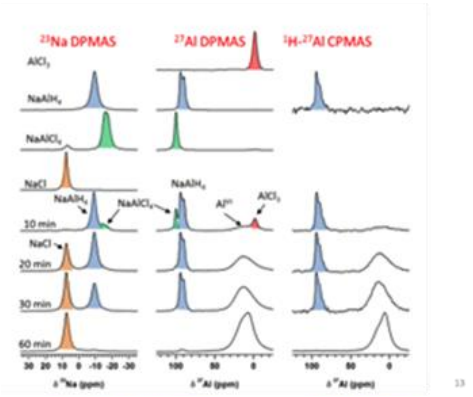
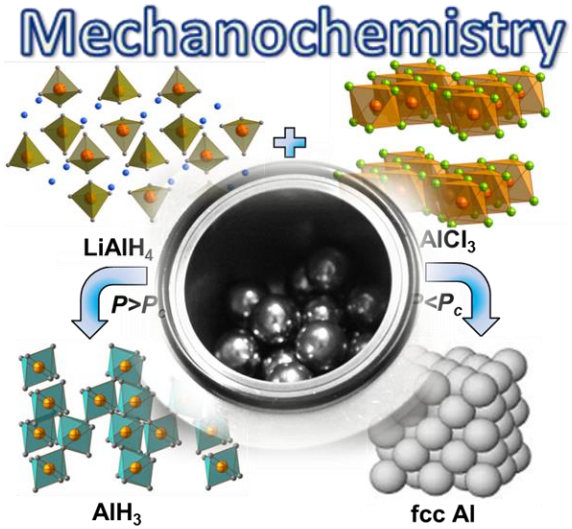
U.S. DEPARTMENT OF ENERGY

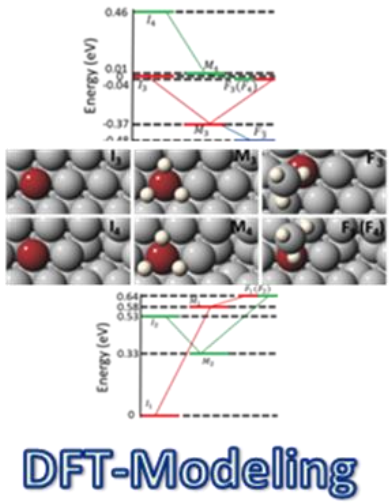
THE Ames Laboratory

Creating Materials & Energy Solutions



Solid-State NMR





DFT-Modeling

Hydrogen Storage Research Capabilities

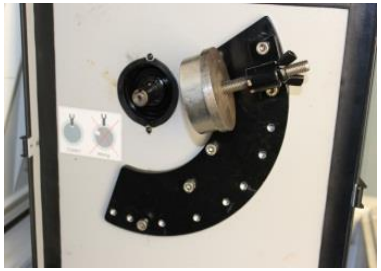
V.K. Pecharsky, D.D. Johnson, M. Pruski, L.S. Chumbley,

Shalabh Gupta, Linlin Wang and Takeshi Kobayashi

IOWA STATE UNIVERSITY
OF SCIENCE AND TECHNOLOGY

Unique High-Pressure Mechanochemistry Capability

Magnetic ball-mill



Mechanical milling (details)

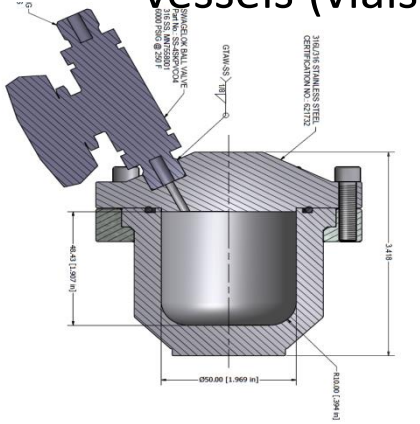
- Temperatures (-30 °C to R.T.)
- Intensity controlled by rotation and magnetic field
- Impact and/or shear mode – Switched by magnet placement
- Ambient, inert or high-P reactive environment.

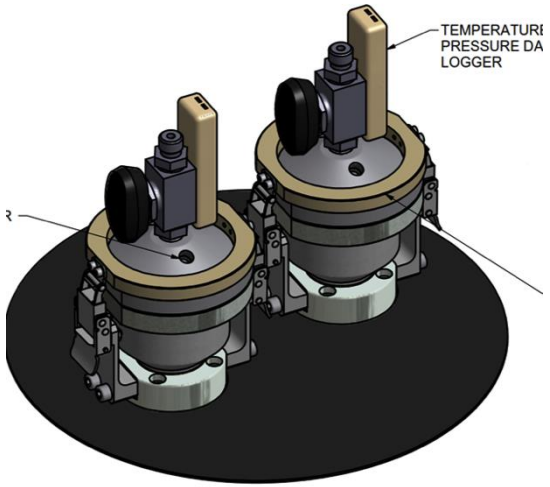
Precise control over the delivery of mechanical energy

High-pressure, High-Energy (Programmable) Milling

Planetary style micro mill (PULVERISETTE 7, Fritsch)

High-pressure vessels (vials)





- Dry or liquid grinding at gas pressures up to 350 bar.
- Rotation speed up to 800 rpm
- Programmable milling

- **Designed up to 350 bar H_2 pressure**
- ***In-situ* monitoring of P and T** during milling (1-300 bar, 23-100 °C)
- 316 steel resistant to H embrittlement
- 440C steel sleeve for wear resistance

Knowledge of critical events during mechanochemical processing

Cryomilling

- Rapid nanostructuring
- Microstructural refinements
- New light-weight alloys

Can introduce H_2 capability!

Milling at 77 K under H_2 atm. is unprecedented!

Understand Mechanochemistry

- Lack of analytical methods to monitor MTs in real time ≡ lack of basic understanding of the mechanisms
- develop analytical tool to facilitate in-situ neutron diffraction characterization of MTs in real time (Bragg and total scattering), in collaboration with ORNL-SNS

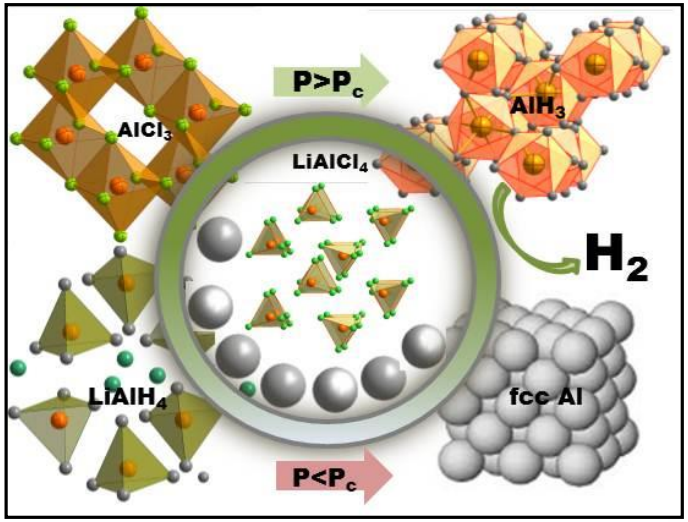
- Science we are after
  - ✓ Identify changes at the atomic length scale
  - ✓ Deduce atomistic mechanisms of MTs critical to BES mission
- Start with VULCAN; later integrate with NOMAD

Potential for a broad use by H-storage community

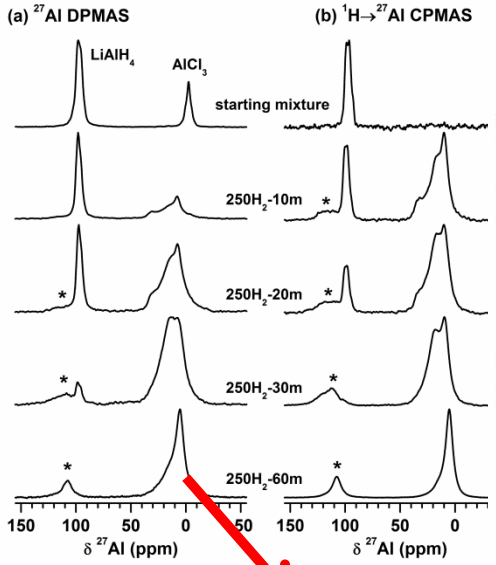
High-Pressure Mechanochemistry: Alane via Metathesis

$$3LiAlH_4 + AlCl_3 \xrightarrow{\text{RT, no ether}} 4AlH_3 + 3LiCl$$

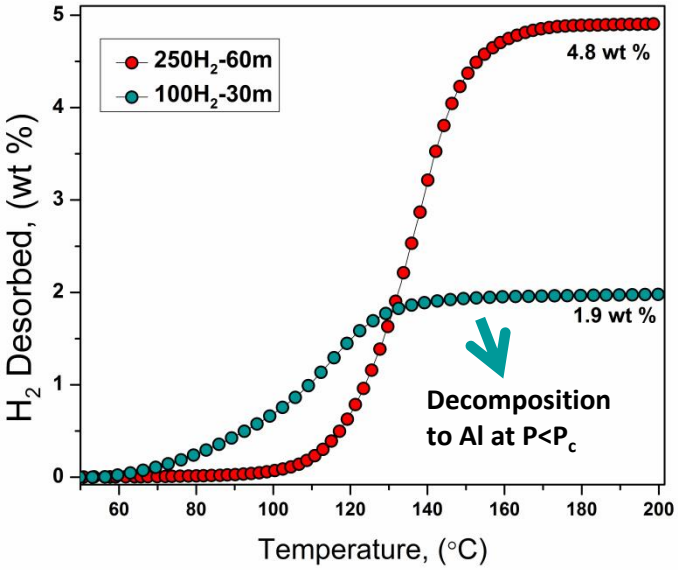
Adduct- free alane



^{27}Al NMR



All Al is 6-coordinated indicating formation of AlH_3



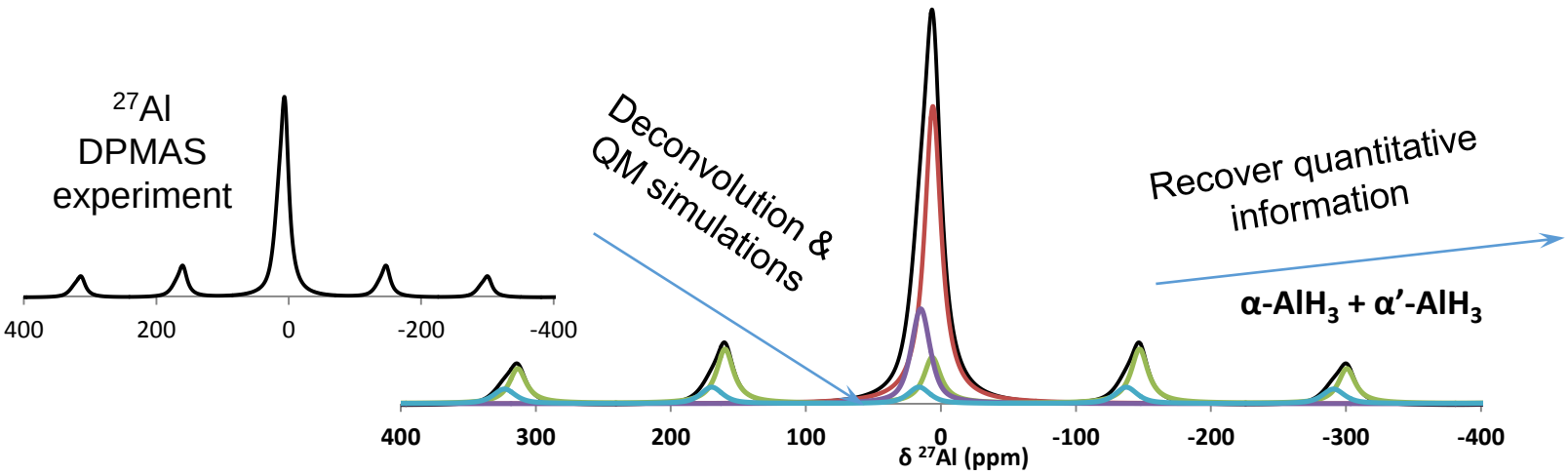
TPD/ Quantitative yields of AlH_3

Gas pressure during ball-milling can alter reaction pathways!

Quantitative SS-NMR

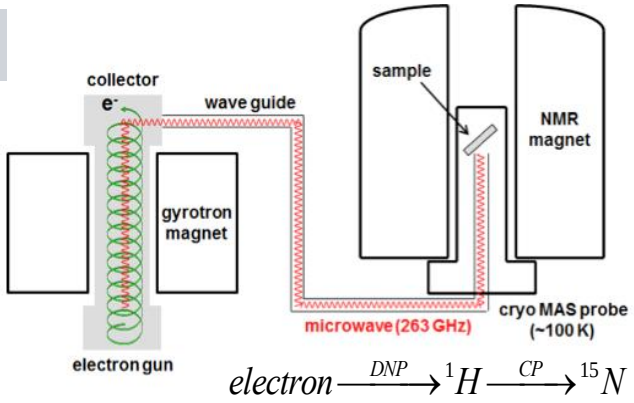
- Deconvolute SS-NMR spectra collected under quantitative conditions
- High-resolution reveals key features
- Simulated spin dynamics addresses quadrupolar coupling

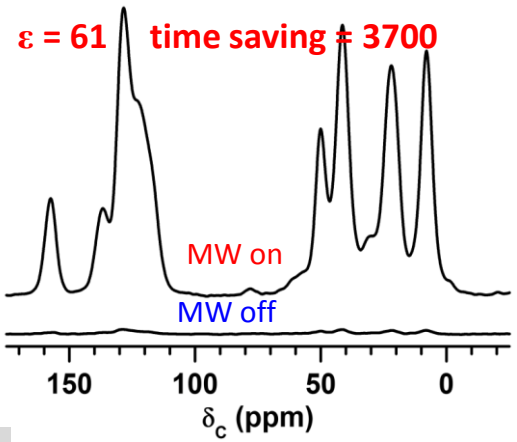
e.g., $4LiAlH_4 + AlCl_3 = 3LiCl + 4AlH_3 + LiAlH_4$



Fully quantitative SSNMR is critical for mechanistic developments

Solid-State (Dynamic Nuclear Polarization) NMR



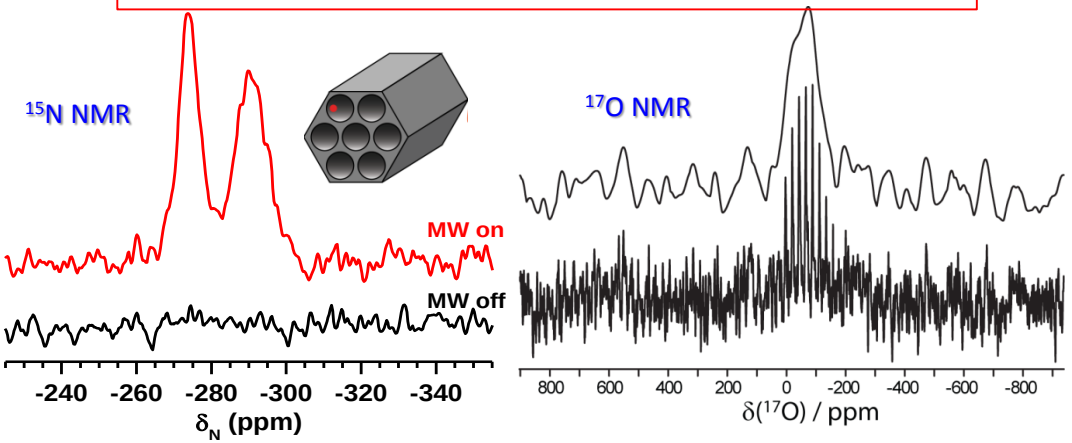


DNP-NMR installed in July 2014
(9.4 T, 263 GHz)

Electron Spin-Resonance (ESR) to excited nuclei enhancements up to $\gamma_e/\gamma_H \approx 660$ or $\gamma_e/\gamma_N \approx 6500$

^{13}C scan of catalytic moieties on silica

DNP-NMR ^{15}N and ^{17}O spectra at natural abundance



SS-NMR: ^{13}C or ^{15}N signal is enhanced by ^{1}H via cross-polarization (CP), yielding ε of 4 (^{13}C) or 10 (^{15}N)

DNP NMR: DNP combined with CP can yield ε of ~2640 (^{13}C) or ~6500 (^{15}N)

✓ **Unique DNP-enhanced NMR provides unparalleled environmental information**

Sensitive Instruments Facility (SIF): Advanced Suite of Instruments

SIF advanced capabilities potentially available for H-storage research

ADVANCED E-BEAM Characterization Instruments

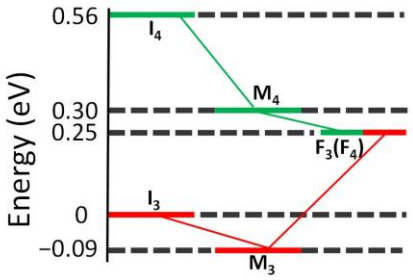
- FEI Teneo LoVac Field Emission SEM (FE-SEM)
- FEI Helios G3 UC Dual-Beam Focused Ion Beam (FIB) and FE-SEM
- FEI Tecnai G2 F20 Scanning TEM (STEM)
- FEI Titan Themis 300 Cubed 300 STEM/TEM

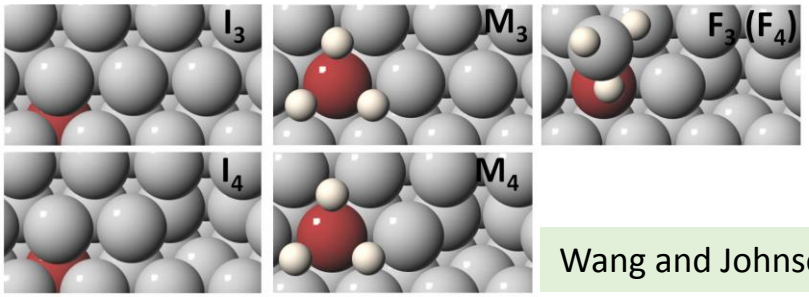
Theoretical Capabilities at Ames Lab

- ❑ **Surface Catalytic Reactions**
  - Defect-mediated Alane formation on Ti-doped Al(111)
- ❑ **Thermal Annealing for Structural Predictions**
  - $NaAlH_4$ and $AlCl_3$ reaction intermediate
- ❑ **Proper Solid-State Nudged Elastic Band for Solid-Solid Transitions**
  - Transformation pathway for Alane polymorphs
- ❑ **Configurational Thermodynamics for Nanoalloy with Adsorbates**
  - Simulating adsorption isotherm (hydrogen evolution reaction, HER)

Defect-mediated Alane Formation on Al(111)

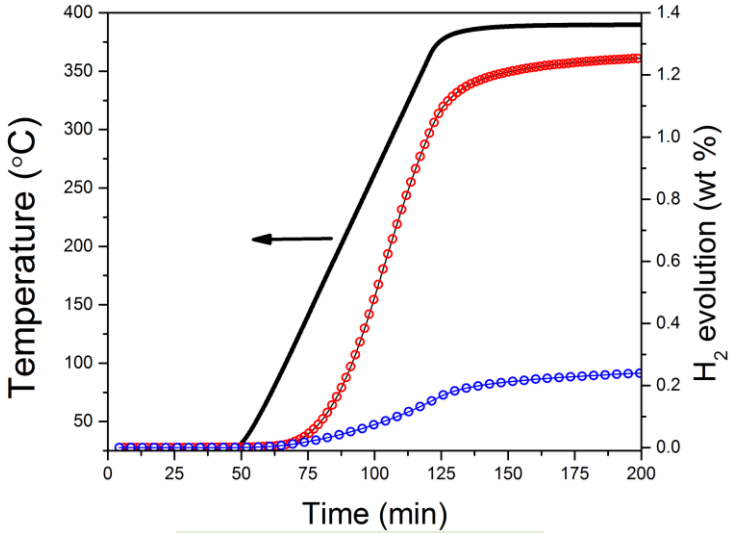
Reaction diagram





Wang and Johnson

Ball-milling: Ti-doped Al



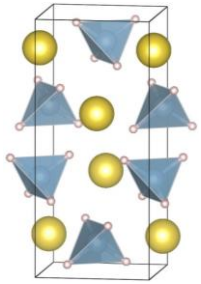
Gupta and Pecharsky

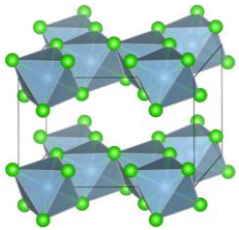
Defects play significant roles

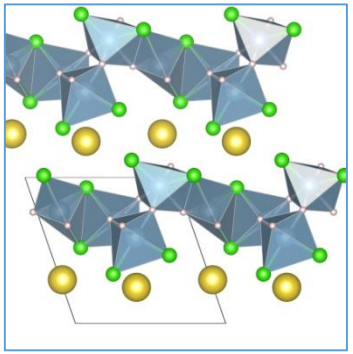
- ✓ **Ti helps dissociate H_2 to facilitate AlH_3 formation**
- ✓ **Al adatom with vacancy make AlH_3 formation exothermic**
- ✓ **Confirmed ball-mill formation under 344 bar of H_2 (a 30-fold reduction of P_{H2}!)**
- ✓ **Coupling theory and experiment to achieve understanding of mechanism**

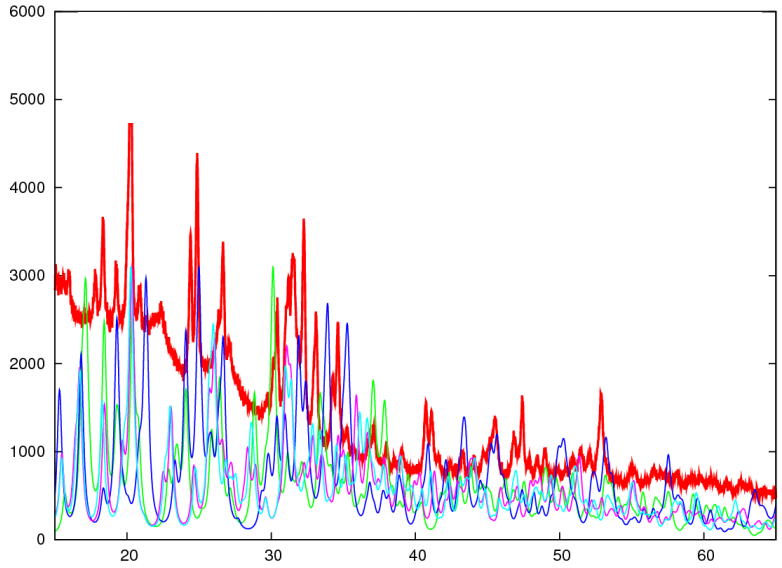
Solve Unknown Reaction Intermediate

$NaAlH_4$ + $AlCl_3$ → $NaAl_2Cl_3H_4$









- Thermal annealing with *ab initio* MD
- PEGS (Eric Majzoub)

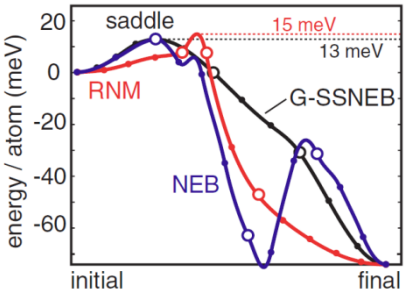
✓ **Knowledge of intermediates is critical for progress, especially in multi-step reactions.**

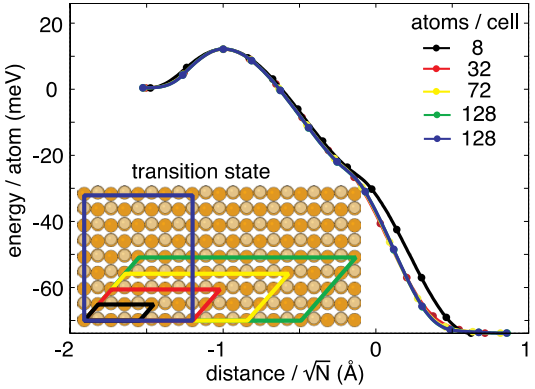
Generalized Solid-Solid Nudged-Elastic Band (G-SSNEB)

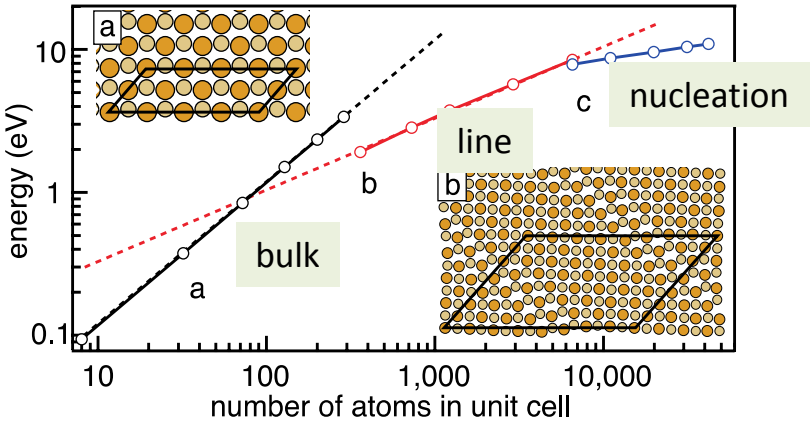
Predicts atomic- and cell-dominated processes, and properly coupling, i.e., *atomic degrees of freedom* versus *cell distortion*, and *nucleation events*.

❑ **Invariant versus size of cell**
– for cell-dominated path

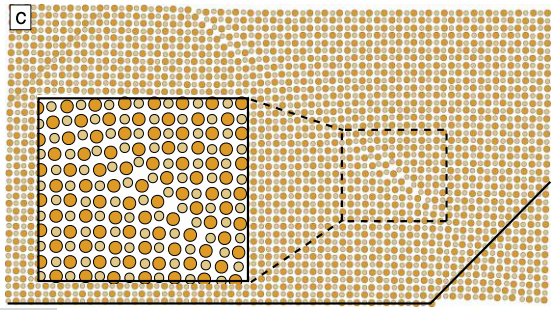
❑ **G-SSNEB jointly handles atomic + cell DOF**
and contains nucleation for LARGE cells







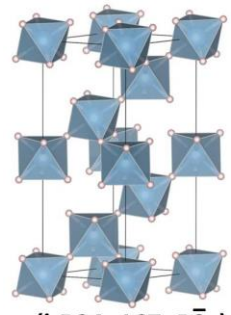
CdSe: *rock-salt to wurtzite*



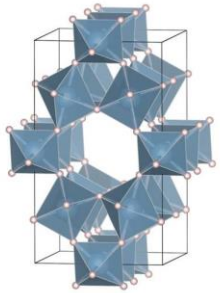
- **Some NEB models decouple DOF that should not be!**
  Original NEB minimizes forces – purely local Trinkle et al. PRL 91 025701 (2003)
  ***Rapid Nuclear Motion* – purely cell distortion** Casperson & Carter PNAS 102, 6738 (2005
- **Alternative NEB models are not CELL INVARIANT!**
- **Transition states are not always SADDLE-POINTS!**
- **Multi-scale modeling for hydrogen storage materials**

G-SSNEB Method: D. Shepard, et al. , J. Chem Phys 136, 074103 (2012)

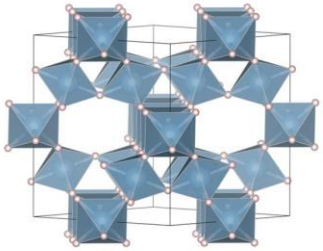
Solid-State Transformations of Alane Polymorphs



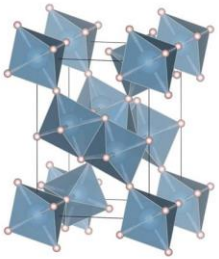
α (hR24, 167, R$\bar{3}$c)



α' (oP24, 63, Cmcm)

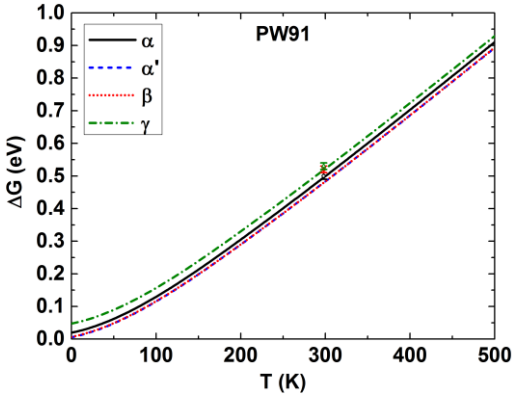


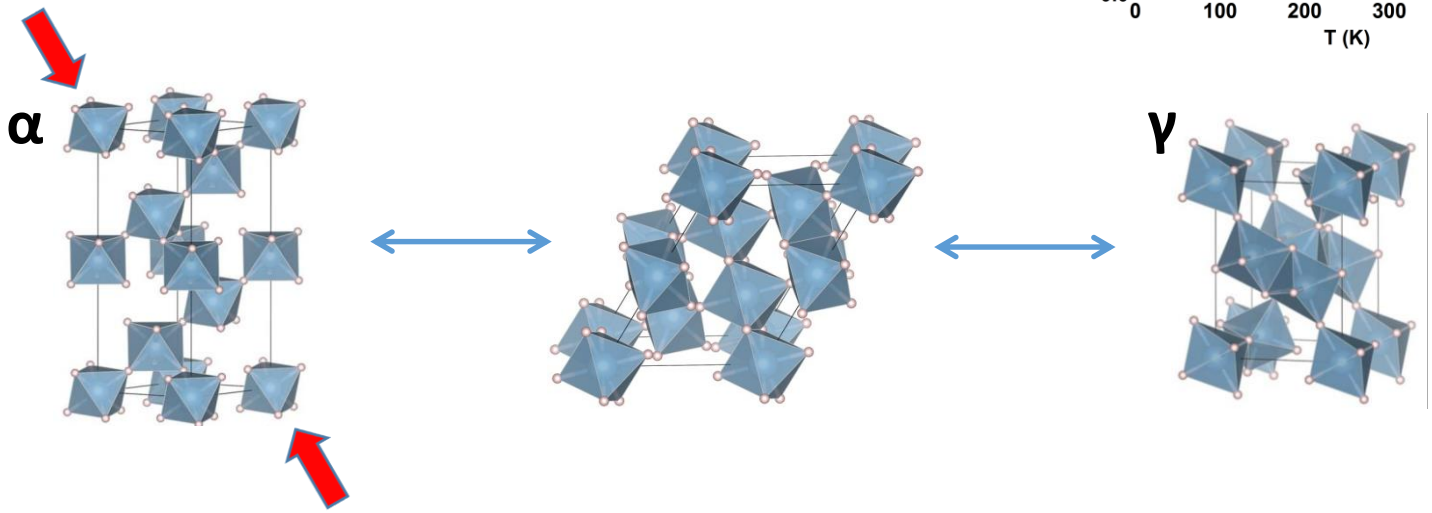
β (cF*64*, 227, Fd$\bar{3}$m)



γ (oP24, 58, Pnnm)

Reaction free energy





- α phase is the most stable against decomposition
- Cell deformation gives edge-sharing Al-H octahedra
- Complex transformation pathways with intermediates for just alane polymorphs

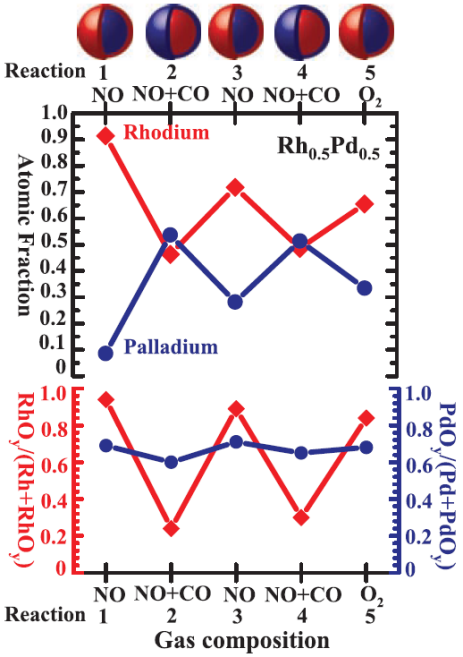
Alloyed Nanoparticle (NP) Configurational Change

PdRh NP core-shell reversal in oxidizing/reducing gas

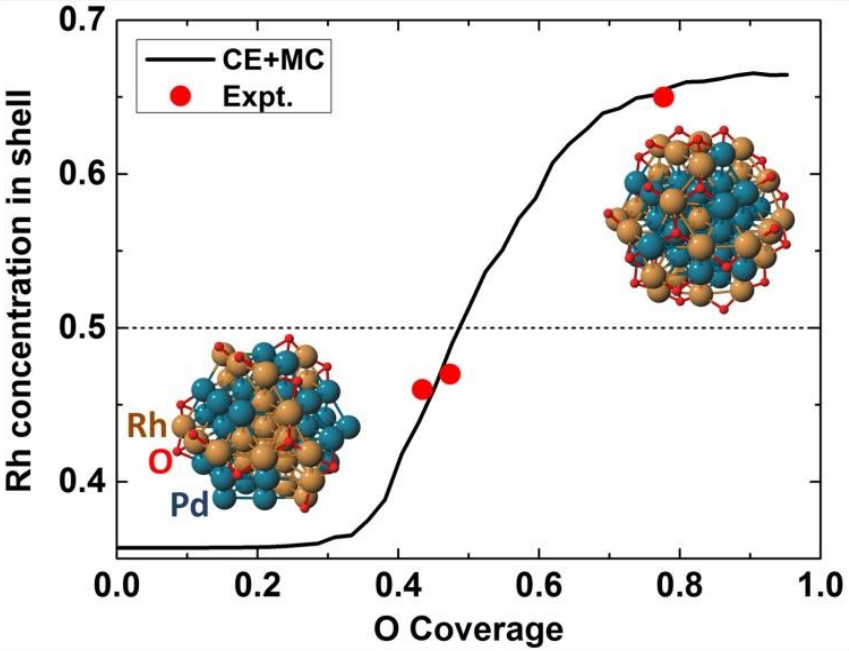
Shell conc. (C^{shell})

AP-XPS

F. Tao, *et al*. *Science* 322, 932 (2008); *JACS* 132, 8697 (2010)



Ab initio theory



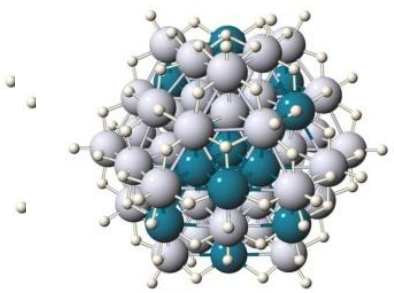
Unique Theoretical Capabilities for Ab Initio Prediction

- ✓ **Alloy configurational thermodynamics for NP *with adsorbates***
- ✓ **Simulating adsorption isotherm on low-coordinated alloy sites**

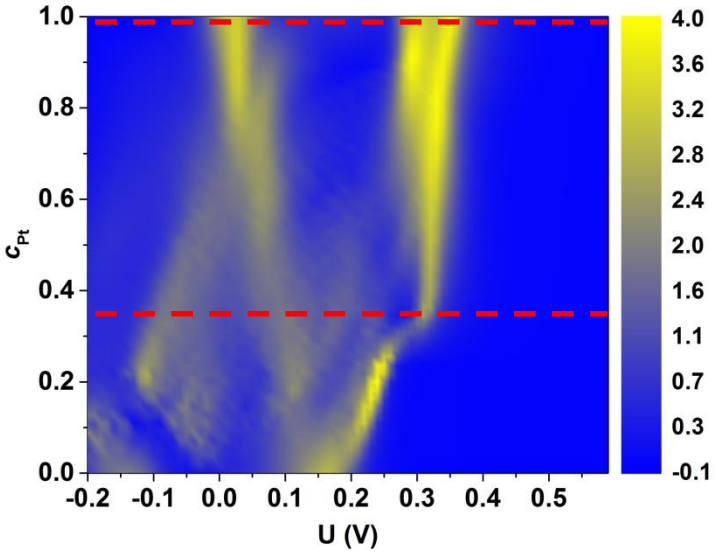
L.-L. Wang, T. L. Tan and D. D. Johnson
PRB 86, 035438 (2012); *JPCC.* 117, 22696 (2013); *Nano Lett.* 12, 4875 (2012); *Nano Lett.* 14, 7077 (2014); ACS Catalysis 5, 2376 (2015); *PCCP 17, 28103* (2015)

INCLUDES: Shape, size, stability, and design of nanolloy catalysts in working condition, for systems with *Component (M) and Site (N)*

Simulated Adsorption Isotherm



Hybrid Ensemble Ab initio Method

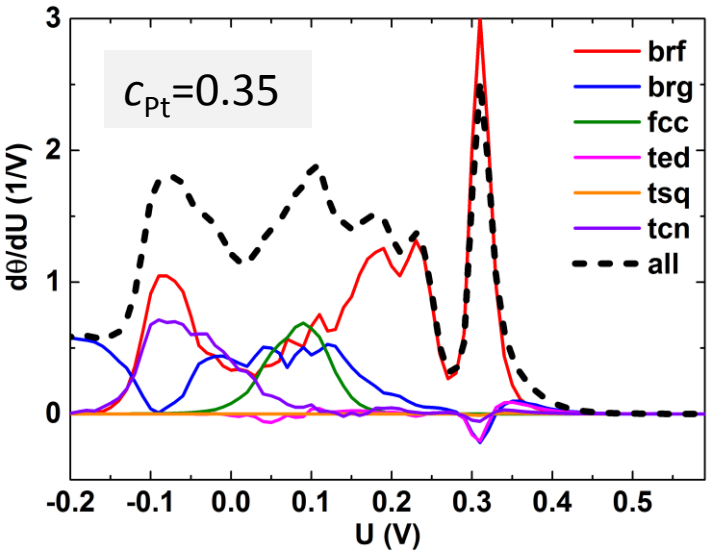


PdPt-H

hydrogen evolution reaction (HER)

- **Pure Pt voltammetry peak positions (V)**

CE+MC	0.40	0.32	0.15
Expt	0.35	0.27	0.12



- ✓ **Fully first-principles predicted isotherms that include correlation effects from low-coordinated alloy sites**
- ✓ **H-adsorption isotherm on alloyed Al nanostructures**

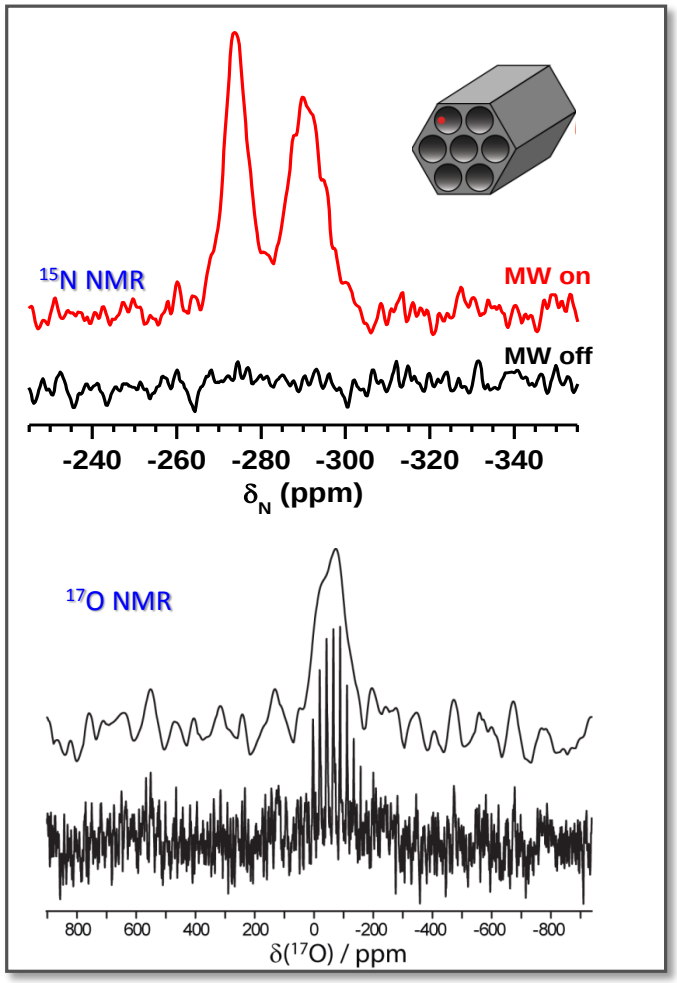
Ames Laboratory H-Capabilities at a Glance

1. State-of-the-art mechanochemistry:
   → P_{H2} = 300-350 bar with T,P monitoring
   → Real-time, in-situ analysis of processes with neutrons (under development)
2. Unique solid-state NMR →
   → Quantitatively accurate
   → DNP-enhanced
3. Accurate theory →
   → Thermodynamics/adsorption isotherms
   → Transformation pathways and intermediates

Questions?

Ames Laboratory DNP-NMR Highlights

DNP SSNMR ^{15}N and ^{17}O spectra of surface species at natural abundance



Examples of scientific achievements enabled by DNP – SS-NMR studies were never before possible:

- 1D and 2D ^{1}H-^{15}N DNP spectra determined the host-guest interactions between metal ions (Pt^{2+} and Cu^{2+}) and a metal-organic framework (MOF).
- DNP surface-enhanced NMR spectroscopy was extended to the ^{17}O nuclide, allowing the facile measurement of undistorted lineshapes, 2D ^{17}O NMR spectra, and ^{1}H-^{17}O distances at natural abundance.
- DNP-enhanced ^{15}N SSNMR was used to describe the mechanism of solid-state thermolysis of ammonia borane.
- DNP-enhanced ^{29}Si SSNMR was used to characterize isolated $(\text{-AlO})_3\text{Si(OH)}$ sites deposited on the $\gamma\text{-}Al_2O_3$ catalyst via atomic layer deposition.
- Molecular binding intermediates on metal nanoparticles were identified, for the first time, by DNP ^{13}C-^{13}C SSNMR.
- Most recently, ^{27}Al SSNMR spectra of surface Al species were detected on alumina thin film of the size on the order of ~1 cm^2.

Ames Laboratory's DNP-enhanced NMR is the only system dedicated to materials studies.