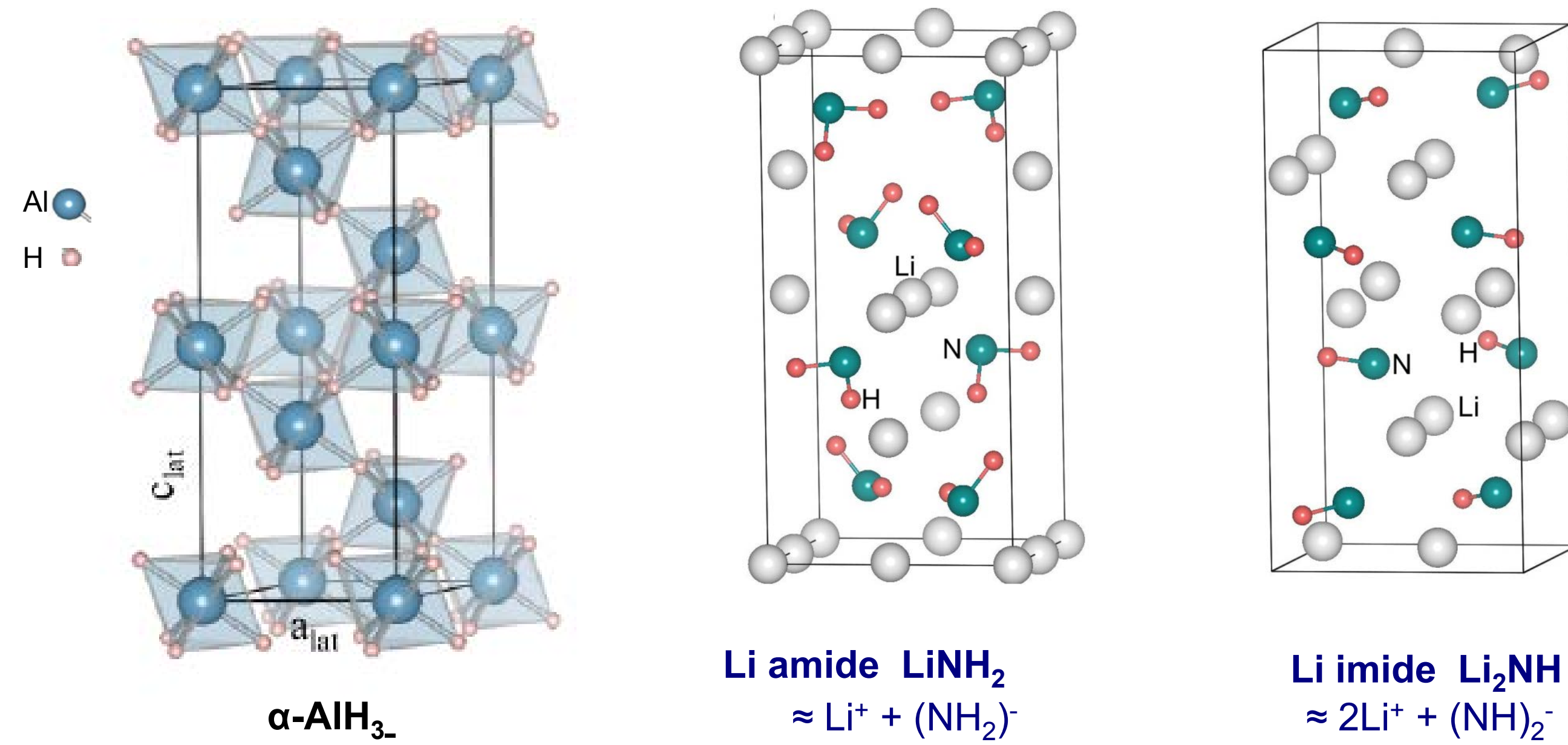


Motivation and challenges

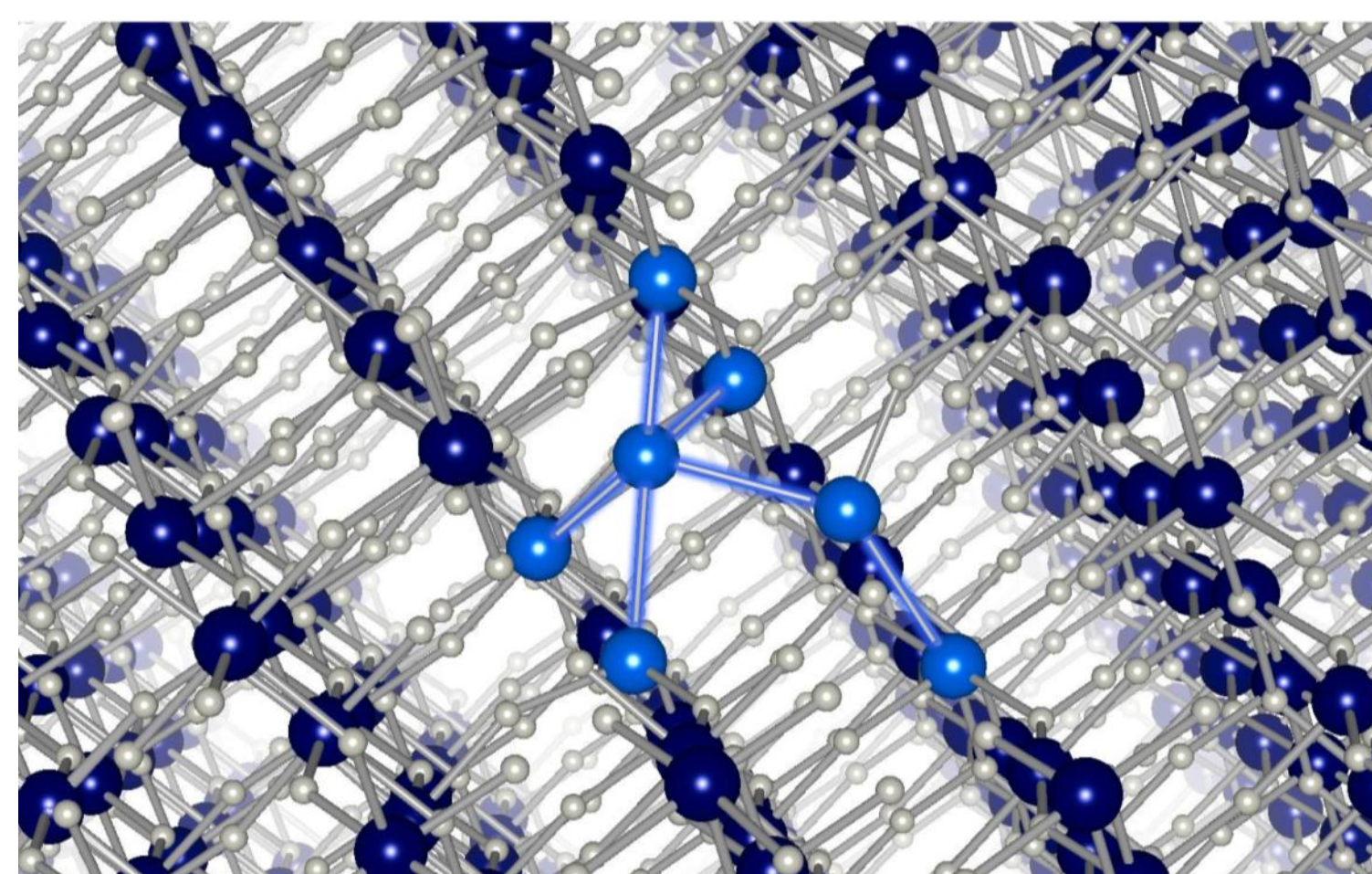
- Metal hydrides and complex hydrides as hydrogen-storage materials
- Build understanding of the fundamental mechanisms that control reversible hydrogenation and dehydrogenation processes in hydrides

Systems of interest: Aluminum hydride (AlH_3) and lithium amide (LiNH_2) as reversible hydrogen-storage materials



Objectives

- Apply state-of-the-art first-principles calculations as well as other simulation techniques to study the microscopic mechanisms that govern mass transport in hydrogen storage materials
- Determine formation energies and migration barriers of defects related to hydrogen uptake and release
- Interpret experimental results based on calculated activation energies
- Investigate the effect of transition-metal additives on hydrogen kinetics
- Study effects of particle size
- Develop guidelines for designing storage materials with improved storage capacities and favorable kinetics



Aluminum metal phase nucleation in AlH_3

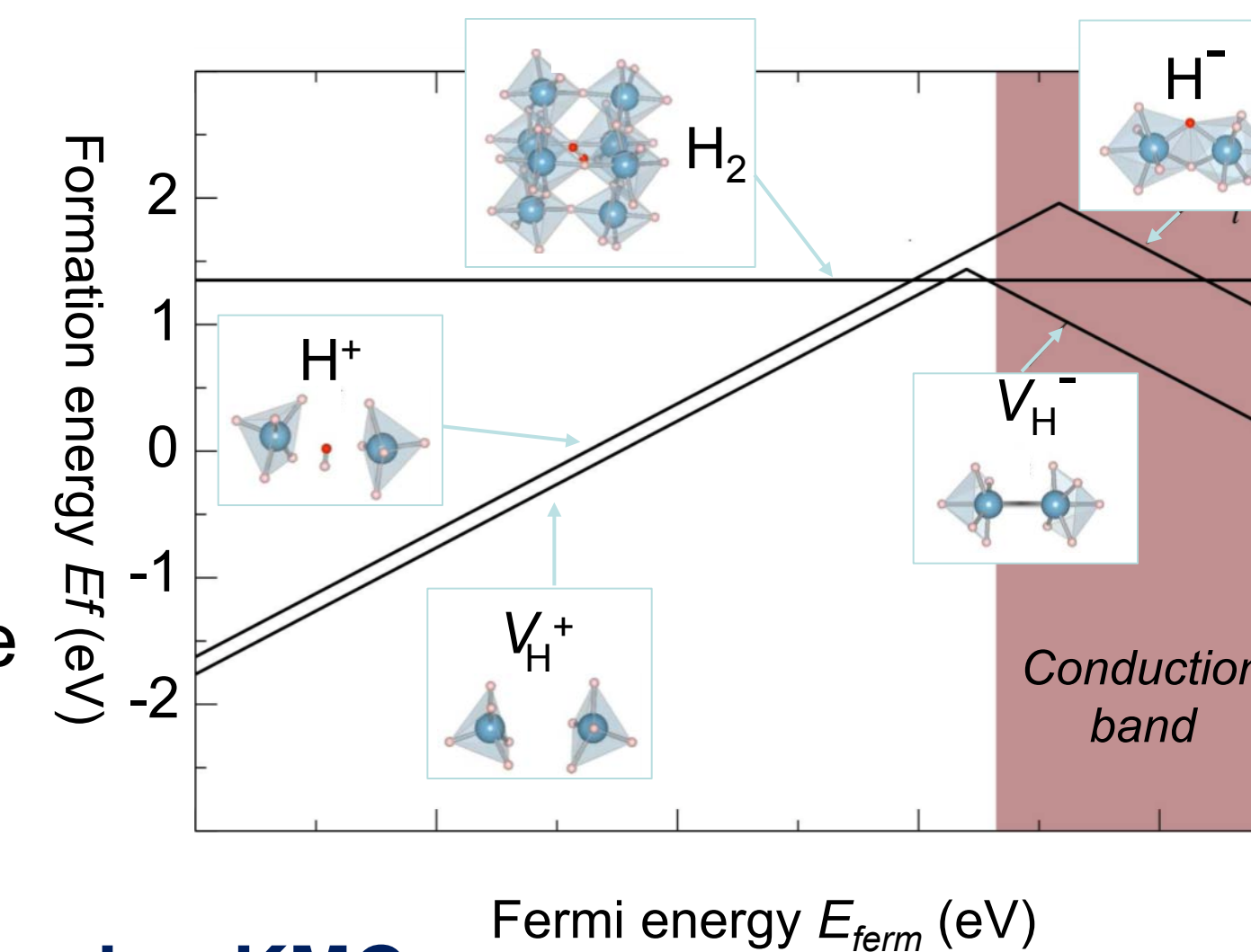
The image shows a cluster of bonded Al atoms in an AlH_3 host crystal. Blue balls: Al; white balls: H.

Methods

- Density functional theory (DFT)
 - generalized-gradient approximation (GGA)
 - screened hybrid functional
 - J. Heyd, G. E. Scuderia, and M. Ernzerhof, J. Chem. Phys, **118**, 8207 (2003); **124**, 219906 (2006)
- Kinetic Monte Carlo (KMC) model based on first-principles results
 - Enables direct comparison with experiment

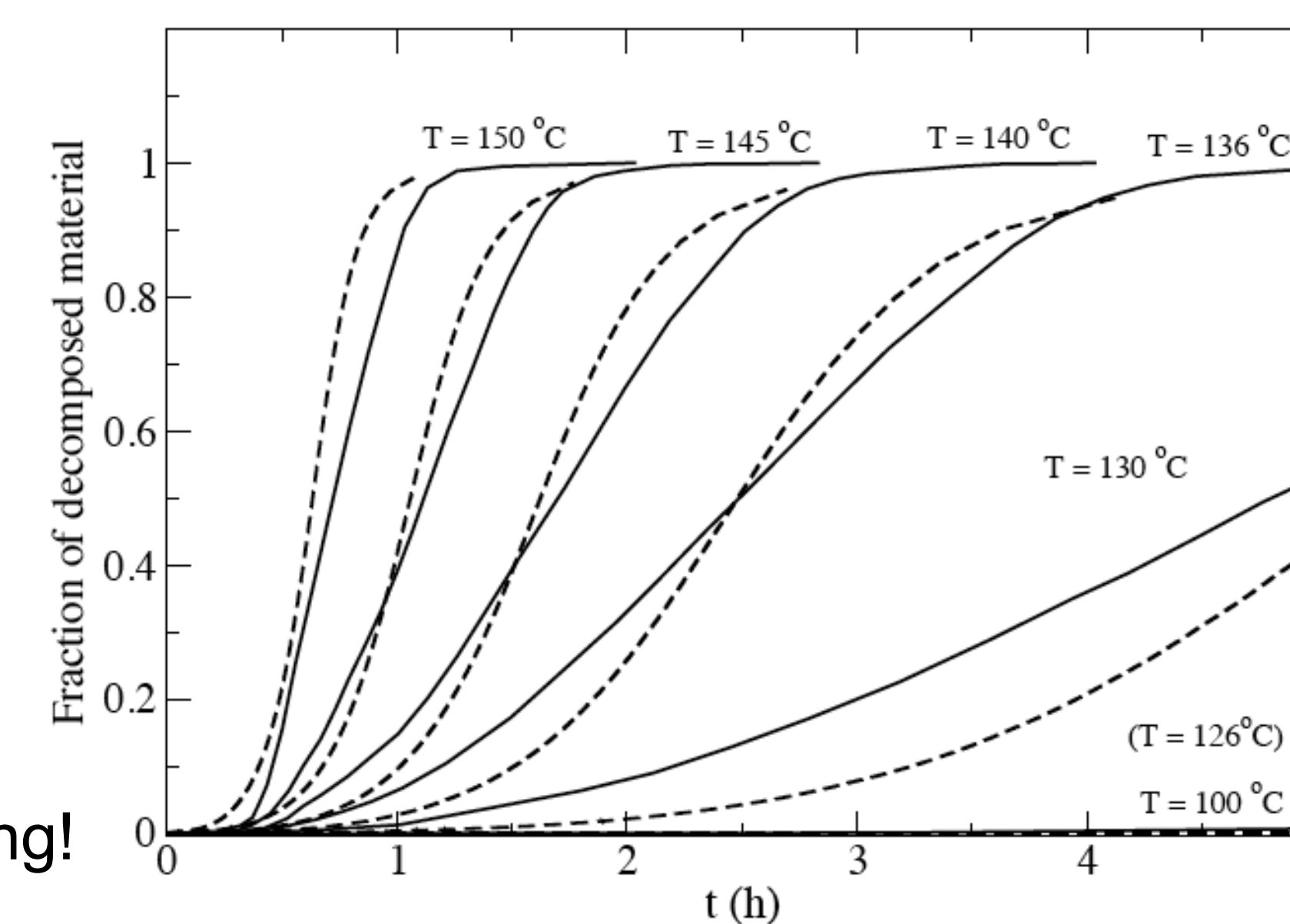
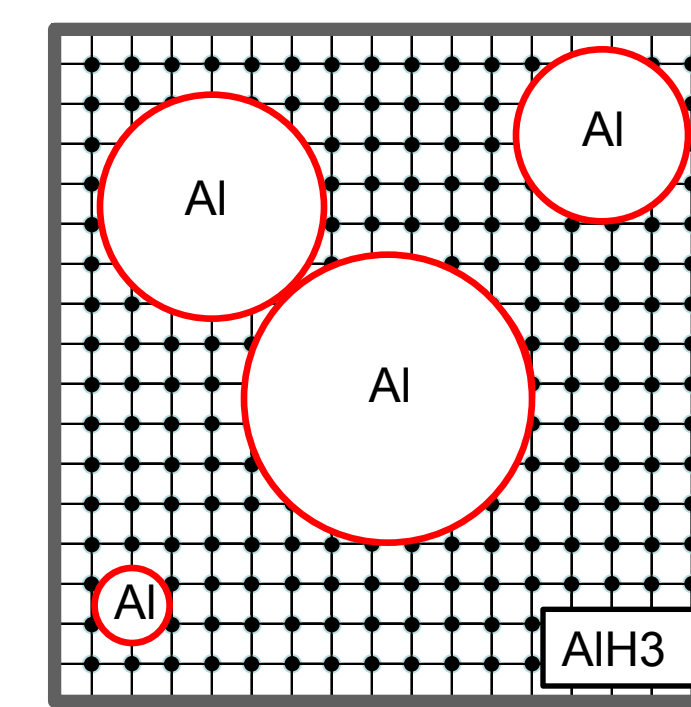
Dehydrogenation of AlH_3

- AlH_3 is thermodynamically unstable at ambient conditions, but kinetic effects inhibit dehydrogenation below 100°C
- Contrary to earlier speculation, surface-oxide layer not responsible for metastability
 - H.Saitoh *et al.*, Appl. Phys. Lett., **93**, 151918 (2008).
- Decomposition of AlH_3 initiates at localized sites throughout the bulk material, as opposed to nucleation at the surface
 - S. D. Beattie *et al.*, Chem. Commun. (Cambridge) **2008**, 4448.
- V_{H}^+ and V_{H}^- key defects in the dehydrogenation process
- V_{H}^+ migrates faster
- Fermi level at the conduction-band minimum ensures the presence of mobile carriers necessary for charge neutrality

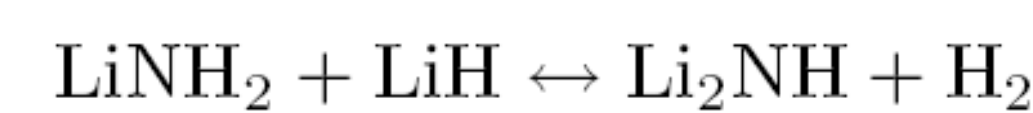


Dehydrogenation kinetics modeled using KMC

- V_{H}^- immobile nucleation centers for Al phase
- V_{H}^+ Random walkers
- Favorable binding energies (trapping energies) as the vacancy clusters grow in size
 - AlH_3 stable for years even without oxide layer
 - KMC results agree with experiment
 - S-shape-like onset of reaction curve does *not* rule out diffusion-limited mechanism
 - Simple rules about shapes of reaction curves can be misleading!



Point defects and diffusion in lithium amide

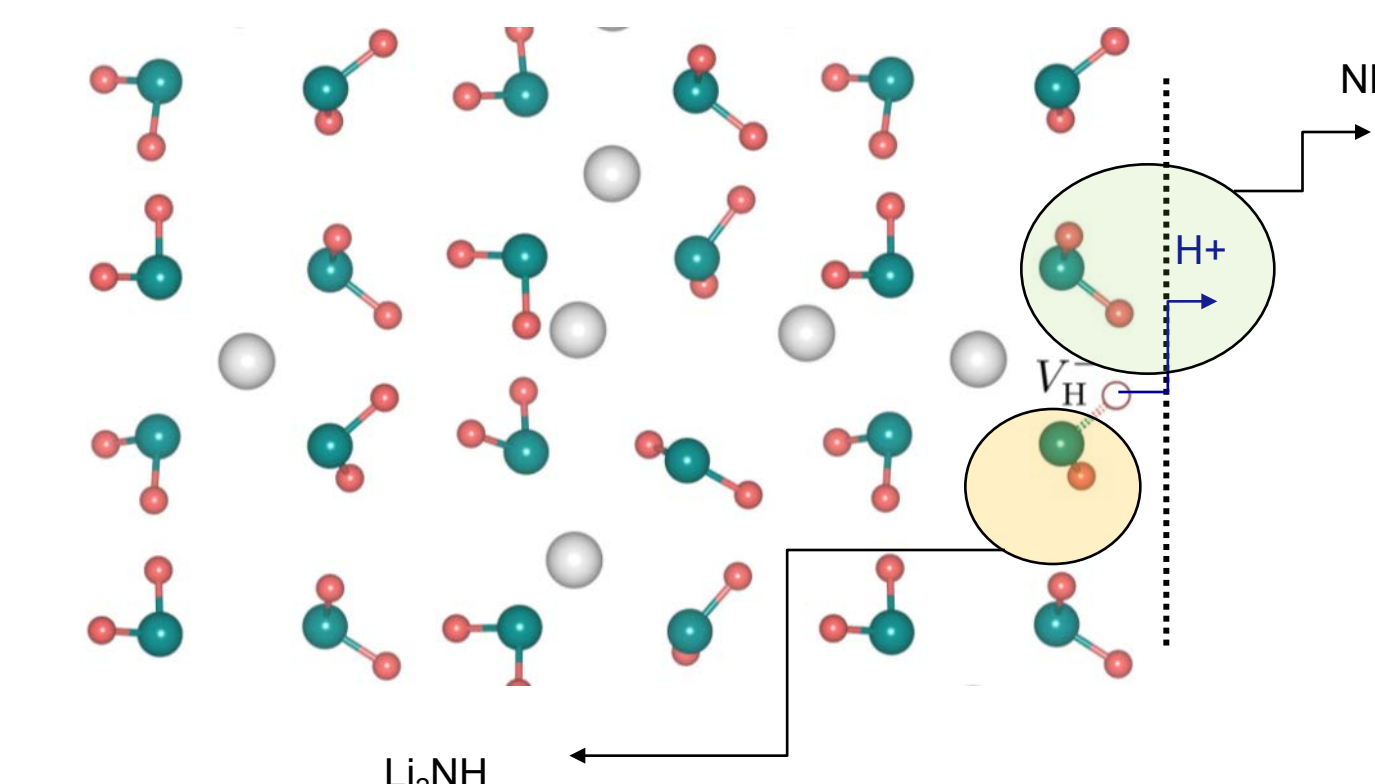


Defect	E^f (eV)	E_m (eV)	Complex	
➢ All possible native defects investigated: structure, energetics, migration	H_i^+	1.28	0.61	
	H_i^-	1.34	0.34	
	V_{H}^-	0.63	0.71	
	$(\text{H}_2)_i$	1.75	0.19	
	Li_i^+	0.51	0.30	
	V_{Li}^-	0.51	0.20	
	Li_{H}^0	0.48	0.71*	$\text{Li}_i^+ + V_{\text{H}}^-$
	H_{Li}^0	1.17	0.61*	$\text{H}_i^+ + V_{\text{Li}}^-$
	$V_{\text{NH}_2}^+$	0.62	0.87	
	V_{NH}^0	0.40	0.87*	$V_{\text{NH}_2}^+ + \text{H}_i^-$
	V_{N}^+	1.64	0.87*	$V_{\text{NH}_2}^+ + (\text{H}_2)_i$
	V_{N}^-	1.77	0.87*	$V_{\text{NH}_2}^+ + 2\text{H}_i^-$

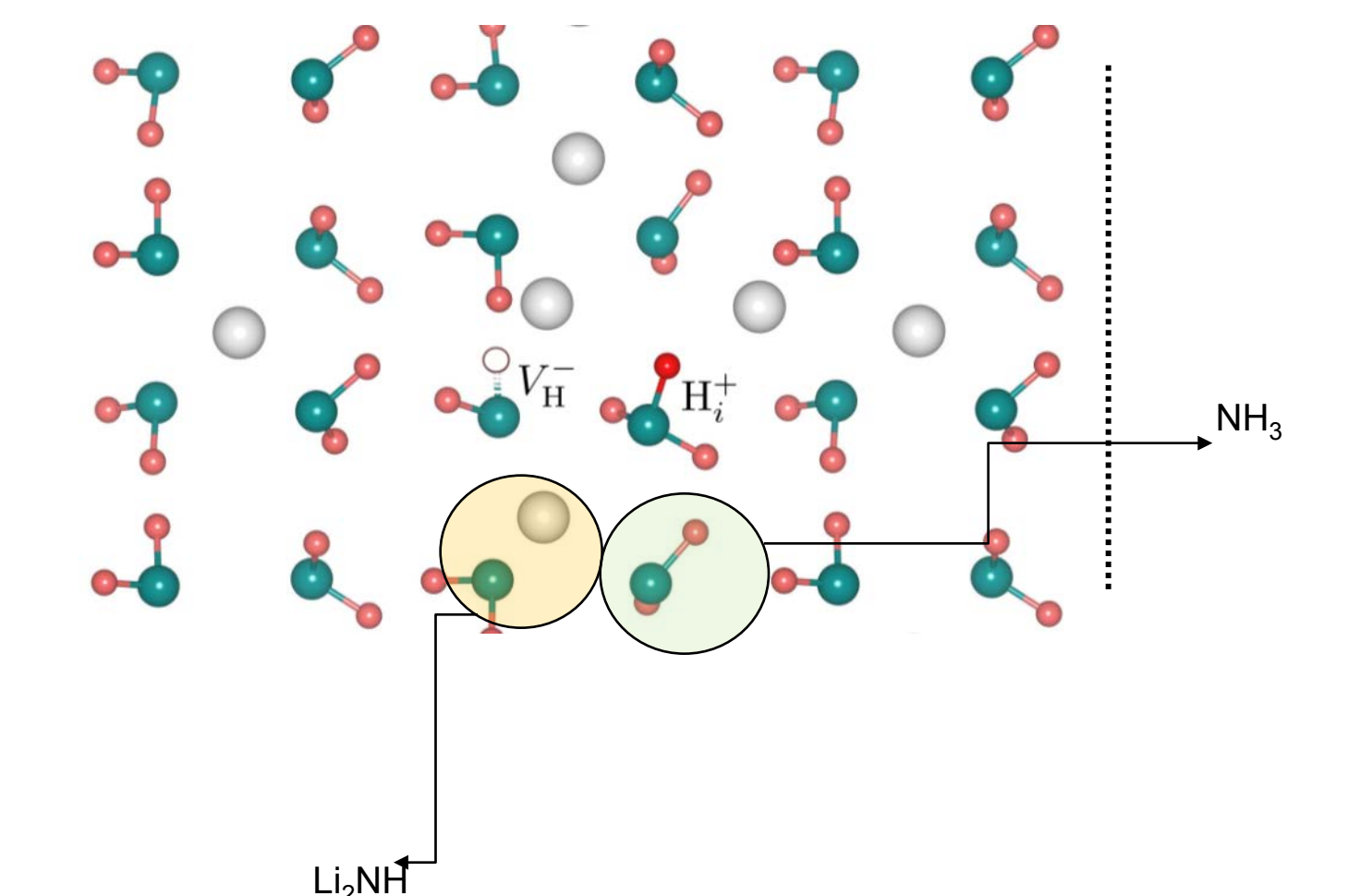
Hydrogen desorption kinetics of lithium amide

- Charge neutrality maintained by Li-related Frenkel pairs
- Two mechanisms for dehydrogenation of LiNH_2 suggested:

Mechanism I (bulk): self-diffusion of $(\text{H}_i^+, V_{\text{H}}^-)$ rate-limiting process



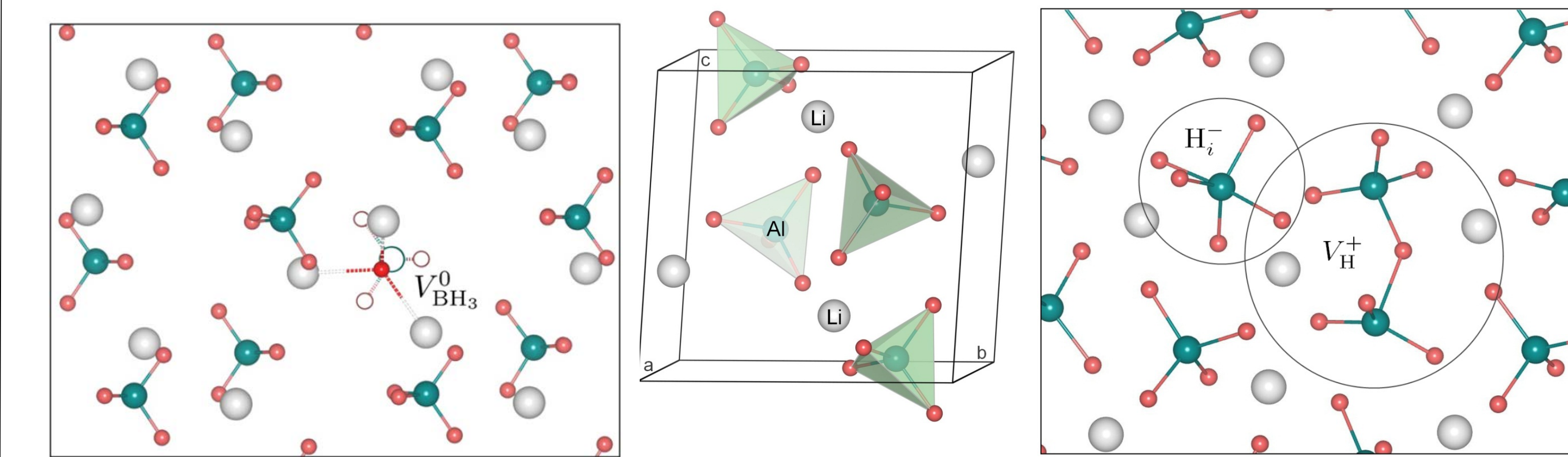
Mechanism II (surface): self-diffusion of V_{H}^- rate-limiting process



- Dominant mechanism for decomposition depends on particle size (specific surface area): explains variation of activation energy with duration of ball milling
- Hydrogen Frenkel pairs at the core of decomposition mechanism

Decomposition mechanisms of LiBH_4 and LiAlH_4

- Comprehensive study of point defects and dehydrogenation mechanisms
- Investigated effects of transition-metal additives



Future directions

- Role of hydrogen-related Frenkel pairs in dehydrogenation kinetics
 - Systematic studies in a range of materials: LiBH_4 , $\text{Li}_4\text{BN}_3\text{H}_{10}$, LiNH_2 , MgH_2 , $\text{Mg}_2(\text{Fe/Ni})$ -hydride, LiAlH_4 , etc.
- Role of transition-metal doping in MgH_2 :
 - Formation energies and migration barriers in Mg_2 -TM and MgH_2 matrix in the dilute limit

Overall summary and impact

- Consideration of **charged** point defects and impurities (and not just neutral states) in hydrides: an essential physics issue previously not addressed
- State-of-the-art first principles calculations to accurately describe defects
- Multiscale modeling to address realistic system sizes and temperature
- Broader conclusions: shapes of reaction curves, particle-size dependence

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K. Hoang, A. Janotti, and C. G. Van de Walle, Phys. Chem. Chem. Phys. **14**, 2840 (2012).