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Atomistic Potentials for Palladium-Silver Hydrides

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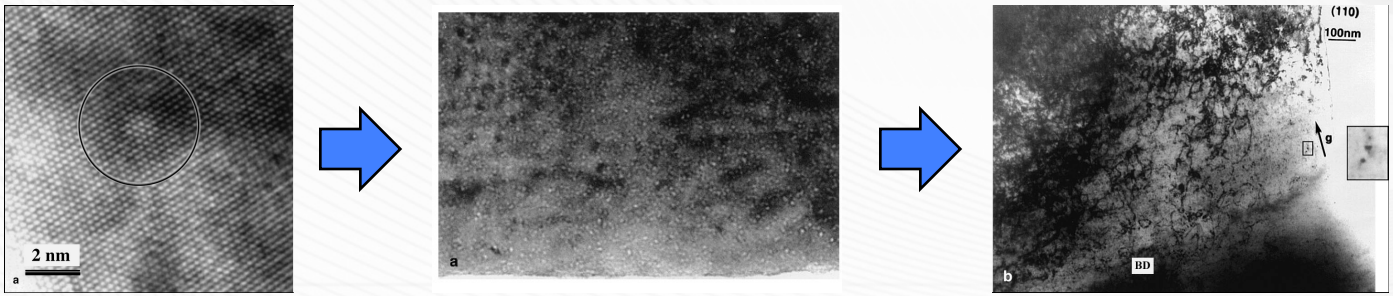
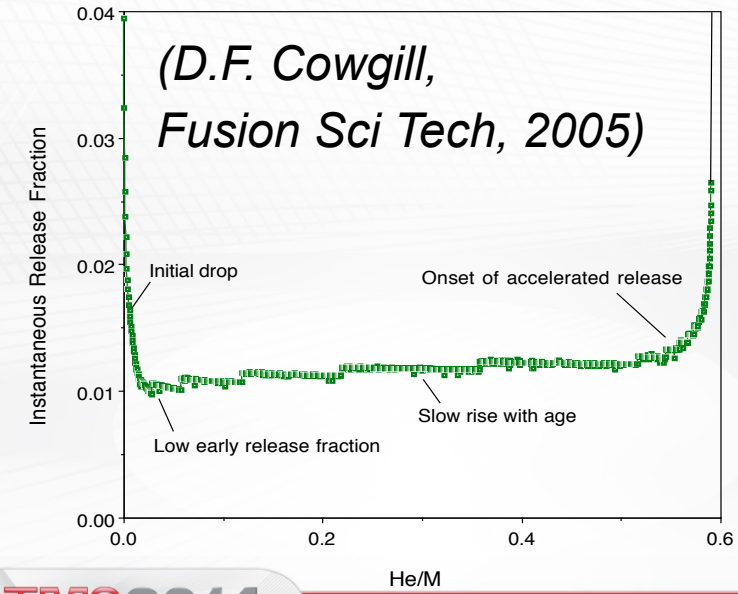
How do hydrogen and hydrogen-isotope storage materials fail?

- Hydrogen (H) and hydrogen-isotopes (D,T) in metals produce a variety of defect-mediated behaviors that can result in deformation, failure and fracture, e.g. H embrittlement (HE), H enhanced localized plasticity (HELP).
- Decay of tritium produces helium (He) atoms that cluster and form bubbles.
- For He in palladium (Pd), He gas is released from the metal at an accelerated rate at some critical concentration of He/Pd.
- Experiments reveal dislocation loops and other defects in these aged samples

Determining the cause of accelerated release of helium gas



(S. Thiébaut et al, J Nucl Mater, 2000)



Our focus:

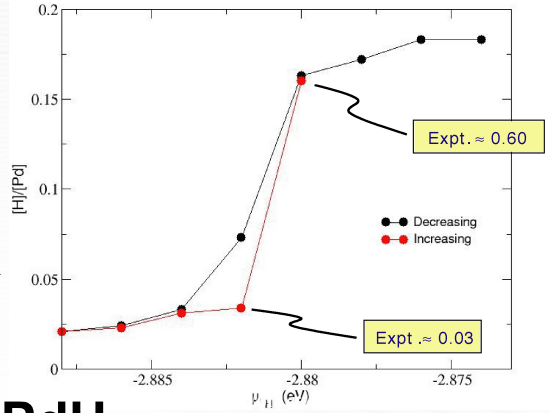
Identify physical mechanisms leading to accelerated release of He gas

We simulate and examine the material defects that originate from having He bubbles in a metal lattice using atomistic modeling methods.

See talk on Wed, Feb 19th at 11:30 am, SD Conv Ctr room 11B

Potentials in the scientific literature

- **Embedded Atom Method (EAM) model by Daw and Baskes (*Phys Rev Lett*, 1983; *Phys Rev B*, 1984)**
  - **Accurate for dilute amounts of H and reasonable for PdH alloy.**
  - **Incorrectly predicts tetrahedral site occupation for high H concentrations.**
  - **Displays only a very small miscibility gap:**



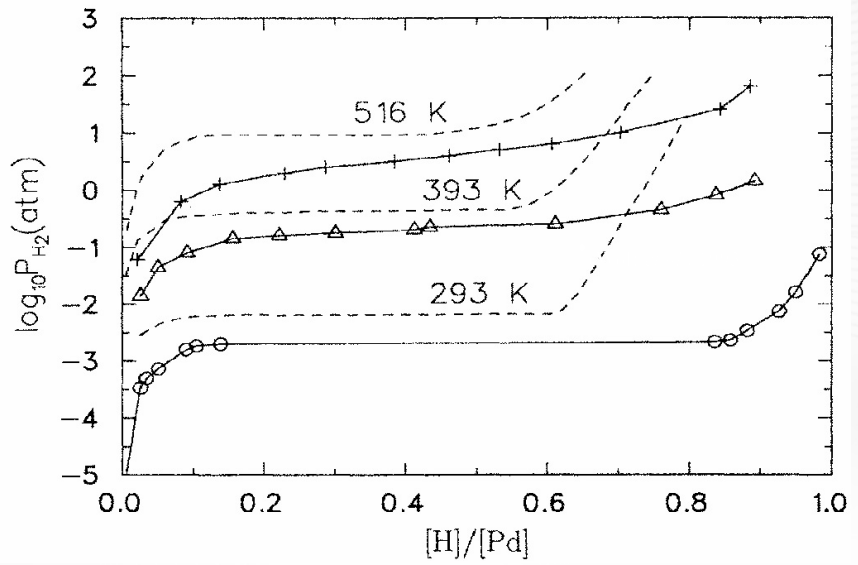
- **Multi-body potential by Zhong, Li and Tománek (*Phys Rev B*, 1991, 1992)**
  - **Accurate for dilute amounts of H in Pd and PdH.**
  - **Agreement on properties of H-covered Pd surfaces.**
  - **Incorrectly predicts tetrahedral site occupation for high H concentrations.**
  - **– Displays no miscibility gap.**

Potentials in the scientific literature

- EAM by Wolf, Lee *et al.* (*Phys Rev B*, 1992, 1993; *Phys Rev Lett*, 1994)
  - Displays qualitatively correct miscibility gap:
  - BUT, functions and parameters for Pd-H and H-H interactions are not in publications! (or anywhere, trust me)

… so, we decided to build our own potential to capture miscibility gap.

Later, developed an interest in exploring Pd-Ag-T alloys to determine if alloying impacts He bubble/gas retention.



Pd-H EAM Model

Start with Pd-Pd interaction by Foiles and Hoyt *(SAND2001-0661)…*

- **Total energy** $E = \sum_{i=1}^{N} F_i(\rho_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ j\neq i}}^{N} \phi(r_{ij}), \qquad \rho_i = \sum_{\substack{j=1 \\ j\neq i}}^{N} \rho^a(r_{ij})$
- **Pd potential functions known**
- **H embedding energy** $F(\rho) = A\cdot\rho\cdot\ln(\rho) + B\cdot\rho$
- **H electron density** $\rho^a(r) = C\cdot\exp(-\delta\cdot r)$
- **H-H and Pd-H pair energy**

$$\phi(r) = \beta\cdot D\cdot\exp\left[-\alpha\cdot(r-r_0)\right] - \alpha\cdot D\cdot\exp\left[-\beta\cdot(r-r_0)\right]$$

Model problems, and solutions…

- **For elemental system, invariances relating the pair potential, atomic charge density and embedding energy functions introduce non-uniqueness:**

$$F(\rho)+k_1\cdot\rho,\qquad \phi(r)-2k_1\cdot\rho^a(r)\qquad F\left(\frac{\rho}{k_2}\right),\qquad k_2\cdot\rho^a(r)$$

Solutions: $k_1=-F'(\rho_0)$ $\qquad \rho_{low}<\rho_{0,i}<\rho_{high},\qquad i=1,2,...$

- **For Pd-H system, properties of selected Pd-H phases do not uniquely determine H properties**

Solution: Include H phase in the fitting of potential parameters

Whenever possible, use analytic functions of composition

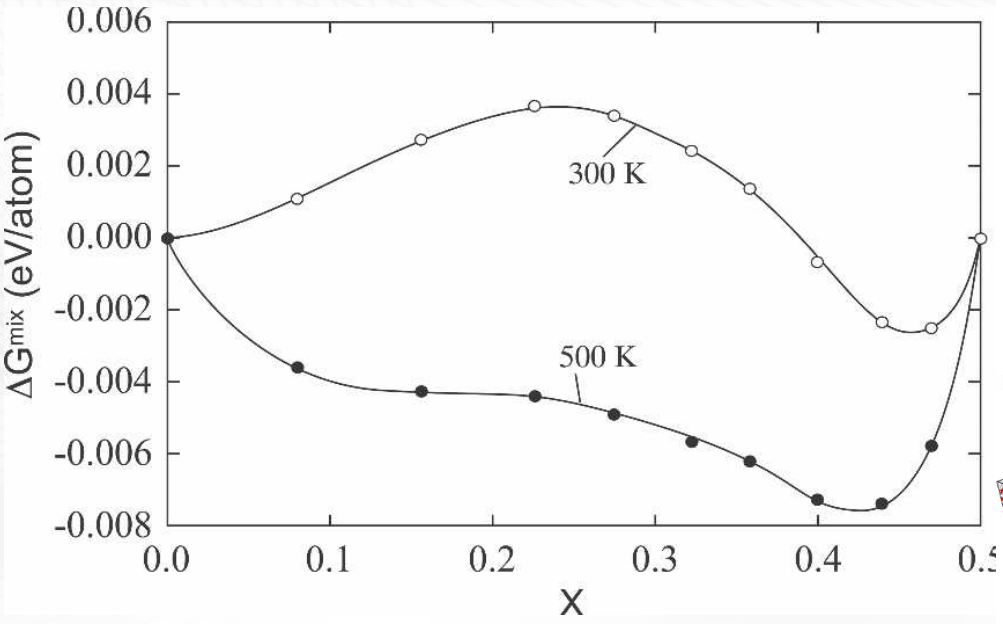
- **OC PdH_x structure: a fully occupied fcc Pd sublattice, and a partially occupied fcc H sublattice at the Pd octahedral interstitial sites. The occupancy probability for the H sublattice is x.**
- **TE PdH_x structure: a fully occupied fcc Pd sublattice, and two partially occupied fcc H sublattices at the Pd tetrahedral interstitial sites. The occupancy probability for the H sublattice is x/2.**
- **Analytical energy as a function of composition can be derived assuming atom distribution is perfectly random.**

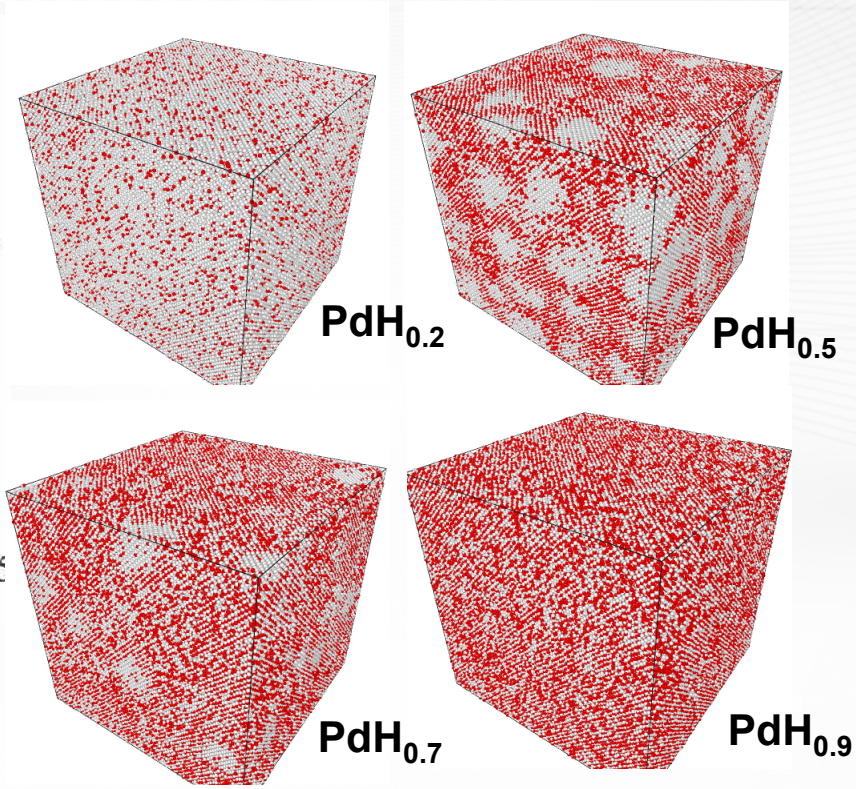
fitEAM Mathematica program

- Mathematica used for its symbolic computation, automated derivation, graphic analysis capabilities, and built-in optimization routines
- Conversion of input Pd potential
- Derivation of analytical expressions for cohesive energy, pressure, bulk modulus, other elastic constants.
- Optimization under constraints using four routines: conjugate gradient, simulated annealing, differential evolution and Nelder Mead methods
- Fitting data includes ab initio estimates of cohesive energy, lattice constant and bulk modulus for various H-compositions. Also, experimental data for elastic constants from Schwarz et al.
- Characterization: heat of mixing, Gibbs free energy of mixing, elastic constants

Success: new potential exhibits (a) miscibility gap

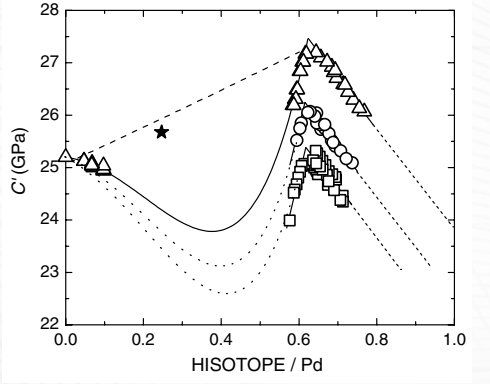
- Miscibility gap exists, cause phase separation into H-rich and H-poor regions (annealed at 300 K for 14,000,000 timesteps)
  - In experiments, α phase = $PdH_{0.03}$ and β phase = $PdH_{0.6}$
  - With the potential, α phase $\approx$ $PdH_{0.00}$ and β phase $\approx$ $PdH_{0.85}$

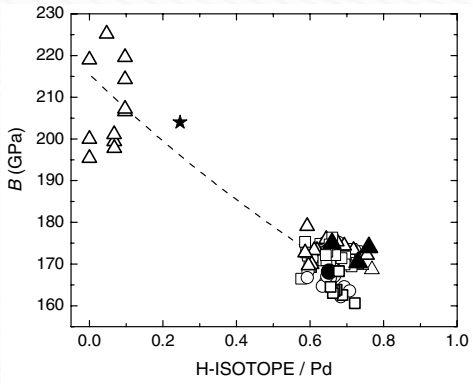


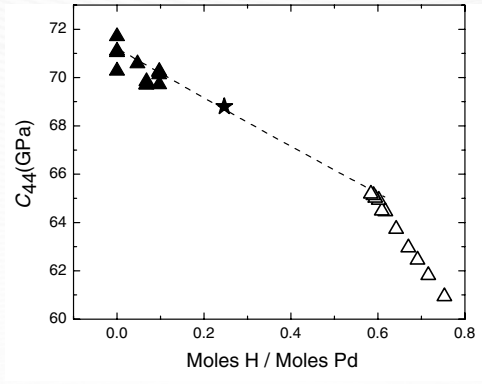


Elastic constants
(weakly used for potential fitting)

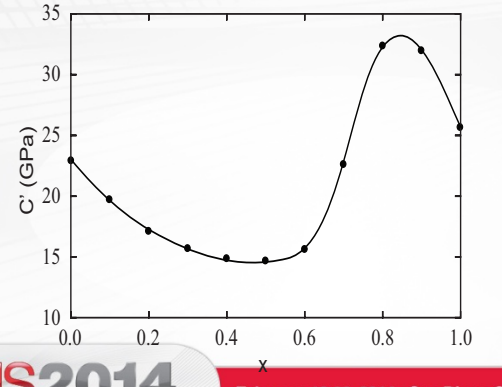
- Good qualitative agreement for C' (=(C11-C12)/2).
- $B_\alpha \sim B_\beta$ and essentially flat for $0.82 \leq x \leq 1$.
- C44 shows a decreasing trend for $0.82 \leq x \leq 1$. Also, a line connecting the α and β regimes has a lower slope that for the high concentration region.

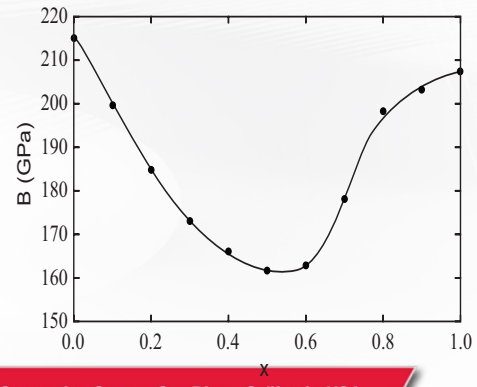


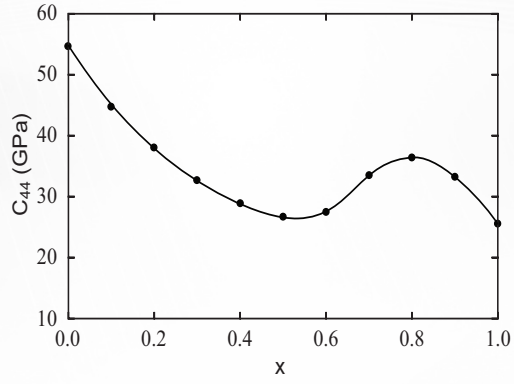




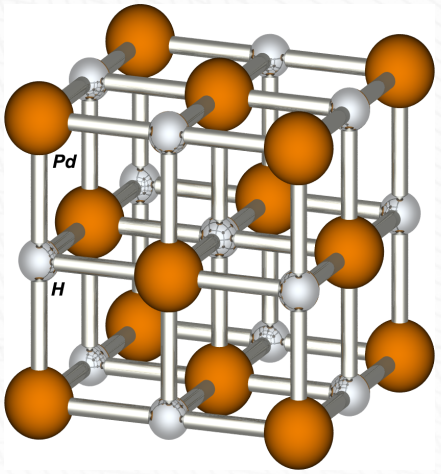
(R. Schwarz et al, Acta Mater, 2005)

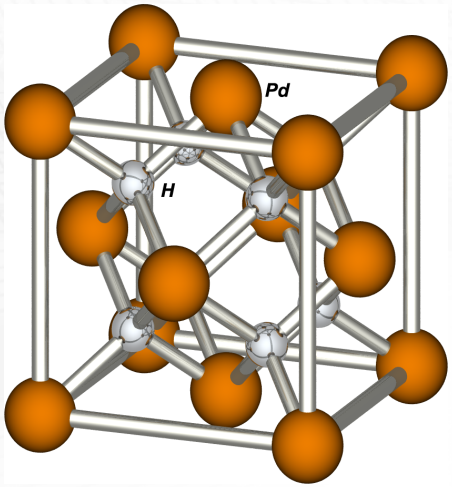


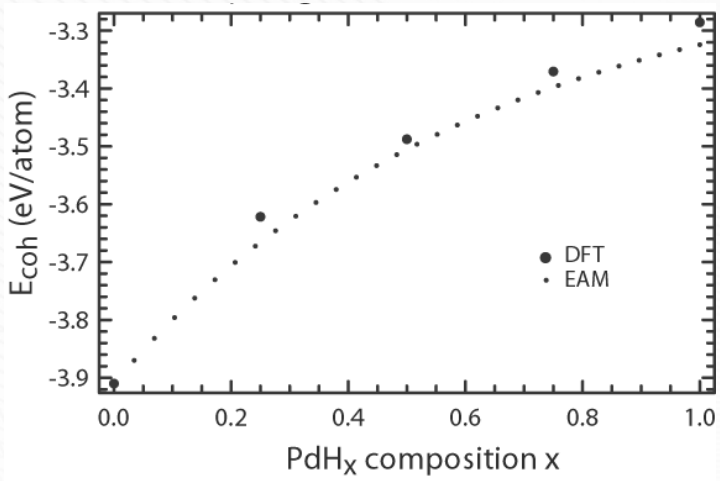


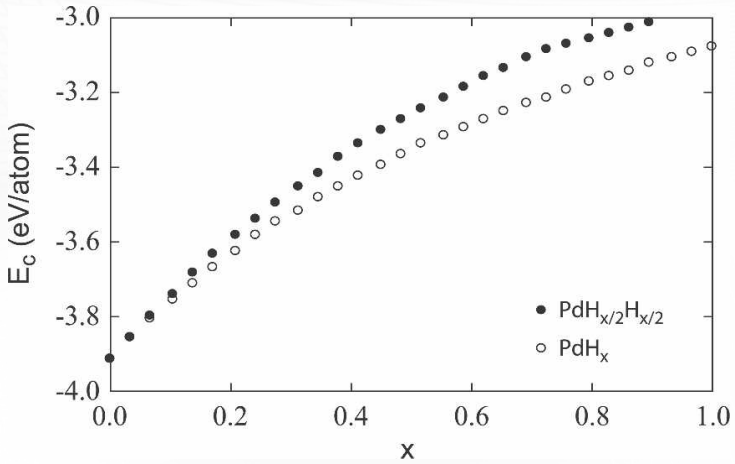


Octahedral site preferred at all H concentrations





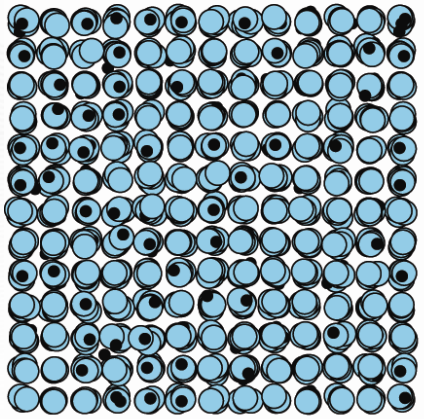




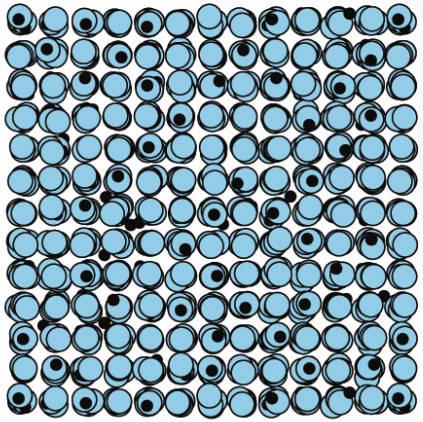
$PdH_{0.784}$ after 8 ps MD annealing at 300 K

Pd • H

octahedral initial H sites



tetrahedral initial H sites

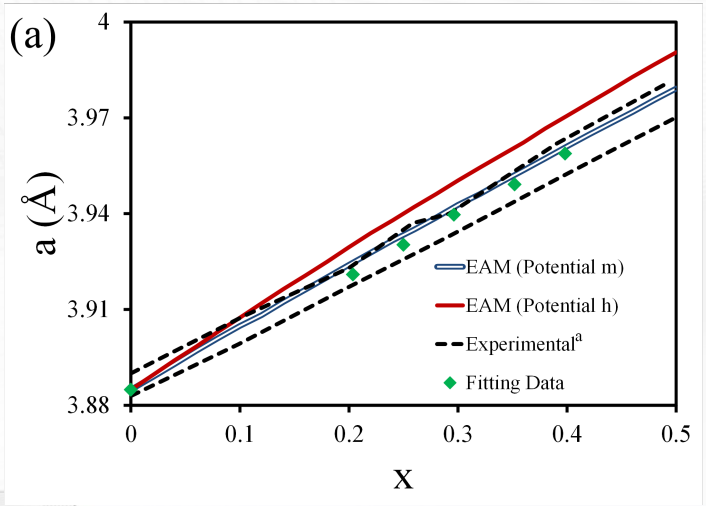


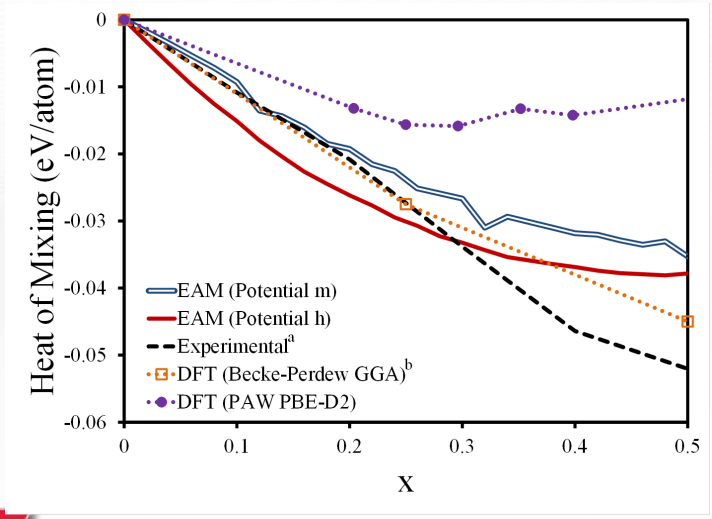
Pd-Ag-H potential development

- Alloying palladium with another metal alters properties
  - Tensile and shear strengths (loop-punching and fracture pressures)
  - Maximum H concentrations (rate of He/M formation)
  - Miscibility gap (single or multiphase material)
- Pd_xAg_{1-x} alloys: not many experimental measurements on bulk properties
- Palladium and silver are completely solid soluble (no intermediate compounds, phase separations)
- Solubility of H into Ag is negligible
- H preferentially occupy interstitial sites near Pd. Experiments on Pd-Au hydrides show an increase in occupied tetrahedral sites with increasing Au concentration
- Adding Ag reduces the miscibility gap, which disappears around 25-30% Ag

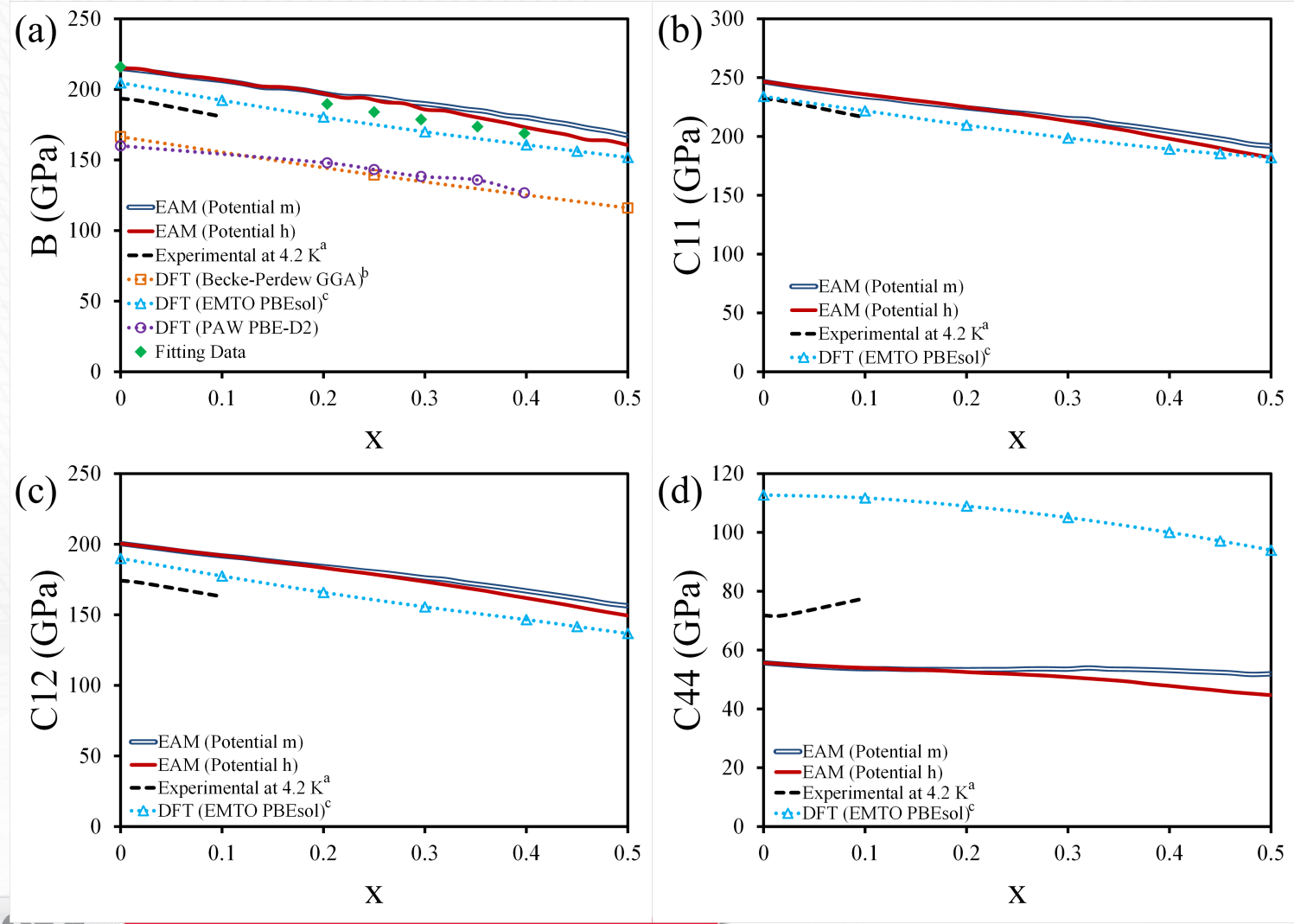
Modeling the Pd-Ag interaction

- Start with EAM potential by Williams *et al* (*MSMSE*, 2006) for Ag
- Pd-Ag interactions fitted using two different functional models (Morse-style (m) and Hybrid (h) of Pd-Pd and Ag-Ag)
- Fitting parameters determined such that properties of the potentials match with lattice parameter, a, and bulk modulus, B, obtained from DFT, and heat of mixing reported experimentally
- Smooth change in properties and favorable mixing results in solid solution



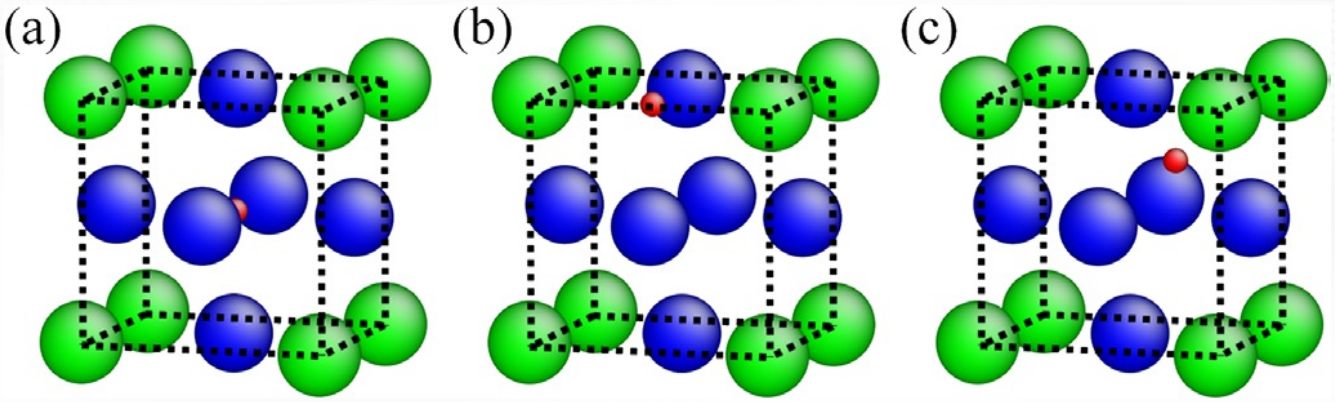


Pd-Ag elastic constants



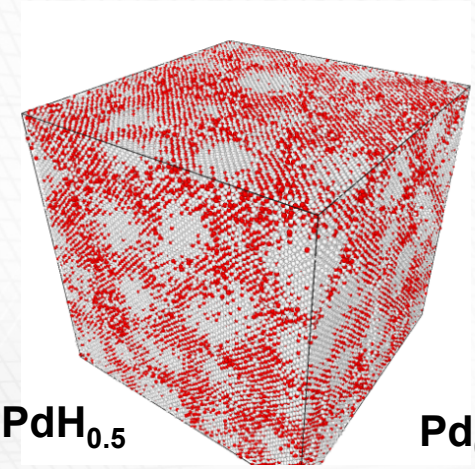
Modeling the Ag-H interaction

- Fitting to a broad range of compositions and bulk properties failed to capture the correct behaviors
  - Averaged system values good, but locally poor and crystallographically unstable
- Ideal Pd_3Ag systems with H added to both octahedral and tetrahedral sites
  - DFT to obtain relaxed structure and relative energy of that structure
  - Fit parameters such that EAM potential matches the DFT results

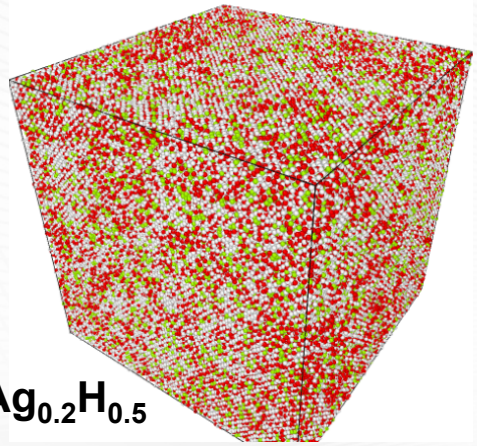


Addition of Ag removes miscibility gap

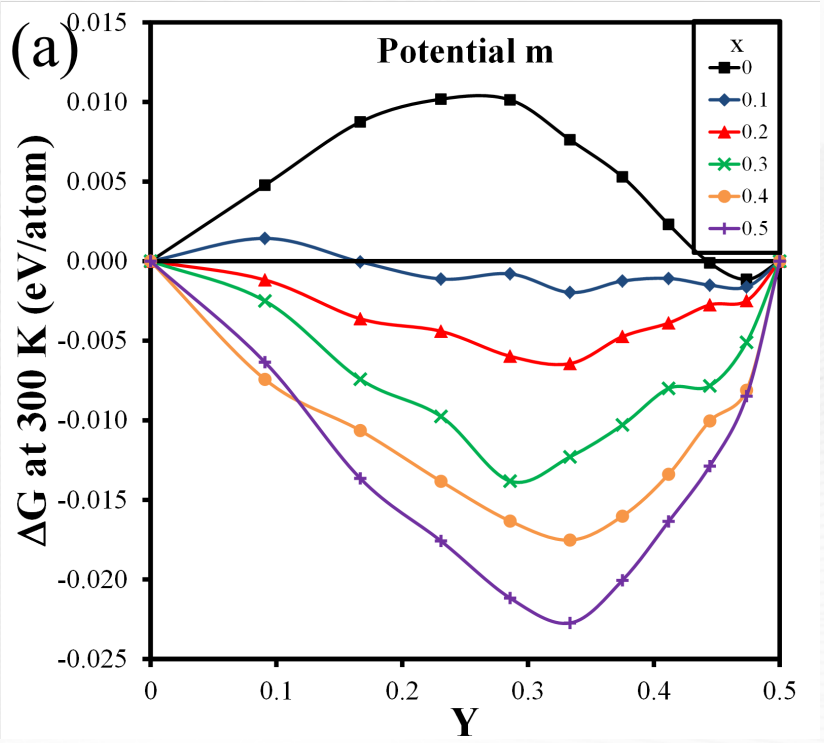
- Loss of miscibility gap noticed between 10% and 20% Ag.
- Experiments show this occurs in real systems at 25% Ag.



$PdH_{0.5}$



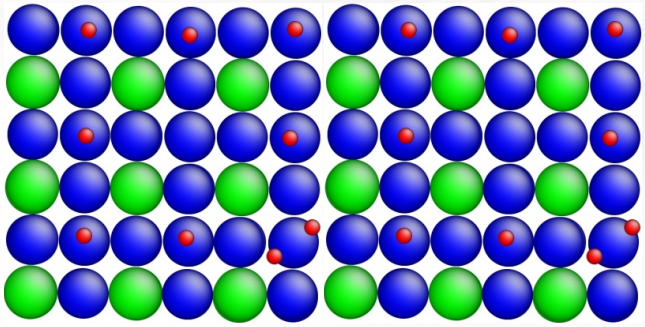
$Pd_{0.8}Ag_{0.2}H_{0.5}$

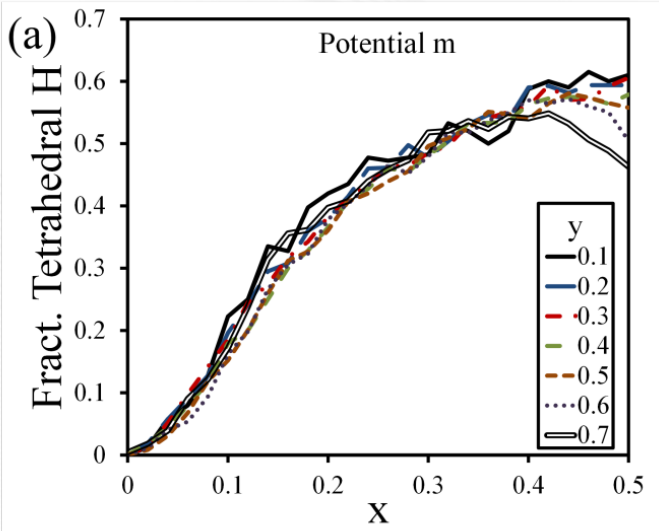


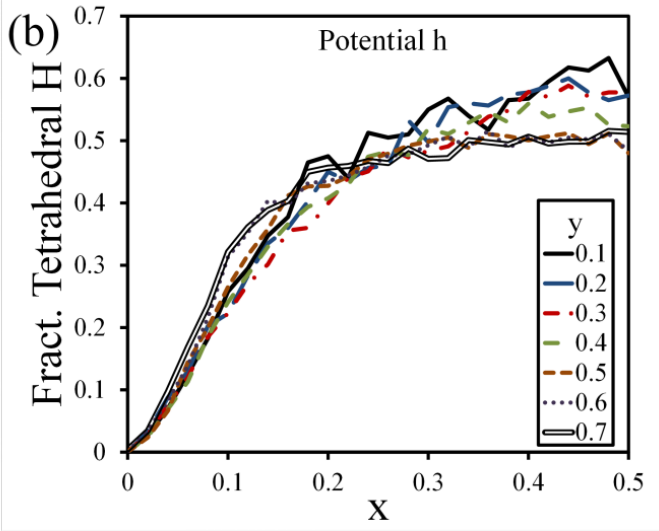
Examination of Gibbs free energy indicates that Morse-style (Pd-Ag) pair function may better represent the loss of the miscibility gap with increasing Ag content.

H interstitial occupancy depends on proximity to Pd atoms

- Occupancy of H in tetrahedral interstitial sites increases as %Ag increases, similar to neutron diffraction data for Pd-Au-D by Nanu *et al*. (*Acta Mater*., 2008).
- H prefers sites near Pd atoms over Ag atoms; Increasing Ag limits favorable H octahedral interstitial sites
- H in tetrahedral sites increases with increasing Ag (like as seen for PdAuH)







Concluding remarks

- Improvement of potential requires additional measurements:
  - Elastic properties of Pd-Ag and Pd-Ag-H alloys
  - Neutron diffraction of Pd-Ag-H would provide a definitive answer on the hydrogen interstitial site occupancy
  - Additional ab initio calculations to investigate long-range interactions between Ag and H, vibrational entropy, and the energy and structure of defects in the hydrides.
  - Ab initio estimates of ideal tensile and shear strengths
- Publications:
  - Pd-H: Zhou *et al*, *J Mater Res*, 23(3), 704-718, 2008
  - Pd-Ag-H: Hale *et al*, *MSMSE*, 21, 045005, 2013
- Simulations performed with Sandia's LAMMPS code (http://lammps.sandia.gov).
- Questions? For further info: jzimmer@sandia.gov