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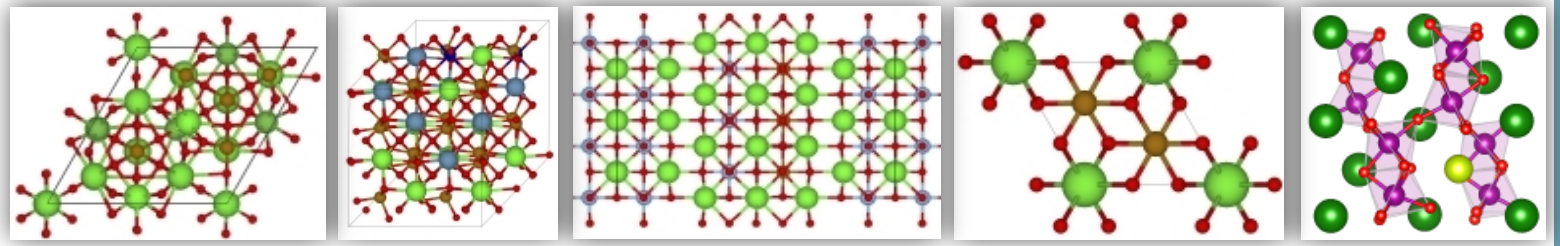
Machine learning driven discovery and modeling of materials for hydrogen storage and generation



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HydroGEN Advanced Water Splitting Materials

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

HyMARC Hydrogen Materials Advanced Research Consortium

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HyMARC Hydrogen Materials Advanced Research Consortium

HydroGEN Advanced Water Splitting Materials

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Experiments

Machine Learning

First principles/DFT

Data infrastructure

Talk Outline

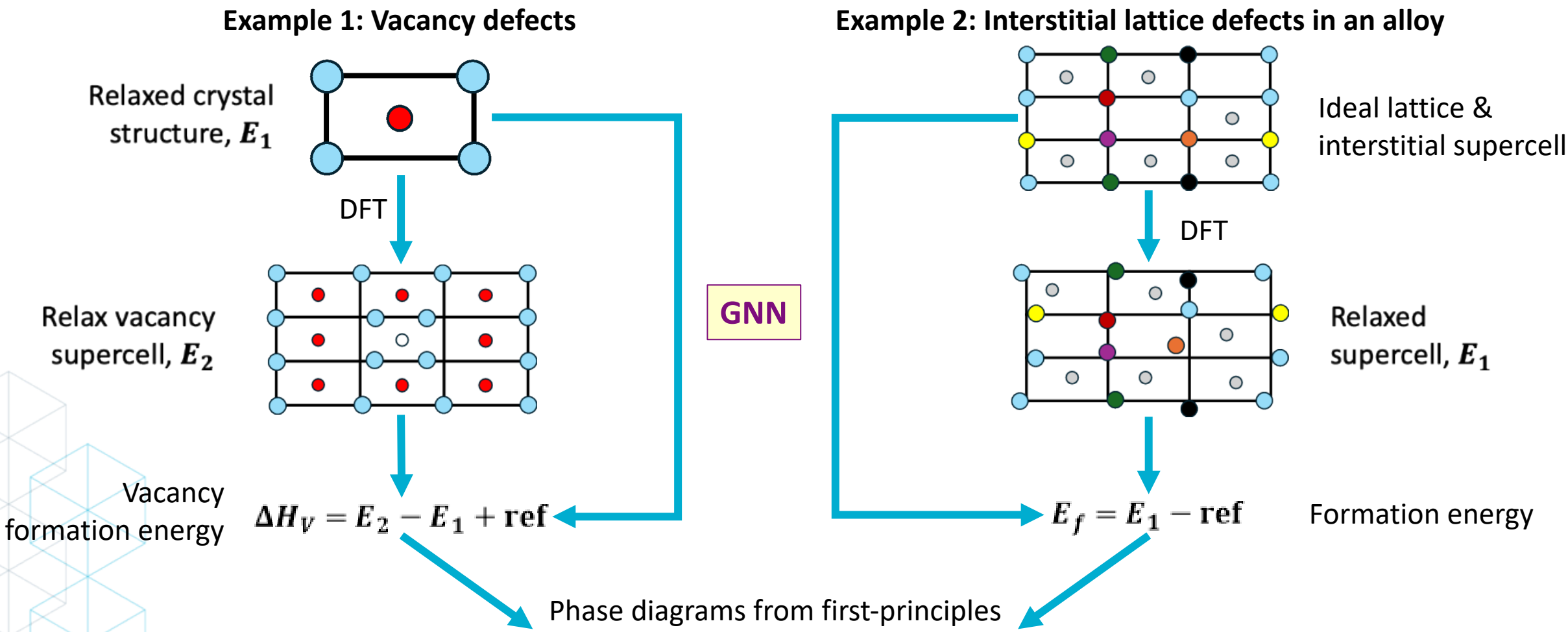
Introduction:
Methodology and applications
- Graph neural networks for modeling & discovering hydrogen energy materials

Part I, H_2 generation:
Accelerated screening of oxides for high-T clean energy applications
- graph neural networks / direct vacancy property predictions / high-throughput screening

Part II, H_2 storage:
Modeling of (super)-hydrides for hydrogen storage and beyond
- graph neural networks / screening + statistical sampling / metal-hydrogen phase diagrams

Central methodology theme: Use graph neural networks (GNNs) as a surrogate model for expensive DFT relaxations in *the limit of low data*

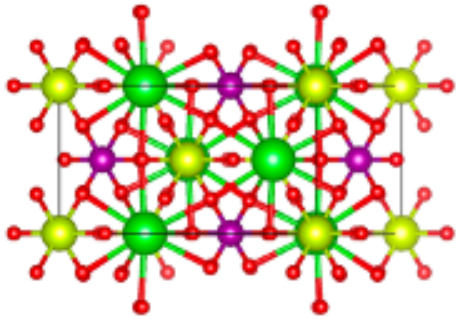
- **Goal**: Predict DFT-relaxed energy of a defected crystal structure from an unrelaxed representation
- For the *most* accurate quantum chemical methods (beyond DFT), we will be data limited for the foreseeable future

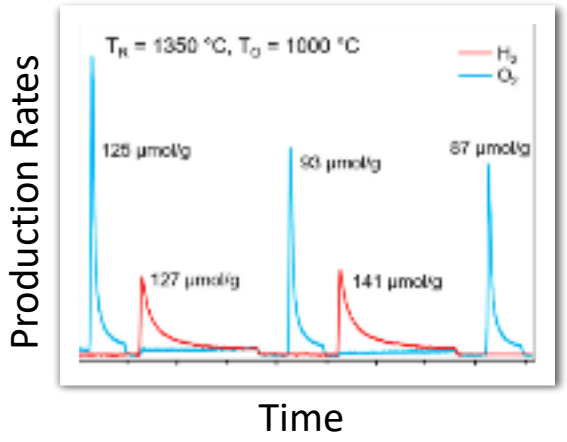


Central application theme: **Experimental** and/or **1st principles calculation** trial-and-error discovery of new & improved hydrogen materials solutions is too costly

Application #1: (High entropy) metal oxides for solar thermochemical (STCH) H_2 generation

$$MO_x \xrightarrow{\Delta} MO_{x-\delta} + \frac{\delta}{2}O_2 \text{ (reduction T)}$$
$$MO_{x-\delta} + \delta H_2O \rightarrow MO_x + \delta H_2 \text{ (oxidation T)}$$

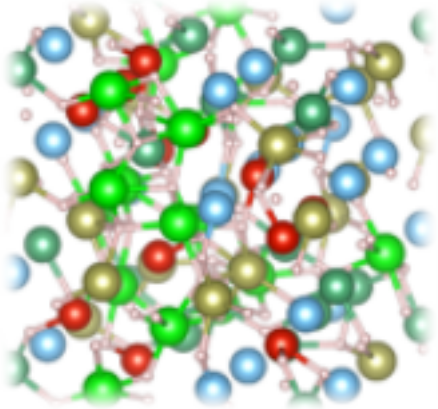


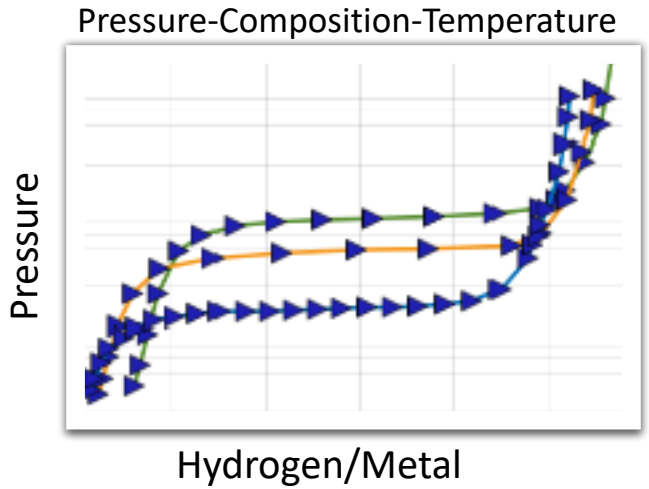


Experiments: Measure H_2 / O_2 production rates
1st principles: Compute ΔH of oxygen vacancy formation

Application #2: Metal (super)-hydrides from (high entropy) alloys

$$M + \frac{x}{2}H_2 \leftrightarrow MH_x$$





Experiments: Measure PCT curves (ΔH, ΔS, and capacity)
1st principles: Low-sample estimation of ΔH

Months to synthesize and fully characterize and test a material
Months to predict *even just a proxy* for performance for a small # of materials

Part I:
Accelerated screening of oxides for high temperature, clean energy applications[1]

Key concepts:

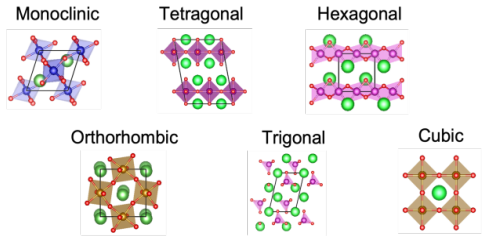
- Graph neural networks to directly predict *relaxed vacancy properties* from the host structure
- High-throughput screening of vacancy formation enthalpies
- New oxides for water-splitting, fuel cells, CO_2 conversion, and thermochemical energy storage

[1] Witman, Goyal, Ogitsu, McDaniel, Lany. *Nature Comp. Sci.* **2023**, (3) 8

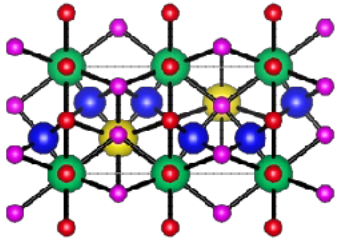
Discovering oxides for clean energy, and specifically solar thermochemical water splitting (STCH) materials

1. **Application**: motivation for H_2 production via solar thermochemical water-splitting (STCH)

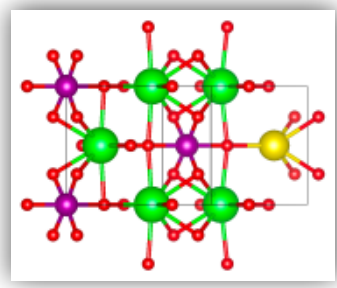
2. **Challenge**: expense of experiments and quantum mechanical based methods



3. **Solution**: surrogate modeling with defect graph neural networks



4. **Screening & validation**: (re)discovery of water-splitting metal oxides



Application: why focus on (green) hydrogen production *without* renewable electrons?

(1) Why H_2?

2022 US Energy demand:
~35% electricity
~20% fuels (cars)
~45% fuels (other)

(2) The mismatch problem

2022 Renewable additions:
~90% electricity
~10% fuels (H_2, biofuels, …)

https://www.eia.gov/energyexplained/us-energy-facts/

(3) Why produce H_2 without electrolysis?

"renewables … are growing quickly enough to meet almost all [growing electricity demand], suggesting we are close to a tipping point for power sector emissions"

As of early 2023, newly added renewable electricity capacity is still just **shy of meeting increasing electricity demand alone**…

(4) High-temperature, concentrating solar power (CSP) is proposed for a variety of decarbonization technologies

2010 LCOE : $0.38/kWh → 2022 LCOE: $0.12/kWh

- Thermal batteries
- Thermochemical energy storage
- CO_2 conversion
- H_2 production via solar thermochemical water-splitting (STCH)

➢ **STCH**: A potential pathway to green H_2 relying only on renewable heat, *not* renewable electrons

CSP in the cinema: In the dystopian sci-fi classic *Blade Runner 2049*, the world apparently went all in on CSP but failed ☹

Challenge: Experiments and calculations to find the best metal-oxides for STCH are difficult and time-consuming

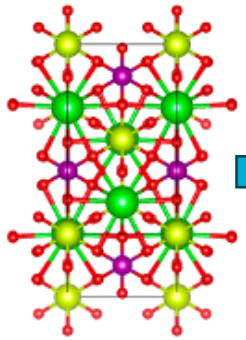
(1) STCH mechanism & experiments

$$MO_x \xrightarrow{\Delta} MO_{x-\delta} + \frac{\delta}{2} O_2 \text{ (reduce ~1400C)}$$

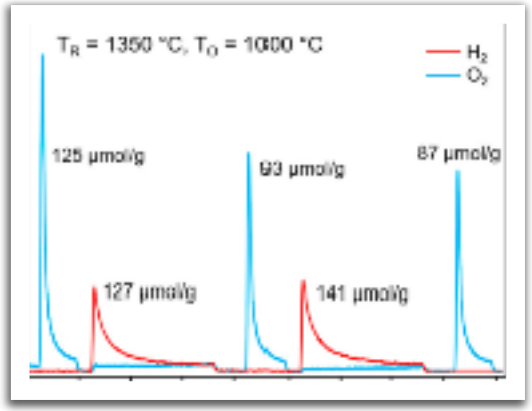
$$MO_{x-\delta} + \delta H_2O \rightarrow MO_x + \delta H_2 \text{ (oxidize ~1000 C)}$$

STCH efficacy first and foremost depends on *oxygen vacancy thermodynamics*

Experimentally measure H_2 & O_2 production:

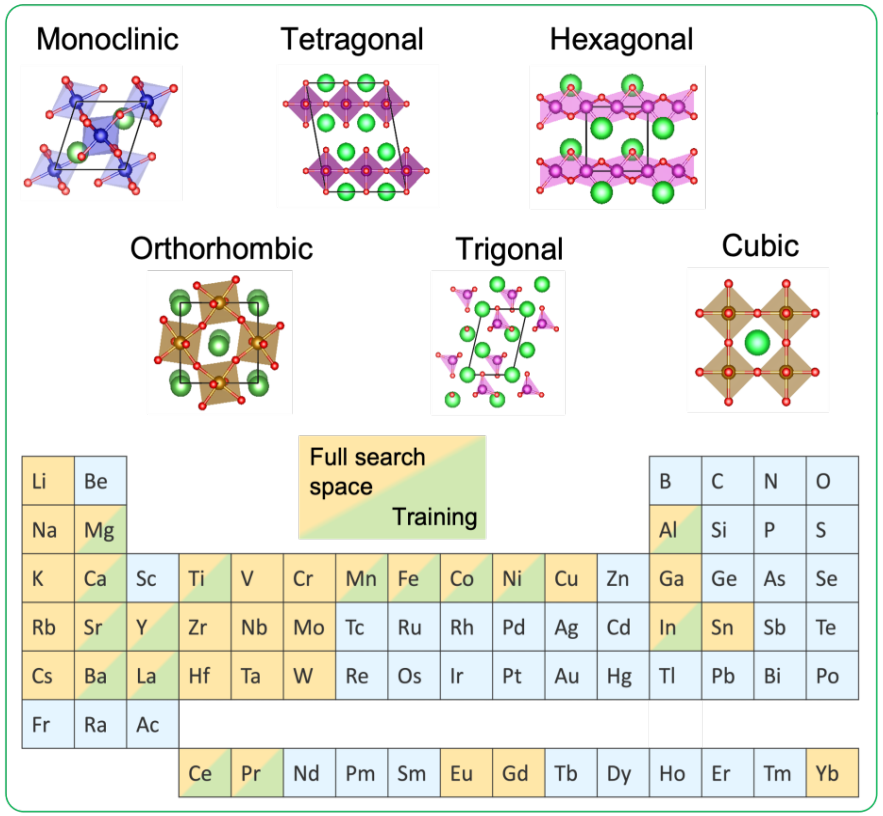


E.g., $Ba_4CeMn_3O_{12}$



Months to synthesize and fully characterize and test a single material

(2) Density functional theory (DFT)-based calculations of oxygen vacancy formation enthalpy (ΔH_{V_O})



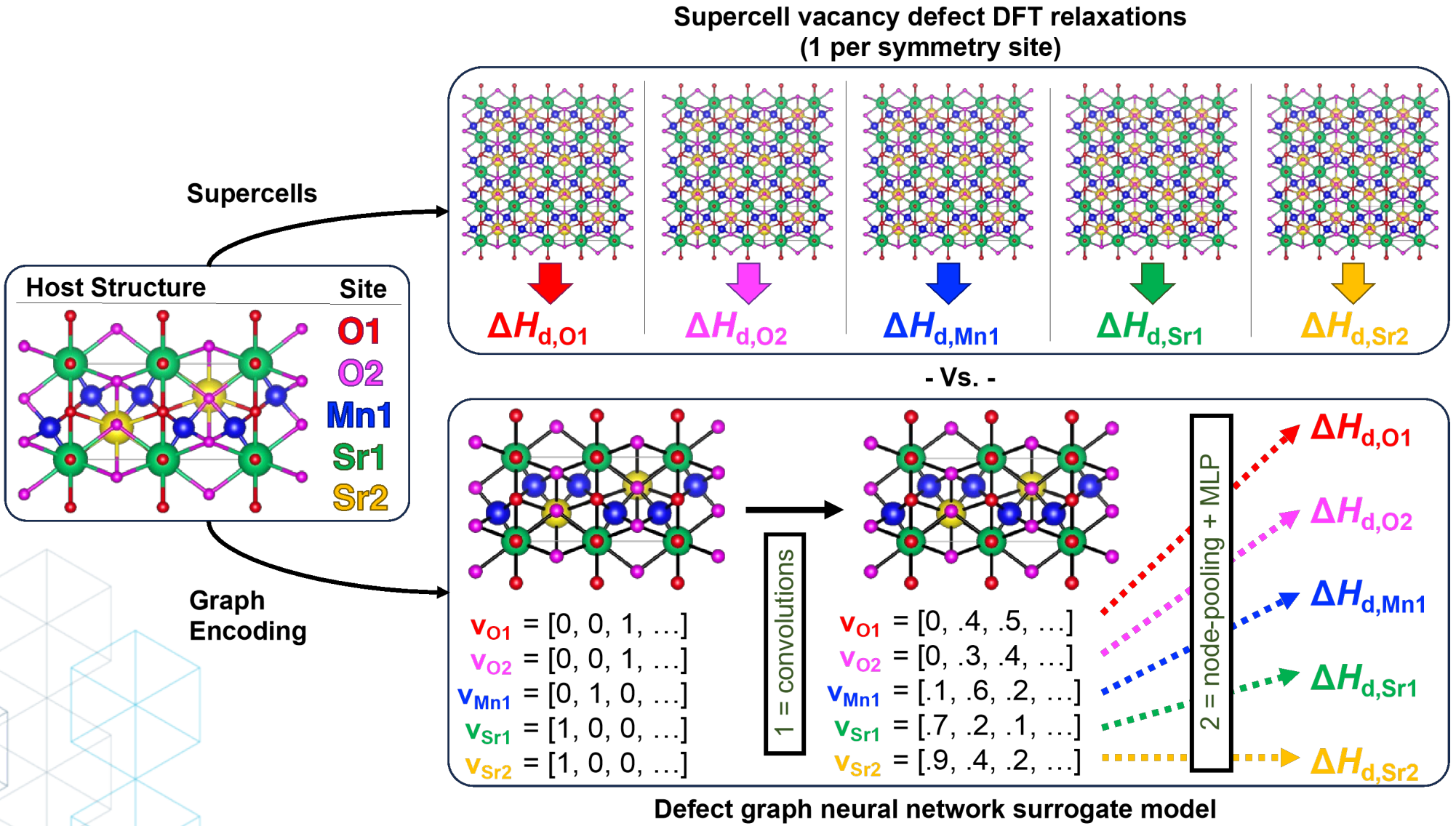
Calculated oxide space:
14 cations
~200 compounds
~1500 vacancy relaxations

~1 years' work

Screening oxide space (Materials Project):
~30+ cations
~10,000s+ compounds
~1Ms+ vacancy relaxations

100s+ years' work…

Solution: A generalizable, defect graph neural network (dGNN) model predicts vacancy formation energies many orders of magnitude faster than DFT



Pros:

- Generalizable (no manual feature engineering)
- Chemistry & structure agnostic
- Improvable w/more data
- Orders of magnitude faster than DFT (milliseconds *vs.* days)

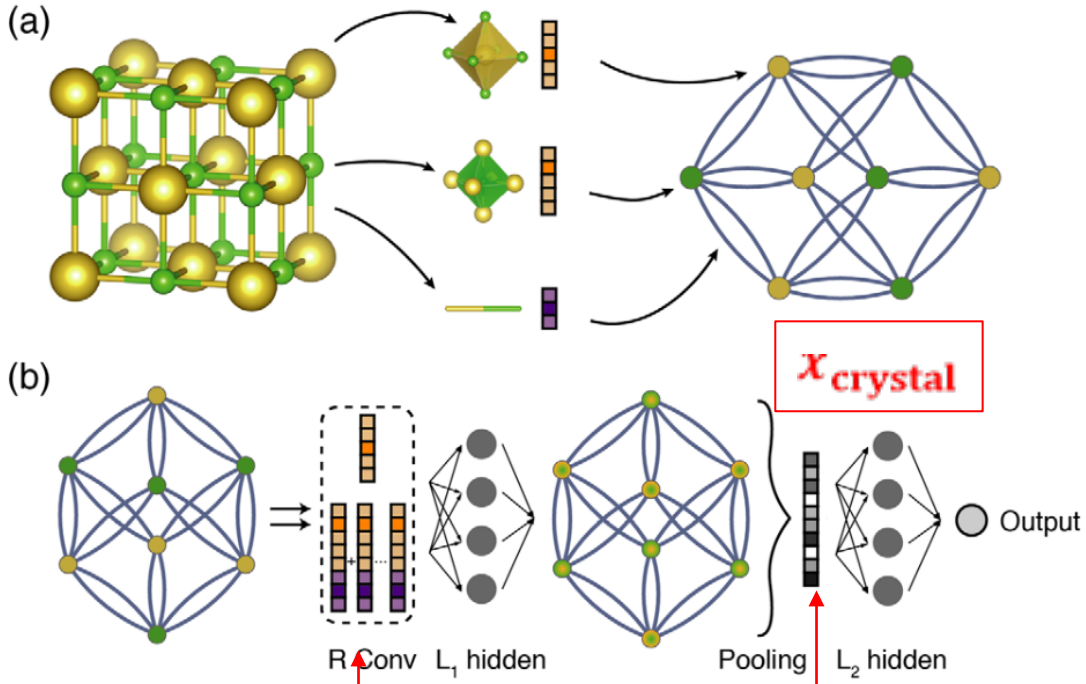
Cons:

- Highly data reliant
- Not interpretable

Automated feature extraction of graph neural networks (GNNs) enables efficient, generalized modeling of vacancy formation enthalpy

Automated feature extraction with GNNs [1]

Interpret crystal as a graph (nodes = atoms, edges = "bonds")



Convolutions over neighbors

Pool **all** atom features to create crystal feature vector

Deriving a "defect GNN" approach[2]

Predict using only host structure, $\boldsymbol{X}_h$, and defect atom index, i'

DFT: $\Delta H_d = E_{\mathrm{DFT}}(\boldsymbol{X}_d) - E_{\mathrm{DFT}}(\boldsymbol{X}_h) + \mathrm{ref}$

ML: $\Delta \widehat{H}_d = f_{\mathrm{GNN}}(\boldsymbol{X}_h, i'; \theta)$

- Example graph: v_1 O — e_{12} — Mn v_2

- Encode the graph (step $t = 0$):

$$\boldsymbol{v}_1^{t=0} = \{r_O, \chi_O, \ldots, s_1\}$$

Accuracy boosting, site-specific inputs (i.e. oxidation state)

- Convolutions ($t = 1 \ldots T$)

$$\boldsymbol{v}_i^{(t+1)} = g\left(\boldsymbol{v}_i^{(t)} + \sum_j \sigma\left(\boldsymbol{z}_{ij}^{(t)}\boldsymbol{W}_1^{(t)} + \boldsymbol{b}_1^{(t)}\right) \odot g\left(\boldsymbol{z}_{ij}^{(t)}\boldsymbol{W}_2^{(t)} + \boldsymbol{b}_2^{(t)}\right)\right)$$

- Property prediction (node pooling):

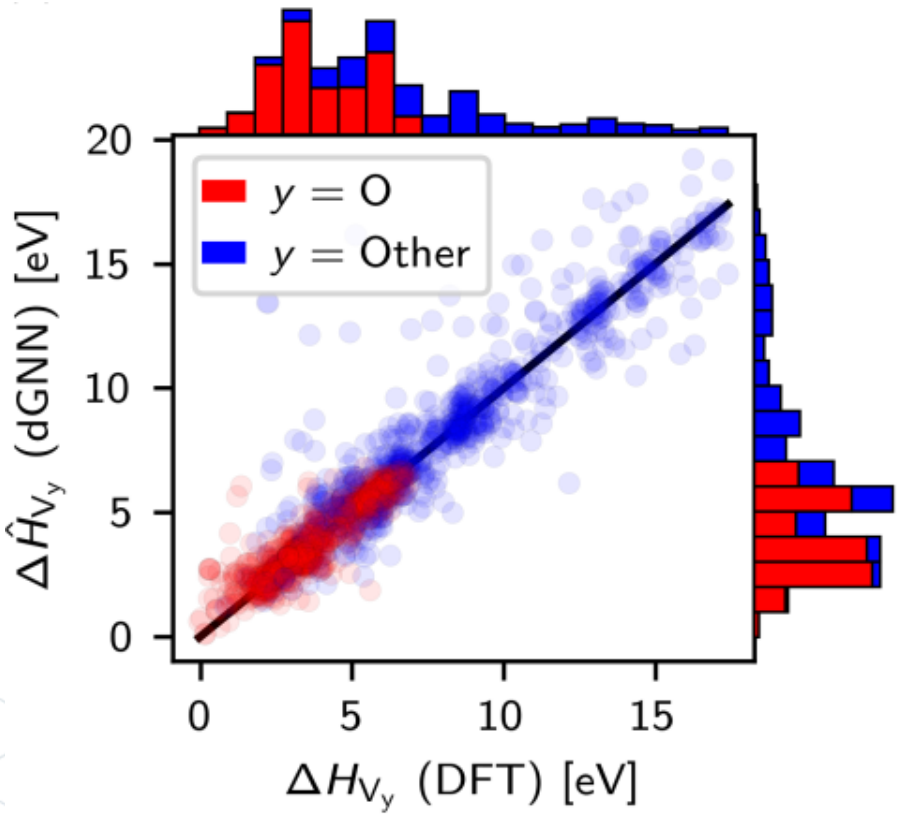
$$\boldsymbol{x}_{\mathrm{defect}} = \sigma\left(\boldsymbol{v}_{i'}^T \oplus \boldsymbol{v}_g \cdot \boldsymbol{W} + \boldsymbol{b}\right)$$
$$\Delta \widehat{H}_d = \boldsymbol{x}_{\mathrm{defect}} \cdot \boldsymbol{W} + b$$

- **Node** pooling at i'
- Can add host's global properties, $\boldsymbol{v}_g$ = {band gap, …}

[1] Xie and Grossman. *P.R.L.* 120 (14), **2018**
[2] Witman, M. et al. *Nature Comp. Sci.* **2023**, (3) 8

Screening & Validation: Improved performance of dGNN with architecture improvements and additional/more diverse training data

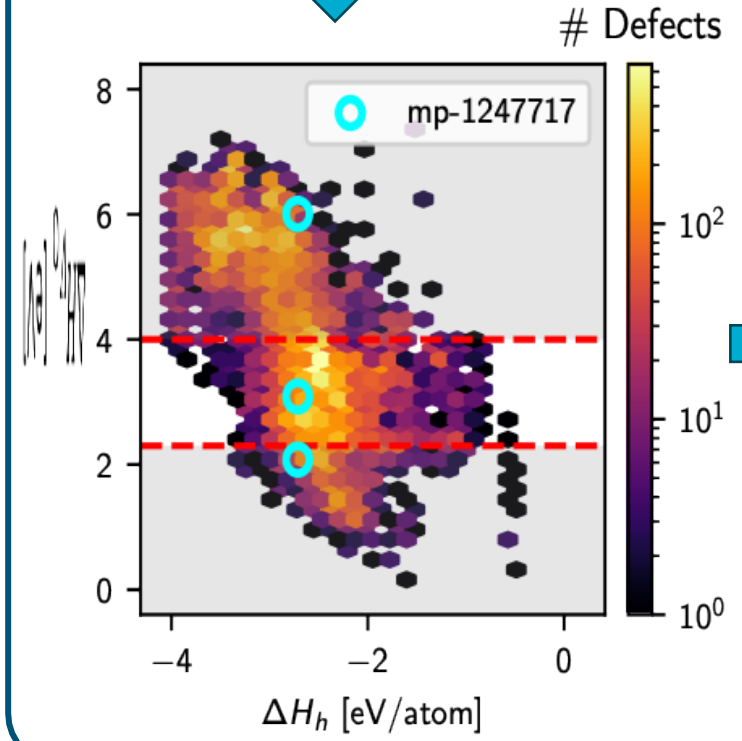
(1) dGNN validation



- Accurate and continually improving oxygen and cation vacancy predictions

(2) Materials screening, down-selection, and experimental validation

- Screen Materials Project oxide space for:
  - Target defect stability: $\Delta H_{V_O} \in [2.3, 4.0]$ eV
  - Target host oxide stability



- Rediscovers known water-splitters (e.g., $Ba_4CeMn_3O_{12}$, …)
- Newly predicted, earth-abundant $BaFe_2O_4$ and $BaFe_{2-x}Al_xO_4$ are *experimentally validated*
- Many additional new materials to be tested (e.g., $Sr_3PrMn_2O_8$, …)

Part I: Key Takeaways

- Accelerated materials discovery made capable by leveraging and adapting state-of-the-art machine learning techniques (GNNs) for defect predictions

  DFT screening = *100s of years* ☹ → dGNN screening = *instantaneous* ☺

- (Re)Discovery of water-splitting oxides made possible (experimental papers coming soon)

- This approach is applicable to wide range of materials/applications (hydrides, nitrides, transition metal dichalcogenides, etc.), so long as we can generate the training data…

Part II:
Modeling of (super)-hydrides for hydrogen storage and beyond[1-3]

Key concepts:

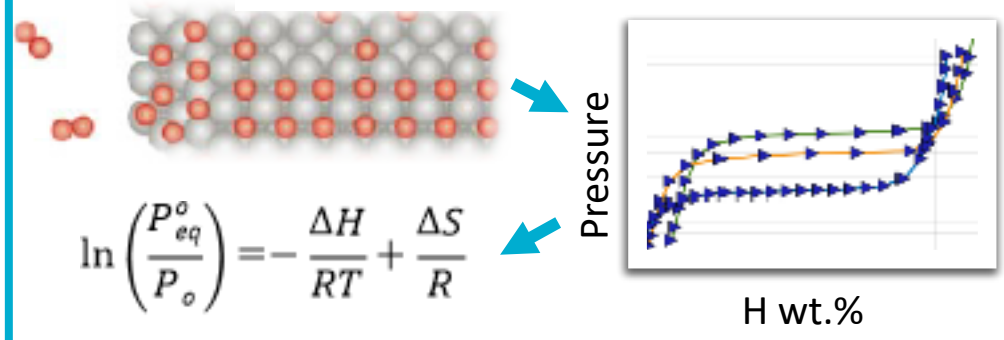
- Graph neural networks on ideal lattices
- High-throughput screening of random alloy/interstitial configurations
- Predictions of thermodynamic properties from first-principles
- Direct calculation of metal-hydrogen phase diagrams

[1] Witman, M. et al. *JPCL,* **2024** (15) 5
[2] Way, L. et al. *In prep*
[3] Guan, P. et al. *In prep*

Explainable machine learning models predict metal hydride thermodynamics

(1) $\ln(P^o_{eq}/P_o)$ target property

H_2 Metal Hydride PCT curves



$$\ln\left(\frac{P^o_{eq}}{P_o}\right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

HydPARK database provides (now ~700 examples):
- Alloy composition, ΔH, ΔS, and $\ln(P^o_{eq})$

(2) Featurization for compositional ML model

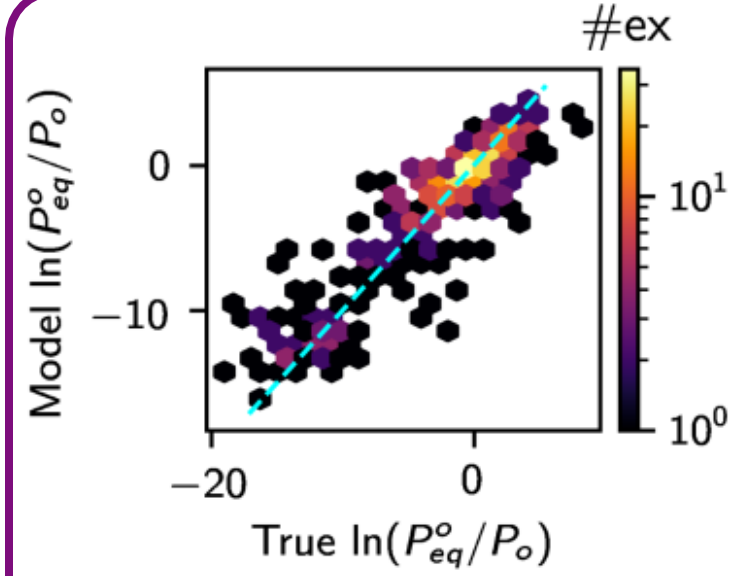
Magpie features[1] -> (mean, stddev., etc) on elemental properties and their at.%

$TiFe_{0.92}Nb_{0.08} \rightarrow$

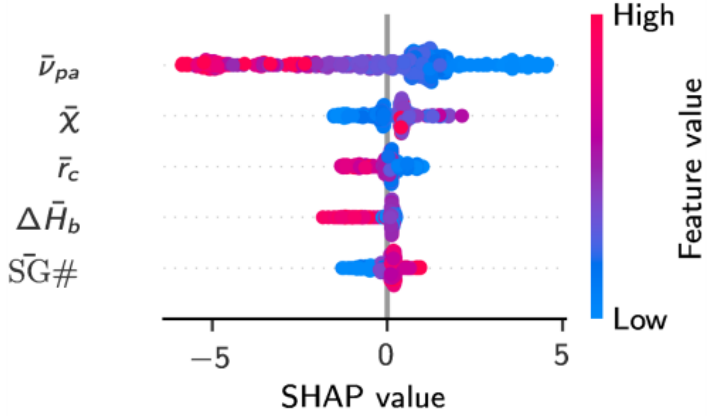
$$\boldsymbol{x} = \{\bar{\nu}_{pa}, \bar{r}_{cov}, \bar{\chi}, \ldots\} \in \mathbb{R}^{145}$$

$\bar{\nu}_{pa} = \sum_i f_i \nu_i$
$\nu_i \equiv$ ground state vol. per atom
$f_i \equiv$ composition frac. of element i

(3) Gradient boosting regression (GBR) model validation and explainability[2-4]



GBR model predicts $\ln(P^o_{eq}/P_o)$ w/MAE ~ 1.5

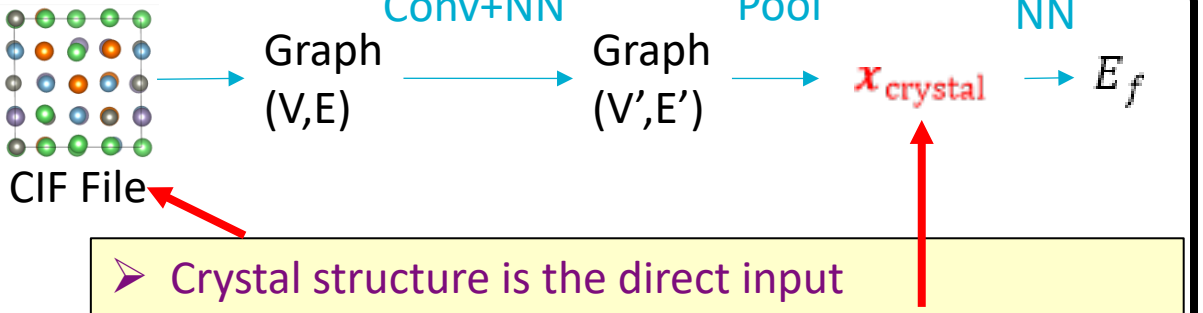


~ linear correlation with $\bar{\nu}_{pa}$:
$\ln(P^o_{eq}/P_o) \approx -m\,\bar{\nu}_{pa} + b$

[1] Ward, L et al. *Comp. Mat. Sci.* **2018**, 152, 60-69
[2] Witman, M. et al. *J. Phys. Chem. Lett.*, 11 (1), **2020**
[3] Witman, M. et al. *Chem. Mater.*, 30 (11), **2021**
[4] Witman, M. et al. *J. Mater. Chem. A.*, 11 (29), **2023**

Graph neural networks (GNNs) on ideal lattice materials provide an attractive platform for high-throughput configurational screening in high entropy systems

GNNs 101: Property prediction from crystal structure input[1]



- Crystal structure is the direct input
- Alleviates the need for manual feature engineering

Model inputs cannot rely on DFT-relaxed configuration

- A model that predicts $\hat{E}_f$ from $\boldsymbol{X}_{\mathrm{DFT}}$ not useful because you would already have $E_{f,\mathrm{DFT}}$:

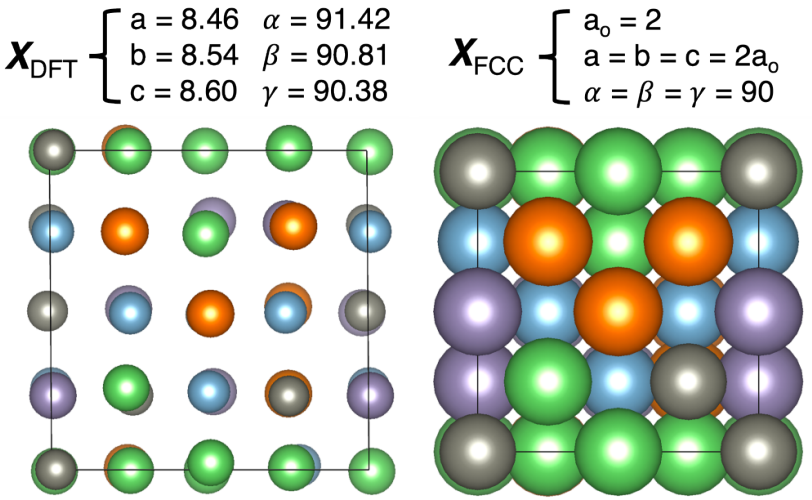
$$\hat{E}_f = f_{GNN}(\boldsymbol{X}_{\mathrm{DFT}}; \theta)$$

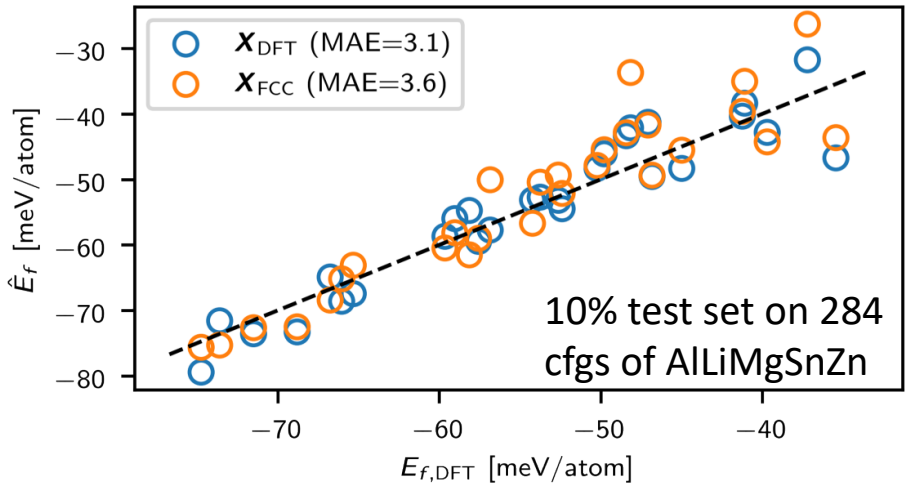
- Derive model inputs (crystal graph) from ideal lattice :

$$\hat{E}_f = f_{GNN}(\boldsymbol{X}_{\mathrm{FCC}}; \theta)$$

$\boldsymbol{X}_{\mathrm{FCC}}$ is trivial-to-generate, so model can be run on millions of random HEA configurations

Negligible loss in performance using ideal representation[2]

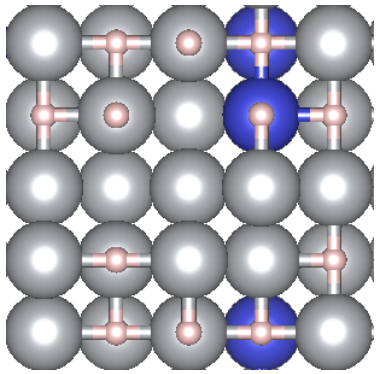




[1] Xie and Grossman. *P.R.L.* 120 (14), **2018**
[2] Witman, M. et al. *J. Phys. Chem. Lett.*, **2024** (15) 5

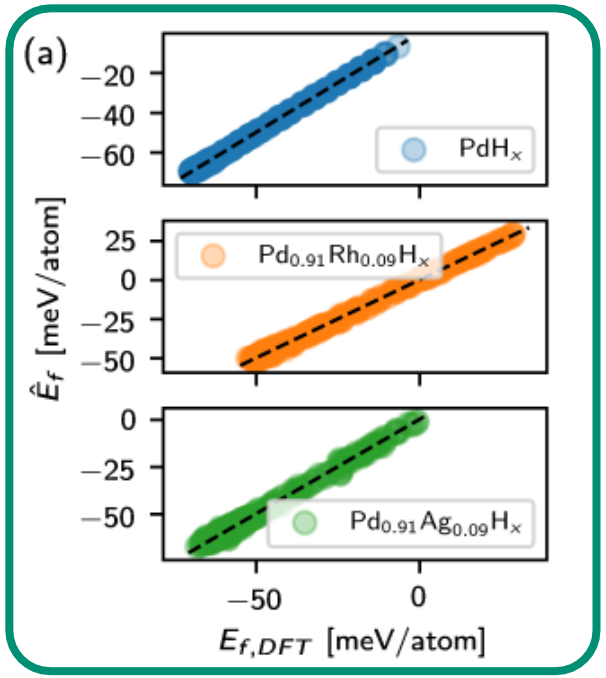
Approach is equally applicable to metal hydrides (random alloy + interstitial occupation)

Ideal FCC hydride representation

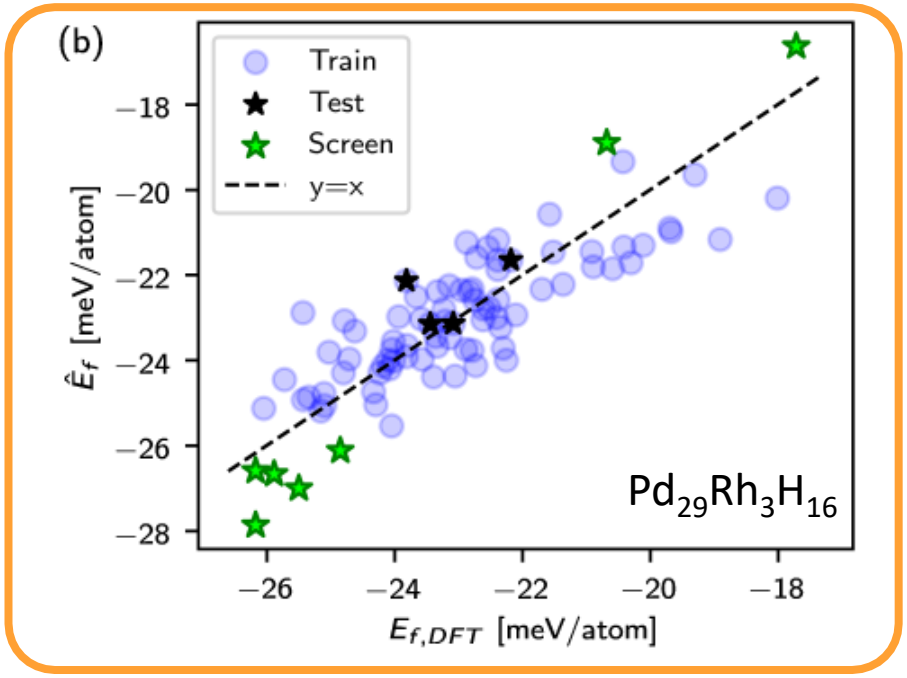


$X_{\text{FCC+INT}}$ for $Pd_{29}Rh_3H_{16}$

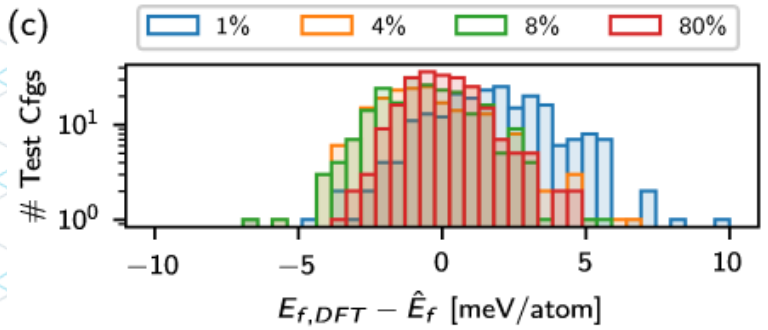
~ 1 meV test MAE for $Pd_{29}\{Rh,Ag\}_3H_x$

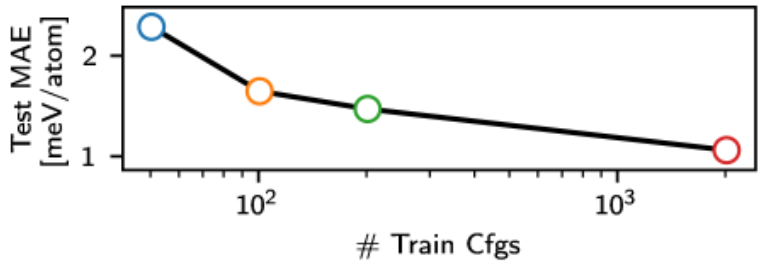


Accurate screening outside train distribution



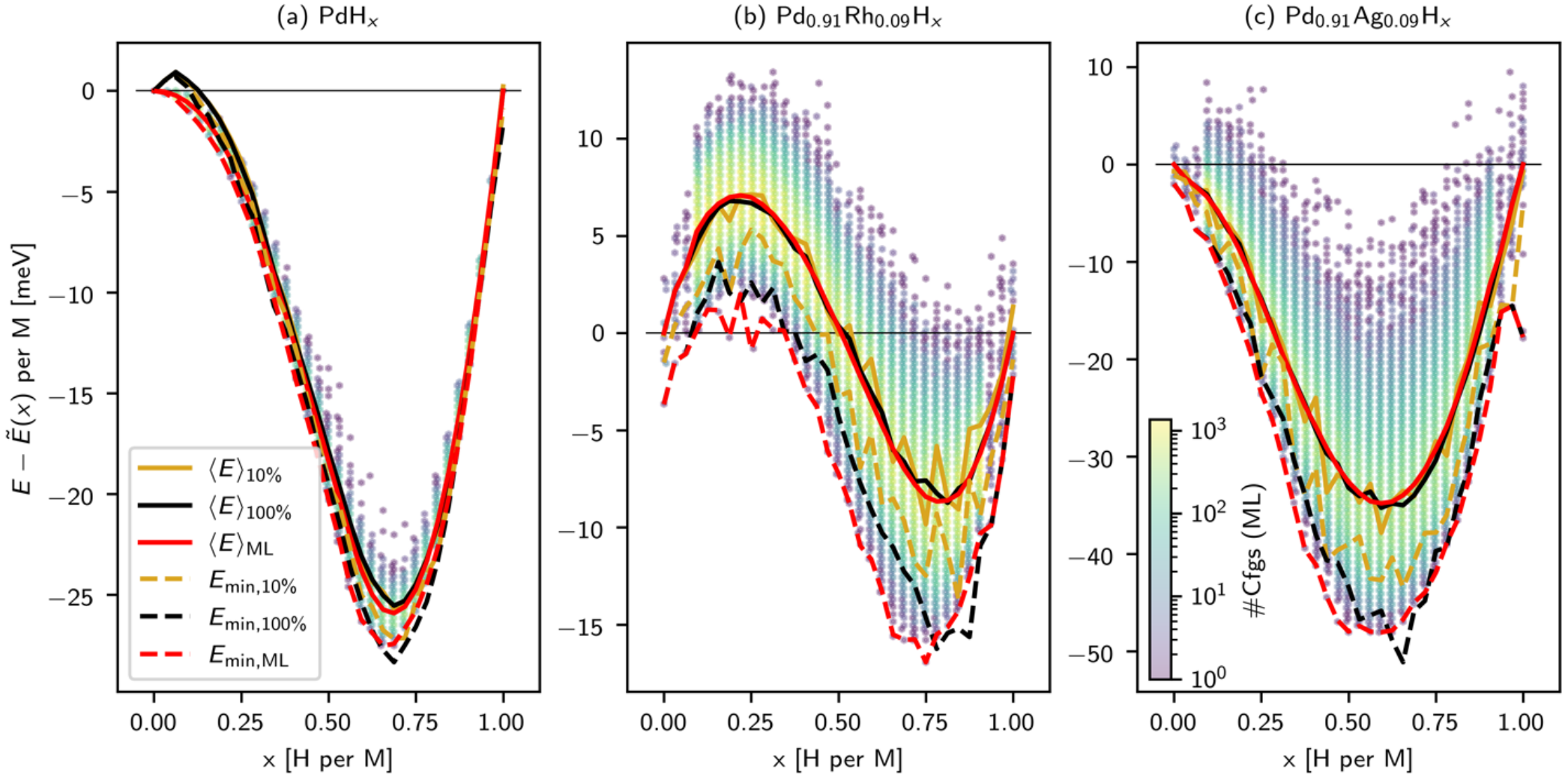
No outlier test set residuals and small MAE despite *small amount of training data*





Models are data-efficient: similar test MAE between 200 vs 2000 train configurations

High-throughput configurational sampling with GNN model identifies lower energy configurations than the brute-force DFT



- ~3,000 DFT cfgs per alloy system needed for $\bar{E}(x)$ convergence (10% of not sufficient)
- ML can screen O(Million) of cfgs, and finds lower energy than anything in training (especially PdRh)

Calculation of PCT curves (metal-hydrogen phase diagram from first principles calculations)

Mean field theory and Boltzmann weighted PCT calculation

Thermodynamic formalism/assumptions:

$$S(x) = k[(1-x)\ln(1-x) + x\ln(x)]$$
$$G(x) = E(x) - TS(x)$$

Energy calculation:

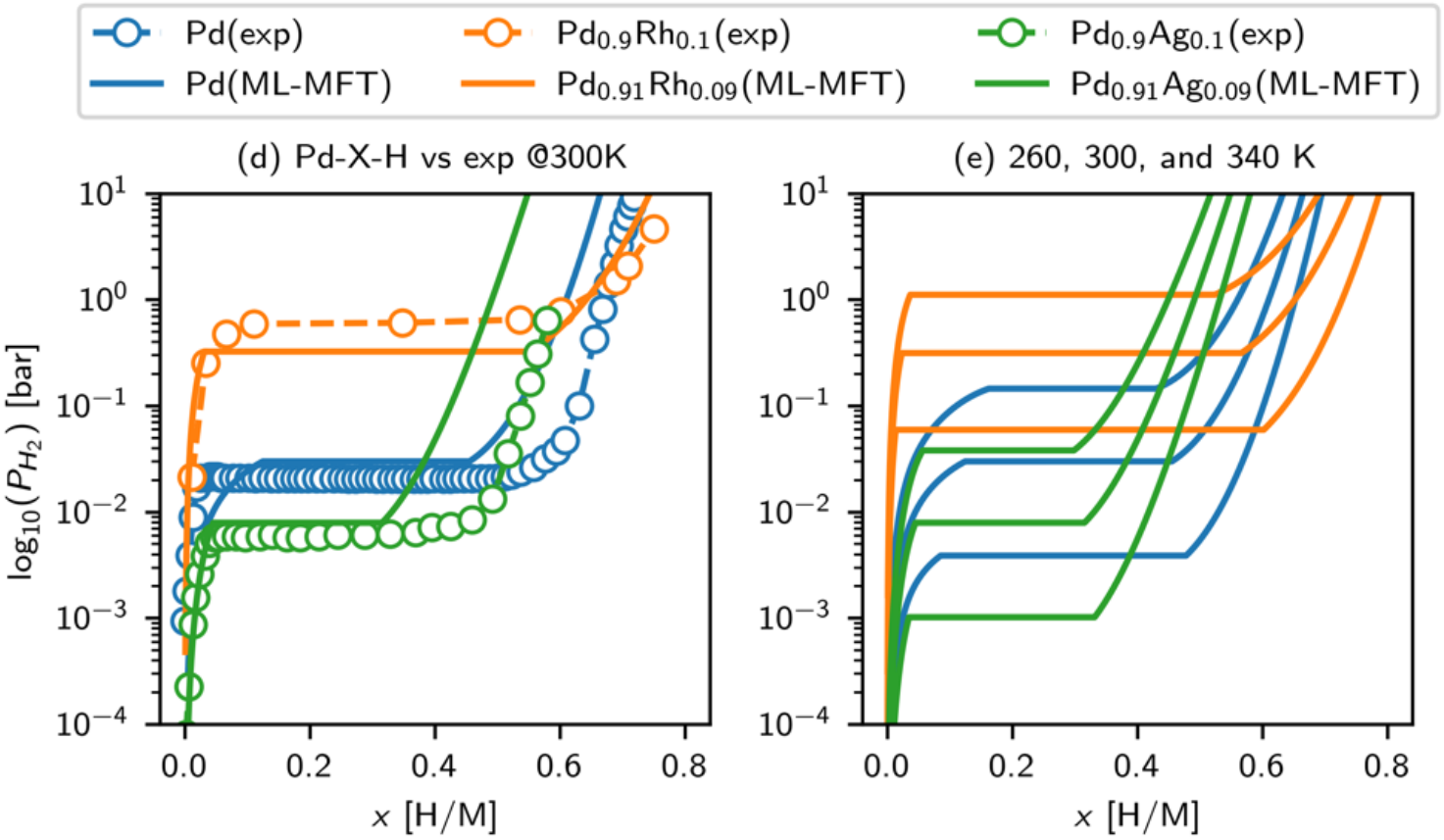
MFT: $E(x) = \bar{E}(x)$

Boltzmann: $E(x) = \frac{\sum_i E_i e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$

PCT:

- fit $G(x)$ to polynomial
- Differentiate w.r.t x $\rightarrow \mu$
- $p = p_0 e^{\mu/kT}$

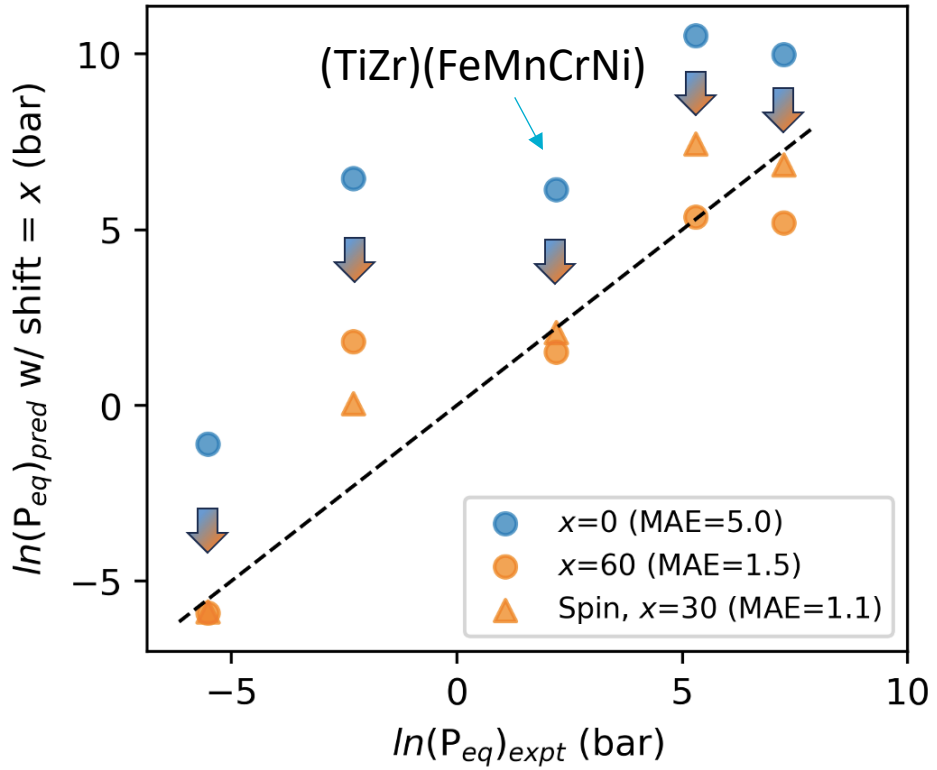
Comparison of computed vs experimental PCT



- Correctly rank plateau pressure, plateau widths, & H/M saturation between alloy systems
- Compute phase envelope

Next steps: Predicting hydrogen phase equilibria in more compositionally complex (super)hydrides

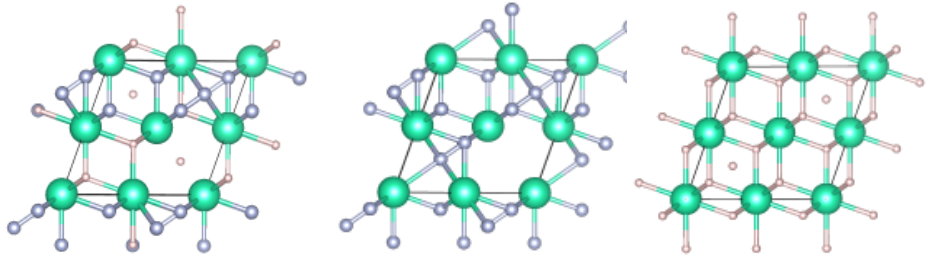
Predicted $\ln(P^o_{eq}/P_o)$ vs. experiment for compositionally complex AB2 alloys[1]



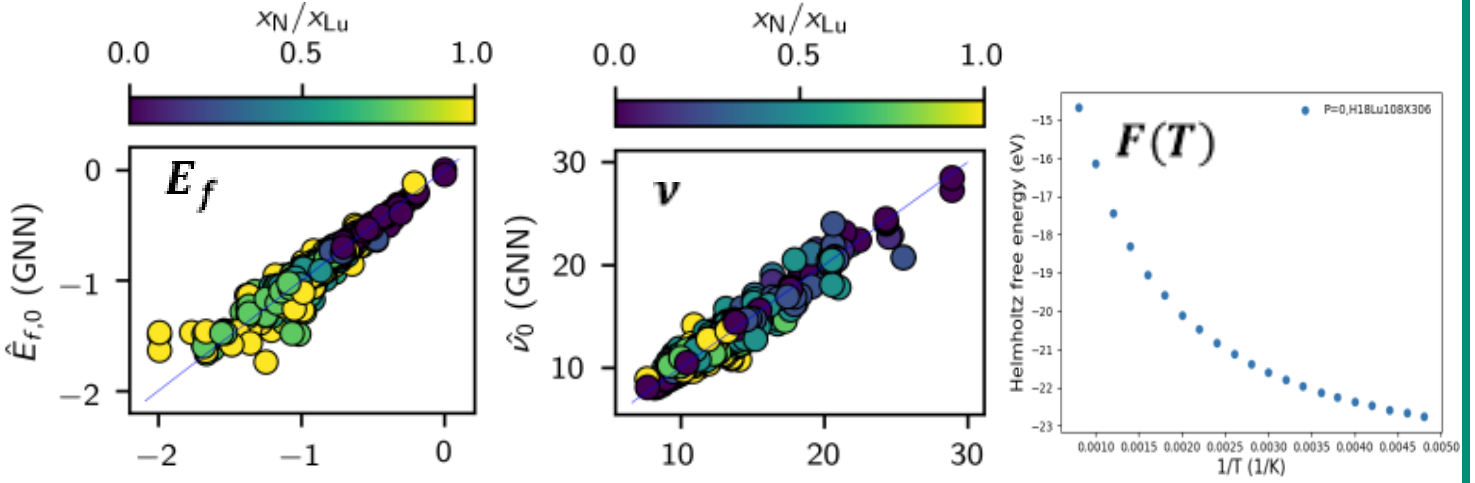
- DFT corrections needed
- Useful for discovering low stability hydrides (high-pressure compression materials)

Multi-interstitial (super)hydrides: $Lu(N,H)_{3-x}$ [2]

1. DFT relaxations of FCC $Lu(N,H)_{3-x}$ (~1,000 calc's)



2. Validate energy *and* volume configurational dependence



3. (μ_N, μ_H) phase diagrams from MC in progress

[1] Way, L. et al. *In prep*
[2] Guan, P. et al. *In prep*

Part II: Key Takeaways

- GNNs make screening of configurational energy landscape in compositionally complex materials tractable

  DFT screening = *100s of years* ☹ → dGNN screening = *instantaneous* ☺

- When coupled to first-principles calculations or simulations, GNNs can power predictions of phase diagrams needed to more wholistically evaluate hydrogen storage performance

- This approach will be particularly useful for predicting/modeling phase equilibria of (super)hydrides under extreme environments (hydrogen pressures) where experimental data is scarce and difficult to obtain

Thank you for your attention!

Questions/comments/collaborations?
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