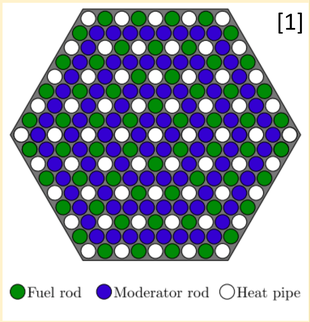
First-principles modelling of hydrogen stability and transport in candidate nuclear microreactor moderator and cladding materials

Aditya Sundar[1], Jianguo Yu[2] and M Nedim Cinbiz[2]

[1]Materials Science and Engineering, University of Michigan, Ann Arbor, MI, 48109, [2]Idaho National Laboratory, ID, 83415

aditya.sundar@inl.gov
adisun@umich.edu

Background and Motivation



Hydrogen containing solid hydride moderators provide efficient neutron moderation and offer compact nuclear reactor designs. However, at high temperatures, hydrogen can desorb from the solid-state moderator which may impact the criticality and operational safety of these reactors. Therefore, it is important to investigate hydrogen stability and transport in solid-state moderator and cladding materials. This helps to establish the operation and safety envelope of these reactors.

In this work, we research the hydrogen retention properties in YH_2 (moderator) and FeCrAl + Al_2O_3 (cladding). The key scientific enquiries of our work are:

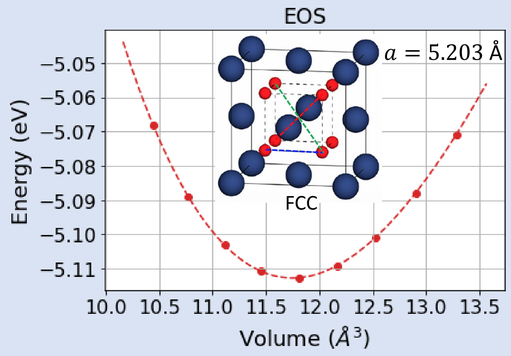
1. What is the temperature dependent self diffusivity of H in YH_2?
2. How do impurities (O) and alloying elements (Cr, Cd, Rb, Ag) affect H retention in YH_2?
3. What are the binding characteristics of H with elements in FeCrAl?
4. Does the charge state of H significantly affect transport in Al_2O_3?

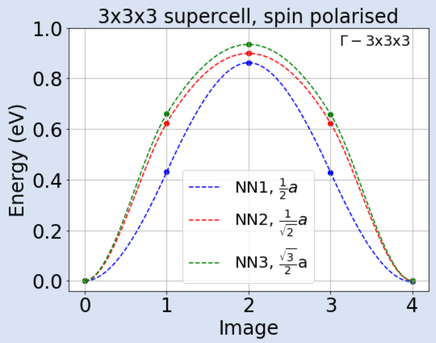
The desired/targeted properties are slow hydrogen diffusion in YH_2 and FeCrAl, so that thermal neutrons can be generated to sustain the fission reaction.

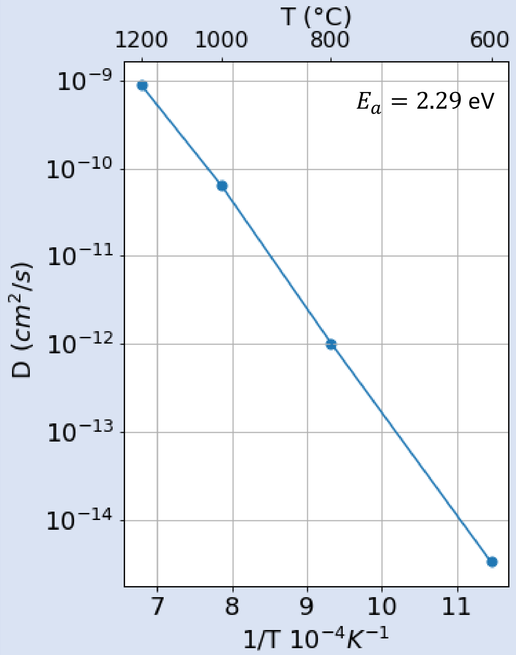
Methodology

1. Density functional theory calculations implemented in VASP, to calculate formation energy and binding energy.
2. Climbing image nudged elastic band (CI-NEB) calculations in VASP, to calculate migration barriers
3. Kinetic monte carlo simulations implemented using a python script

Hydrogen stability and transport in YH_2







Vacancy formation energy

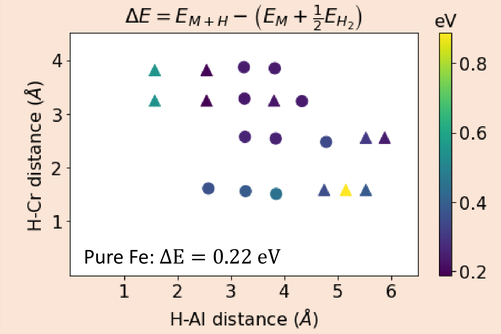
$$E_f(V_H) = [E(S_V) + \epsilon_{ZPE}] - [E(S) + \epsilon_{ZPE}] + \frac{1}{2}\left[E_{H_2} + \epsilon_{ZPE} - TS_{\text{t+r+v}}\right] = 1.38 \text{ eV}$$

All energy barriers within 0.8 to 1.0 eV,

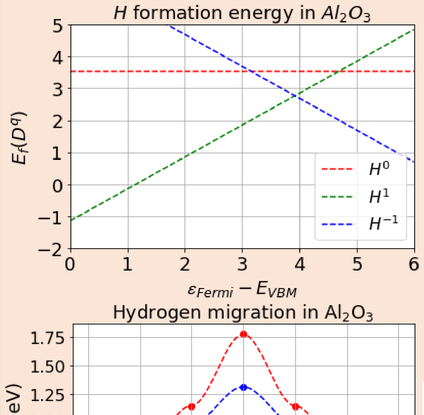
For 3D KMC, frequency $\nu = 10^{13}/s$
6 NN1, 12 NN2, 4 NN3 paths

$$D = \frac{1}{6}\frac{|\bar{r}_t - \bar{r}_0|^2}{\Delta t}$$

Hydrogen stability and transport in FeCrAl + Al_2O_3

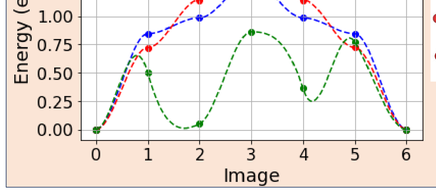


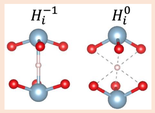
- Repulsive interaction[2] between H and Fe-Cr-Al
- H is not soluble in FeCrAl alloys[3]



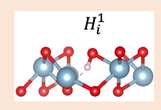
$$E_f(H^q) = E_{total}[Al_2O_3 + H^q] - E_{total}[Al_2O_3] - \frac{1}{2}[E_{H_2}] + q(E_{VBM} + \epsilon_{Fermi})$$

H^1 and H^{-1} are predominant charge states



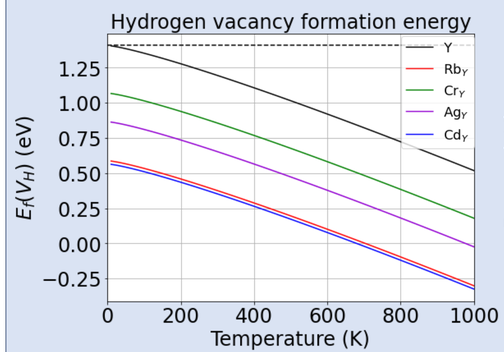


Symmetric energy profiles[4].



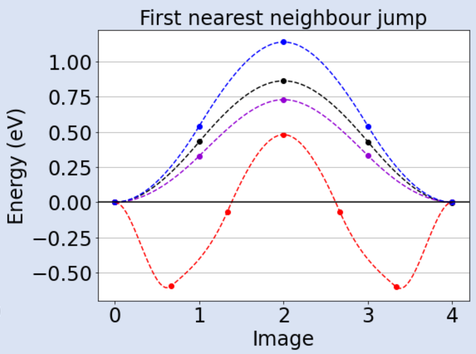
Asymmetric energy profile.

Impurities and alloying elements in YH_2

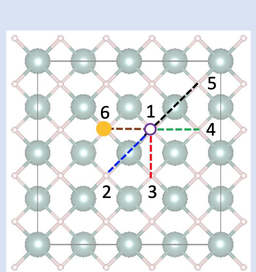


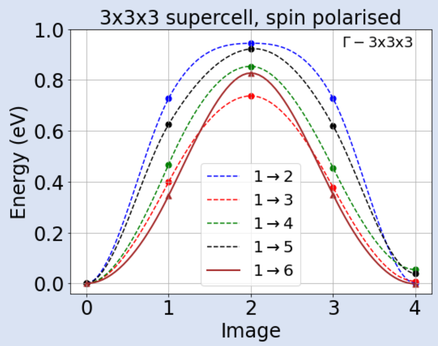
Thermodynamically easiest to form H vacancy near substitutional elements Cd and Rb

$E_f(V_H) = \sim 0.6$ eV at 0 K



NN1 jump barrier in YH2 = 0.86 eV
NN1 jump barrier with Cd or Rb = 1.1 eV





The filled yellow circle represents an O atoms. The empty circle represents a vacancy on the interstitial sites. For the shown hopping paths, the barrier varies by ±0.1 eV compared to pure YH_2.

Conclusion

1. YH_2 is a promising nuclear moderator, as shown by the large activation energy barriers (~2.3 eV) from KMC simulations.
   - Alloying with Cr, Ag, Cd, Rb has a negative effect on H retention
2. FeCrAl is a strong candidate for application as cladding material due to low H solubility.
   - Cr/Al addition makes the metal-H interactions even more repulsive (H binding energy is more positive).
   - Passive Al_2O_3 also poses high energy barriers for H transport

Future work

1. Improving KMC simulations by calculating quantum corrections to the energy barriers in YH_2.
2. Hydrogen binding energy calculations with Ti and Y as minor alloying elements in FeCrAl.
3. Searching for other promising moderators and cladding materials using DFT

References

[1]. Shivprasad et al., J. Alloys Compounds 826, 153995 (2020), [2]. Jiang et al., Physical Review B 70, 064102 (2004), [3]. Samin et al., Physical Review B 99, 014110 (2019), [4]. Yu et al., J. Chem. Phys. 134, 064111 (2011)