Effects of point defects and impurities on kinetics in $NaAlH_4$

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Support: DOE
University of California Energy Institute

DOE Theory Focus Session on Hydrogen Storage Materials
San Francisco, California
March 24, 2008

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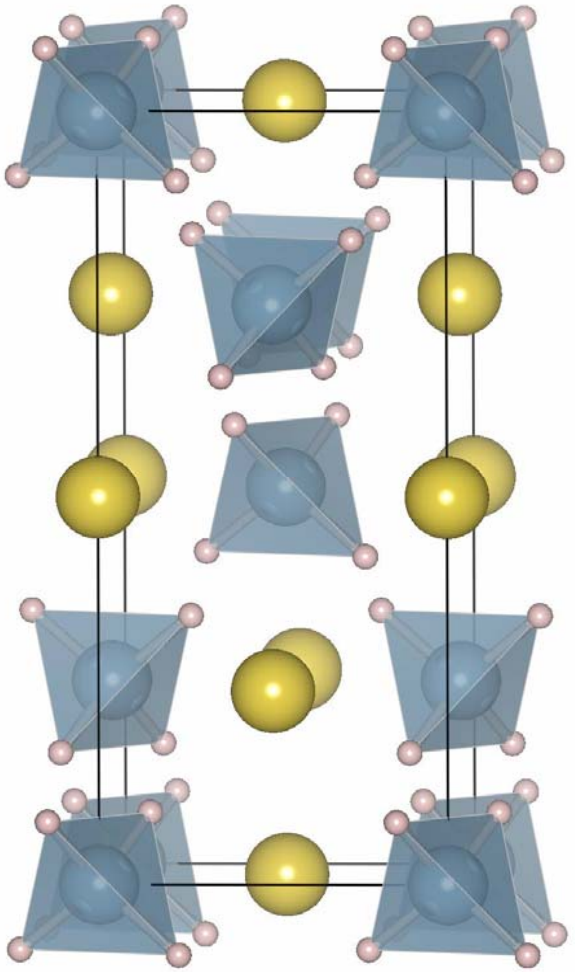
Sodium Alanate

- **Viable hydrogen storage material (5.6 wt%)**

  $NaAlH_4 \leftrightarrow 1/3\ Na_3AlH_6 + 2/3\ Al + H_2$

  $Na_3AlH_6 \leftrightarrow 3\ NaH + Al + 3/2\ H_2$

- **But: reactions slow**
  - Only happen at too high temperature
- **Addition of transition metals (Ti) was found to speed up kinetics**
  - Bogdanovic *et al.*, J. Alloys. Compd. **253**, 1 (1997).
  - Explanation?



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Hydrogen in storage materials

- **Calculations of bulk properties**
  - Formation enthalpy, …
  - Valuable information, but does not directly address kinetics
- **How does dehydrogenation take place?**
  - "One hydrogen at a time"
  - Imagine fully hydrogenated material as starting point
- **Treat hydrogen as a "defect"**
  - Move one hydrogen
    - » Hydrogen interstitial
    - » Hydrogen vacancy
  - Point defects well known to be involved in diffusion
  - May also serve as nucleation sites for new phases
- **Study with first-principles computations**
  - Formation energies
    - » Likelihood of a certain defect occurring
  - Diffusion

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Calculations

- **Density functional theory (DFT) (VASP)**
  - Generalized gradient approximation (GGA) for exchange-correlation
  - Projector augmented wave (PAW) pseudopotentials
  - VASP
- **Plane-wave expansion with cutoff 450 eV**
- **96-atom supercell geometry**
  - 2 x 2 x 2 k-point grid
- **$NaAlH_4$:**
  - Insulator, E_g = 4.75 eV (GGA); 6.9 eV (quasiparticle calculation)
    - » Peles *et al.,* Phys. Rev. B **70**, 165105 (2004).
  - Formation enthalpy: -48.9 kJ/mol H_2

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Formalism

- **E_{form}: formation energy**

  Concentration:

  $$C = N_{sites} \exp [- E_{form}/kT]$$

- **Example: Hydrogen interstitial**

  $$E_{form}(H_i) = E_{tot}(NaAlH_4{:}H_i) - E_{tot}(NaAlH_4) - \mu_H$$

  μ_H: energy of hydrogen in reservoir, i.e., H chemical potential

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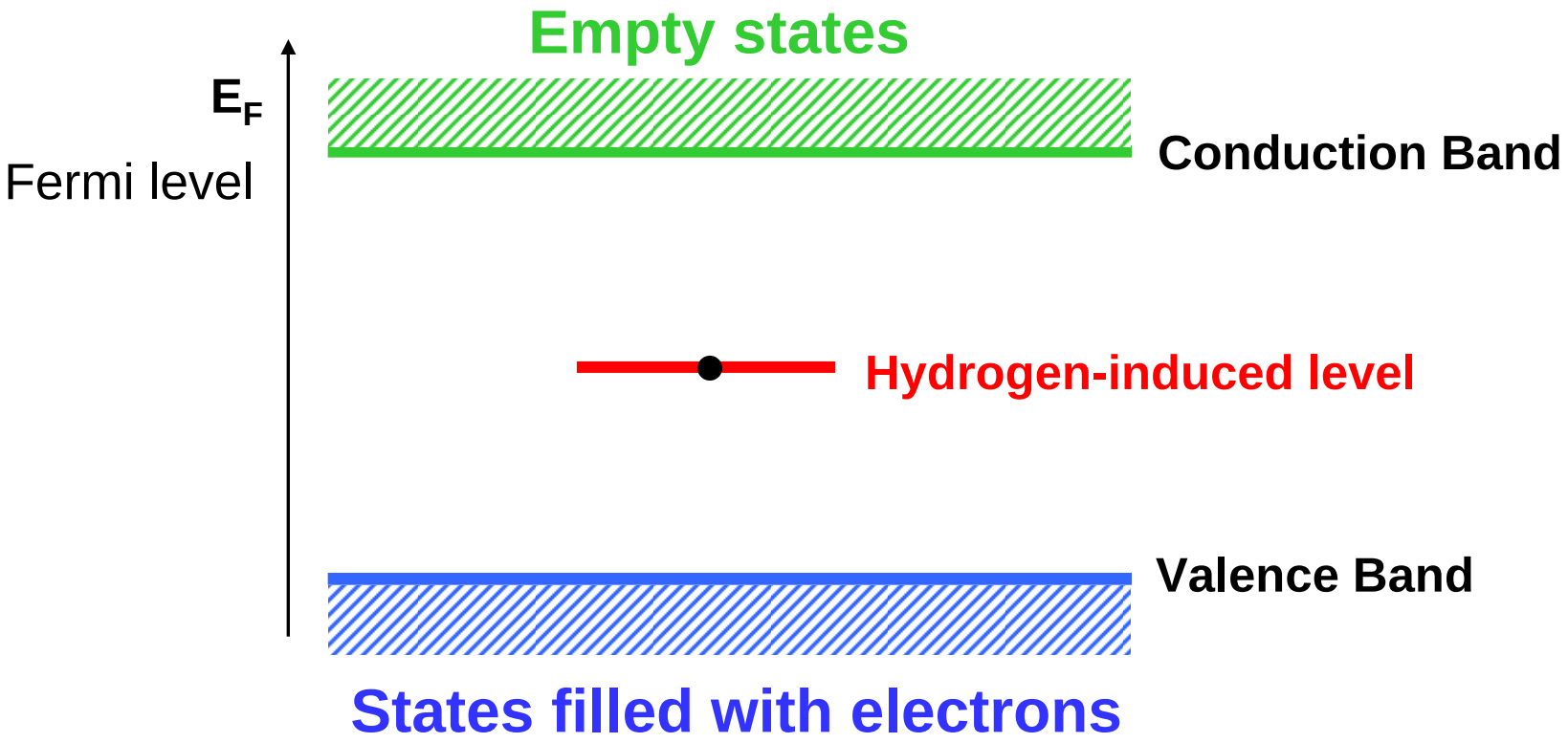
Hydrogen defect in an insulator



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- **H interstitial in *positive charge state***

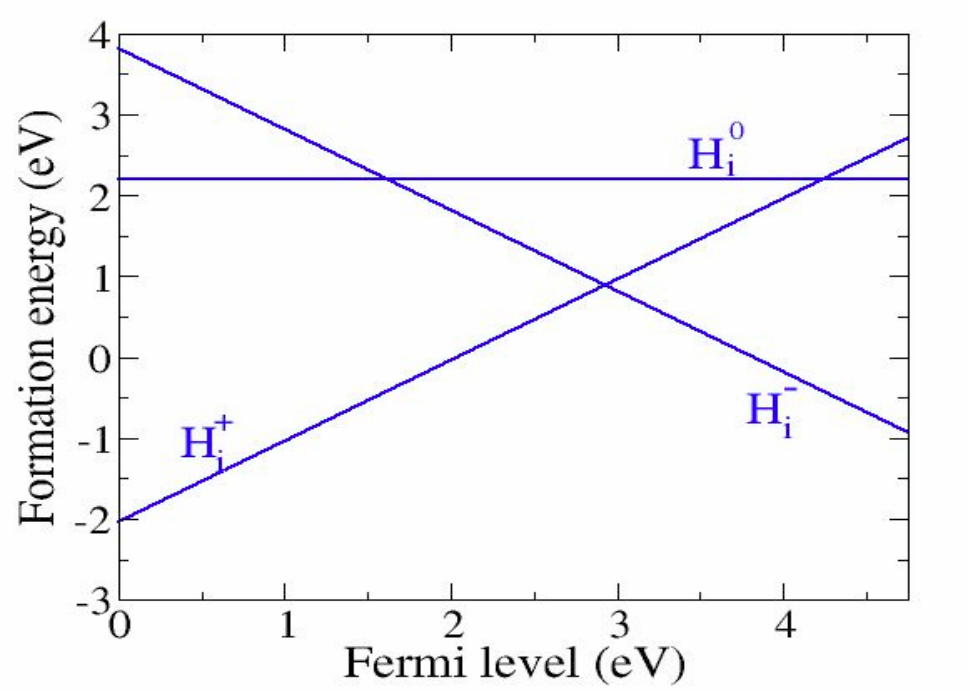
  $$E_{form}(H_i^+) = E_{tot}(NaAlH_4{:}H_i^+) - E_{tot}(NaAlH_4) - \mu_H + \mu_e$$

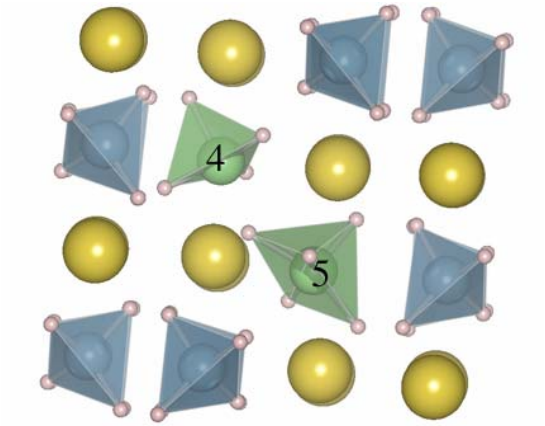
  μ_e : energy of electron in its reservoir, i.e., the Fermi level

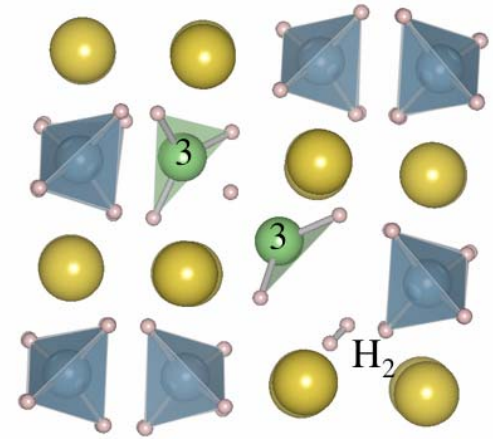
- **H interstitial in *negative charge state***

  $$E_{form}(H_i^-) = E_{tot}(NaAlH_4{:}H_i^-) - E_{tot}(NaAlH_4) - \mu_H - \mu_e$$

Hydrogen interstitials in $NaAlH_4$

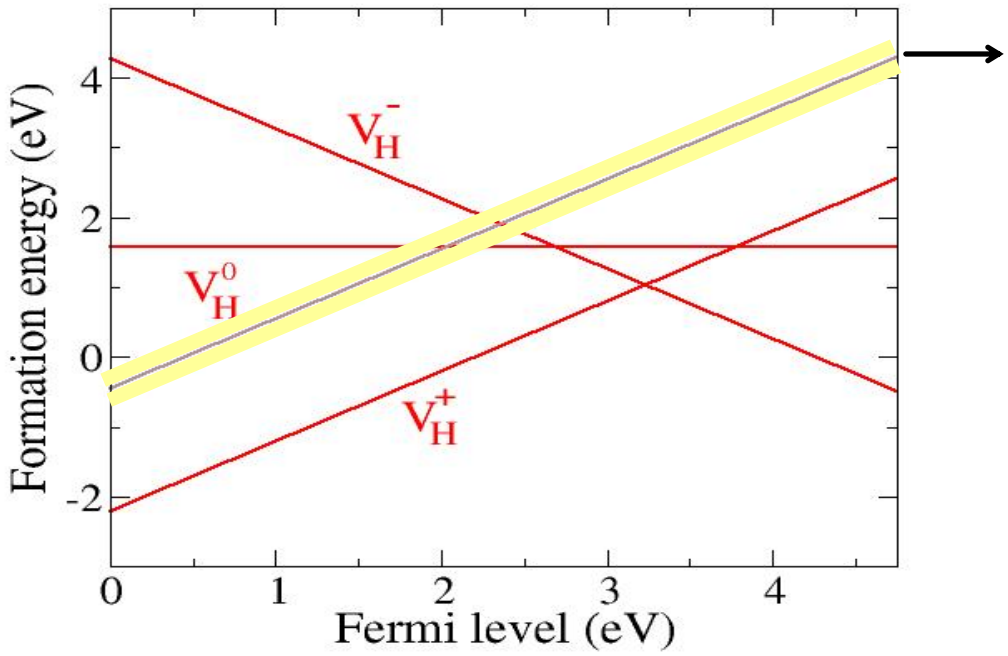






Hydrogen vacancies in $NaAlH_4$

- Remove a hydrogen atom: create a vacancy



V_H^+ without relaxation

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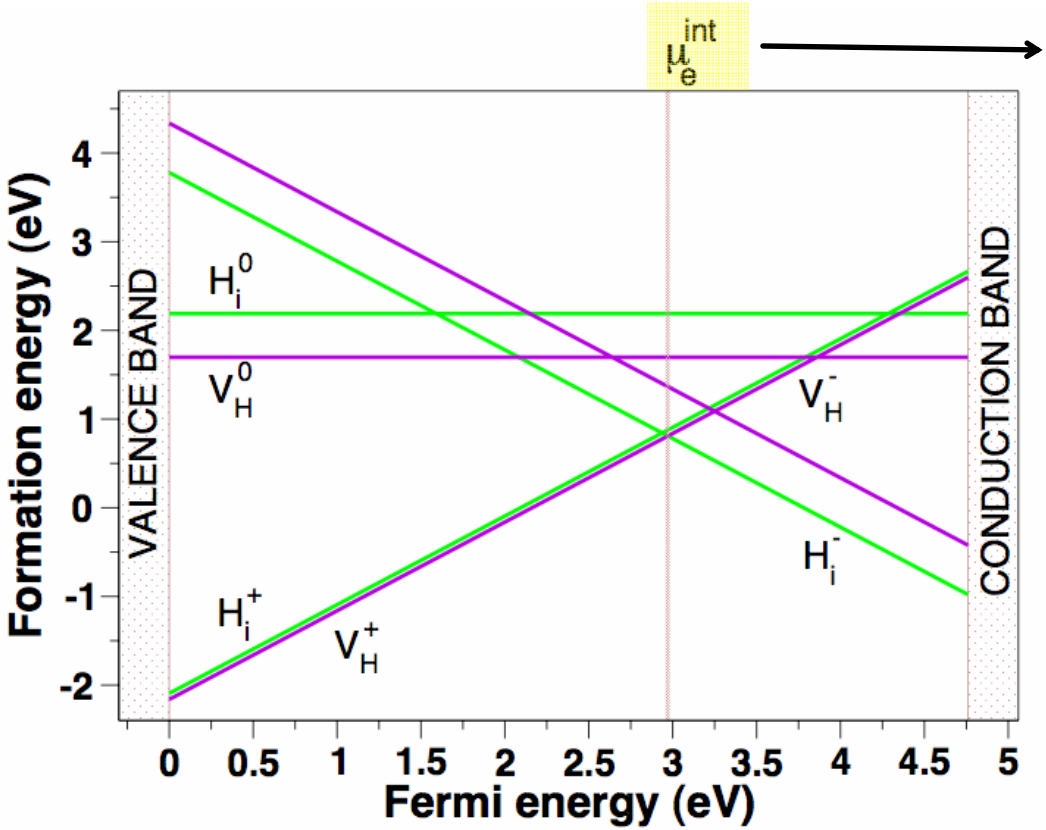
Interstitials *and* Vacancies

- H_i and V_H simultaneously present
- Charge neutrality!
  - Equal number of + and – defects



μ_e "pinned" at position where formation energies are equal

$E_{form}(V_H^+) = E_{form}(H_i^-)$

$= 0.81$ eV

At 100 °C:

$c\,(V_H^+) = c\,(H_i^-) \approx 10^{11}$ cm^{-3}

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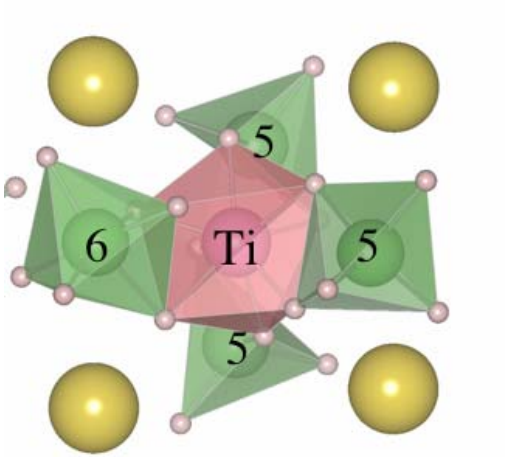
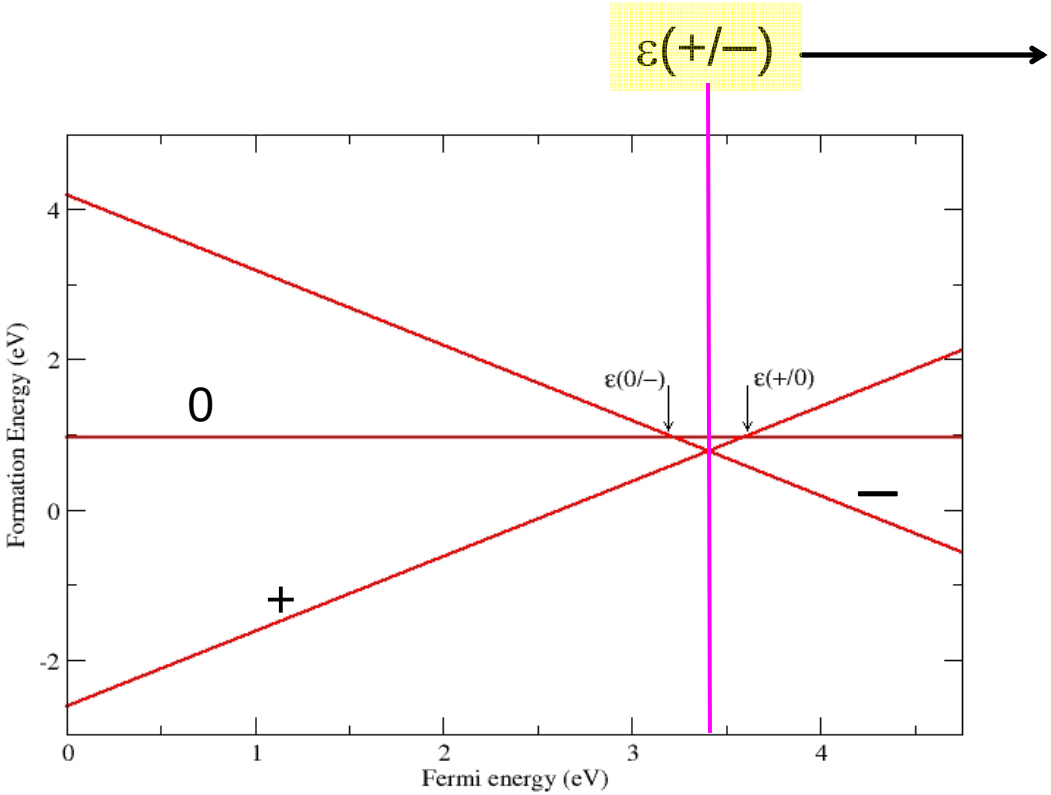
Titanium

- **Most stable on Al site**
- **Can occur in different charge states**





μ_e "pinned" at position where + and – have equal formation energies

(irrespective of Ti concentration, as long as exceeds defect concentration)

$\mu_e = \varepsilon(+/-) = 3.41$ eV

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A note on formation energies…

- Some papers in the literature seem to (implicitly or explicitly) assume that if a calculated formation energy is positive, the impurity will not incorporate.
- This is not correct. Remember:

  $C = N_{sites} \exp [- E_{form}/kT]$

- A *finite* positive formation energy can lead to a finite concentration.
- In fact, if the formation energy were *negative*, the material would be unstable in the presence of the impurity!

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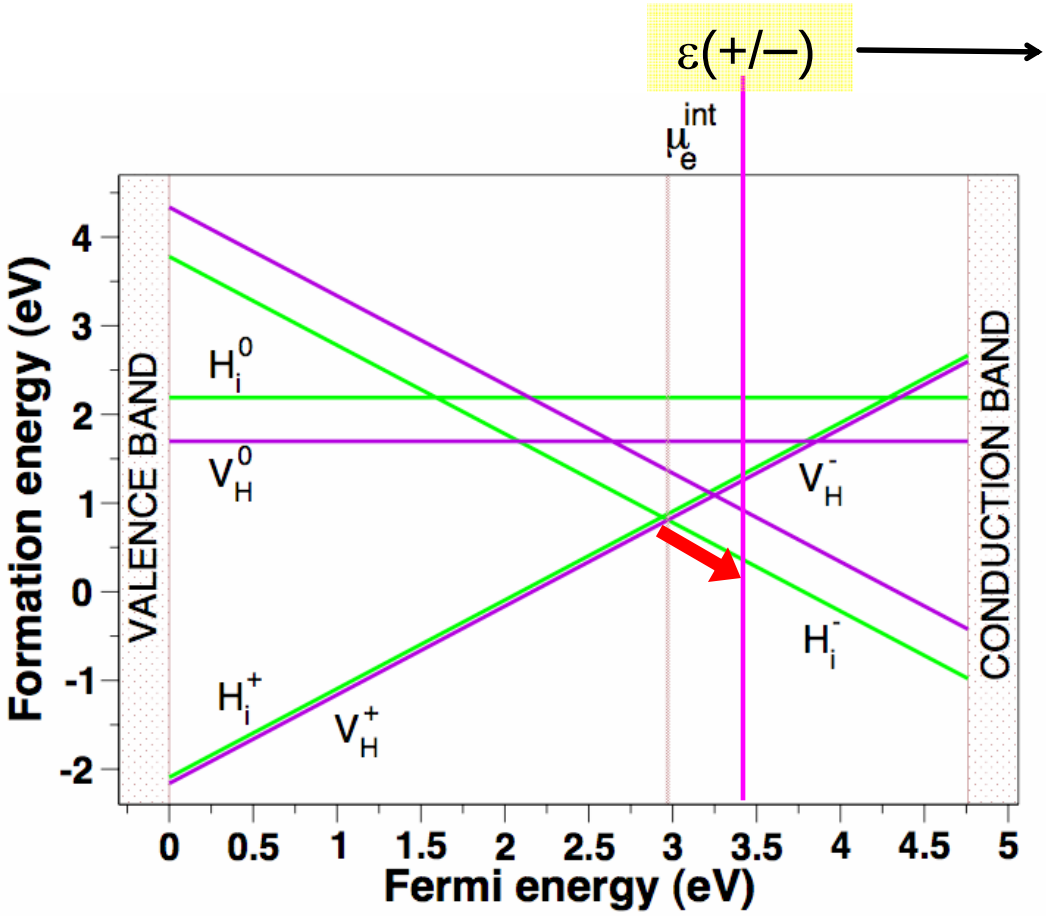
Interstitials & Vacancies *and* Titanium

- **Presence of Ti shifts μ_e away from μ_e^{int}**
- **Lowers formation energy of the defects!**



μ_e "pinned" at 0.44 eV higher value ⇒

$E_{form}(H_i^-) = 0.81 - 0.44$ eV

$= 0.37$ eV

At 100 °C:

$c\,(H_i^-) \approx 10^{17}$ cm^{-3}

(6 orders of magnitude higher than without Ti!)

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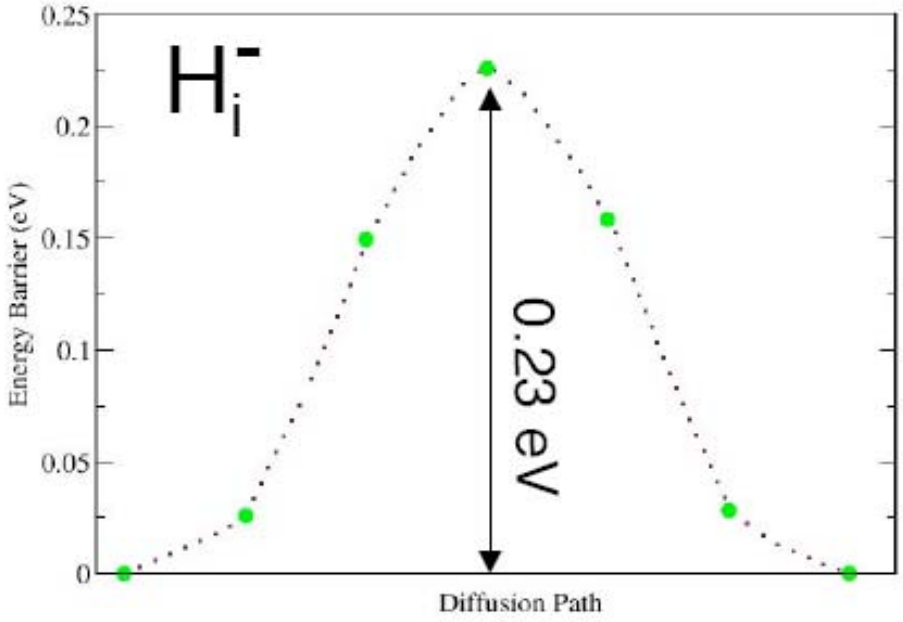
Diffusion

- Once the defects are created, they can move very fast
- Calculations of diffusion barriers



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Enhancement of kinetics

- **Ti: electrically active**

  $\Rightarrow$ shifts the Fermi level

  $\Rightarrow$ lowers formation energy of hydrogen-related defects (H_i^-)

  $\Rightarrow$ increases the concentration of the defect

  $\Rightarrow$ increase in self-diffusion

  $\Rightarrow$ allows achieving a given concentration of defects at a lower temperature

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Enhancement of kinetics

- **Typically several mol % of Ti are added (>10^{20} cm^{-3})**
  - Only small fraction of added Ti is needed to achieve the effect!
  - Adding Ti adversely affects the hydrogen weight capacity.
- **Experimentally:**
  - Several Ti-related species have been detected
  - Only a minute fraction of the total Ti produces the observed enhancements
    - » Sandrock *et al.*, J. Alloys Compd. **339**, 299-308 (2002).
    - » Kuba *et al*., J. Mater. Res. **20**, 3265–3269 (2005).
  - Ti-Al alloy formation
    - » Presence of these alloys is not required in order to achieve a significant enhancement in the kinetics of the alanate
    - » Kuba *et al*., J. Mater. Res. **20**, 3265–3269 (2005).
- **Adding large amounts of Ti is unnecessary**

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Enhancement of kinetics

- **Kinetics of hydrogen-related point defects is intimately tied to the decomposition reaction**
  - Decrease in the activation energy for hydrogen diffusion: $\Delta\mu_e$ = 0.44 eV = 42 kJ/mol
  - Experimentally observed change in activation energy for Ti-doped alanate compared to pure alanate: ~40 kJ/mol
    - » Sandrock *et al.*, J. Alloys Compd. **339**, 299-308 (2002).
- **Enhancement is independent of the amount of added Ti**
  - …as long as the Ti_{Al} concentration exceeds the concentration of hydrogen-related defects

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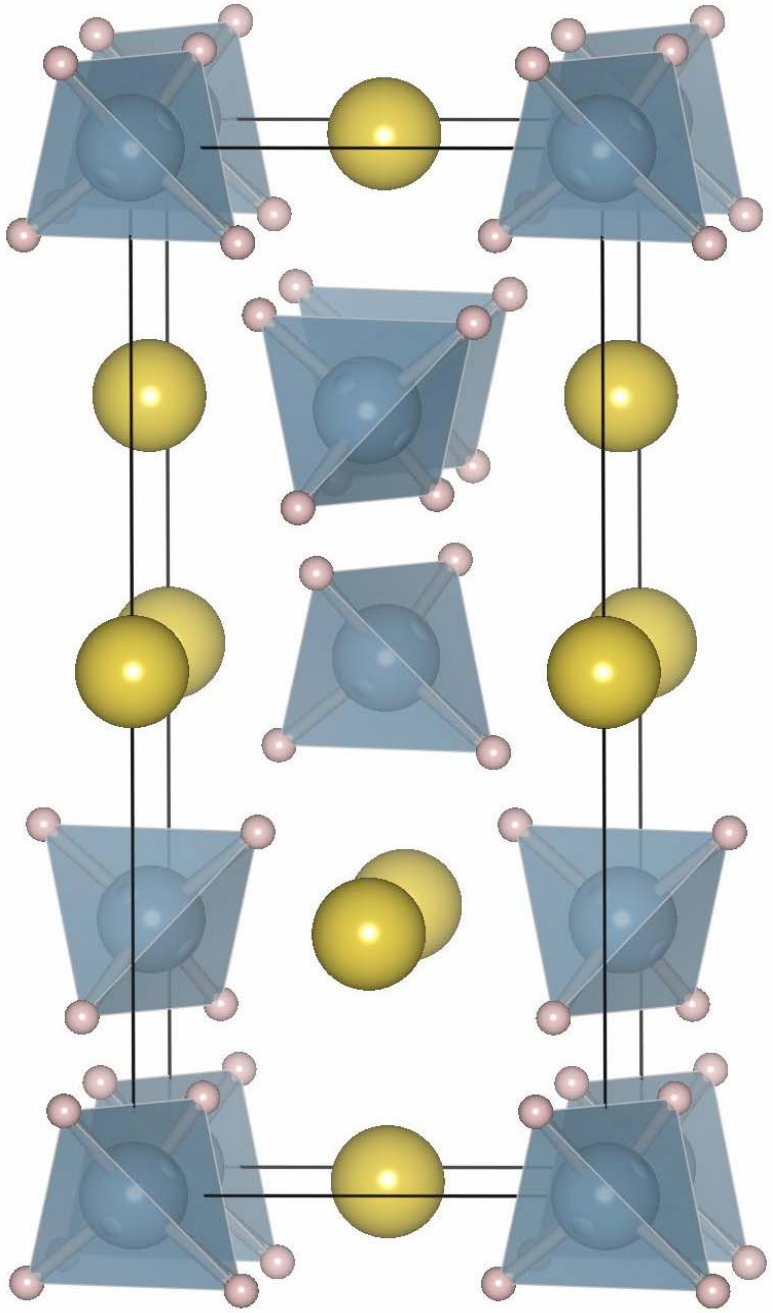
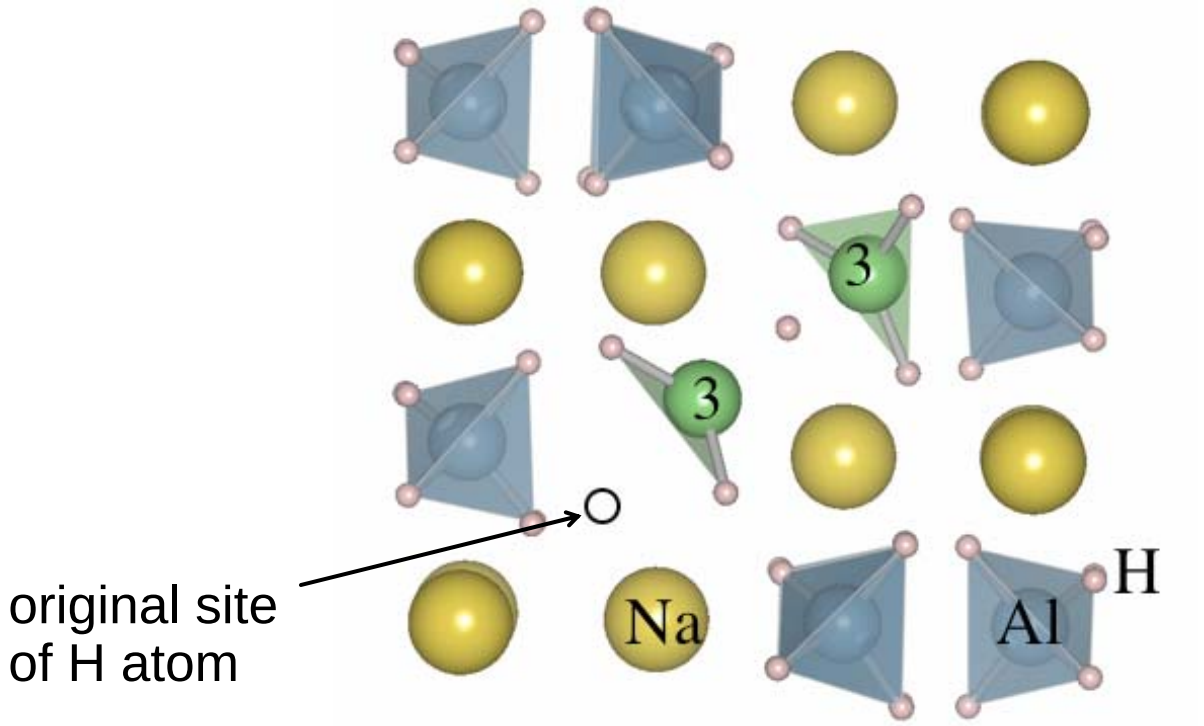
Defect Geometry

- Hydrogen-related defects induce large changes in lattice geometry
- May serve as nucleation sites for formation of new phases



Hydrogen vacancies

- V_H^+: formation of two planar AlH_3 complexes with a H atom in between



- V_H^-: structural rearrangements much smaller

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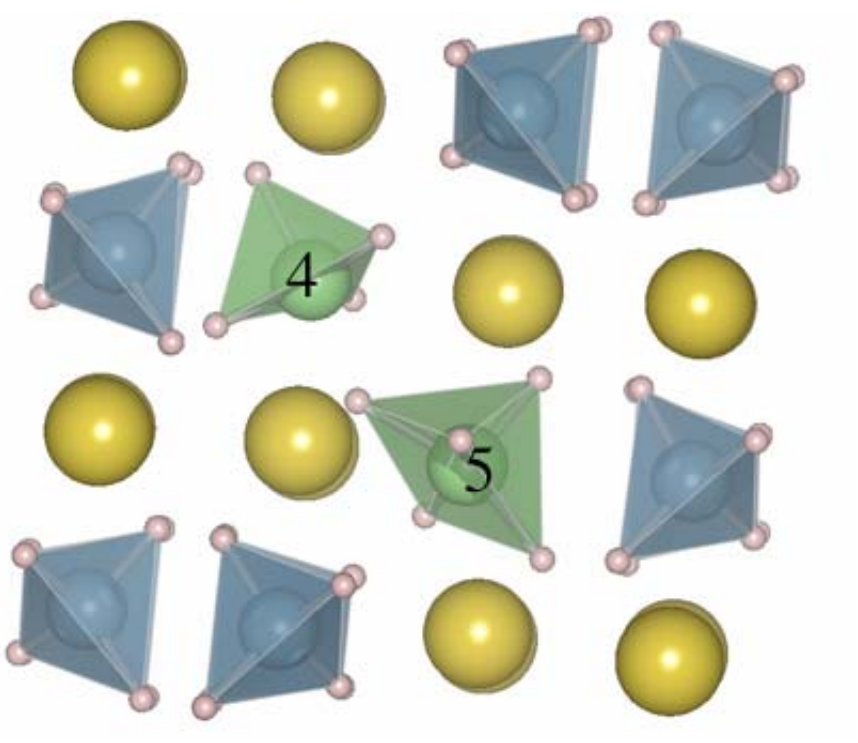
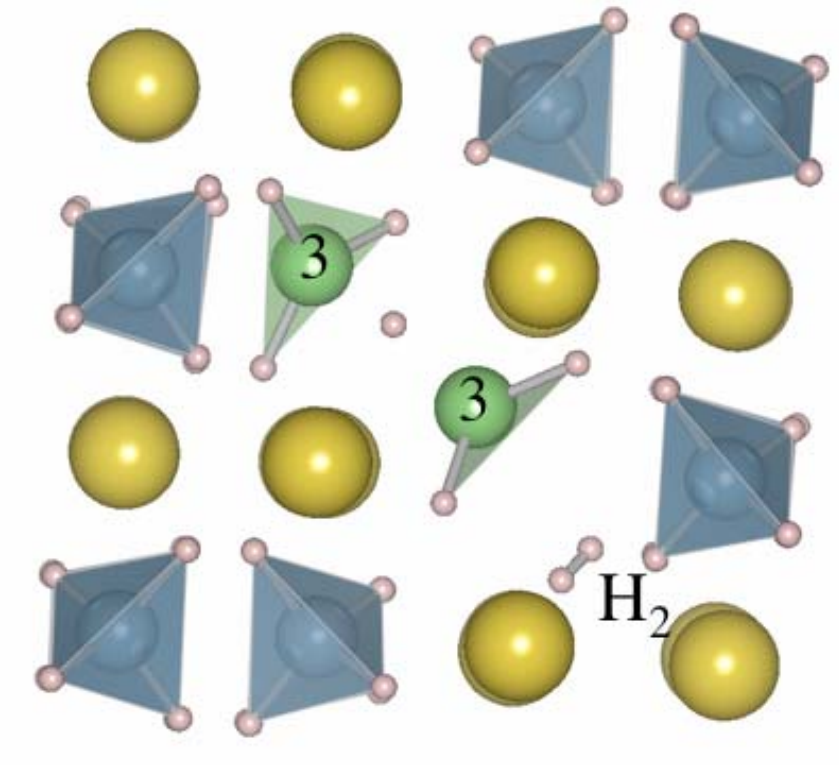
Hydrogen interstitials

H_i^-



H_i^+



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Conclusions

- **Point defects play important role in kinetics of $NaAlH_4$**
  - Vacancies, interstitials
  - Mediate hydrogen transport
  - Large structural relaxations
  - Charged
  - Formation energies changed due to doping with transition metals
  - Consistent with observed effects of Ti, Zr incorporation
- **References:**

  - A. Peles and C. G. Van de Walle, J. Alloys Compds. **446-447**, 459 (2007).
  - A. Peles and C. G. Van de Walle, Phys. Rev. B **76**, 214101 (2007).

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