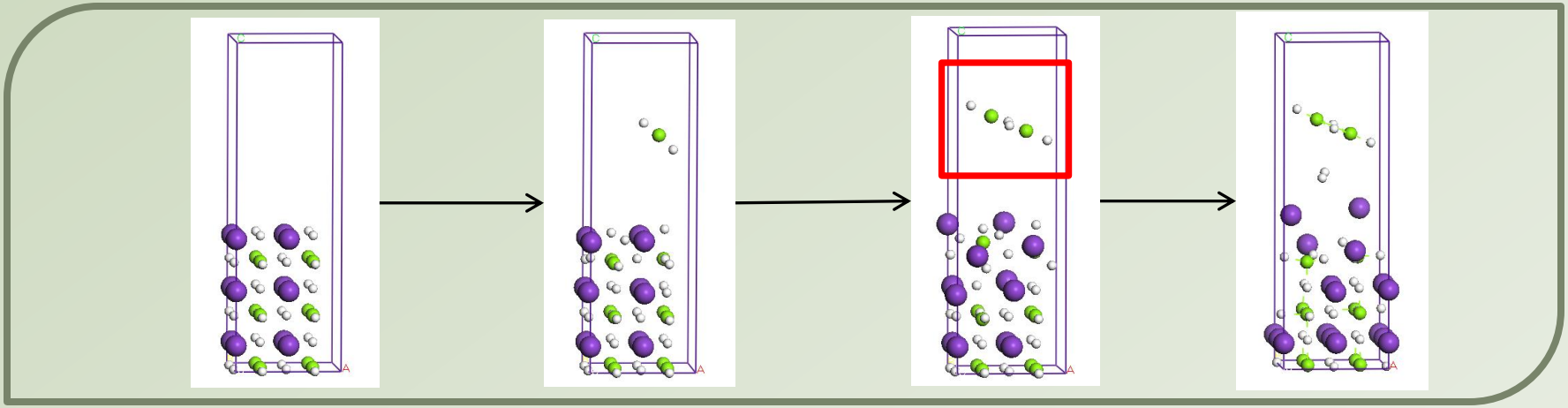
(Energy in eV)	Surface Mg	Surface K
E_T: 1 H removed	1.35	1.23
E_T: H_2 removed	1.67	2.19
E_T: 2 H_2 removed	3.21	3.97

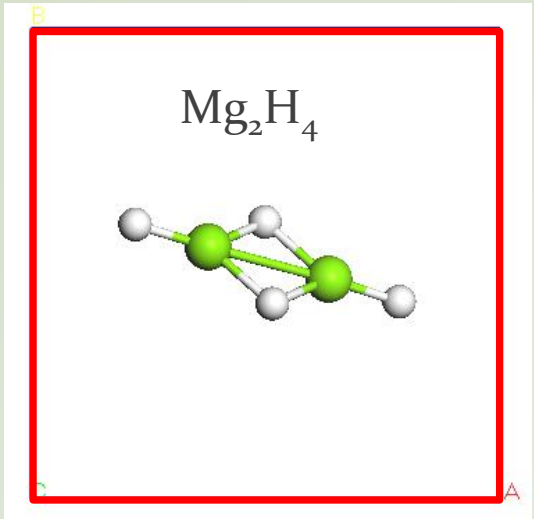
H_2 removed from surface-Mg

E_T = change in total energy

Reactions

Reaction 1



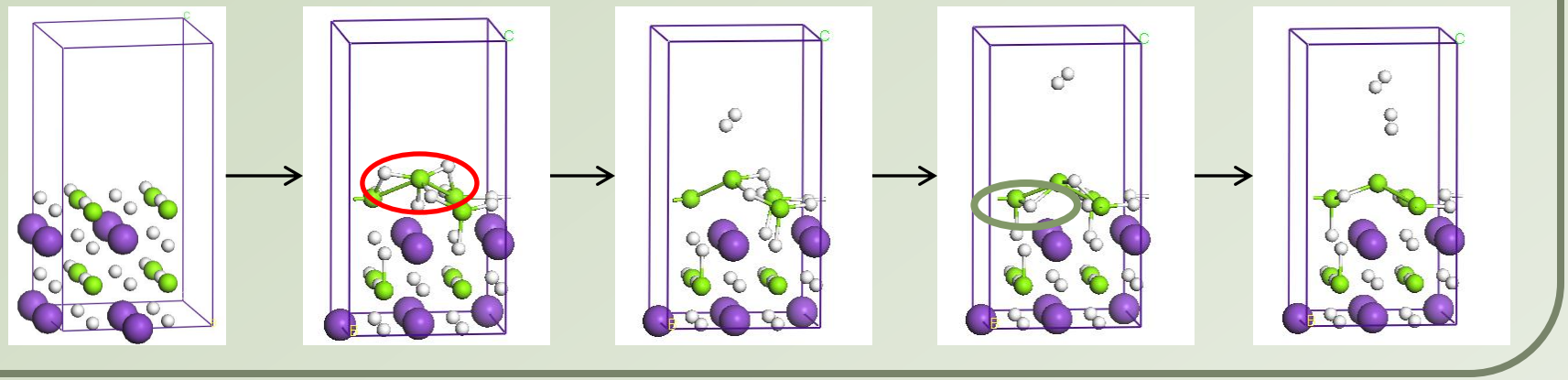


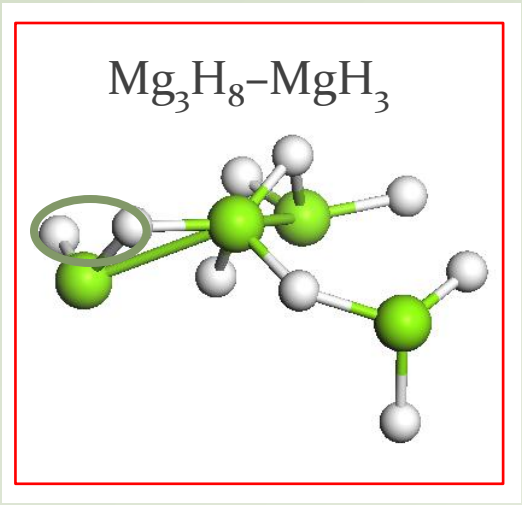
(Energy in eV)	Surface Mg	Surface K	Reaction 1
E_T: 1 H removed	1.35	1.23	
E_T: H_2 removed	1.67	2.19	6.09
E_T: 2 H_2 removed	3.21	3.97	
Barrier for H_2	2.93	2.53	8.47

- Lower ΔE_{dehyd} – smaller attraction of H to surface
- Lower activation barrier – easier for H_2 to leave surface

Reactions

Reaction 2





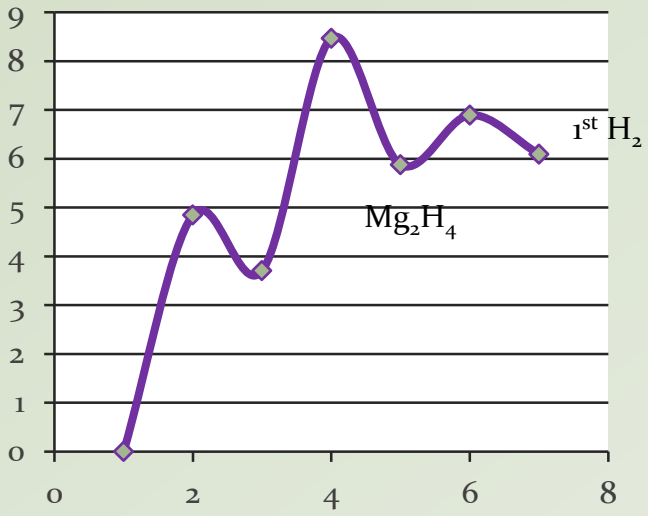
(Energy in eV)	Surface Mg	Surface K	Reaction 1	Reaction 2
E_T: 1 H removed	1.35	1.23		1.30
E_T: H_2 removed	1.67	2.19	6.09	2.07
E_T: 2 H_2 removed	3.21	3.97		2.93
Barrier for H_2	2.93	2.53	8.47	2.48
Barrier for 2 H_2				3.31

Reactions

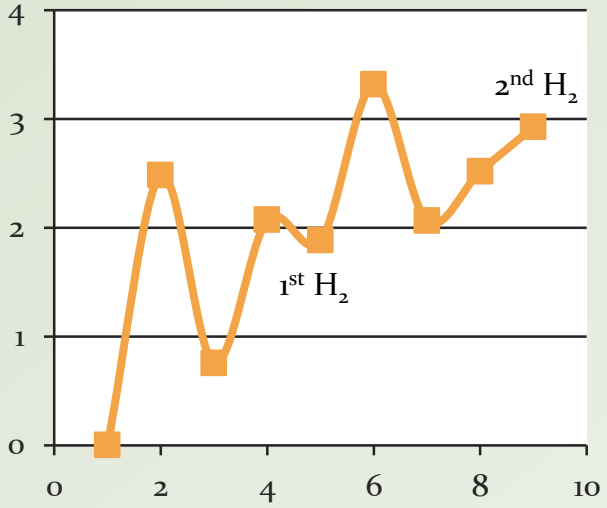
- In terms of 0 K energy:

Energy (eV)

Reaction 1 (Mg_2H_4)



Reaction 2 (Mg surface bonding)

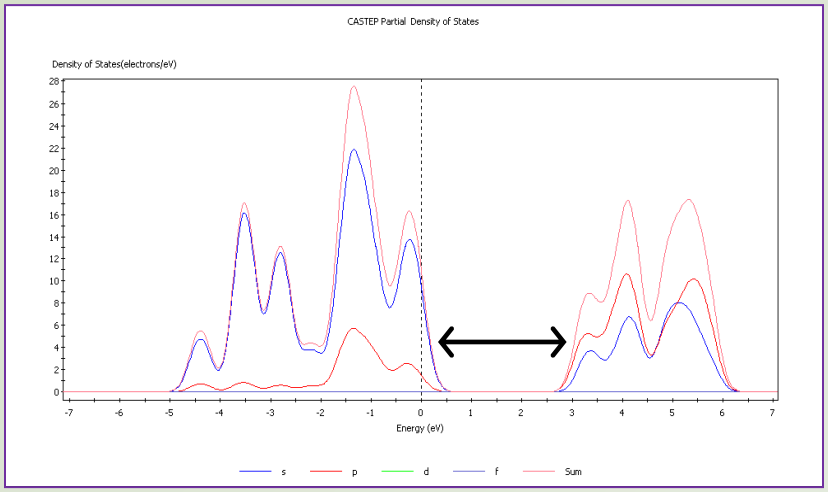


Reaction Coordinate

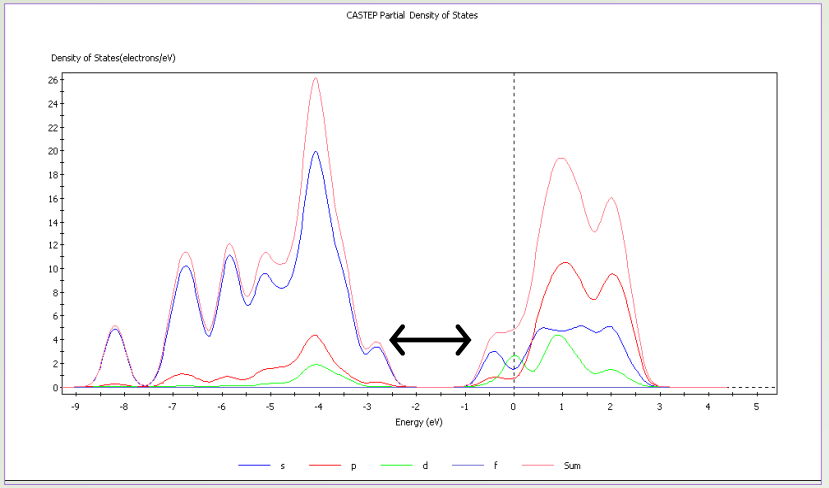
Ti-dopants

- Common dopants: Fe, Ni, Ti, V, Nb
- Our choice: Ti
- Smaller band gap with dopant

Pure Surface



Doped Surface

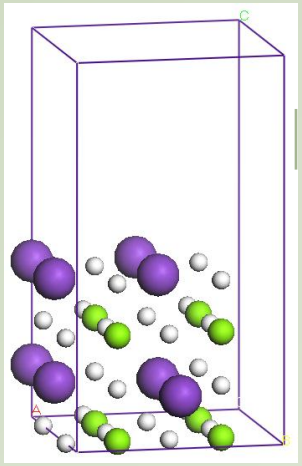


Location of Ti

- A compound with the metal is reacted with the hydride
- Ti will settle in the most energetically stable spots
  - thermal energy
- 0 K energy used to calculate:
  - cohesive energy: E(structure) – ∑E(parts)
    - compares the stability of similar structures
  - doping energy: E_{cohes}(structure) – E_{cohes}(doped structure)

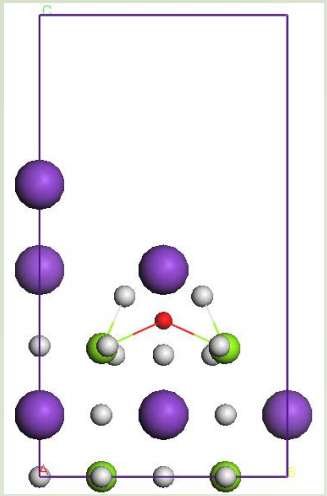
Possible locations of Ti

Surface-K ('K')



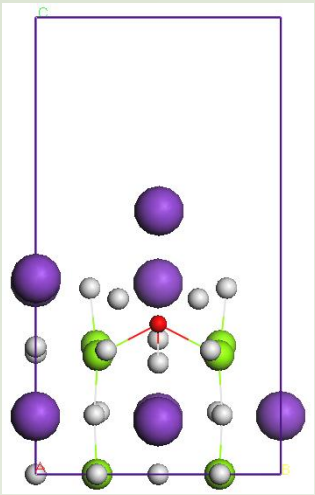
$Ti \rightarrow K_K$:

K – K ion site

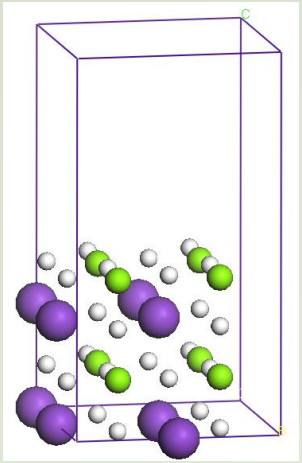


$Ti \rightarrow K_I$:

I - interstitial

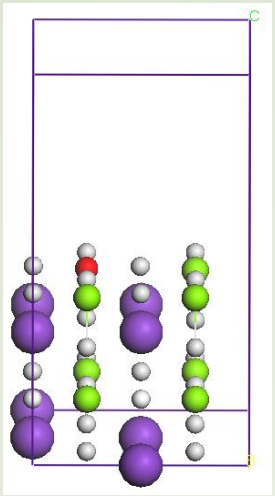


Surface-Mg ('M')

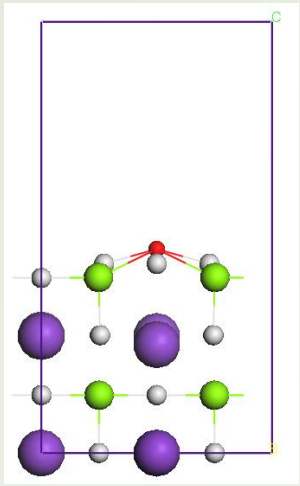


$Ti \rightarrow M_{Mg}$:

Mg – Mg ion site

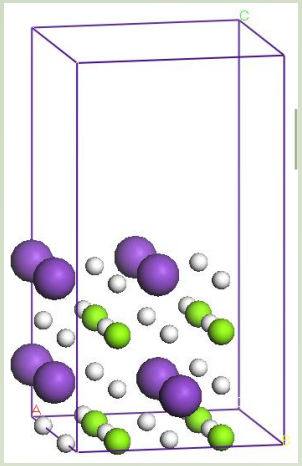


$Ti \rightarrow M_I$:



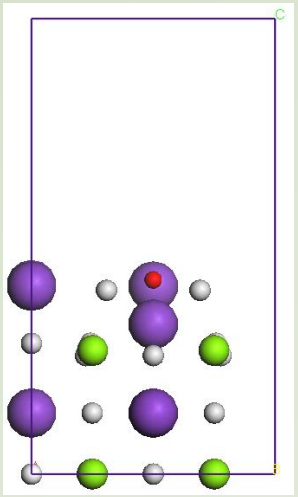
Location of Ti

Surface-K ('K')

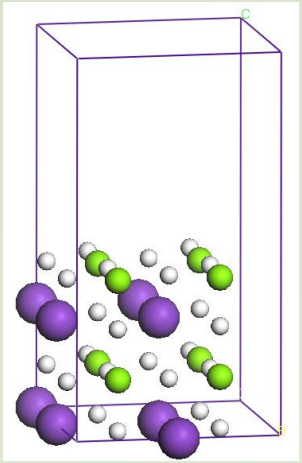


$Ti \rightarrow K_T$:

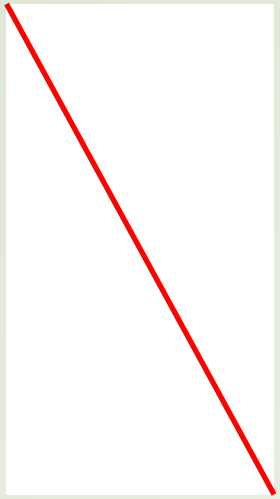
T – above cation site



Surface-Mg ('M')



$Ti \rightarrow M_T$:



- was not a possible structure

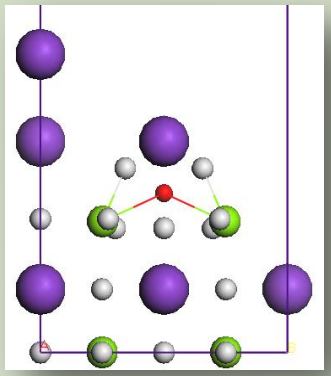
Location of Ti

Stable E_{coh}: > pure case

Favorable E_{dop}: small

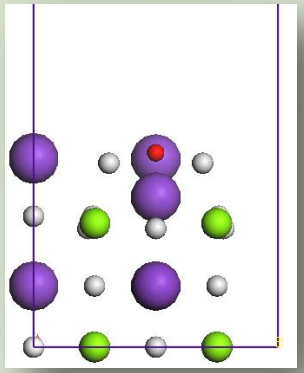
Ti → K_K :

Cohesive E > pure case
Doping E = 3.1 eV



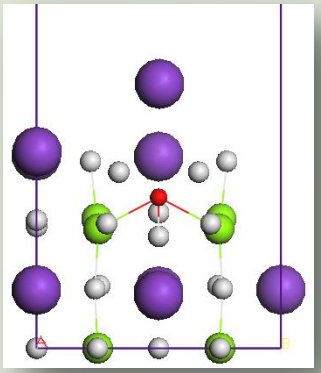
Ti → K_T :

Cohesive E < pure case
Doping E = - 1.7 . eV



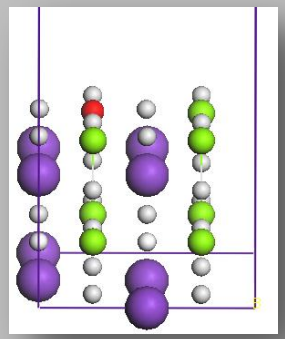
Ti → K_I :

Cohesive E > pure case
Doping E = 3.8 eV



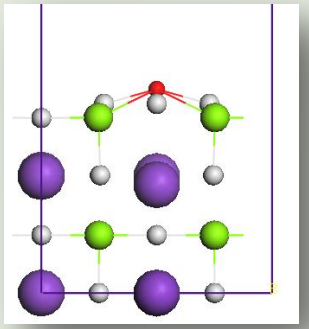
Ti → M_{Mg} :

Cohesive E > pure case
Doping E = 2.9 eV



Ti → M_I :

Cohesive E > pure case
Doping E = 4.2 eV



Effect of Ti on dehydration

	Ti-doped site	H bonds broken	Dehydrogenation energy (eV)	Average (eV)
Surface-K	None	H-Mg	1.23	
	Replacing K	H-Ti / H-Mg	0.55	0.45
		H-Ti	0.35	
	Interstitial	H-Ti	0.32	0.34
		H-Mg (1st layer)	0.32	
		2 H-Mg (2nd layer)	0.40	
Surface-Mg	None	2 H-Mg	1.39	
	Replacing Mg	H-Ti / H-Mg	1.26	1.07
		2 H-Mg	0.88	
	Interstitial	H-Ti / 2 H-Mg	0.59	0.67
		2 H-Mg	0.75	

Conclusions

- Ti is most likely to substitute a cation already in the surface
- Ti improves the chances of hydrogen leaving the surface
- Mg-Mg bonds formed before H_2 release may lower activation barriers.

- In future:
  - find activation barriers on doped surfaces
  - study more possible reaction paths

Acknowledgements

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