

Atomistic Simulations of Hydrogen Storage in Metal Hydrides and Nanoporous Sorbents

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Outline

■ Metal Organic Frameworks

- Simulation methods for H₂ adsorption in MOFs
- Validation and predictions for existing MOFs
- Where and how H₂ adsorbs in MOFs—volume density of states

■ Metal Hydrides

- Thermodynamics of destabilized metal hydrides
- Calculation methods
- Reaction enthalpies: Test systems and predictions
- Entropic contributions & van't Hoff plots
- Kinetic issues: Dissociation of H₂ on Mg₂Si



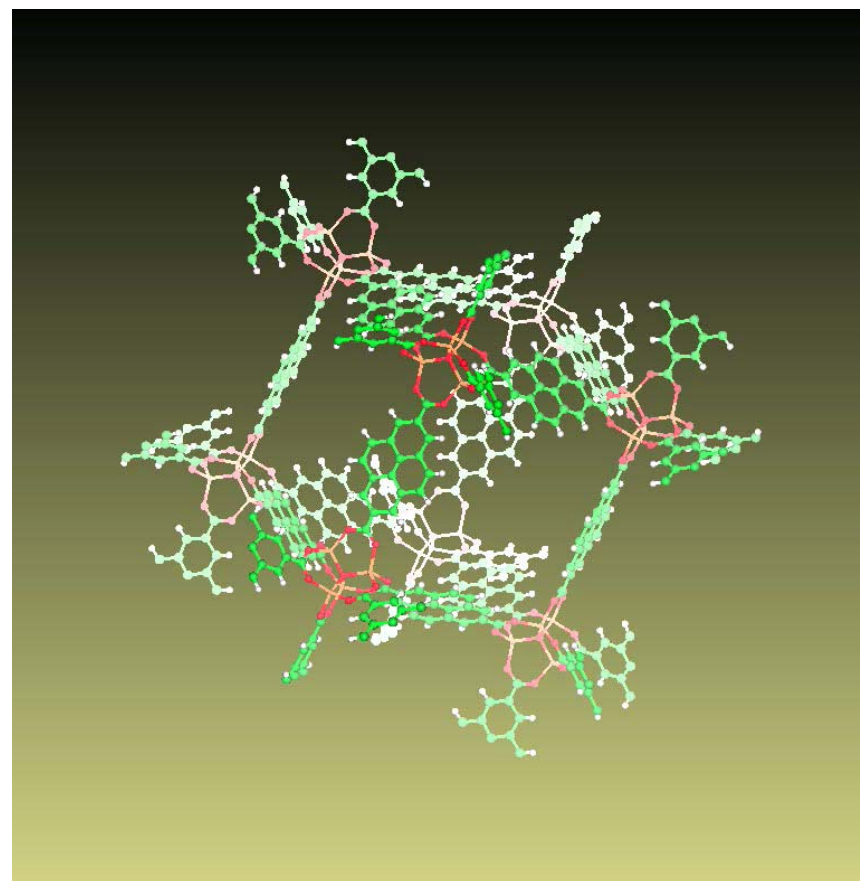
Why study H₂ adsorption in MOFs?

- Metal organic frameworks have been found to be very good adsorbents for **methane**.
 - Snurr and collaborators have found that **computer simulation** results for methane compare very well with experiments, and predicted the structure of a new material with a very large methane adsorption.
- **Experiments** of H₂ adsorption on MOFs at 77 K (Rosi et al., Rowsell et al.) and 298 K (Rosi et al.) indicate that these materials are promising candidates for meeting the DOE targets.



Metal Organic Frameworks

- Metal-oxide vertices held together with organic linkers
- Easy to synthesize
- Stable under a wide range of temperature and pressures
- Large effective surface area (many sites for adsorption)
- Comparatively light
- Can be tailored by changing metal groups, ligands, & organic linkers



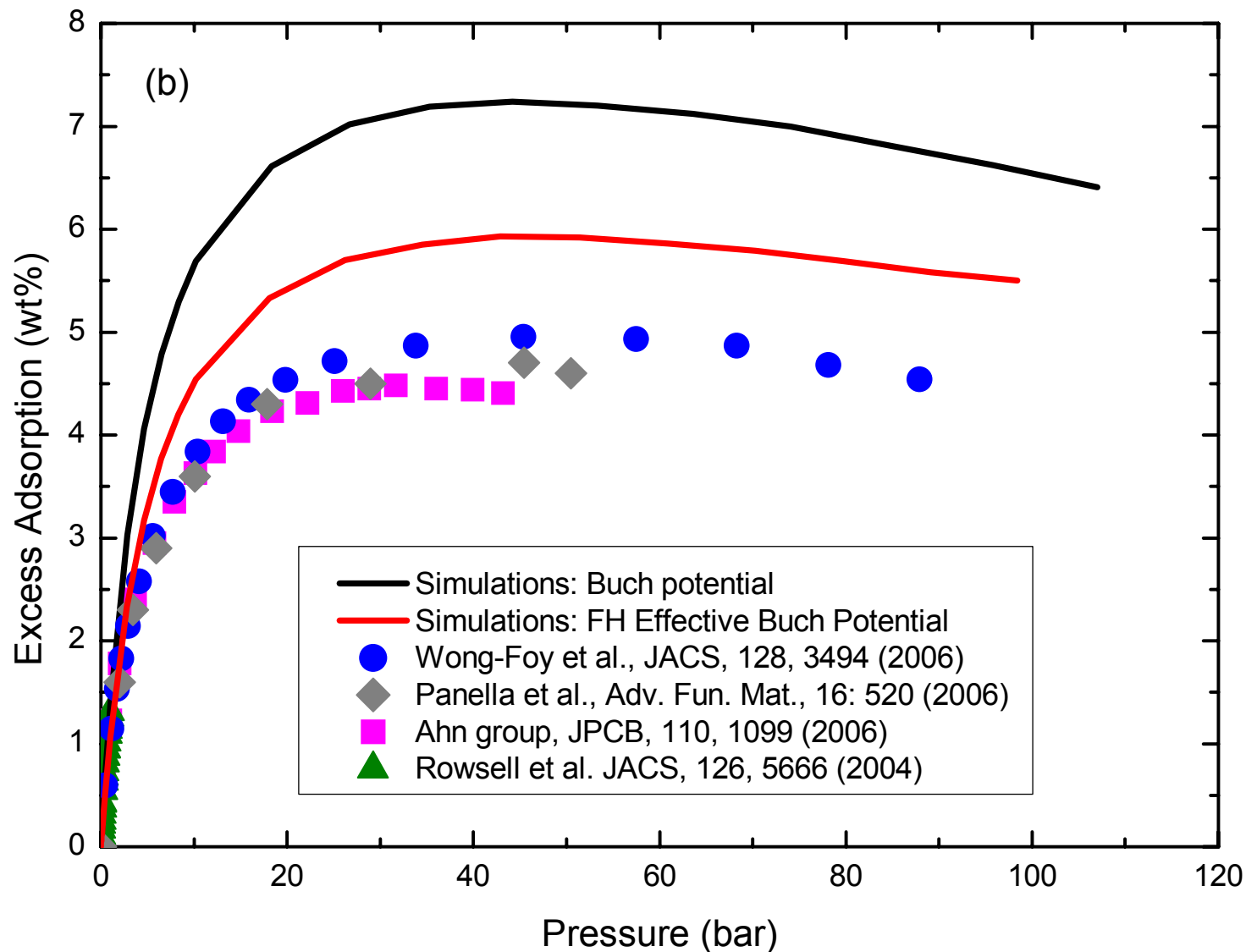
Structure of IRMOF-14

Modeling Hydrogen Adsorption in MOFs

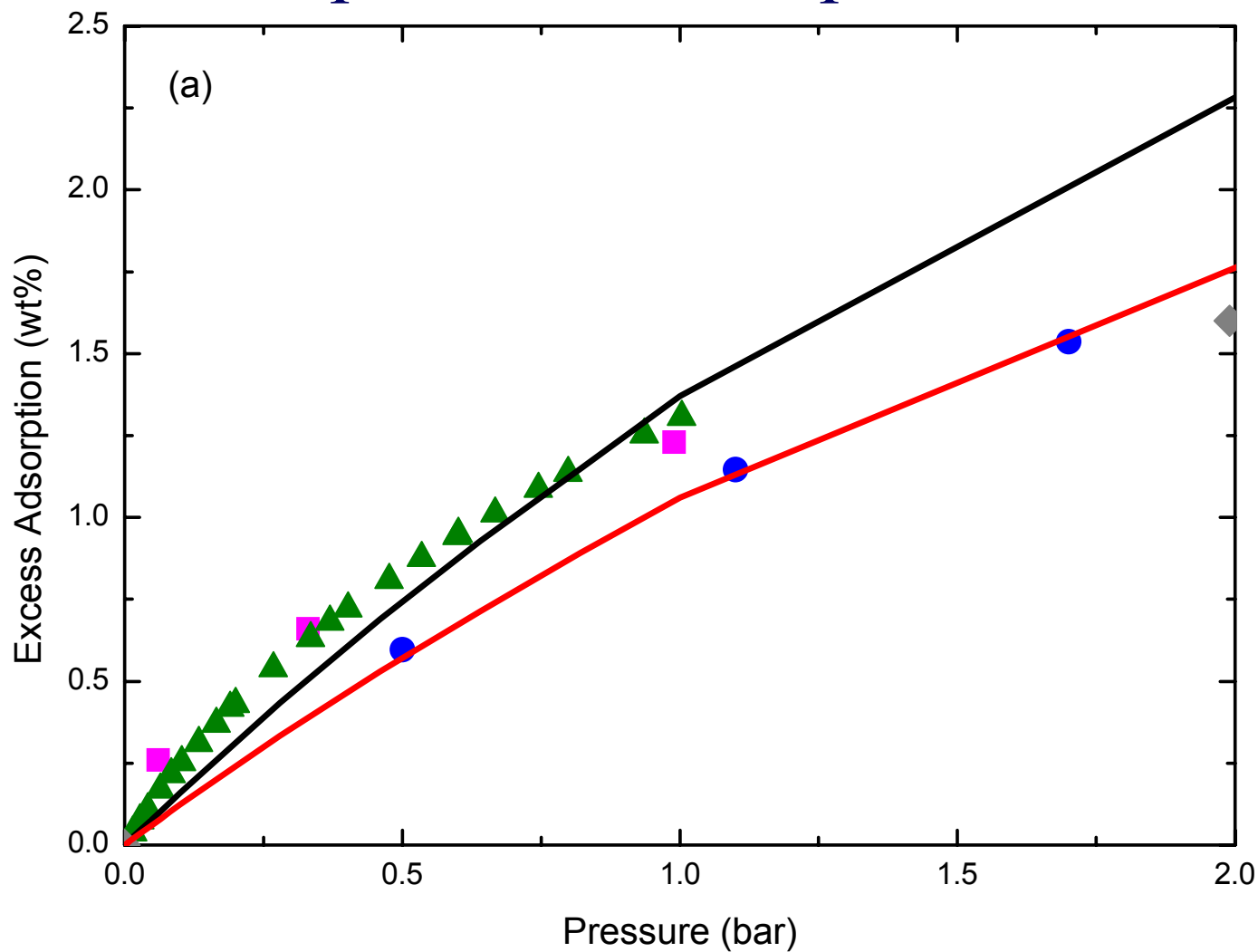
- Structure of the MOFs: rigid framework obtained by XRD experiments
- Solid-fluid potential: standard UFF force field
- Fluid-fluid potential: Buch potential: Spherical, $\epsilon = 34.7$ K, $\sigma = 2.96$ Å
- Computational technique: grand canonical Monte Carlo
 - Quantum diffraction effects at 77 K treated by path integral Monte Carlo and the Feynman Hibbs effective potential approximation.



Adsorption Isotherms for H₂ on IRMOF-1 at 77K: Comparison with Experiments

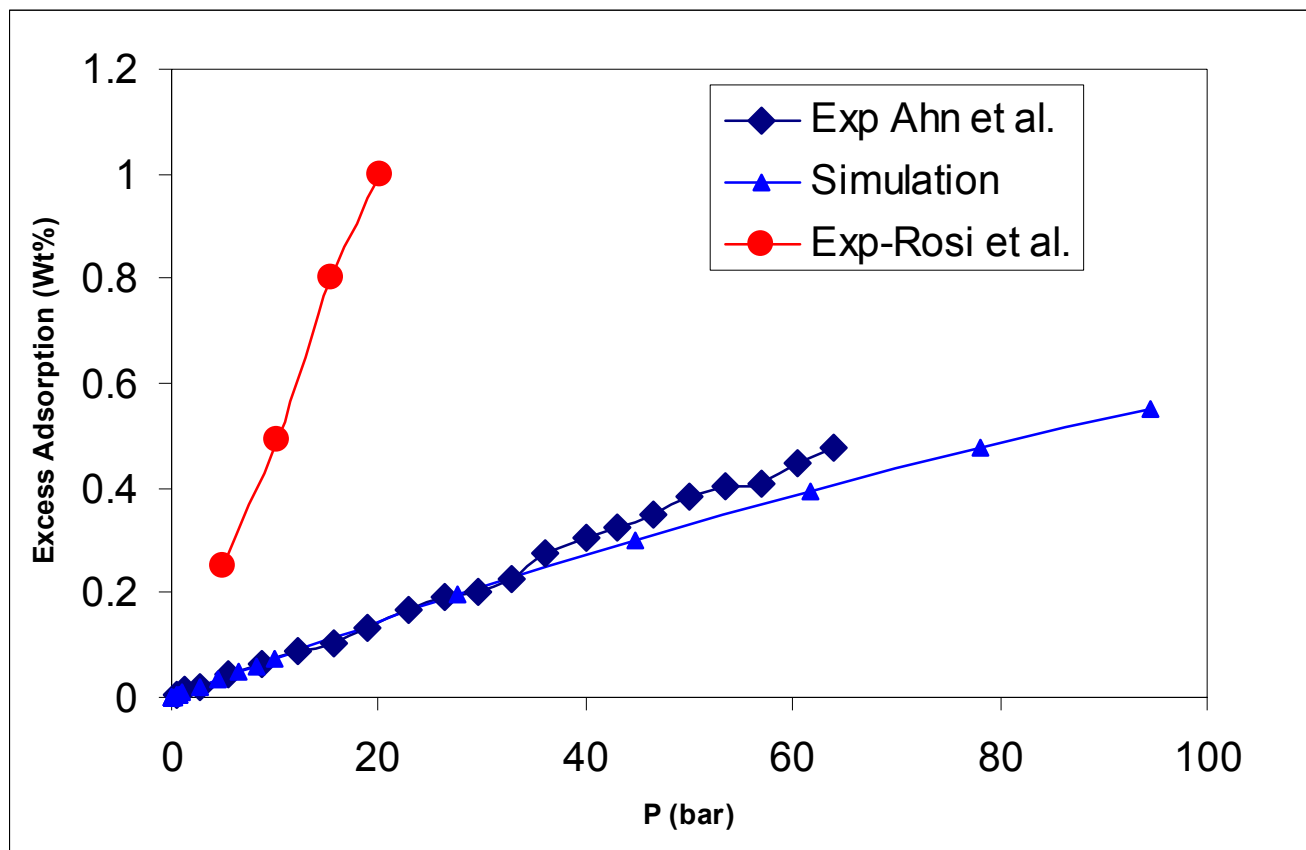


Adsorption Isotherms for H₂ on IRMOF-1 at 77K: Comparison with Experiments

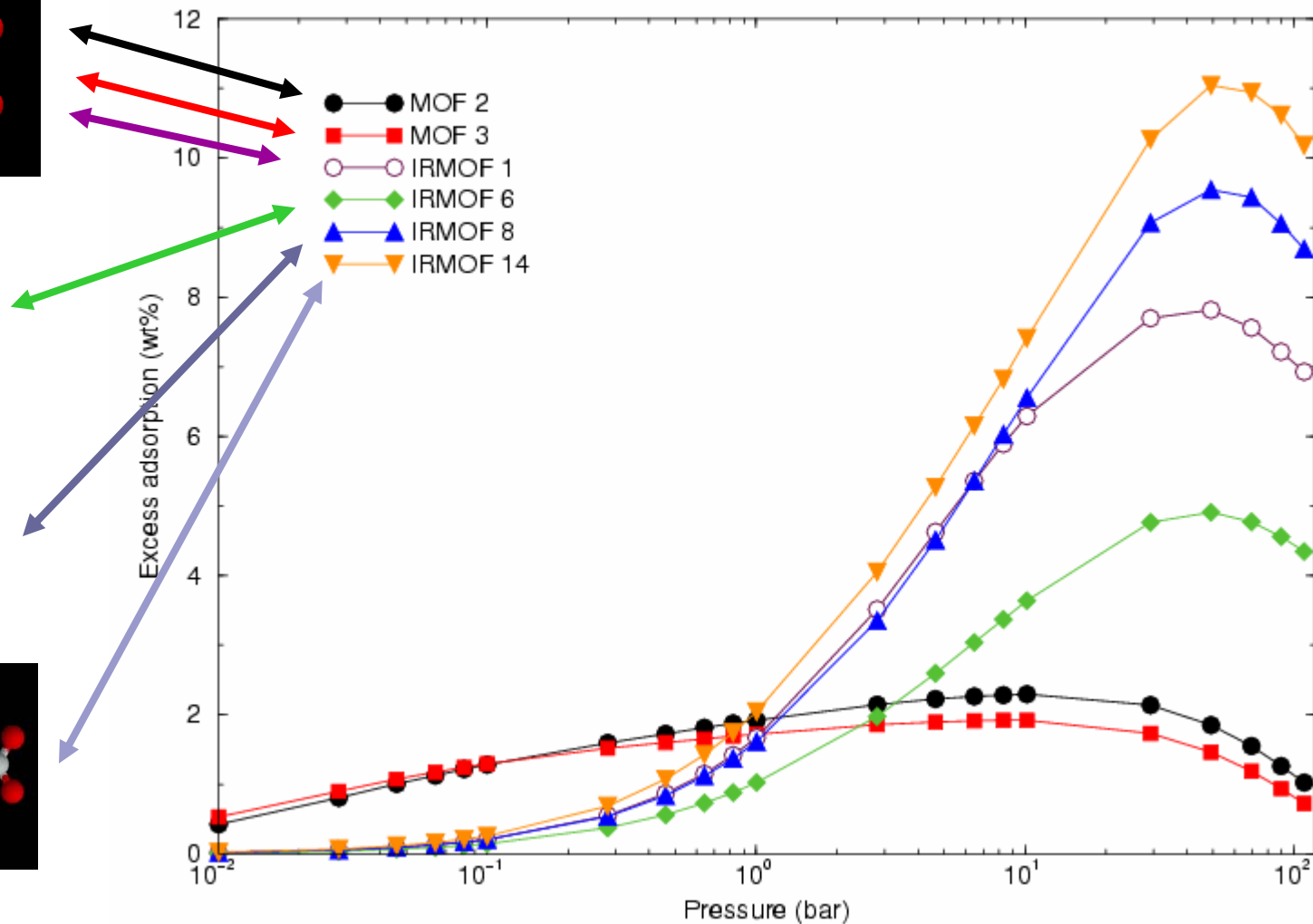
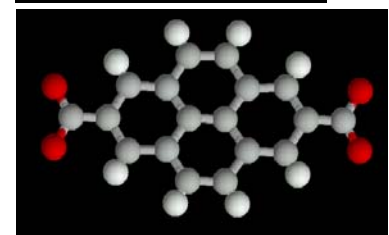
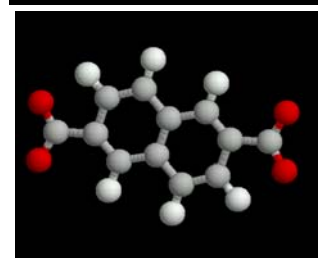
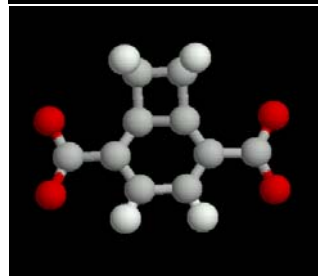
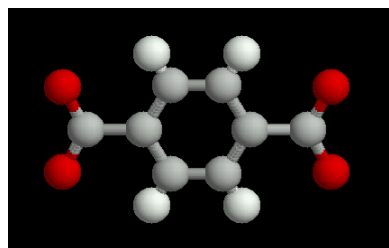


H₂ Adsorption in IRMOF-1 at 298 K

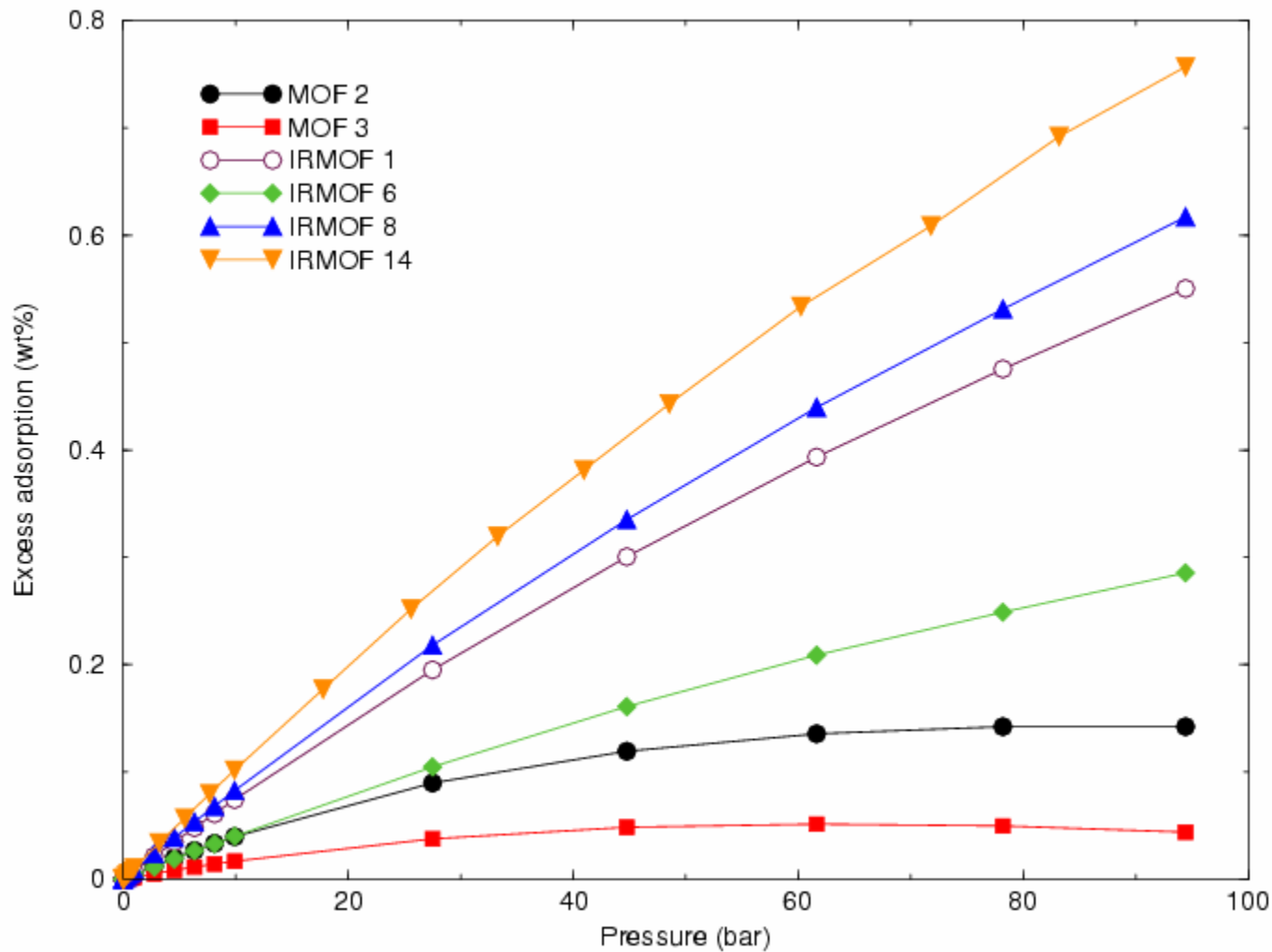
- Experimental data by Rosi et al. (O. Yaghi's group) published in *Science*, **300**, 1127 (2003)
- Simulation data are predictions, no adjustable parameters
- Experimental data of Ahn et al., *JPCB*, **110**, 1099 (2006).



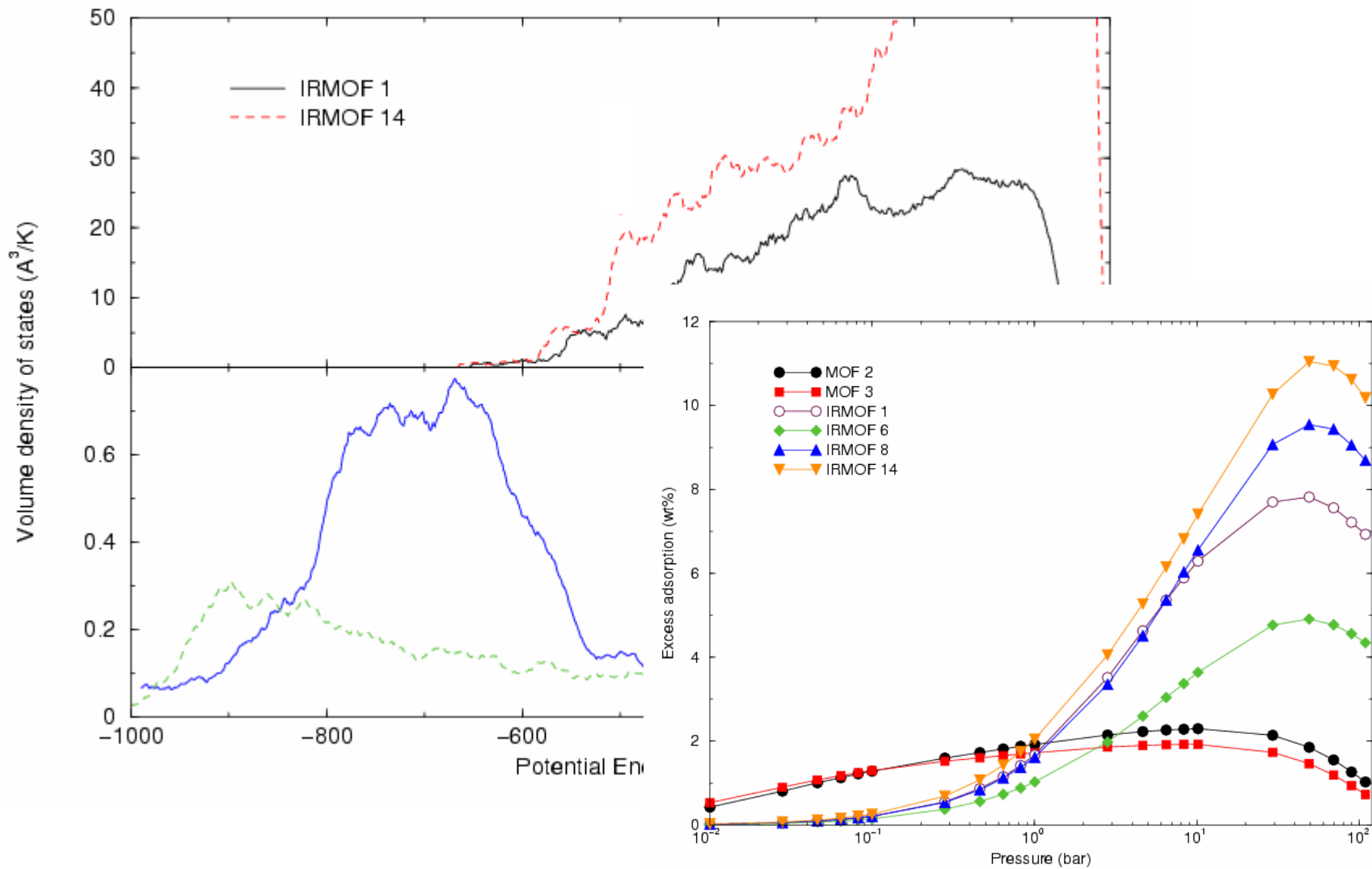
Prediction: Excess Adsorption at 77K



Prediction: Excess Adsorption at 298K



Volumetric Density of States



What are the Properties of Ideal Adsorbents?

- $\Delta G = \Delta H - T\Delta S < 0$.
- Estimate of ΔS : an ideal gas at 100 bar minus one degree of freedom at 298 K: $-T\Delta S \sim 1600$ K (13 kJ/mol).
- One would need high volumetric density of states available in the PES at an energy $U = \Delta H \sim T\Delta S$ to have large adsorption.
- MOF 2 and 3 have sites at almost the right energy, but low volume density of states.
- IRMOFs have a high volume density of states, but for energies that are too weak.



Conclusions—MOFs

- The computer simulations are in fairly good agreement with many experiments on MOFs.
- Problems with experiments have been identified by comparison with simulation data.
- The MOFs we have tested **do not** meet the DOE requirements at 298K.
 - The volume available for adsorption is large enough.
 - The energy of the adsorption sites is too weak.
- Computer simulations will be useful to estimate the adsorption properties of MOFs yet to be synthesized.
- Stronger adsorption are needed, e.g., unsaturated metals, spillover.



Why Metal Hydrides?

- Metal hydrides can have very high volumetric densities, much higher than liquid H₂.
- Hydrides of period 2 and 3 metals can also have very high gravimetric densities.



So Why Not Metal Hydrides?

- Temperatures required for dehydrogenation
- Reversibility
- Heat management



Thermodynamics of H₂ Storage in Metal Hydrides

Zuttel, Mater. Today **6** (2003) 24; Grochala & Edwards, Chem. Rev. **104** (2004) 1283

A useful way to characterize a metal hydride is the temperature at which the material is in equilibrium with 1 bar H₂:

$$\Delta G = 0, \text{ so } \Delta H = T \Delta S$$

For a large number of simple metal hydrides, $\Delta S \sim 130 \text{ J K}^{-1} \text{ mol}^{-1}$

For some complex metal hydrides (e.g. LiBH₄), $\Delta S \sim 100 \text{ J K}^{-1} \text{ mol}^{-1}$

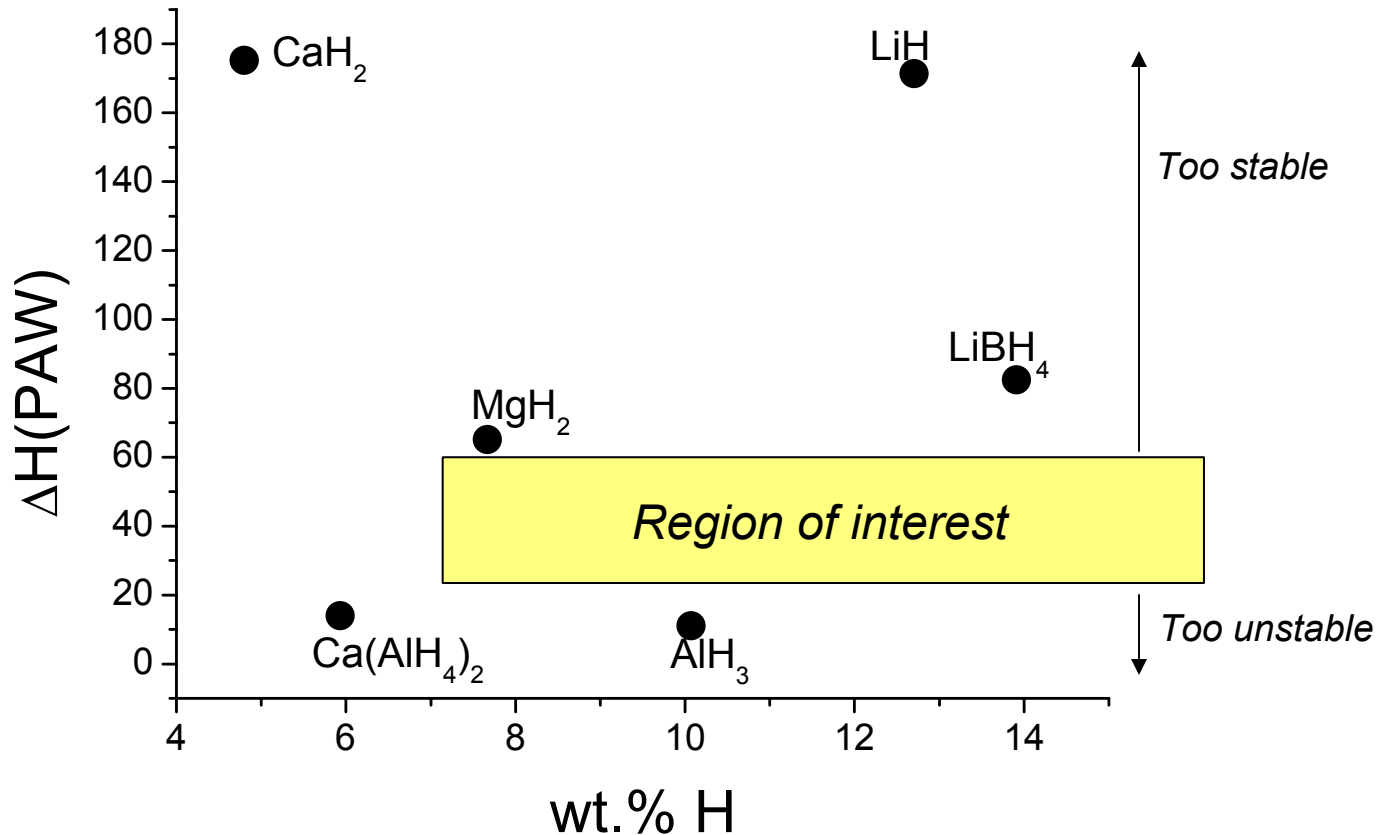
$$100 < \Delta S < 130 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$25 < T < 150 \text{ }^\circ\text{C}$$

$$30 < \Delta H < 60 \text{ kJ/mol H}_2$$



Thermodynamics of H₂ Storage in Metal Hydrides



Some metal hydrides satisfy density requirements but not thermodynamic requirements



Destabilization of Metal Hydrides

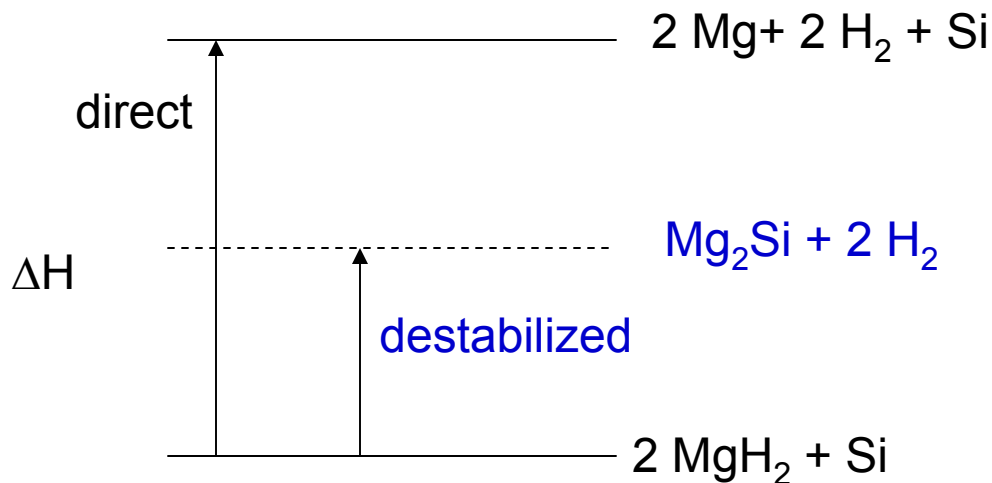
Original concept introduced by Reilly & Wiswall for Ni hydrides.
(Reilly & Wiswall Inorg. Chem., **6**, (1967) 2220)

Recent application of this concept to light metal hydrides by Vajo et al.
(J. J. Vajo et al., J. Phys. Chem. B **109** (2005) 3719; **108** (2004) 13977).

Direct reaction: $\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$ ($\Delta H = 64 \text{ kJ/mol H}_2$; 7.7 wt.% H)

Destabilized reaction:

$2 \text{MgH}_2 + \text{Si} \rightarrow \text{Mg}_2\text{Si} + 2 \text{H}_2$ ($\Delta H = 37 \text{ kJ/mol H}_2$; 5.0 wt.% H)



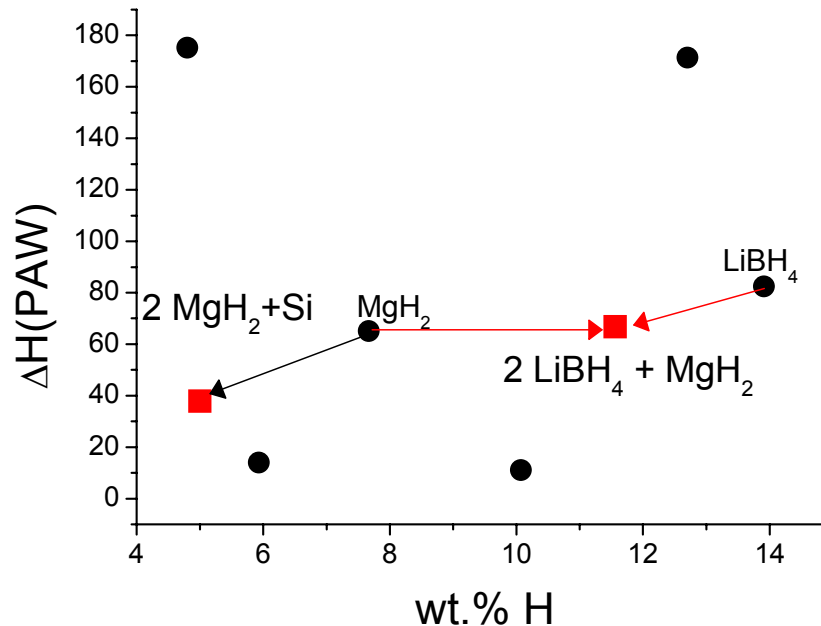
Destabilization of LiBH₄

(J. J. Vajo et al., J. Phys. Chem. B **109** (2005) 3719; **108** (2004) 13977)

Direct reaction: $\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + 3/2 \text{H}_2$ ($\Delta H = 82 \text{ kJ/mol H}_2$; 13.91 wt.% H)

Destabilized reaction:

$2 \text{LiBH}_4 + \text{MgH}_2 \rightarrow \text{MgB}_2 + 2\text{LiH} + 4 \text{H}_2$ ($\Delta H = 67 \text{ kJ/mol H}_2$; 11.56 wt.% H)



Practical Limitations of Destabilized Metal Hydrides

Rapid kinetics are required both for H₂ production and hydrogenation

However, *strong* kinetic limitations are observed for hydrogenation in both destabilized systems:

$\text{Mg}_2\text{Si} + \text{H}_2 \rightarrow 2 \text{MgH}_2 + \text{Si}$ not observed even under extreme conditions

$2 \text{LiBH}_4 + \text{MgH}_2 \rightarrow \text{MgB}_2 + 2 \text{LiH} + 4 \text{H}_2$ gives ~9 wt.% reversible storage, but only at $T > 250 \text{ }^\circ\text{C}$ (with Ti used as catalyst with ball-milled materials)

(J. J. Vajo et al., J. Phys. Chem. B **109** (2005) 3719; **108** (2004) 13977)



Challenges

Identify other destabilization schemes with favorable thermodynamics

Many schemes can be considered, but thermodynamic data are unavailable for most compounds of interest.

Goals of our work:

- Identify reaction schemes yielding > 7 wt.% H_2 with $30 < \Delta H < 60$ kJ/mol H_2
- Understand origin of kinetic limitations, specifically for $Mg_2Si + H_2$



Screening Destabilization Schemes With DFT

Plane wave Density Functional Theory (DFT) is well suited to treating hydrogen interactions with metals

Examples:

H solubility and diffusion through CuPd alloys (Kamakoti et al., Science **307** (2005) 569)

H diffusion in ordered intermetallics (Bhatia et al., J. Phys. Cond. Matt. **16** (2004) 8891)

H solubility in Al (Wolverton et al., Phys. Rev. B **69** (2004) 144109)

Our calculations:

- Vienna *ab initio* Simulation package (VASP)
- GGA functional with PAW approach (USPP gives similar results)
- Convergence reached with energy cutoff and *k*-space sampling
- All solid state structures fully optimized within experimental space group



What is Density Functional Theory?

Molecular orbital method is “an approximate solution to an exact equation”

$$H\Psi = E\Psi; \quad E = E[\Psi]$$

-Many-body problem is impossible to solve exactly

DFT is “an exact solution to an approximate equation”

$$E = T_s[n] + U[n] + V[n] + E_{xc}[n]; \quad E = E[n(r)]$$

-Exact form of E_{xc} is unknown



First-Pass Estimation of ΔH : Limitations

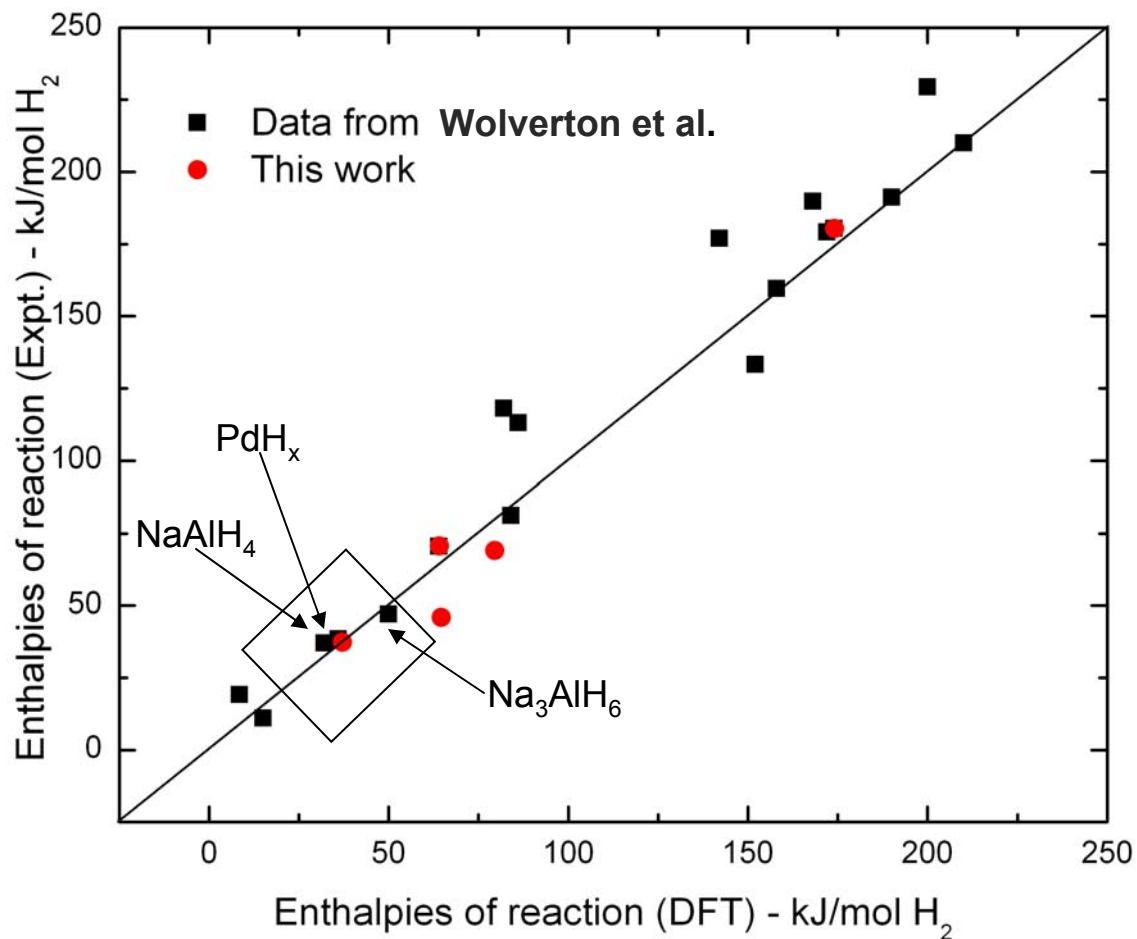
- Accuracy of DFT
- Approximate $\Delta H \approx \Delta E$
- All calculations at $T = 0$ K
- Heat capacities needed for finite T
- No zero point energy corrections
- Phonon density of states needed to compute free energies & equilibrium pressures



Accuracy of DFT-based Values of ΔH

(Wolverton et al., Phys. Rev. B **69** (2004) 144109)

Experimental data available for many high Z metal hydrides (e.g. Sc, Pd, Ni, etc.)



RMS deviation in DFT results is 15 kJ/mol H₂ ;
this is sufficiently accurate for screening purposes

A DFT-based Database of Reaction Enthalpies

We have optimized the crystal structures of 51 solid materials listed in Wyckoff or Pearson comprised of Al, B, Ca, Li, Mg, Si, or H:

Al, Al₁₂Mg₁₇, Al₂Ca, Al₂Ca₃Si₂, Al₂CaSi₂, Al₂Li₃, AlB₂, AlH₃, AlLi, AlLi₃N₂, AlLiSi, AlN, Sc, Sc₅Si₃, ScB₂, ScB₁₂, ScH₂, ScN, ScSi, ScSi₂, Al₂Sc, Al₃Sc, AlSc₂, Li₃ScN₂, Ca₂LiSi₃, Ca₂N, CaB₆, CaH₂, CaLi₂, CaLiSi₂, CaMg₂, CaSi, Li, Li₁₂Mg₃Si₄, Li₃N, Li₅N₃Si, LiBH₄, LiH, LiN₃, LiNH₂, Mg, Mg₂Si, Mg₃N₂, MgB₂, MgB₄, MgH₂, Si, SiB₆, B

Full crystal structure of Ca(AlH₄)₂ is not known experimentally. We used *ab initio* prediction of Løvvik (Phys. Rev. B **71** (2005) 144111)

LiBH₄ transforms from *Pnma* at low T to *P6₃mc* at 384 K
(Soulie et al., J. Alloys Compounds 346 (2002) 200)

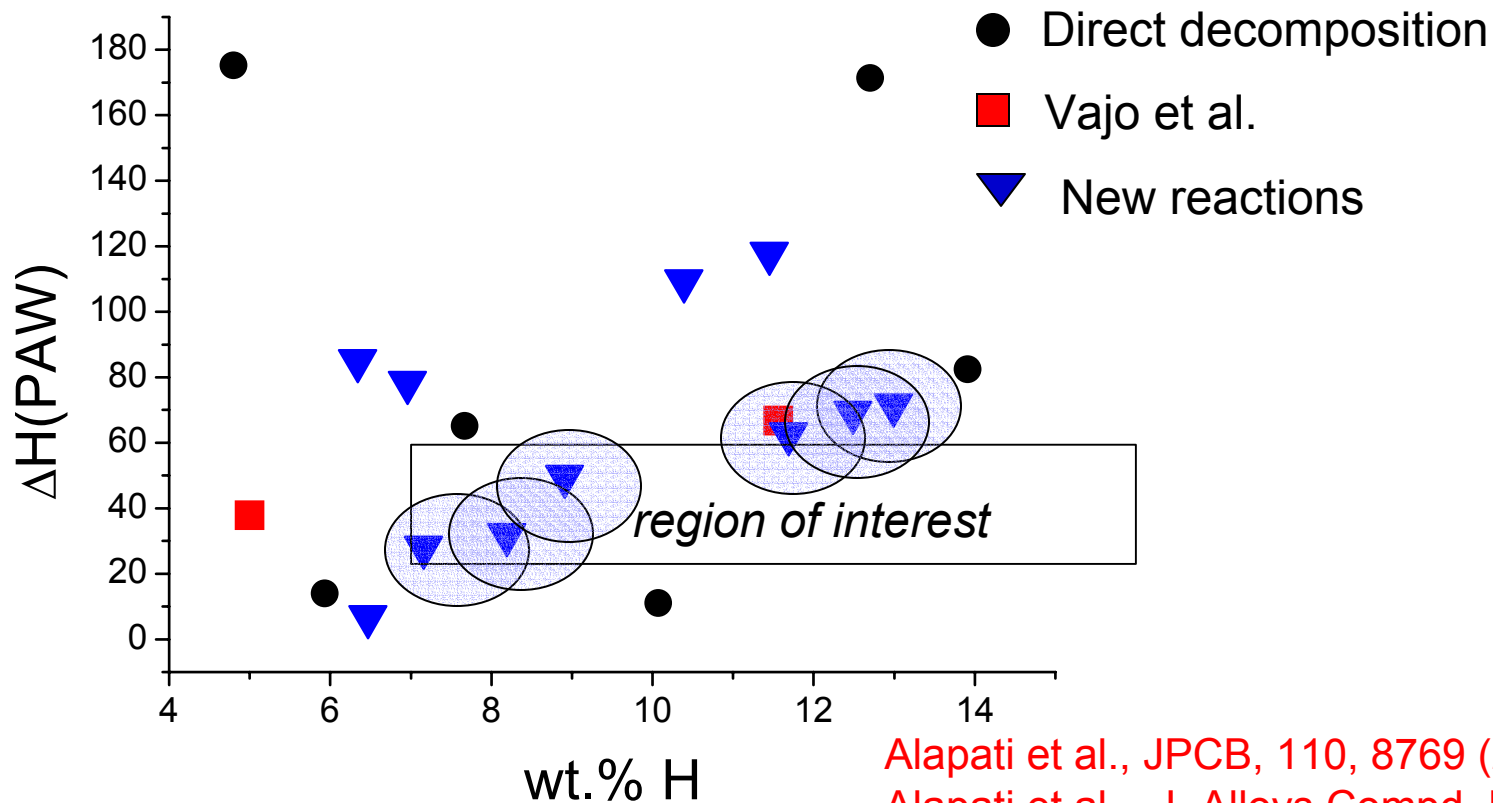
Results below are for *Pnma* form (giving higher ΔH than *P6₃mc*)

Li₅N₃Si has very large unit cell with partial atomic occupancies. DFT calculations performed with two materials with compositions Li₅₄N₃₂Si₁₀ and Li₅₃N₃₂Si₁₁ with Si distributed randomly.

Using this DFT-based database, we have considered >100 reactions that have not previously be evaluated as potential H₂ storage schemes.



Reactions of Interest



Six new promising destabilization schemes identified – all have high densities & promising thermodynamics.

Most schemes (not shown) are less promising for either storage density or thermodynamic reasons (or both).



Promising Reactions

Reaction	wt.% H ₂	ΔH (USPP)	ΔH (PAW)
$3 \text{ LiNH}_2 + 2 \text{ LiH} + \text{Si} \rightarrow \text{Li}_5\text{N}_3\text{Si} + 4 \text{ H}_2$ (10/11 Si atoms)	7.16	29.8/19.2	34.2/23.3
$4 \text{ LiBH}_4 + \text{MgH}_2 \rightarrow 4 \text{ LiH} + \text{MgB}_4 + 7 \text{ H}_2$	12.46	66.8 (o) 57.5 (h)	69.2 (o) 59.9 (h)
$7 \text{ LiBH}_4 + \text{MgH}_2 \rightarrow 7 \text{ LiH} + \text{MgB}_7 + 11.5 \text{ H}_2$	12.99	69.2-73.1 (o) 59.2-63.1 (h)	71.5-75.5 (o) 61.5-65.5 (h)
$\text{CaH}_2 + 6 \text{ LiBH}_4 \rightarrow \text{CaB}_6 + 6 \text{ LiH} + 10 \text{ H}_2$	11.69	60.3 (o) 50.4 (h)	62.7 (o) 52.9 (h)
$\text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{LiMgN} + 2 \text{ H}_2$	8.19	29.7	31.9
$\text{ScH}_2 + 2 \text{ LiBH}_4 \rightarrow \text{ScB}_2 + 2 \text{ LiH} + 4 \text{ H}_2$	8.91	--	49.7



DFT calculations gave the $T = 0$ enthalpy. Is this enough?

$$G \cong U_0 + U_{ZP} + U'_{vib}(T) - TS_{vib}(T) + PV$$

DFT total energy

harmonic approximation using PHONON code (Parlinski)

Ideal gas law

Ackland, *J. Phys. Condens. Matt.*, **14** (2002) 2975

Equilibrium pressure for decomposition reaction given by

$$P = P_0 \exp\left(\frac{-\Delta G(T)}{RT}\right).$$

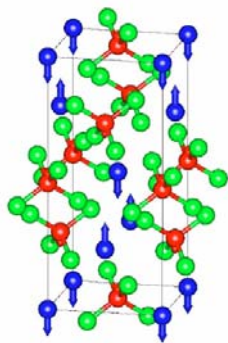


Validation of DFT + Phonon Approach

Calculate Van't Hoff Plots to predict equilibrium pressure for the reaction at any temperature T



Enthalpy Changes $\Delta H(T=0)$



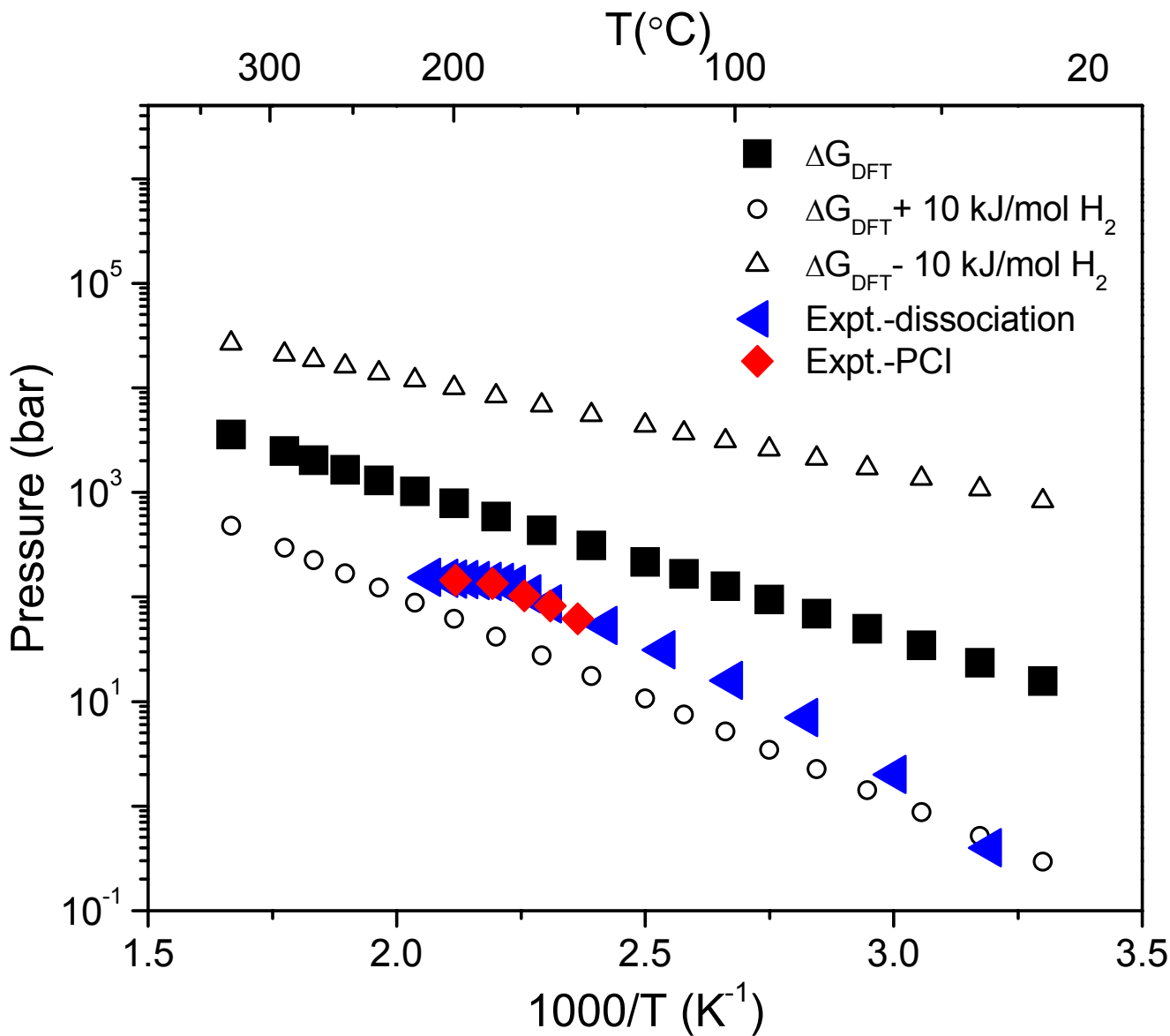
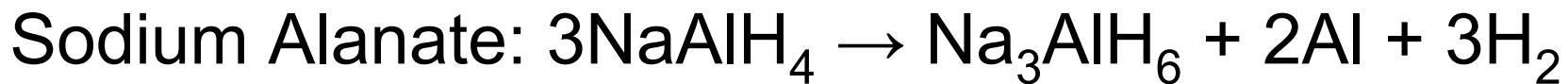
PHONON code¹ direct lattice method

→ C_v and Entropy S



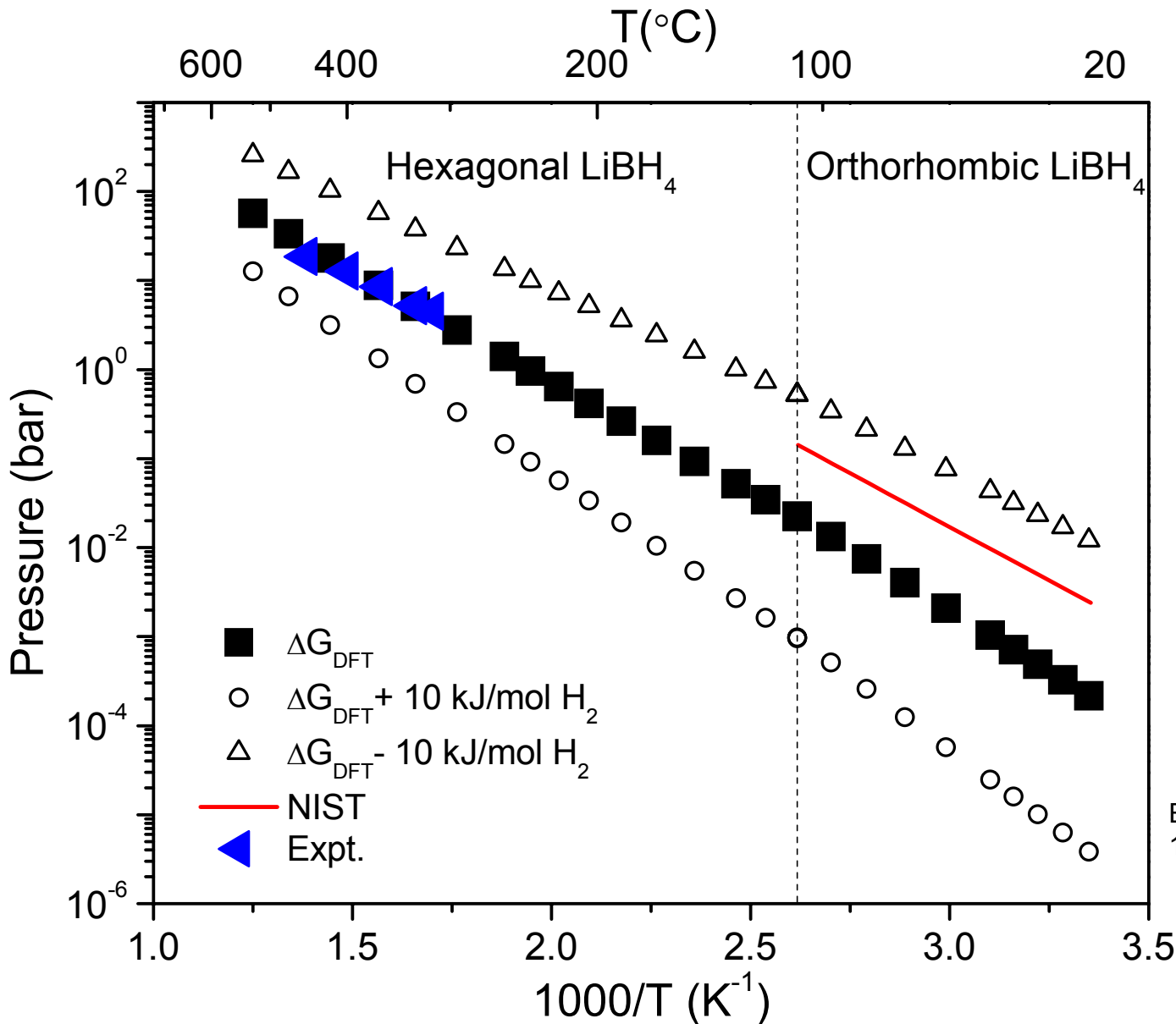
Changes in *Gibbs Free Energy* ΔG

1. K. Parlinski, Software PHONON 2005



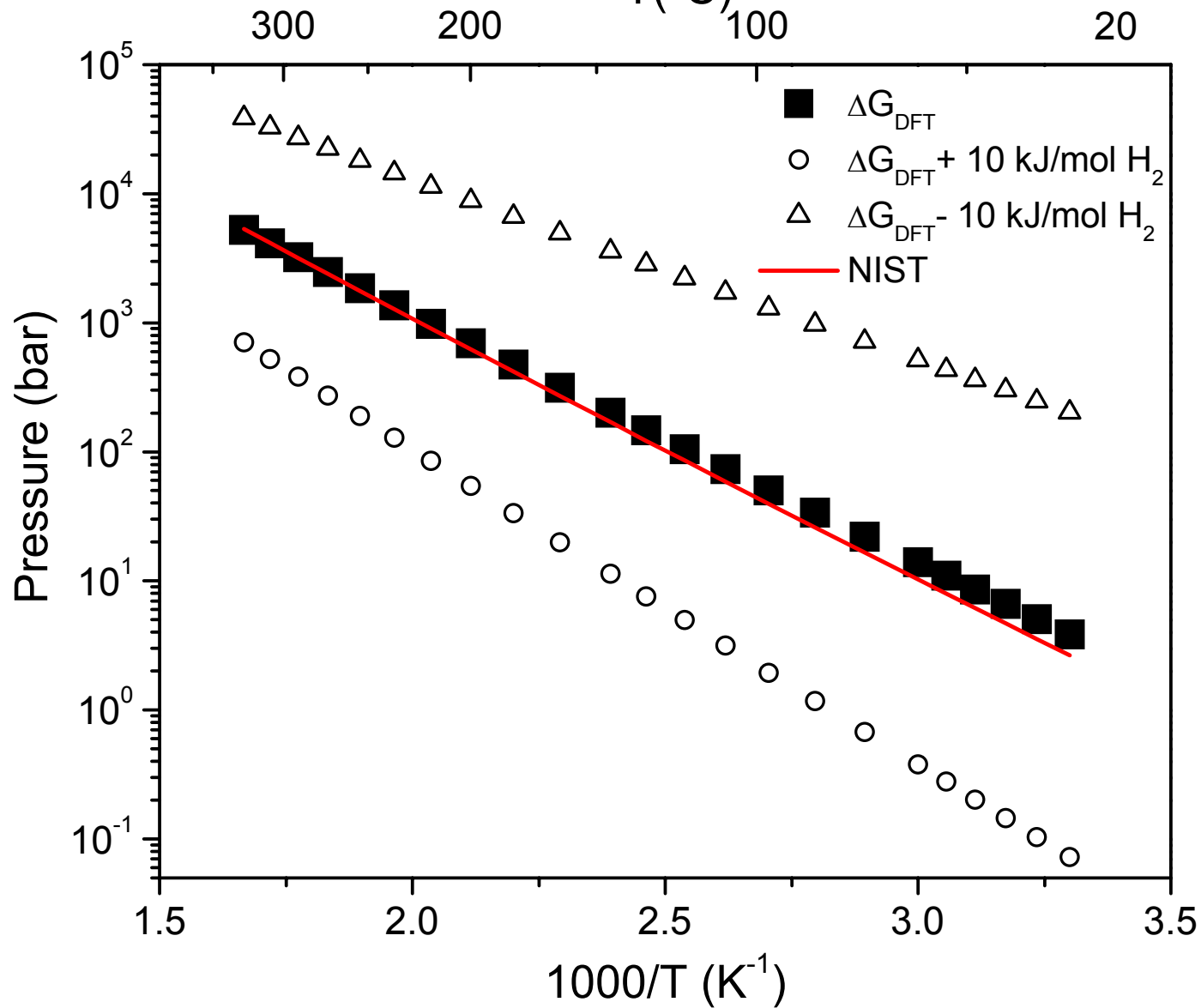
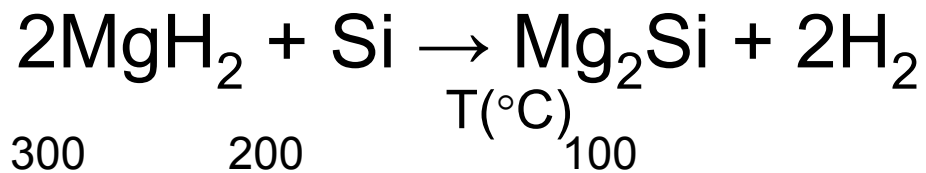
Exp: Bogdanovic et al.,
 J. Alloys Compd. 302,
 36 (2000)

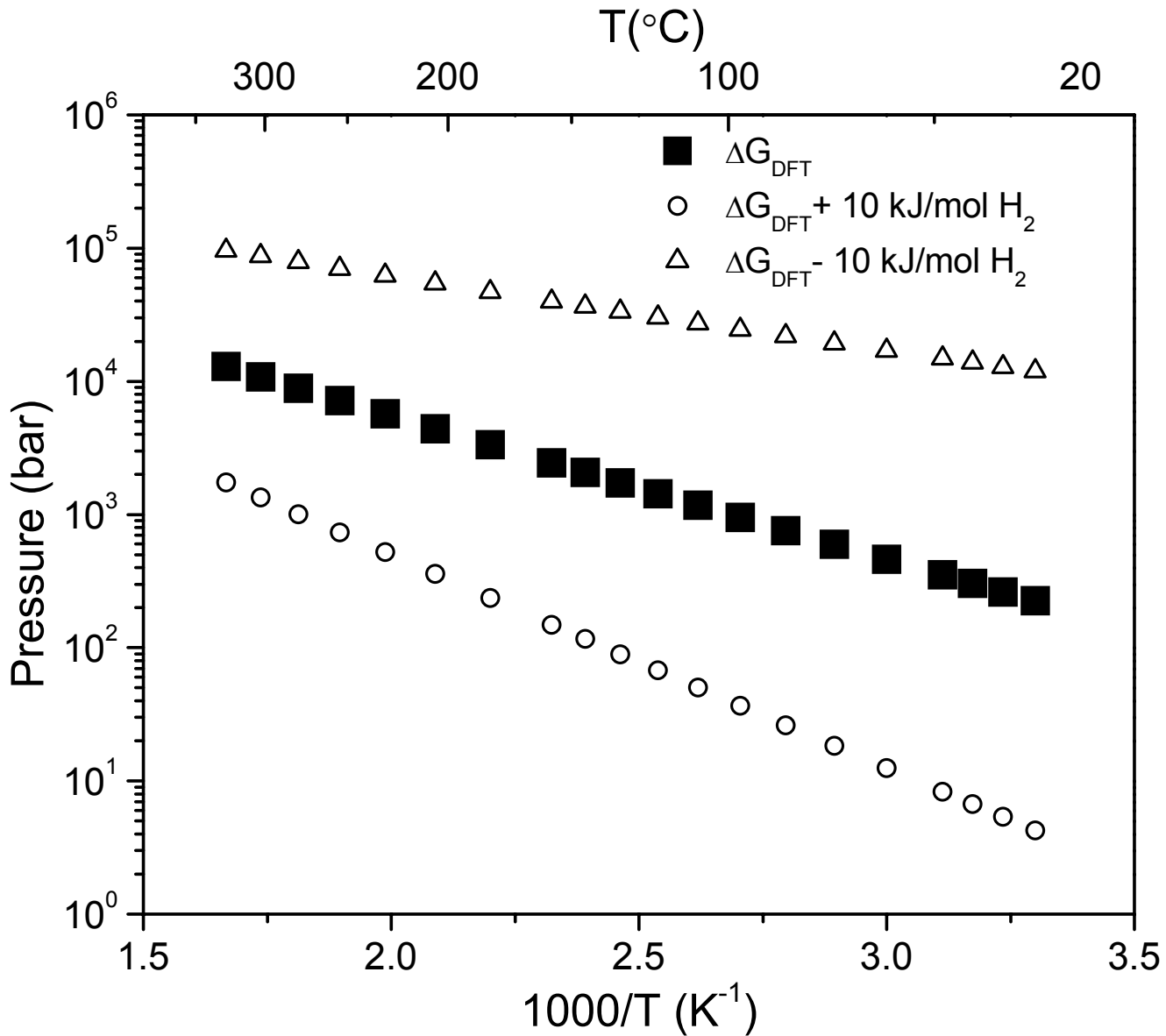
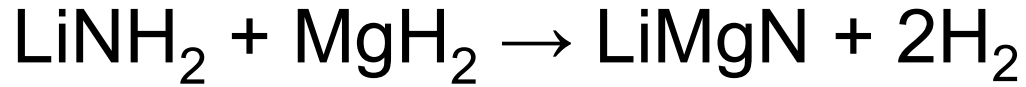


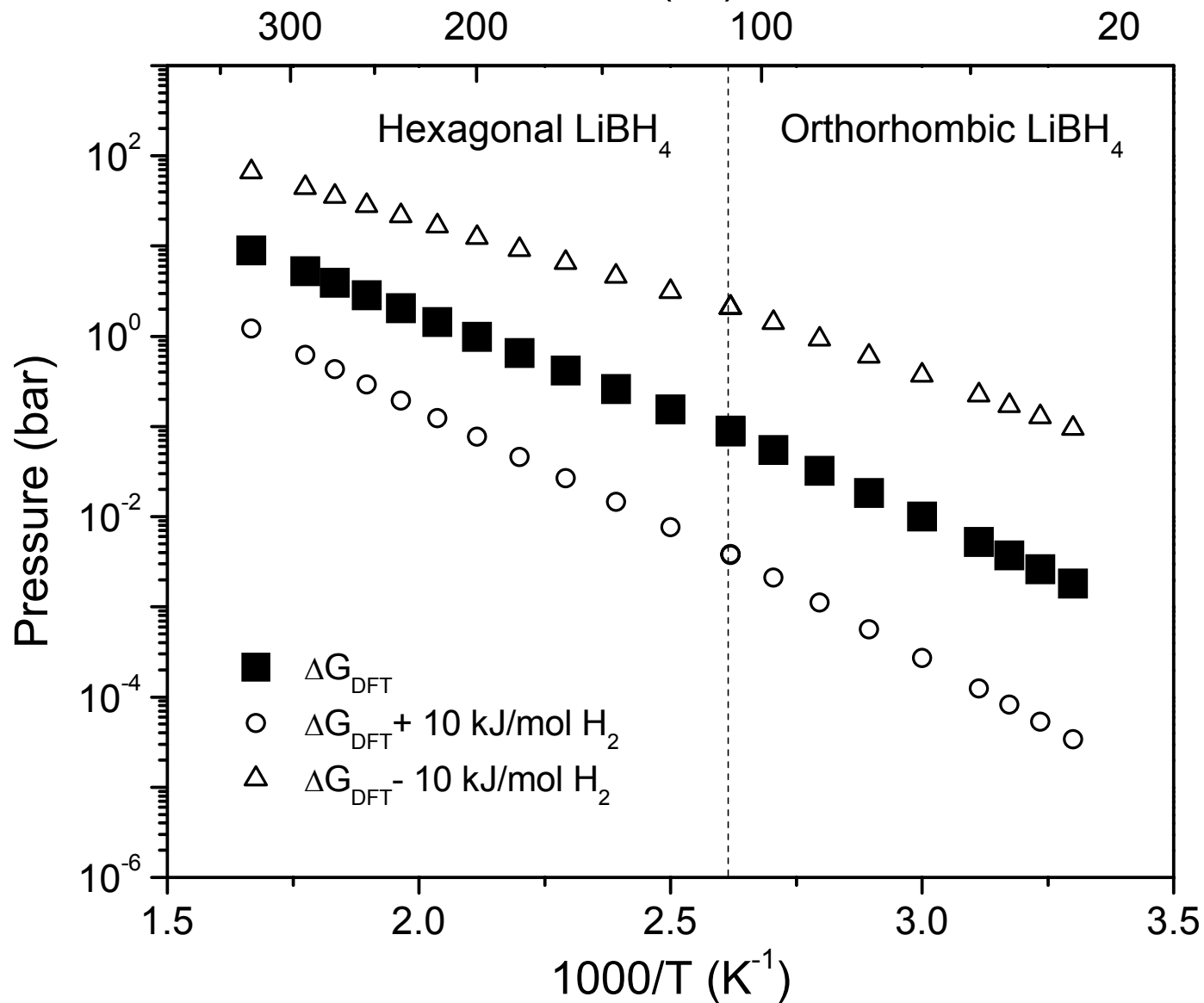
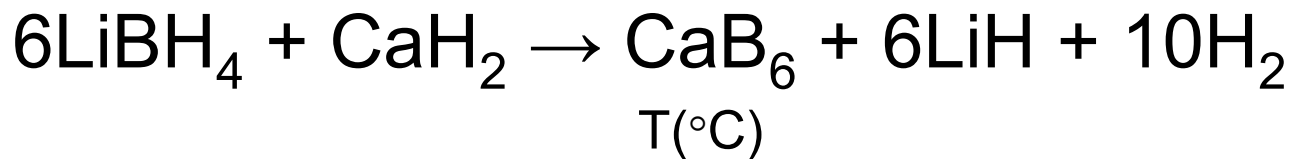


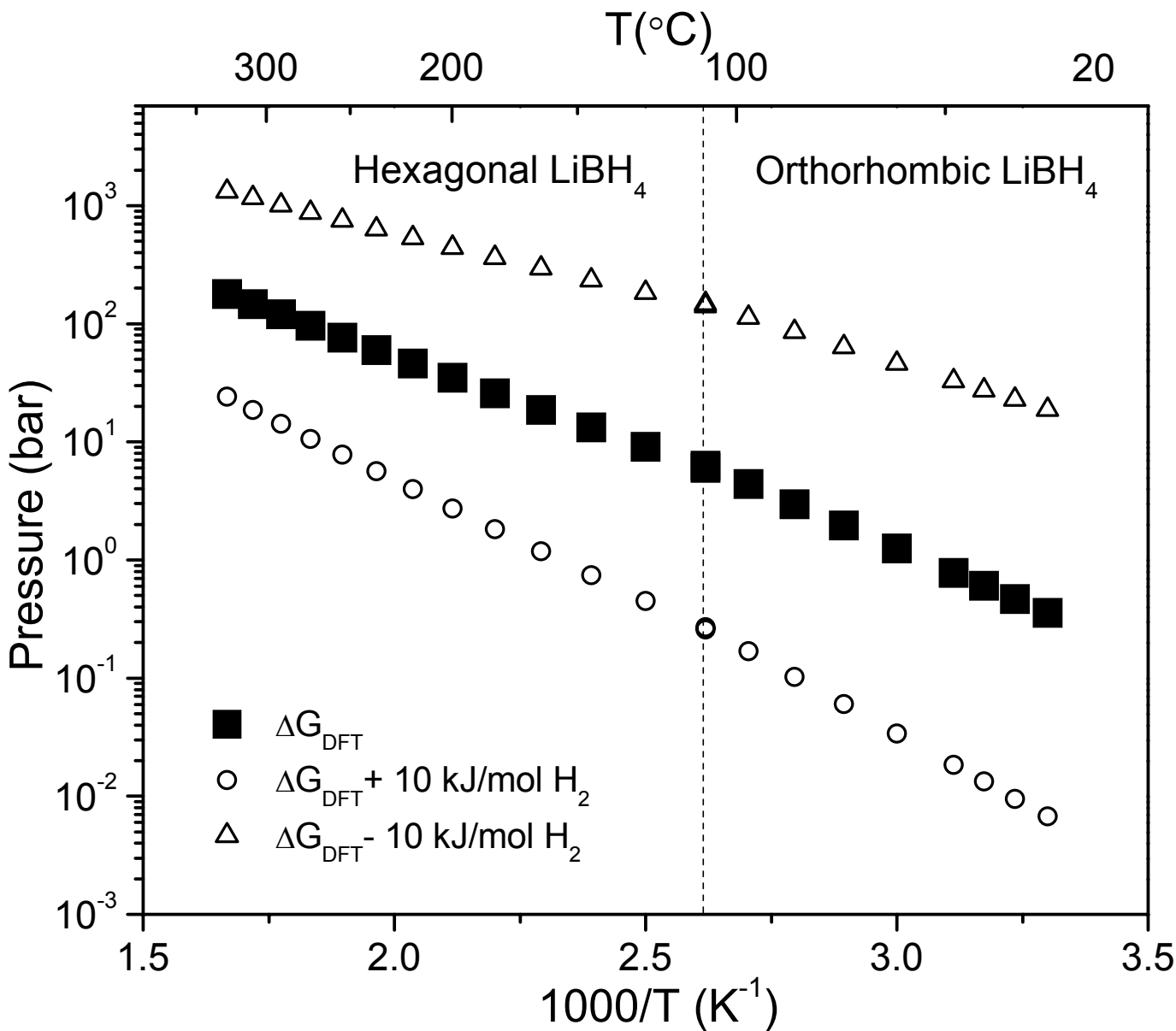
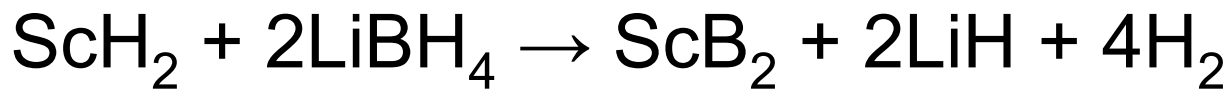
Exp: Vajo et al. JPCB
109, 3719 (2005)











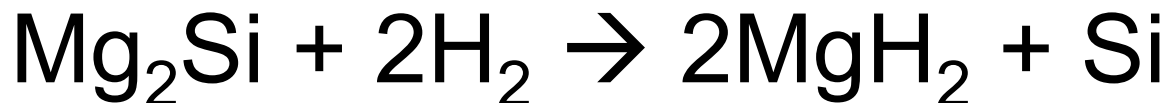
Prediction of Vapor Pressures

- $\text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{LiMgN} + 2\text{H}_2$
 - Pressure probably too high
- $4\text{LiBH}_4 + \text{MgH}_2 \rightarrow 4\text{LiH} + \text{MgB}_4 + 7\text{H}_2$
 - Pressure probably too low
- $7\text{LiBH}_4 + \text{MgH}_2 \rightarrow 7\text{LiH} + \text{MgB}_4 + 11.5\text{H}_2$
 - Pressure probably too low
- $6\text{LiBH}_4 + \text{CaH}_2 \rightarrow \text{CaB}_6 + 6\text{LiH} + 10\text{H}_2$
 - Pressure probably too low
- $\text{ScH}_2 + 2 \text{LiBH}_4 \rightarrow \text{ScB}_2 + 2 \text{LiH} + 4 \text{H}_2$
 - Just about right! ~1 bar @ 50 °C

Experiments on these materials are needed!

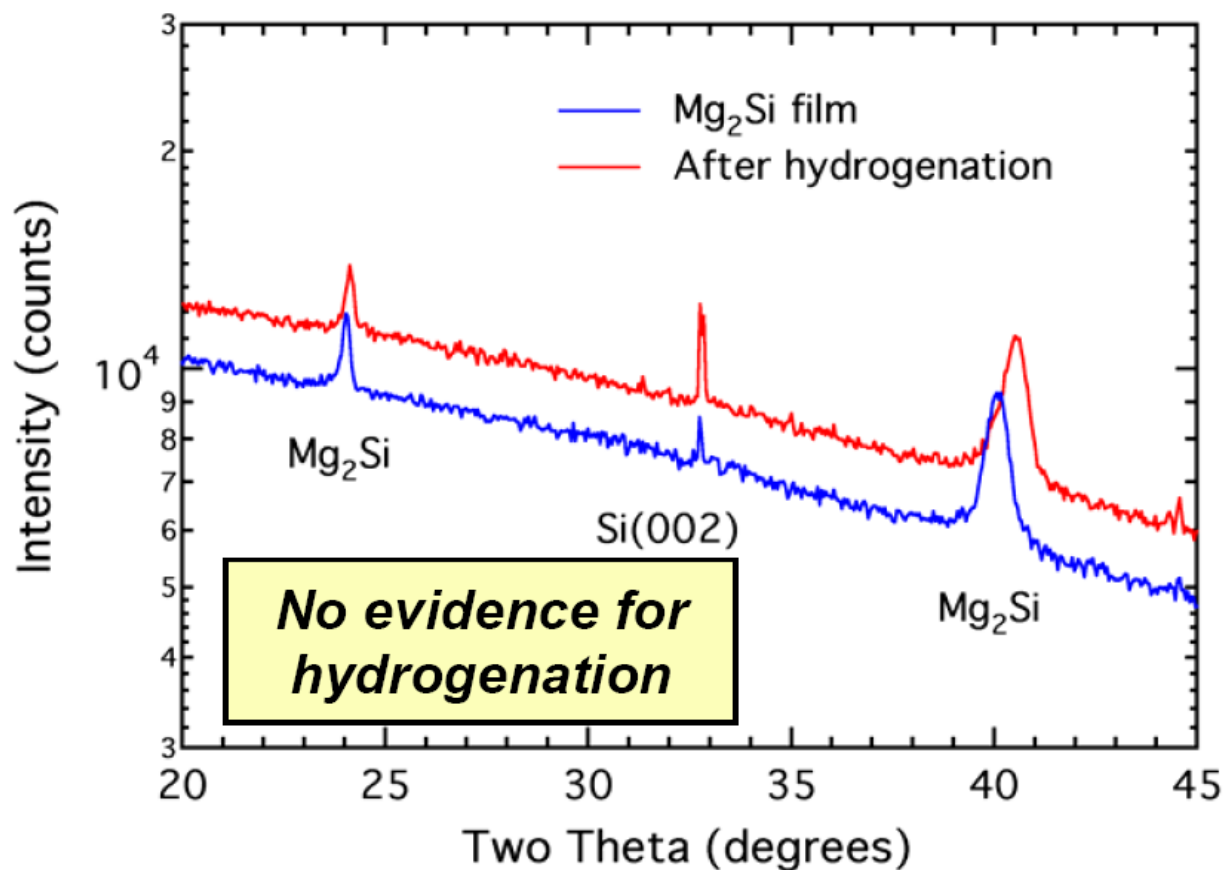


Kinetics of Reversibility:



Strong kinetic limitations observed in destabilized reactions studied to date:

$\text{Mg}_2\text{Si} + \text{H}_2 \rightarrow 2\text{MgH}_2 + \text{Si}$ not observed—even under extreme conditions



H₂ Dissociation on Mg₂Si Surfaces

One possible kinetic barrier to $\text{Mg}_2\text{Si} + \text{H}_2 \rightarrow \text{MgH}_2 + \text{Si}$ is the dissociation of H₂ on surfaces of Mg₂Si

Large barriers to H₂ dissociation are known to exist on Mg(0001)
(T. Vegge, Phys. Rev. B 70 (2004) 035412)

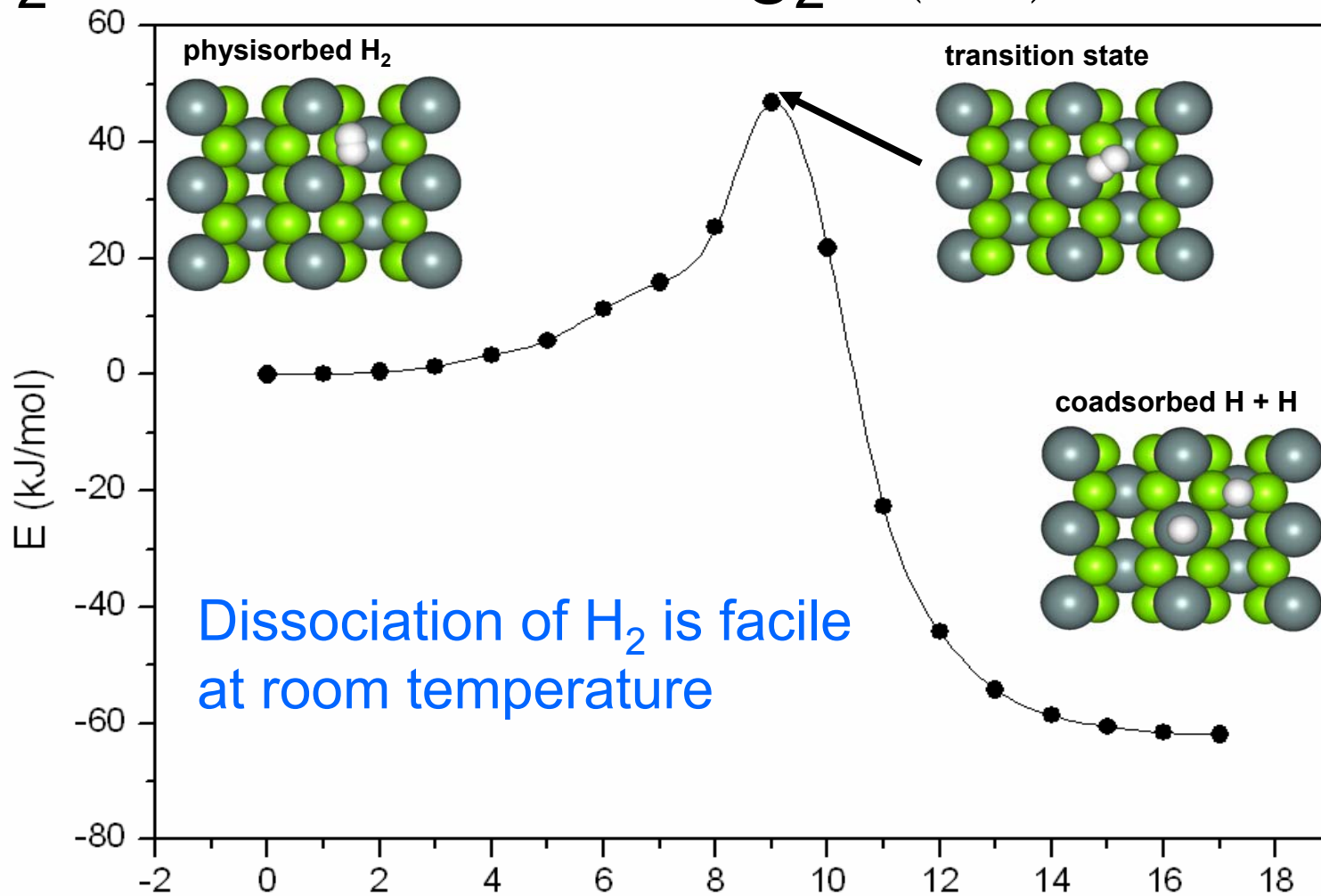
This hypothesis can be disproved if facile pathways for H₂ dissociation are identified

Our strategy is to compute the most favorable binding sites for H-atoms and H₂ on Mg₂Si($\bar{1}10$) and then to find possible dissociation pathways using the *Nudged Elastic Band method** within VASP. The Mg₂Si($\bar{1}10$) surface is very likely to be present in equilibrium Mg₂Si crystals. It is lower in surface energy than other low index surfaces.

*H. Jónsson et al. Surf. Sci. **324**, 305 (1995)



H₂ Dissociation on Mg₂Si($\bar{1}10$)



Dissociation of H₂ is facile
at room temperature

Energy barrier to H₂ dissociation is 45 kJ/mol (39 kJ/mol after ZP corrections)
cf. ~110 kJ/mol on Mg(0001) (T. Vegge, Phys. Rev. B 70 (2004) 035412)

H₂ Dissociation on Mg₂Si

H₂ dissociation rates can be estimated using Transition State Theory
(T. Vegge, Phys. Rev. B 70 (2004) 035412)

TST dissociation rate/surface site at P_{H₂} = 1 bar:

T = 20 °C → rate is > 1 s⁻¹

T = 300 °C → rate is > 1000 s⁻¹

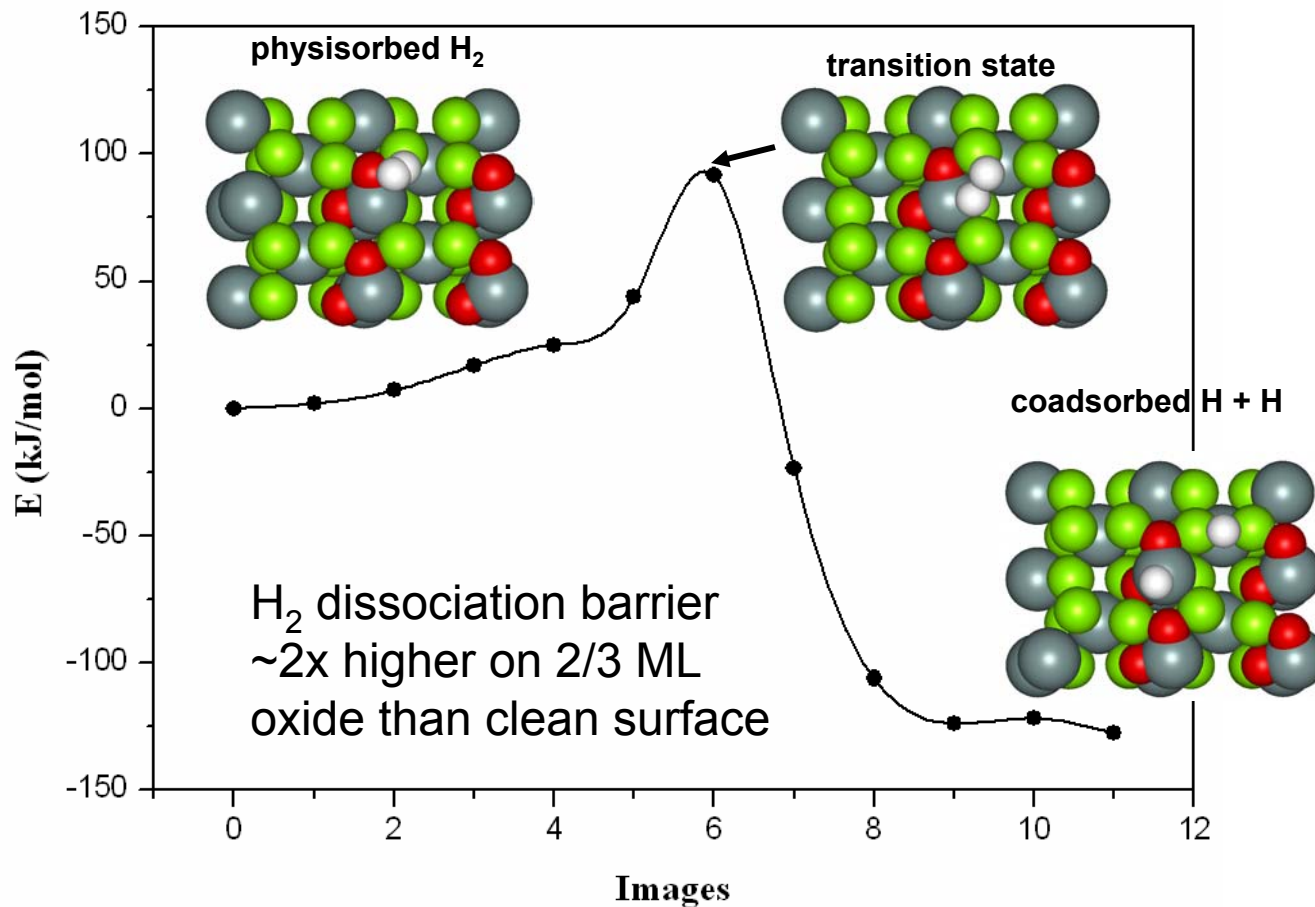
H₂ dissociation appears to be facile on Mg₂Si($\bar{1}10$)
so H₂ dissociation is not the rate limiting step in Mg₂Si hydrogenation

Many other atomic-scale processes must still be considered before a complete description of the overall hydrogenation reaction is available

- Oxide overlayer formation?
- Formation of MgH₂ from the hydrogenated surface?
- Segregation of MgH₂ and Si?

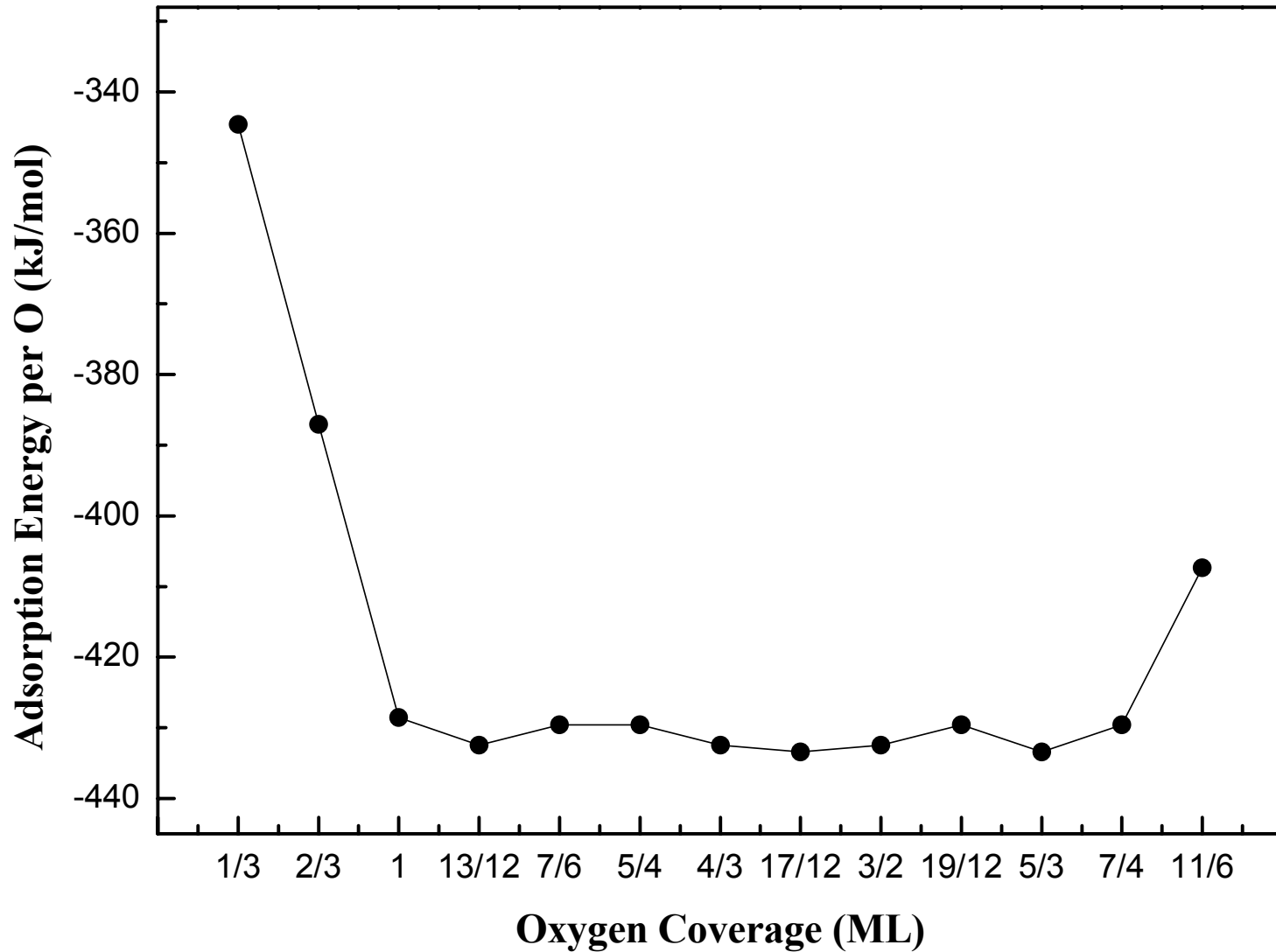


Oxide Formation on the Mg_2Si Surface: 2/3 Monolayer Coverage

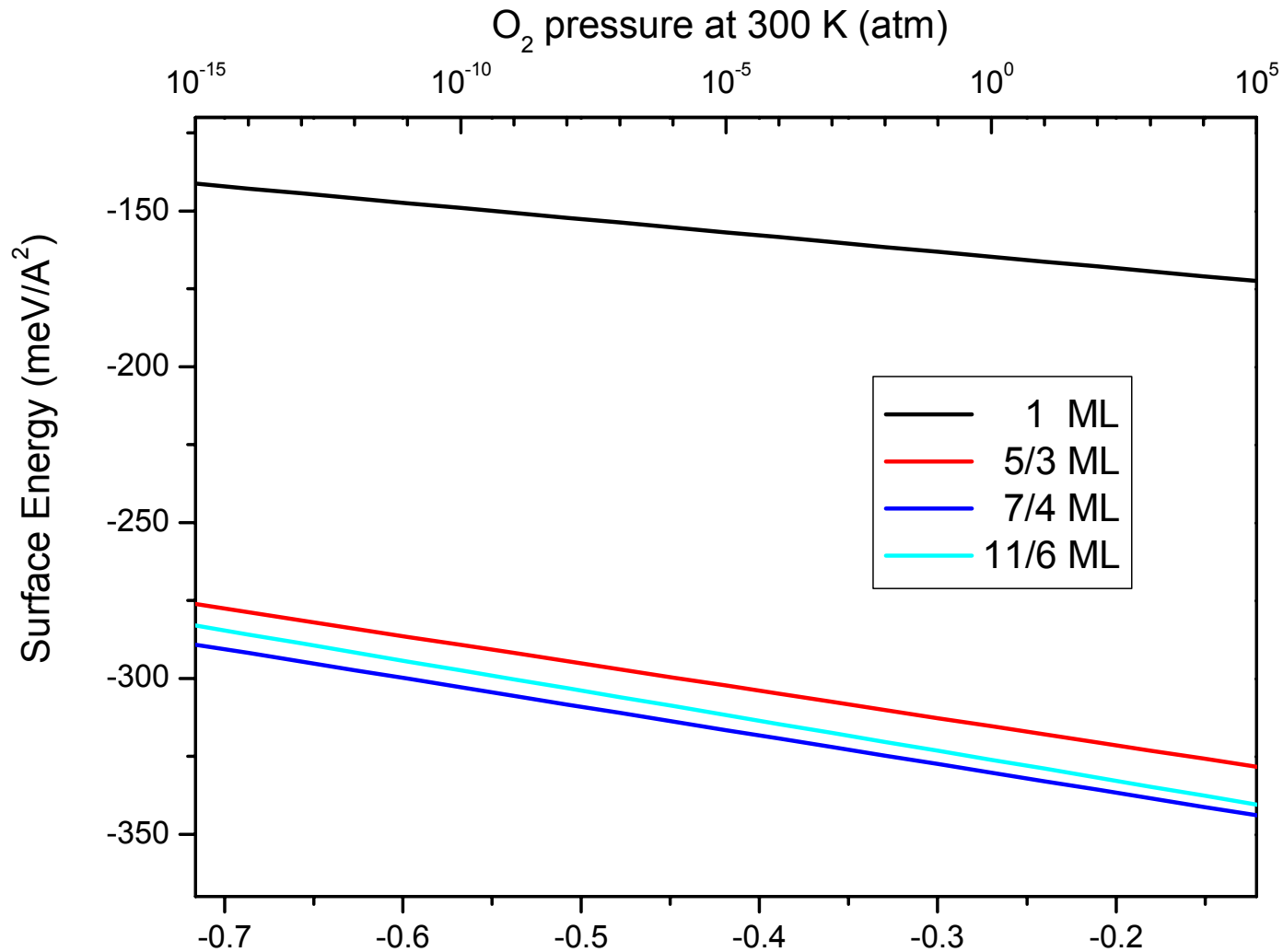


**Energy barrier to H_2 dissociation is 92 kJ/mol
(80 kJ/mol after zero point energy corrections)**

Energetics of Oxide Formation On Mg_2Si



What is the Extent of Oxide Formation?

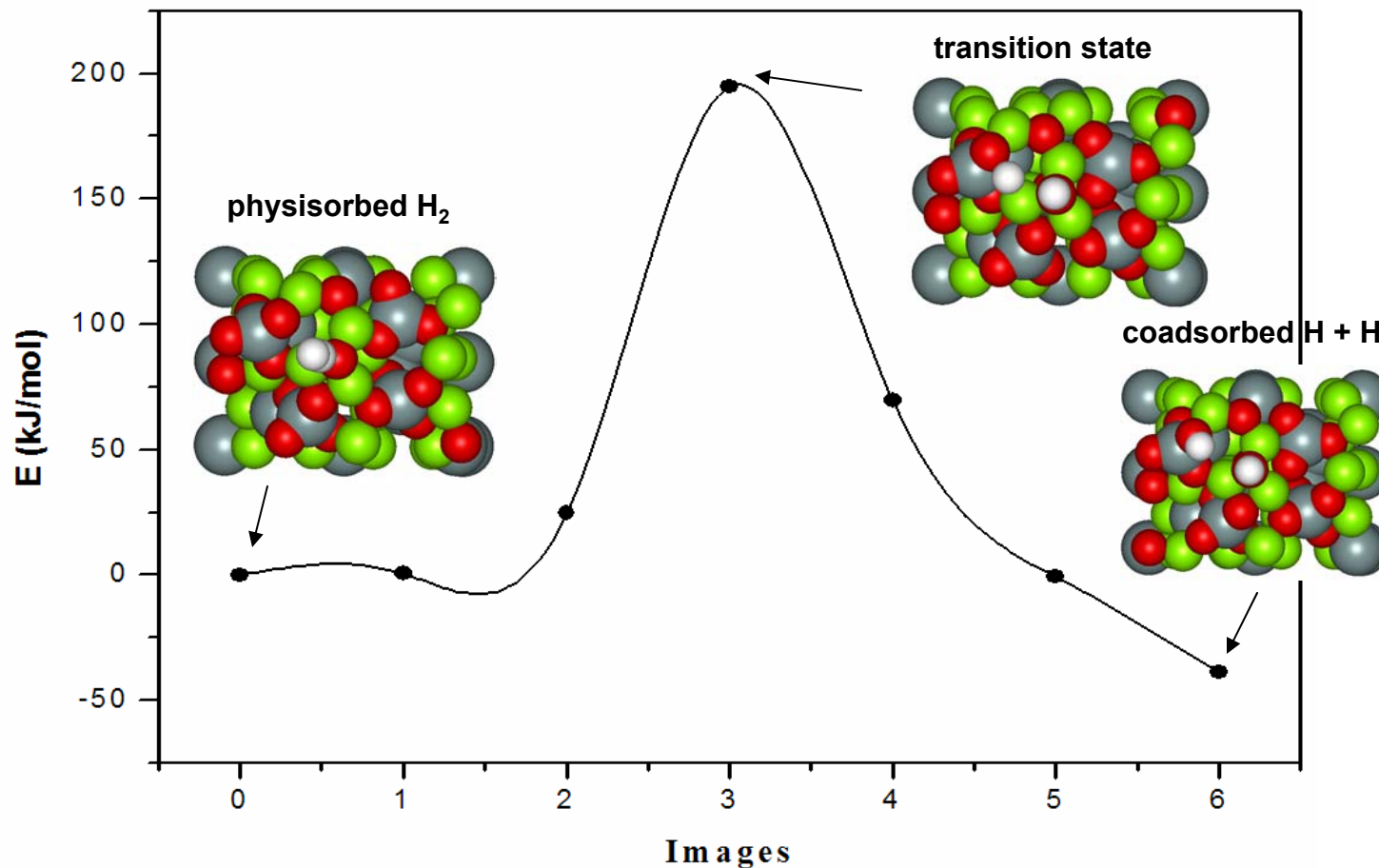


$$\gamma = \frac{1}{2A} \left[E^{\text{slab}} - \frac{1}{2} N_{\text{O}} E_{\text{O}_2} - N_{\text{Mg}_2\text{Si}} E_{\text{Mg}_2\text{Si}}^{\text{bulk}} - N_{\text{O}} \mu_{\text{O}}(p, T) \right]$$

O chemical potential (eV)



Energy barrier to H₂ dissociation on the 7/4 ML oxide surface is 195 kJ/mol



Conclusions—Metal Hydrides

- Destabilized metal hydrides are perhaps the most promising known materials for achieving high density reversible storage of H₂
- Our DFT-based database has allowed several hundred additional reactions to be screened based on reaction enthalpy.
- Six promising examples have been identified, plus a larger number of metastable reaction schemes.
- Entropic terms may be included through calculating the phonon density of states.
- Calculated van't Hoff plots are in reasonable agreement with experiments



Conclusions—Metal Hydrides

- Facile dissociation of H_2 should be observed on the clean Mg_2Si surface.
- Surface oxide formation is very exothermic.
- Surface oxides inhibit adsorption and dissociation of H_2 on Mg_2Si .
- Calculations are in accord with experiments indicating that ball milling under a hydrogen atmosphere is required to hydrogenate Mg_2Si . (Janot et al., Intermetallics, 14, 163 2006)



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- F. E. Pinkerton
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- DOE Metal Hydride Center of Excellence.

