DFT Study of the Effect of 3*d* and 4*d* Transition Metals on $NaMgH_3$ Complex Metal Hydride for Hydrogen Storage Applications

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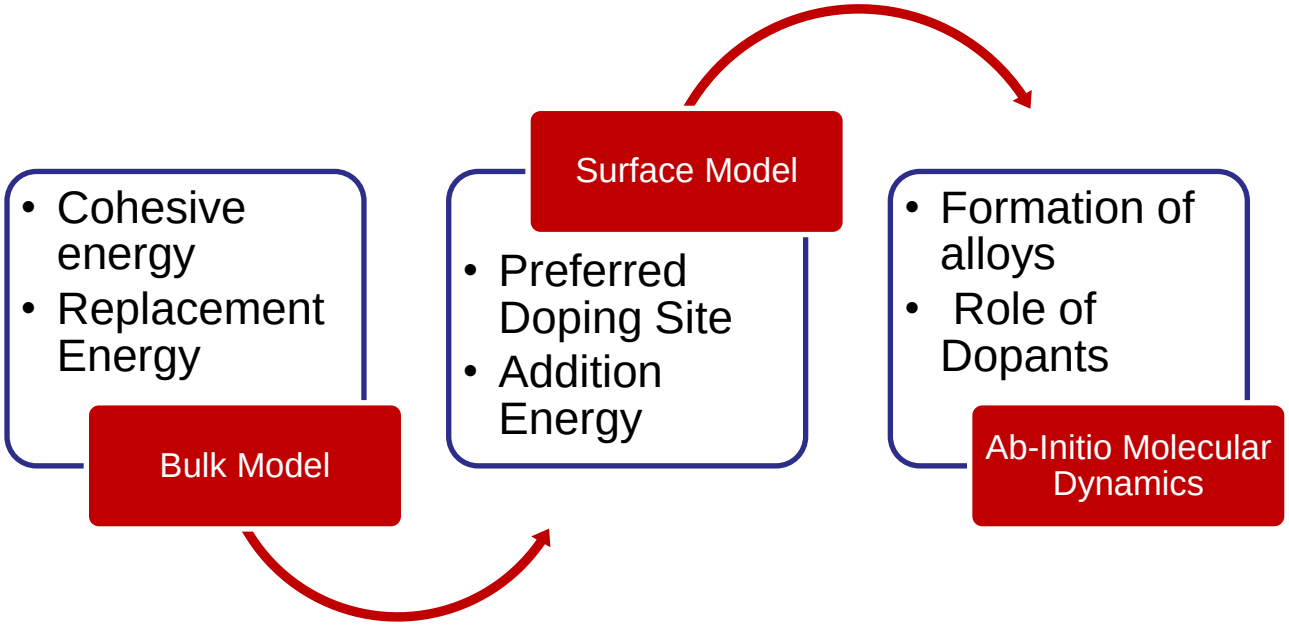
Overview

- Introduction
- Methodology
  - Bulk Model
  - Surface Model
- Results
  - Geometry Optimization
  - DFT-Molecular Dynamics
- Conclusions
- Acknowledgements

Complex Metal Hydrides

- **Goal** : Improve ability to design materials for hydrogen storage/explore wide range of promising hydrogen storage systems
- **Method** : First-principles investigation of effect of catalytic additives in structural dynamics of bulk and surface models in Complex Metal Hydrides (CMHs)



Hydrogen Storage

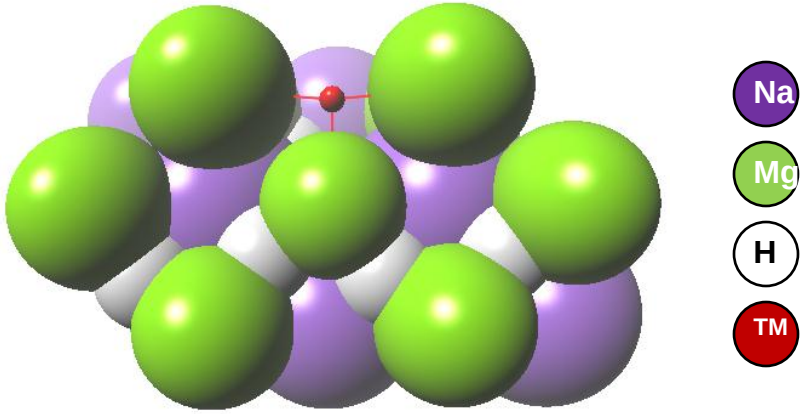
CMHs currently under study:

$NaMgH_3$,

<u>Decomposition of $NaMgH_3$</u>

$NaMgH_3 \rightarrow NaH + MgH_2$

*6 % wt. hydrogen capacity

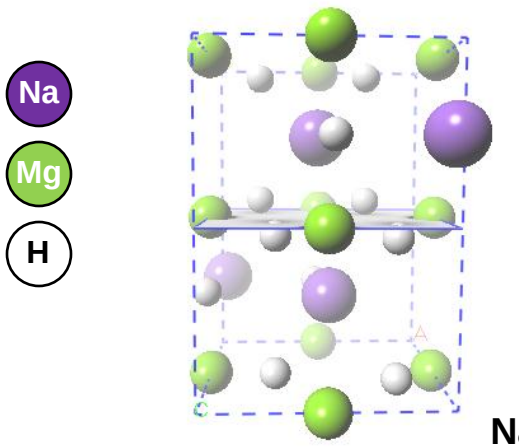


<u>Research Opportunity</u>

- **Higher H mobility** in this material due to their perovskite structure cause improved hydrogenation rates compared to pure MgH_2
- These structures may enhance kinetics and reversibility and inhibit toxic gas side products compared to borohydride, amide, and alanate compounds

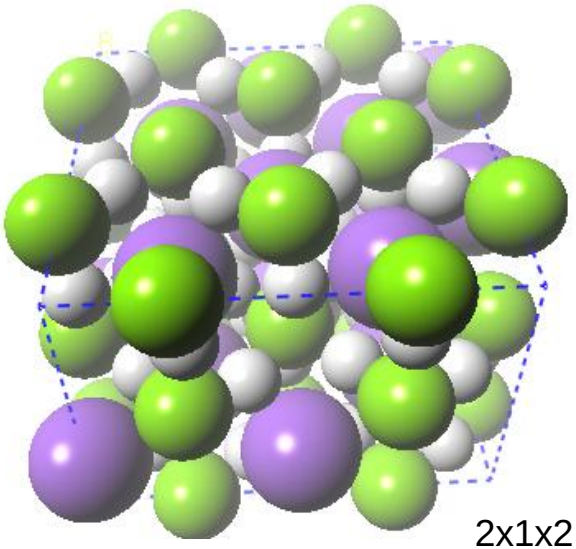
$NaMgH_3$

- **Complex Metal Hydrides** have attracted interest, experimental findings show that decomposition temperature for CMHs can be modified by introduction of additives



$NaMgH_3$ Unit Cell

- **Structure and Dynamics**
  Overall goal of First Principles calculations for 3d/4d-Transition Metal **Doping** is to determine**:**
  - Structural stability
  - Preferred doping site
  - Cohesive energy



2x1x2 **Supercell**

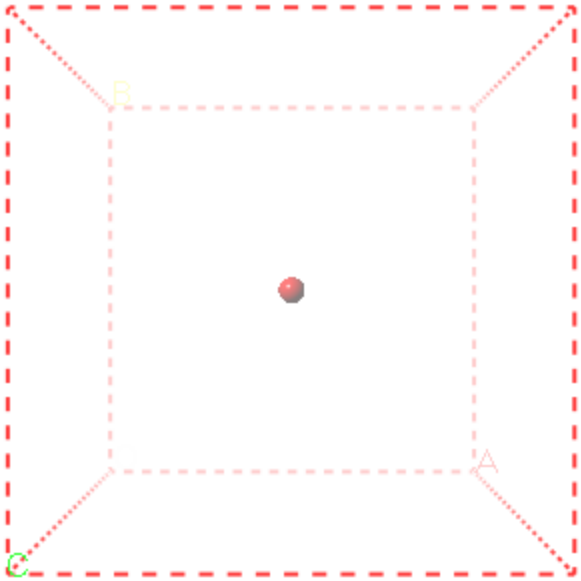
Modeling Approach

- First principles calculations done with Density Functional Theory (DFT)
  - Generalized gradient approximation (GGA)
    - PW91 for Geometry Optimization
    - PBE for Single-Point Energy Calculations
  - All the simulations successfully completed are performed using the plane wave pseudo-potential implementation of DFT as applied in the CASTEP® module of the Materials Studio® suite from Accelrys
  - DFT coupled MD is used to study the behavior of the system in canonical and microcanonical ensembles at high temperatures (423 K & 448 K)
    - NVT and NVE Ensembles
    - Gamma K-pt sampling

Methods

Cohesive Energies for Models

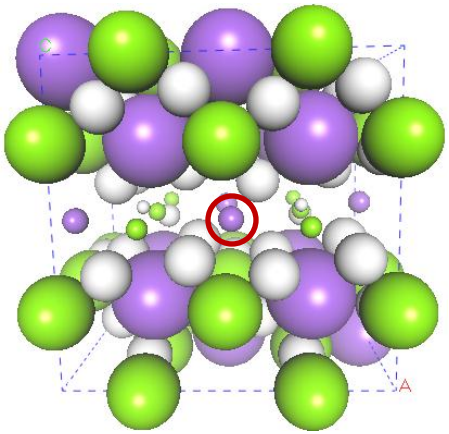
- Energy of free neutral atoms is calculated by placing an atom in a 10Å x 10Å x 10Å box with gamma Kpt set and E_{cutoff} = 400 eV
- Energy of atoms with unpaired electrons is obtained through spin-polarized simulations
- $\mathbf{E_{add/sub} = (E_{Doped\ system} - E_{pristine\ system})/N}$
- $\mathbf{E_{cohesive} = E_{total\ system} - \sum E_{free\ neutral\ atoms}}$



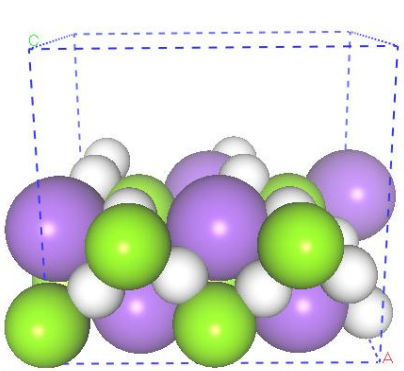
Titanium atom placed in a 10Å x 10Å x 10Å box

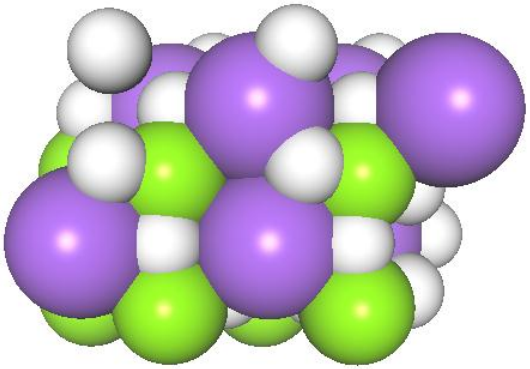
Models

- $NaMgH_3$ Bulk Models with Na @ Na site replaced with 3d/4d dopants
- $NaMgH_3$ 2 Layer Slabs
- Ti→@Na site
- Ti→@Hollow site
- Ti→@ Bridge site (Top of Na)
- Ti→@ top of Hollow Site
- Ti→@ Mg Site
- H removed from Pure model



2x1x2 supercell consisting of 16 f.u.

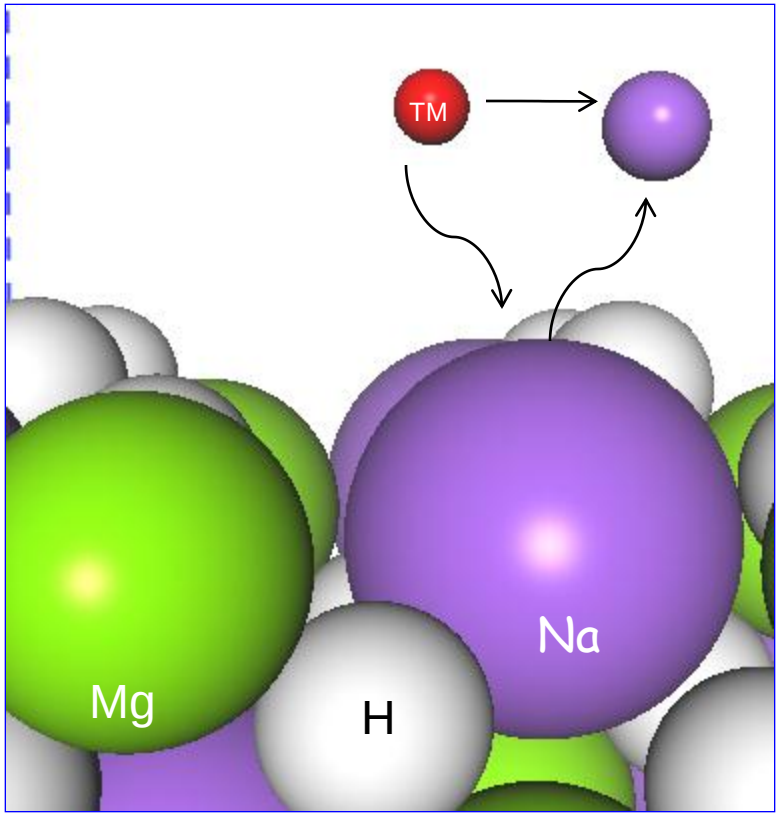




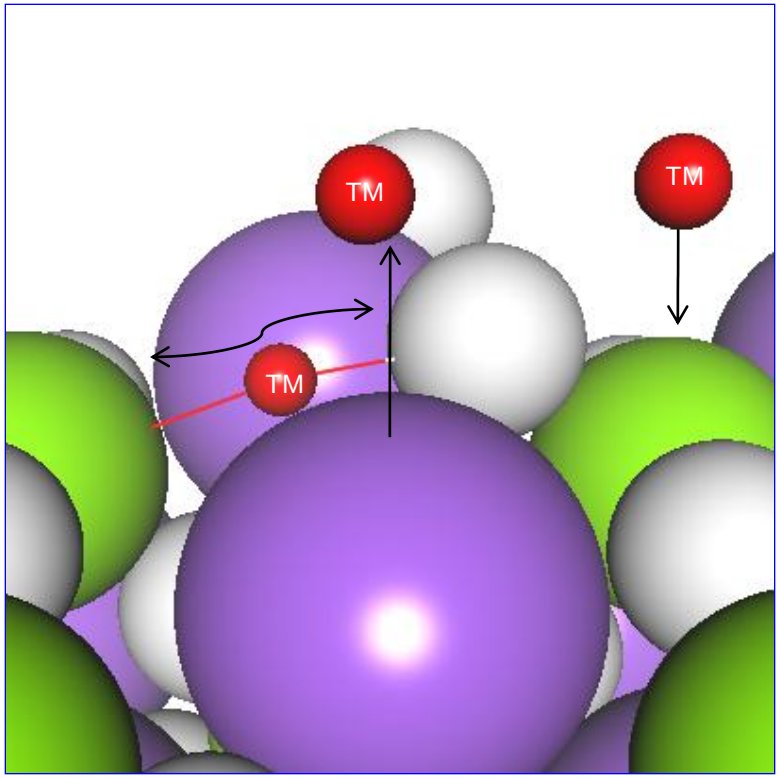
Two layered 001 surface with 5.40 Å vacuum gap (8 f.u.)

Models

Surface Models with Possible Sites for Dopants



Transition Metal at Na site

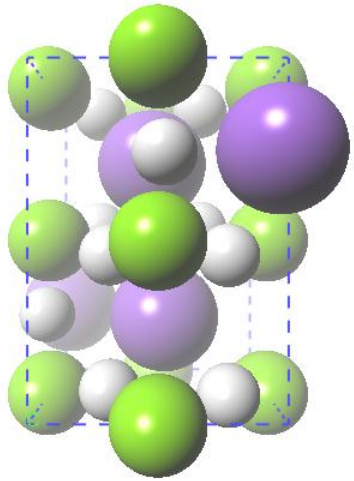


Transition Metal at hollow, Mg, and bridge site

Pure Crystal Structure

Structural and Electronic Properties of Pure Crystal Structure

- Ground State Structure
  - Geometry optimization performed for the orthorhombic structure using (PW91/USPP/400 eV)
  - Convergence check with respect to kinetic energy cutoff and k-point mesh
  - Lattice parameters, bond lengths and angles in agreement with experimental results. Δ Volume = <0.20%



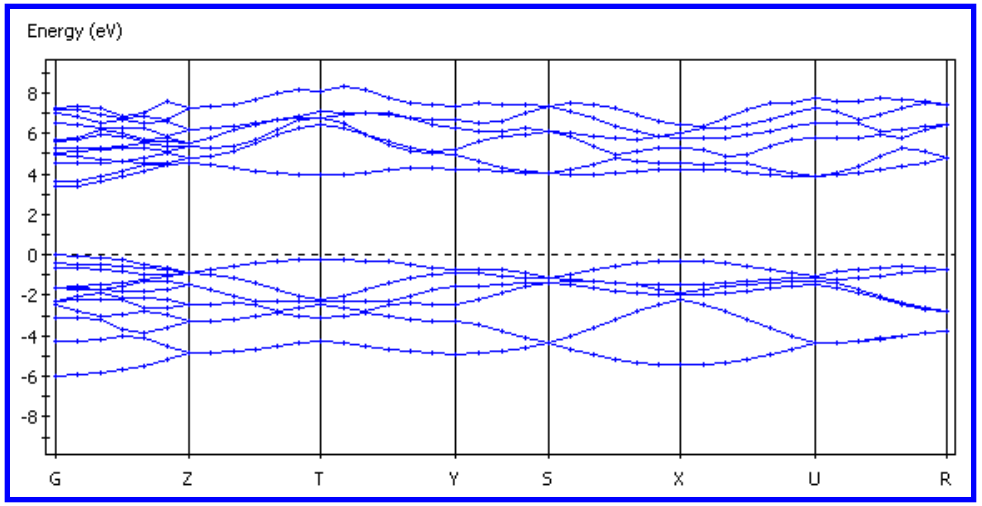
$NaMgH_3$ Optimized Cell, consisting of 2 f. u.

Lattice Constant	Lattice Parameter (Å) Experimental	DFT-PW91 Results
a	5.463	5.48
b	7.703	7.68
c	5.411	5.40

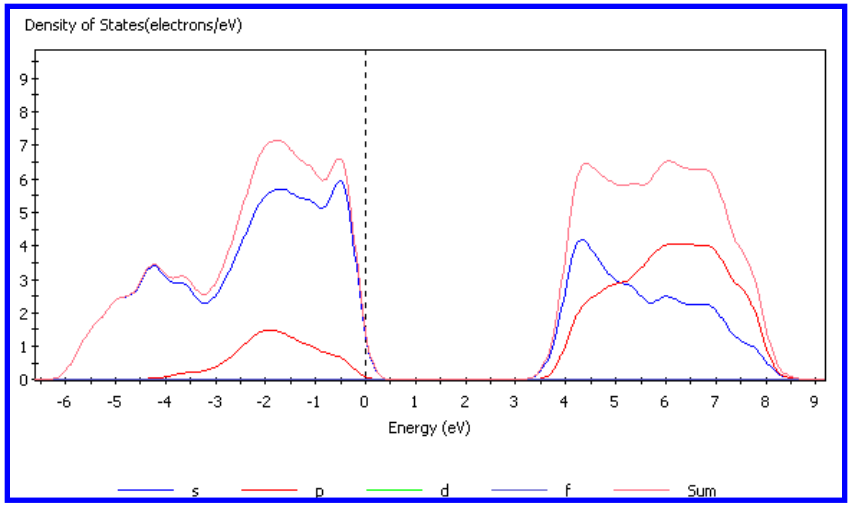
Pure Crystal Structure

Structural and Electronic Properties of Pure Crystal Structure

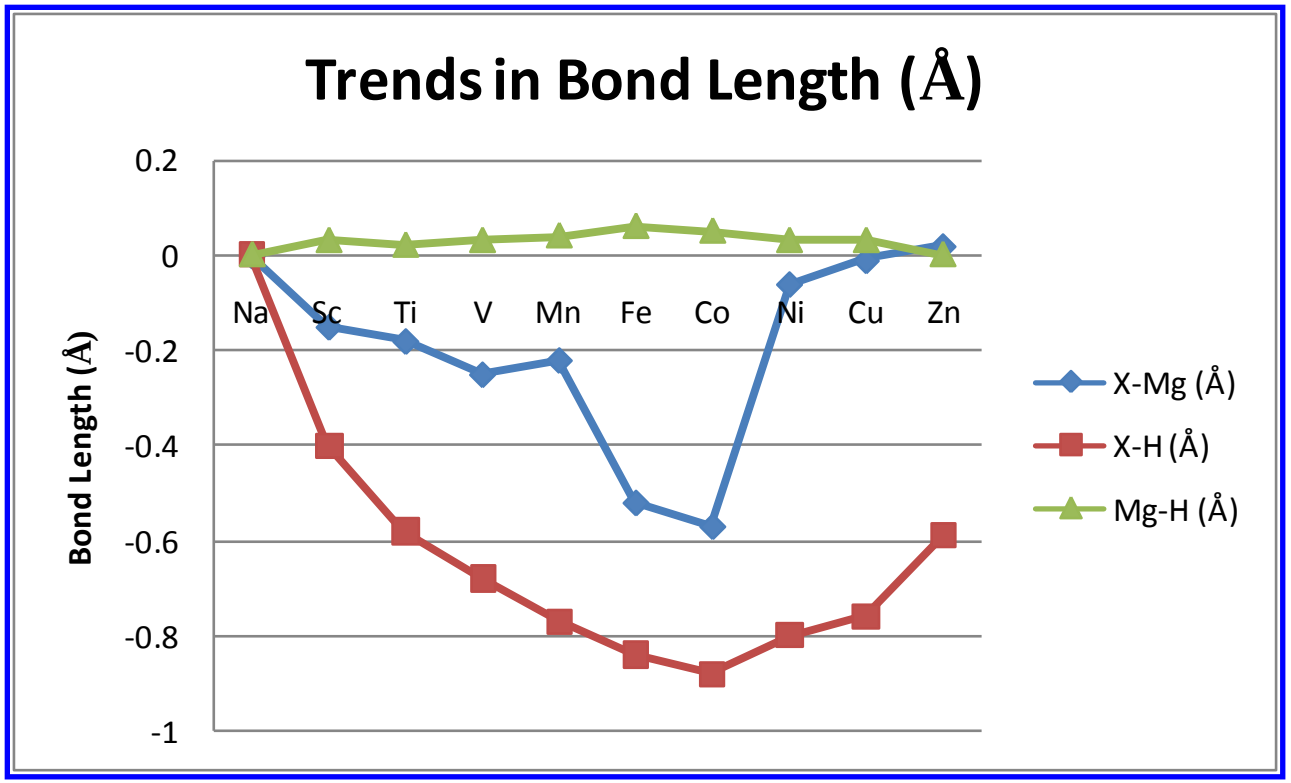
- Electronic Properties
  - Insulator with energy gap of 3.35 eV. Similar to values found in literature (3.3-3.5 eV)

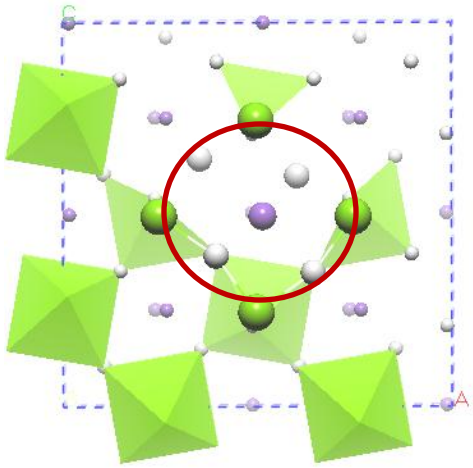


- Electronic Properties
  - Partial Density of States (PDOS) shows Interaction between Na and MgH3 is ionic and that between Mg and H comprises both ionic and covalent character.



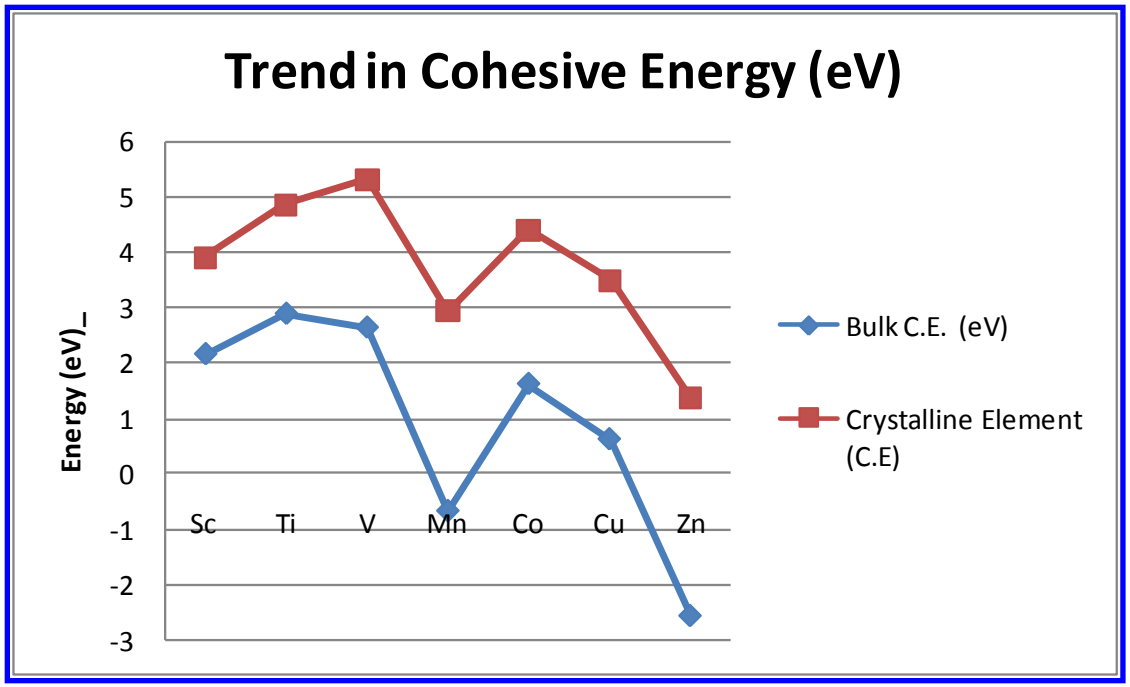
Bulk Model Results for 3d Transition Metals

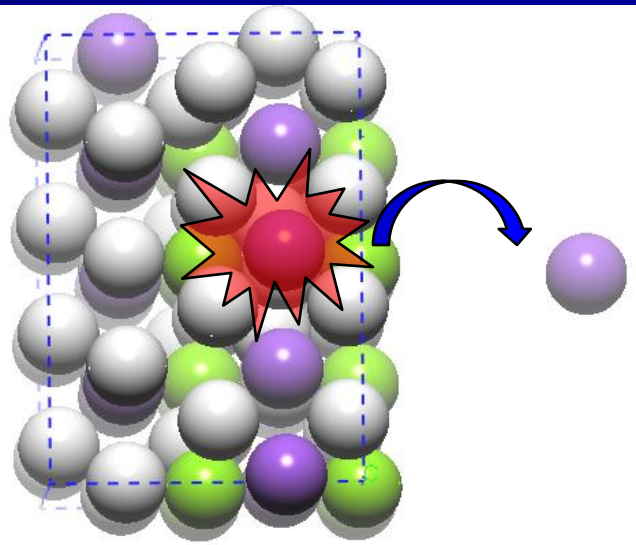




- Where X : Na, Sc, Ti, V, Mn, Fe, etc
- Elongation and possible weakening of Mg-H bond when Ti, V, Mn, Fe, and Co substitutes Na at Na site

Bulk Model Results for 3d Transition Metals (continued)



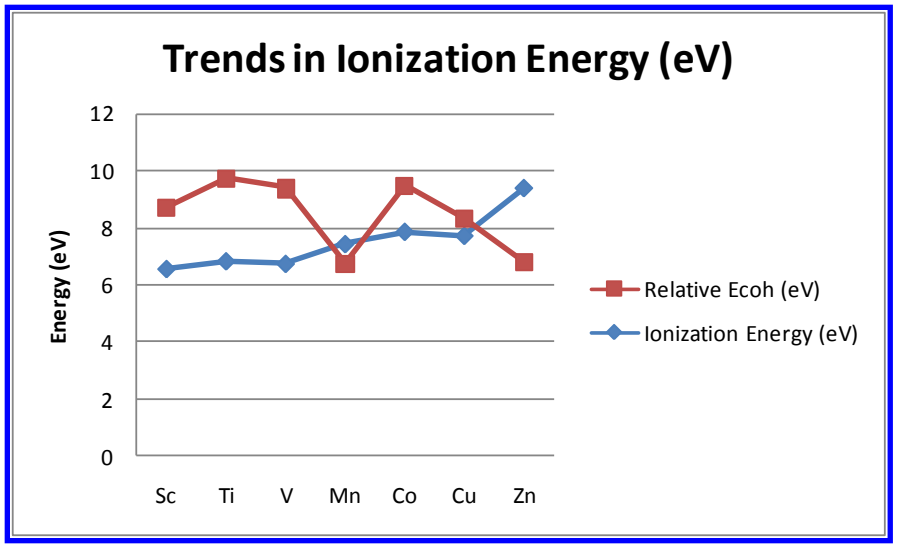


➢*Cohesive Energy is calculated relative to the pure model

➢The higher the cohesive energy in crystalline element, the higher the energy in bulk model.

➢$E_{cohesive} = E_{total\ system} - \sum E_{free\ neutral\ atoms}$

Bulk Model Results for 3d Transition Metals (continued)

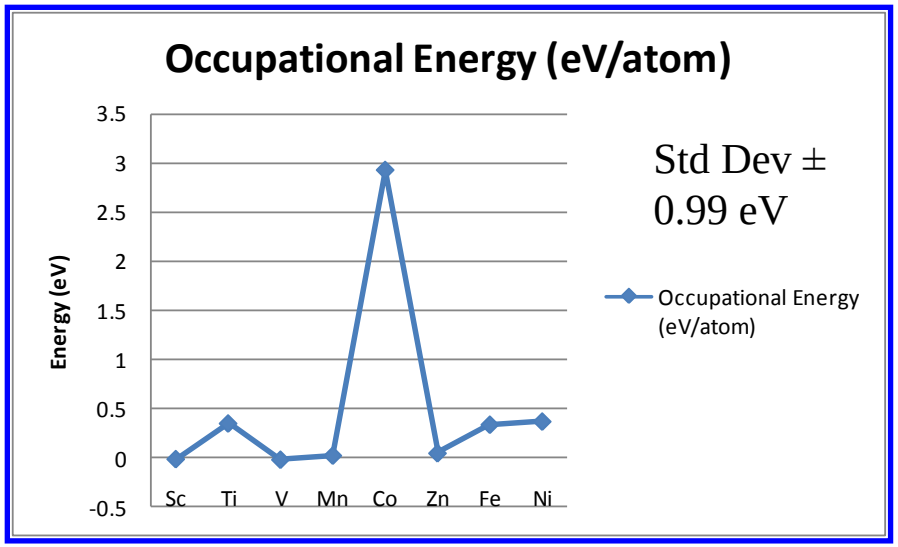


- Ti and Zn for further study, representing LHS and RHS of periodic table

- $E_{add/sub} = (E_{Doped\ system} - E_{pristine\ system})/N$

- Transition elements with higher ionization potential (RHS) lowers cohesive energy of system, leading to destabilization of the bulk model

- Elements in LHS show increased association with Mg and H



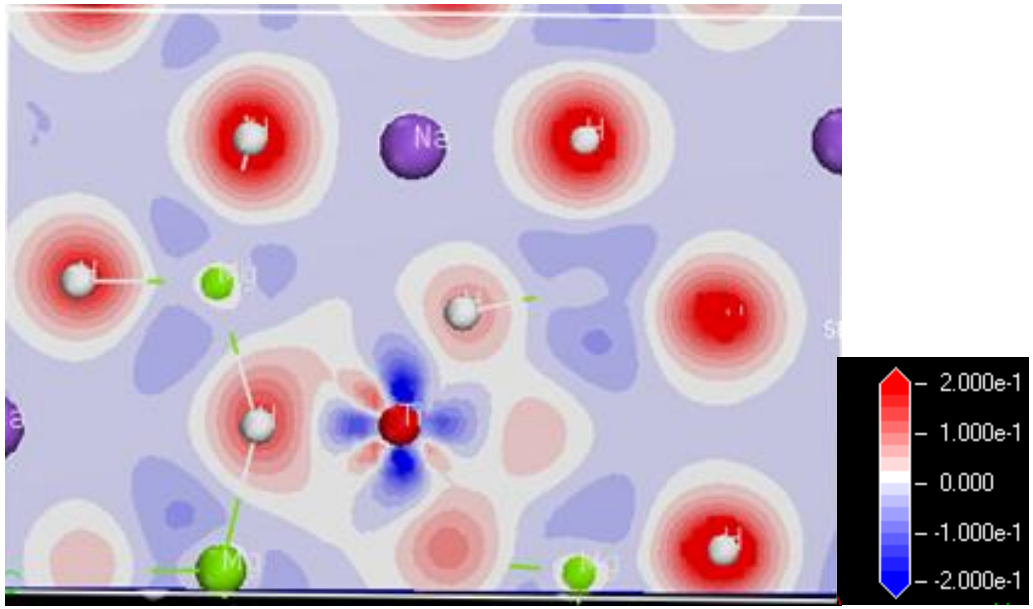
Bulk Dehydrogenation Energy Comparison (Ti/Zn)

Model	Dehydrogenation Energy (eV)/H_2
Pure	0.00*
Zn-doped	-1.31*
Ti-doped	-1.38.

*Energy relative to Pure Model

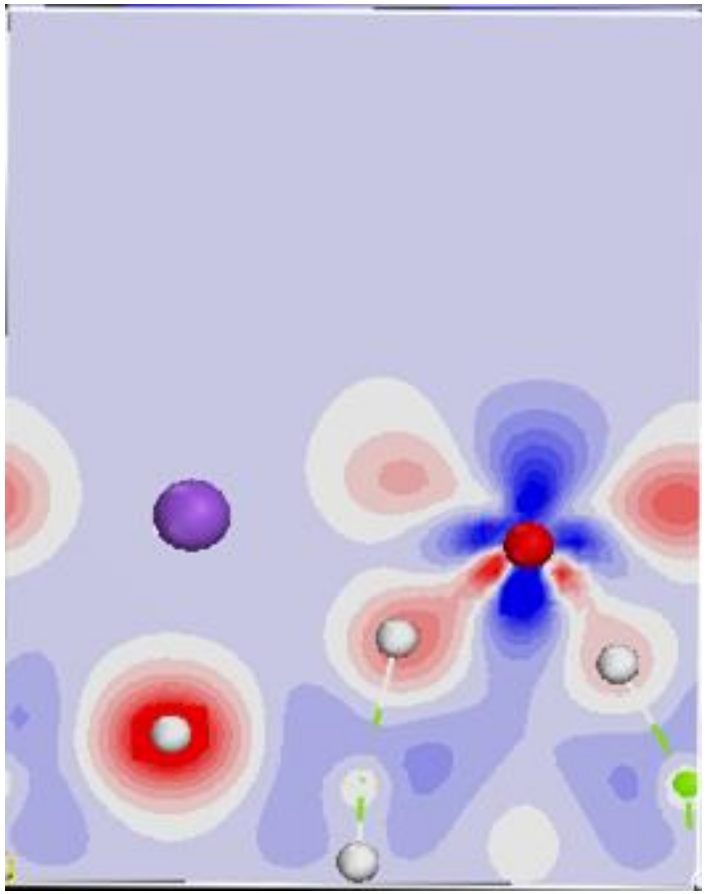
$$\Delta E = E(X)Na_{15}Mg_{16}H_{48} - (E(X)Na_{15}Mg_{16} + 24EH_2)$$

Surface Density Difference Map (Ti-doped)



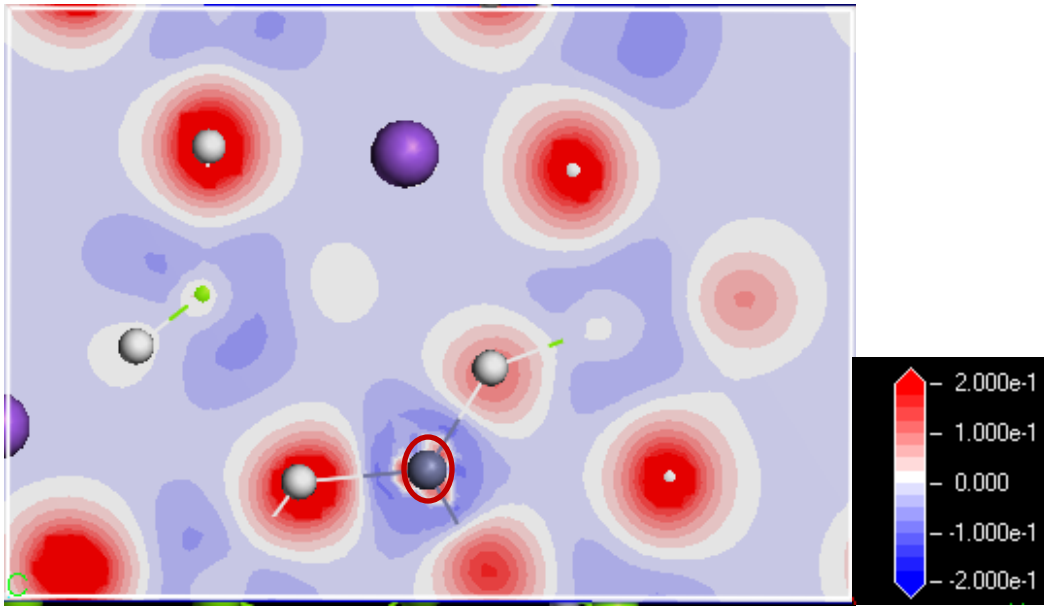
(View parallel to x and y axis)

- Loss of electrons is indicated in blue, while regions rich in electrons are indicated in red. White colors indicate regions with small changes in the electron density

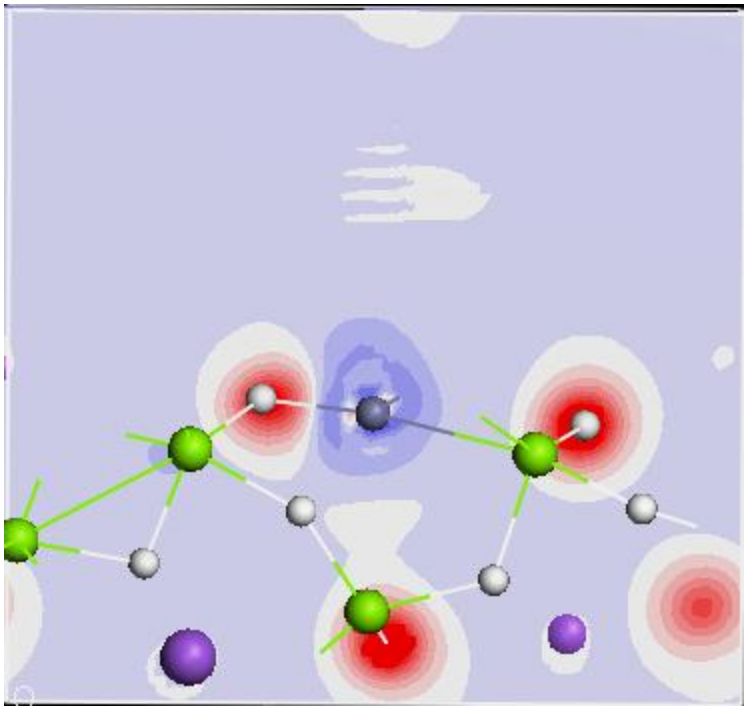


(Side View)

Surface Density Difference Map (Ti-doped)



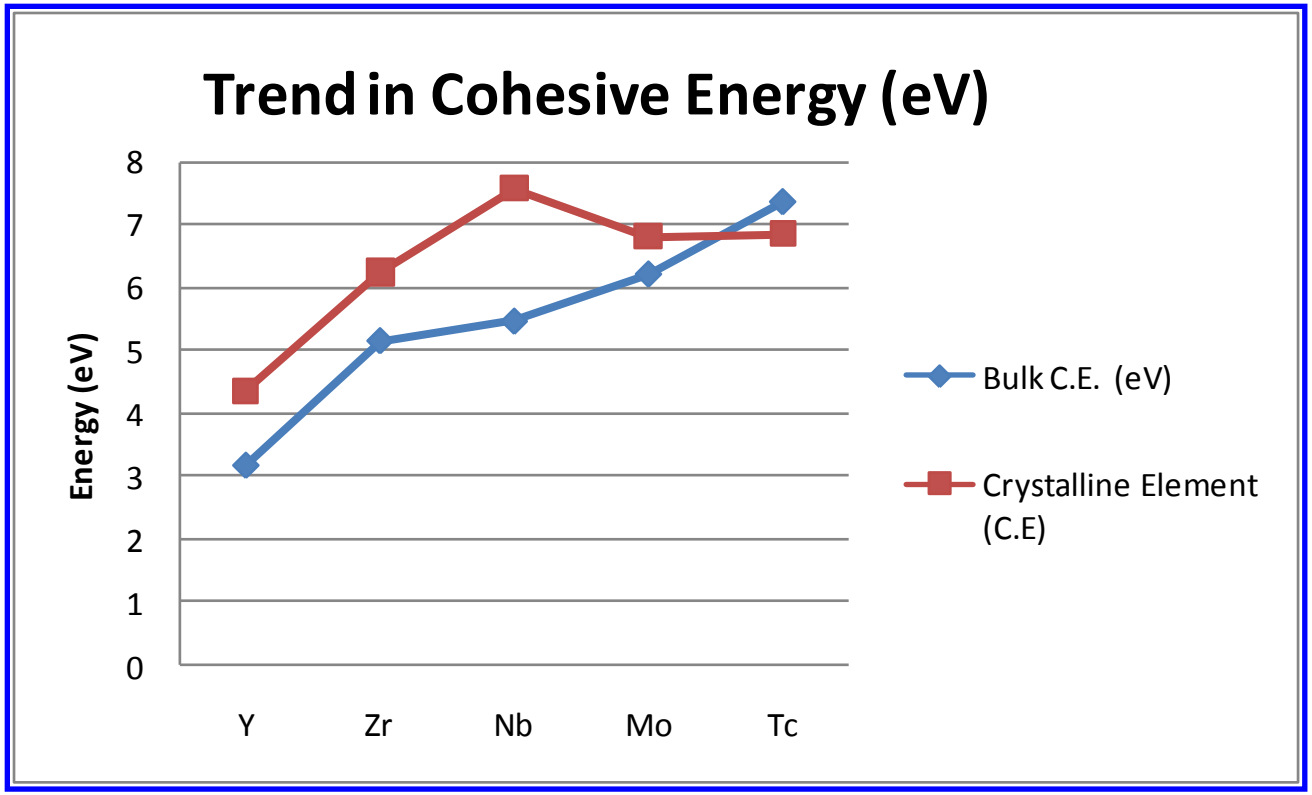
(Top View)



(Side View)

- Blue region in Ti-doped model is more intense.
- Signaling greater depletion of electrons to surroundings

Bulk Model Results for 4d Transition Metals



- For the 4d block, all the models show a high positive cohesive energy with respect to the pure model
- Models are stable, formation of alloys is possible
- Tc has a C.E. 2.5 times greater than Ti

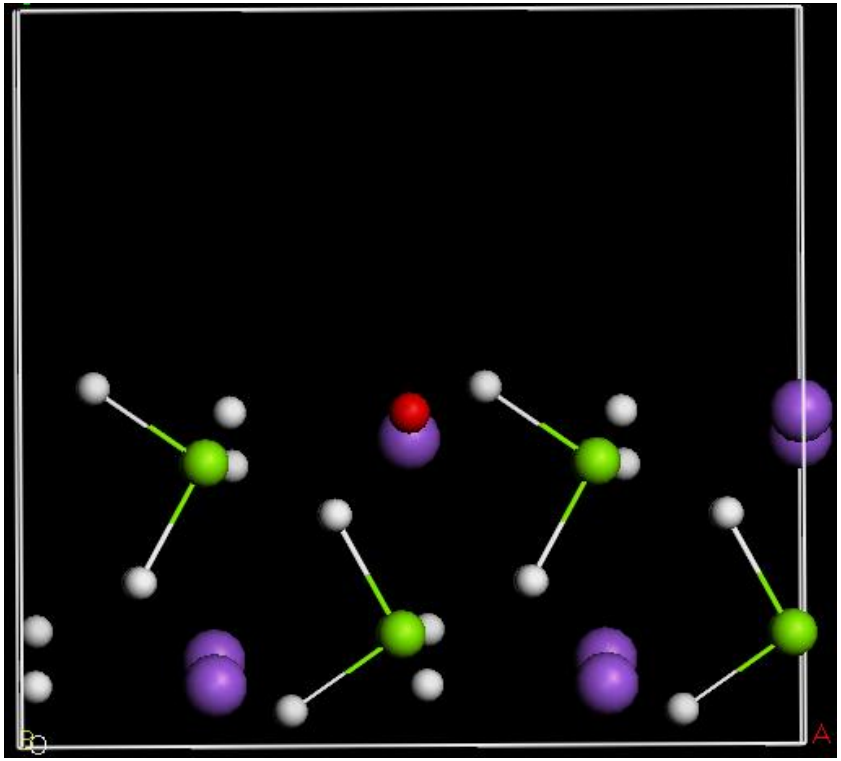
(001) Surface Energy

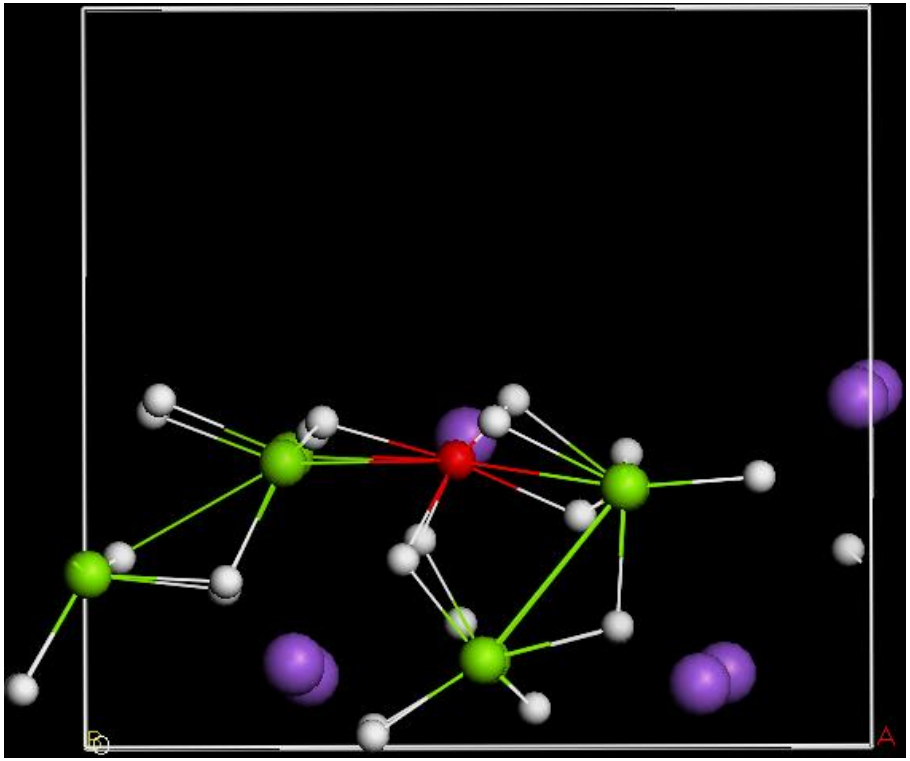
Site	System	E_{coh} (eV)	$\triangle E_{add}$(eV/ atom)
Ti@ Na site	$TiNa_7Mg_8H_{24}$	4.60	-
Ti @ Hollow Site	$TiNa_8Mg_8H_{24}$	5.47	0.13
Ti@ Top Na site	$TiNa_8Mg_8H_{24}$	3.22	0.08
Ti@ Top Hollow Site	$TiNa_8Mg_8H_{24}$	3.22	0.08
Ti@ Mg Site	$TiNa_8Mg_7H_{24}$	4.23	0.11
H removed from Ti@ Na site	$TiNa_7Mg_8H_{23}$	3.05	-
H removed from Pure model	$Na_8Mg_8H_{23}$	-3.46	-

- ** Cohesive energy is relative to pure model
- **Most favorable models : Ti @ Na site and Ti @ Hollow site**
- Ti@ Top Hollow site and Ti @ Top Na site have same cohesive energy
- Ti@ Mg site is more favorable than Top Hollow and Top Na site
- More favorable to remove hydrogen from Doped model

(001) Surface Geometry Optimization

Surface Models: Possible formation of alloys resulting from doping – Ti @ Na





$TiMg_4H_6$

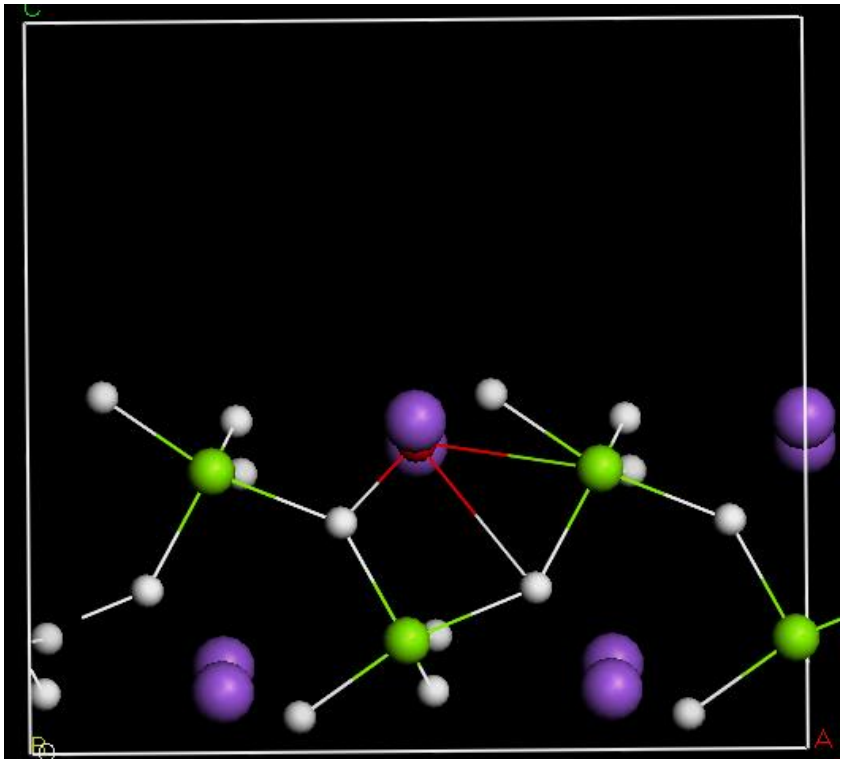
Avg Bond Length (Å) :

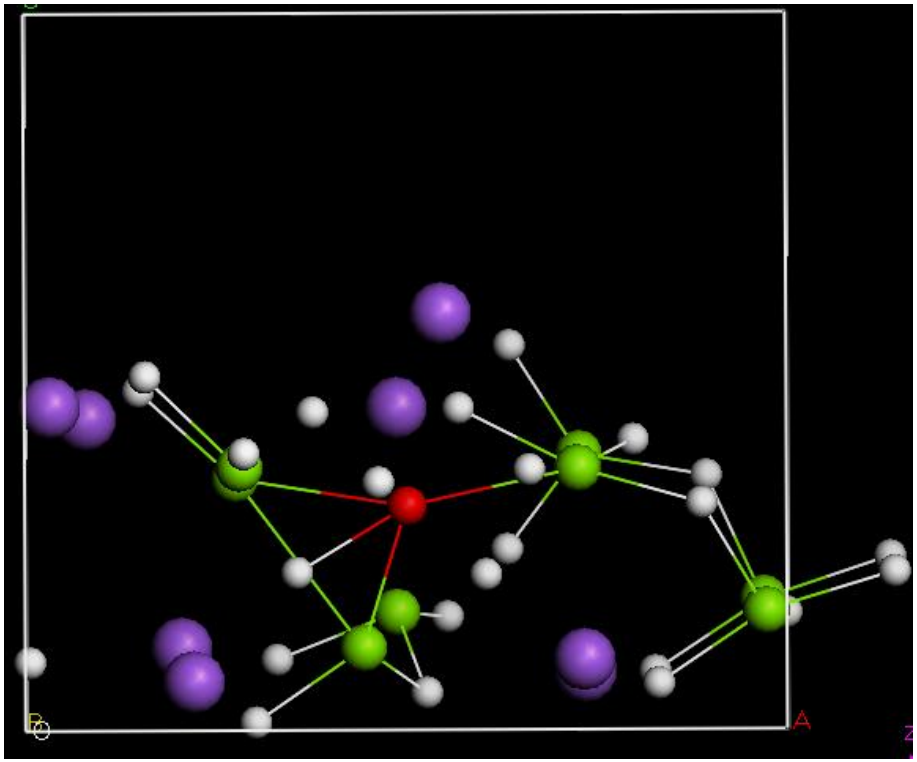
Ti-H = 1.90

Ti-Mg = 3.04

(001) Surface Geometry Optimization

Surface Models:– Ti @ Hollow Site





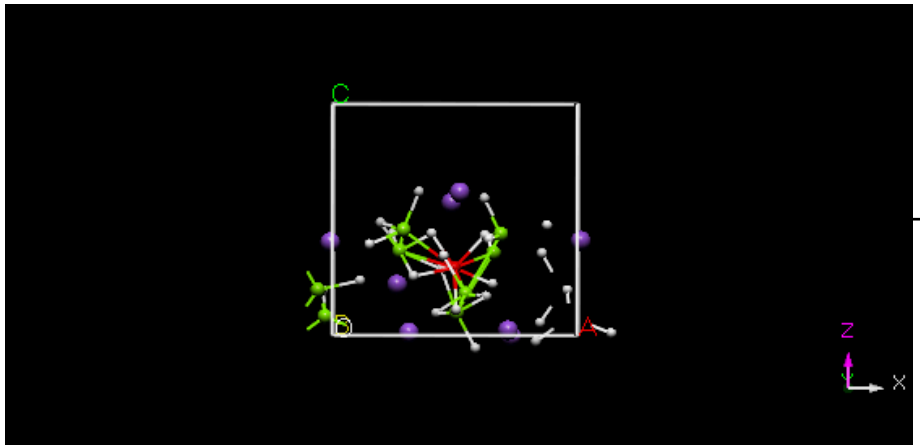
$TiMg_5H_7$

Avg Bond Length (Å) :

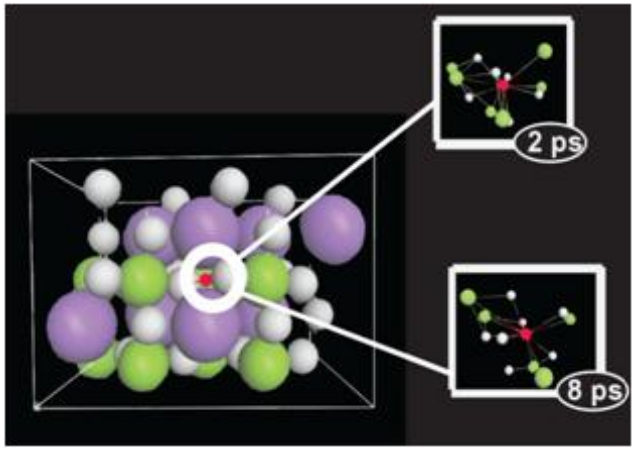
Ti-H = 1.93

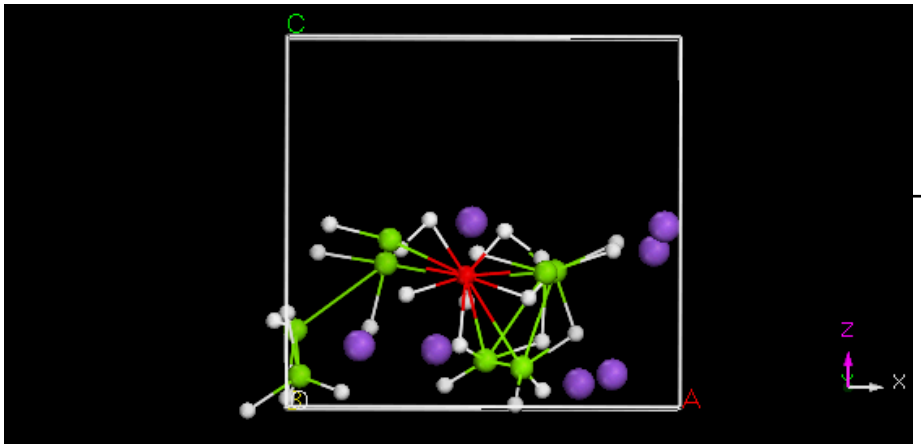
Ti-Mg = 2.94

Dynamic Results : (Ti) $NaMgH_3$

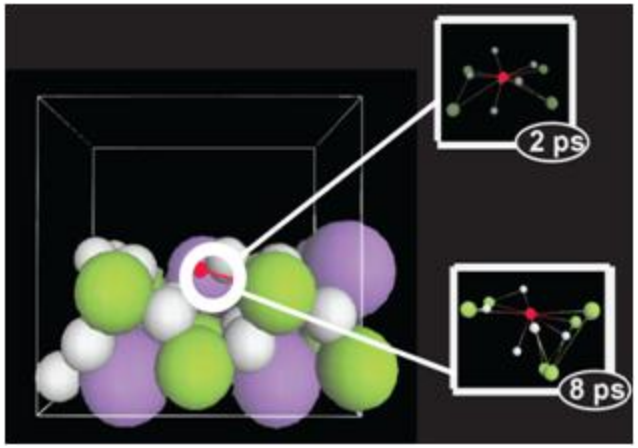


DFT-MD @ Interstitial Site





DFT-MD @ Na Site



Conclusion

- Cohesive Energy may be useful physical quantity for evaluating hydrogen desorption ability

- High Ionization energy of RHS dopants is responsible for thermal stability

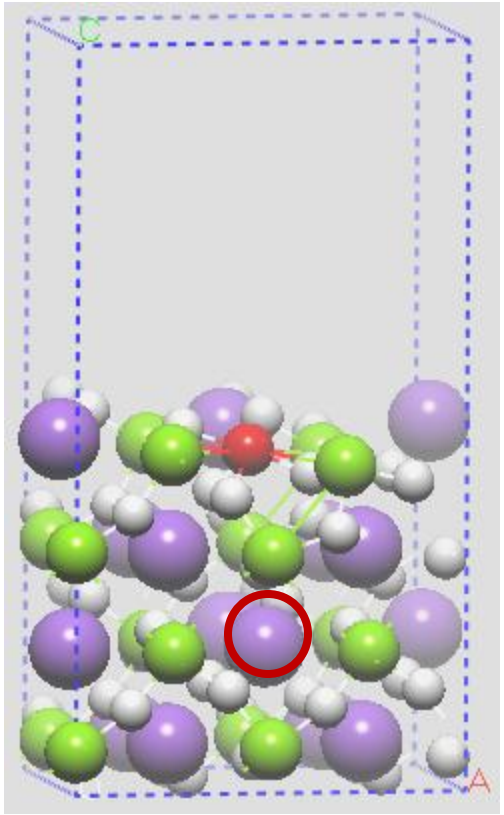
- Site preference of dopants determined by cohesive energy, atomic size and ionization energy

- Ti-Mg_xH_x complexes are observed after geometry optimization of doped-surface models

- DFT coupled MD simulations show the existence of Ti-Mg_xH_x,

- Substitution and addition energy of surface models show that Ti @ Hollow site and Ti @ Na lattice site have almost equal energies
- Ti-doping helps increase hydrogen mobility (hopping)
- Hydrogen mobility is not rate-limiting process in this system

Future Work : Synergistic Effect of TMs as Co-Dopants



Surface

Sub-Surface

Bulk

- Study this system with Zn as co-dopant
- Study Hydrogen Desorption from surface with Ti at surface and Zn at the bulk site (Core-Shell model)
- Determine the rate-limiting step in hydrogen desorption from surface
- Molecular Dynamics on Zn-model and other dopants such as C

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