

Thermodynamic Modeling of Complex Solid Solutions in the Lu-H-N System via Graph Neural Network Accelerated Monte Carlo Simulations

Pin-Wen Guan^{✉,*}, Catalin D. Spataru, Vitalie Stavila, Reese Jones[✉], Peter A. Sharma[✉],
and Matthew D. Witman[†]

Energy Nanomaterials Department, *Sandia National Laboratories*, Livermore, California 94551-0969, USA



(Received 18 September 2024; accepted 23 June 2025; published 2 September 2025)

Metal hydrides are important across diverse applications, such as hydrogen storage, batteries, gas sensors, nuclear reactions, and high-temperature superconductivity. Previous computational studies of metal hydrides under extreme pressures, e.g., $O(10^2)$ GPa, usually treat them as stoichiometric compounds without considering interstitial lattice disorder. As pressures become more moderate in the $O(10^0)$ GPa and below range, hydrogen disorder at interstitial lattice sites becomes prominent, e.g., in the N-doped Lu hydride that was recently claimed superconducting near 1 GPa. Further adding compositional complexity from alloying and/or multielement interstitial occupation makes elucidating pressure- and temperature-dependent observables intractable by first-principles calculations alone. We therefore propose a lattice graph neural-network surrogate modeling approach to predict configuration- and pressure-dependent equation-of-state properties. Their efficiency permits Monte Carlo simulations to calculate Gibbs energies and pressure-dependent phase diagrams, thereby revealing insights into the synthesis conditions required for achieving desired phase equilibria. We demonstrate this concept for the compositionally complex cubic Lu(H,N,Va)₃ system where three constituents (hydrogen, nitrogen and vacancy) have disordered multielement interstitial occupancies and insights into pressure-dependent phase equilibria are critically needed, e.g., N-doping levels can significantly lower dehydrogenation temperatures and provide a new strategy to optimize hydrogen-storage alloys. This work can improve the thermodynamic understanding of the Lu-H-N system and help rational synthesis of N-doped Lu hydrides, but more generally demonstrates an efficient approach to model pressure-dependent thermodynamics of multicomponent solid solutions.

DOI: [10.1103/bsxd-qtph](https://doi.org/10.1103/bsxd-qtph)

I. INTRODUCTION

Enormous progress has been made in recent years in the pursuit of room-temperature superconductors, mainly driven by metal hydrides. Near-room-temperature superconductor was predicted [1,2], synthesized [3], discovered [4], and subsequently confirmed [5] in the La-H system for the first time. In addition, the same theoretical techniques that led to the discovery of superconductivity in LaH₁₀ predict even higher-temperature superconductors such as Li₂MgH₁₆ with T_c as high as approximately 470 K at 250 GPa [6]. However, creation of these superhydrides requires megabar (>100 GPa) pressure, which is a significant hurdle for large-scale synthesis. Therefore, lowering

the pressure for synthesizing these novel materials is a crucial milestone in the pursuit of practical room-temperature superconductivity [7], with several approaches proposed, including optimized chemical precompression [8], impurity doping in hydrides [9–12], and combining multiple stimuli (e.g., pressure and electrochemical potential) [13,14]. An especially remarkable report was the claim of room-temperature superconductivity at near-ambient pressures in N-doped Lu hydrides [15], which subsequently stimulated a rush [16–25] trying to clarify and reproduce the superconducting phase whose structure is reported to have an FCC Lu lattice but with undetermined stoichiometry and atomic positions of H and N. However, these verification efforts, no matter experimental or computational, have not reproduced the claim and the original study has since been retracted. The difficulty of characterizing the material under such extreme conditions and subsequent lack of knowledge of the exact phase(s) present in the original experiment drastically exacerbated the difficulty for subsequent studies to reproduce it.

To facilitate solving similar future problems, which are not unique to the Lu-N-H system in question or specific

*Contact author: pguan@sandia.gov

†Contact author: mwitman@sandia.gov

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](#) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

to applications of hydrides for superconductivity, we introduce a general workflow for predicting temperature- and pressure-dependent phase equilibria in a given multielement, interstitiated lattice type. We demonstrate this by addressing a remaining open question of how N, along with H, is incorporated into the interstitials of the Lu FCC lattice. Specifically, the pressure-composition-temperature (PCT) phase behavior of the Lu-N-H system has yet to be predicted, i.e., the expected N and H concentrations as a function of N and H chemical potentials (temperatures and partial pressures). More generally, quantitative prediction of PCT behavior [26–28] is difficult due to the computational cost of density functional theory (DFT) and the required high-throughput sampling of the potential energy surface of hydrogen and metal alloy interactions; nonetheless, tractability has been demonstrated for simpler metal hydride systems at near ambient pressures by combining machine learning surrogate models for DFT and first-principles thermodynamics [29]. However, PCT prediction becomes even more difficult if a metal or alloy is open to multiple species that can populate its interstitials (i.e., H and N) or if the pressure range to be modeled is sufficiently high that the pressure contribution to the enthalpy is non-negligible.

Our goal is therefore to generally address both challenges in a unified computational workflow so that PCT behavior of high-pressure, multielement interstitial hydrides can be more rapidly predicted. We will demonstrate this for the cubic Lu(H,N,Va)₃ system, but expect

its applicability to translate to other materials science domains relying on (high-pressure) interstitial incorporation in intermetallic alloy lattices. Modern machine-learning techniques offer the ability to accurately approximate high-dimensional functions [30], opening up new possibilities for solving “curse of dimensionality,” a key challenge in materials science. We propose the use of graph neural networks (GNNs) [31–33] as surrogate models to directly predict computationally expensive DFT-relaxed properties from an unrelaxed crystallographic representation [29,34,35], specifically the zero-pressure *relaxed* formation energy, $E_{f,0}$, and specific volume, v_0 , using just the idealized (i.e., *unrelaxed*) FCC crystallographic lattice and coordinates as inputs. This sufficiently accurate and fast surrogate model for $E_{f,0}$ and v_0 , trained on a reasonable number (approximately 1200) of DFT relaxations, enables the extensive sampling required by lattice model Monte Carlo to estimate free energies dependent on composition, pressure and temperature. From this, different types of phase equilibria and thermodynamic properties can be calculated. Additionally, we propose a new doping strategy to optimize hydrogen-storage alloys based on thermodynamic modeling. By facilitating the assessment of thermodynamic stability of high H-content hydrides, we anticipate this general approach will help with future rational design strategies to reduce the extreme pressures needed for their synthesis, as well as provide an efficient approach for thermodynamic modeling of multicomponent solid solutions as an alternative to the conventional

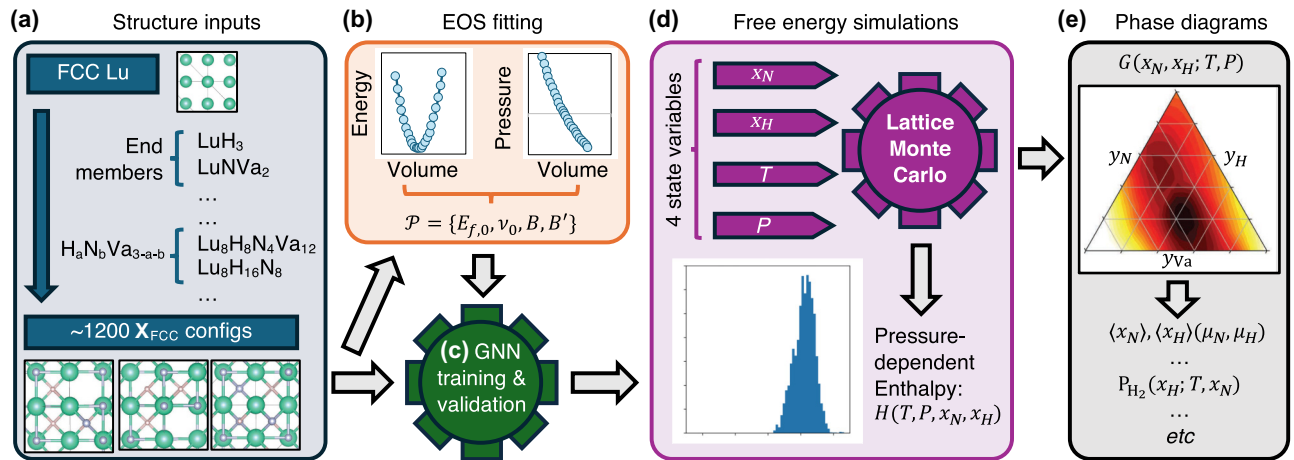


FIG. 1. Graphical summary of the machine-learning-accelerated workflow for calculating pressure-dependent thermodynamics of compositionally complex solid solutions. (a) Solid-solution configurations on an idealized lattice, $\mathbf{X}_{\text{FCC}}$, are first generated by sampling different end member and intermediary compositions. (b) Configuration-dependent energy and pressure vs volume curves are fit to an equation of state to extract a set of four parameters, $\mathcal{P}$: zero-pressure formation energy ($E_{f,0}$), zero-pressure volume (v_0), bulk modulus (B), and pressure-derivative of bulk modulus (B'). (c) GNN surrogate models are trained to predict these properties using $\mathbf{X}_{\text{FCC}}$ as input. (d) A multitude of lattice Monte Carlo simulations across fixed composition, temperature, and pressure are performed using the GNN models. (e) Gibbs free energies as a function of composition, temperature, and pressure are computed, from which relevant macroscopic properties can be computed (which may be complicated to experimentally extract), such as expected composition as a function of chemical potentials, $\langle x_N \rangle, \langle x_H \rangle (\mu_N, \mu_H)$, or the temperature-dependent equilibrium hydrogen pressure as a function of concentrations, $P_{\text{H}_2}(x_H; T, x_N)$.

method based on cluster expansion (CE) [36]. Finally, we conclude with some insights into current limitations and the promising opportunities for extending this work in the future.

II. RESULTS AND DISCUSSION

Our workflow for computing pressure-dependent thermodynamics in compositionally complex solid solutions is graphically summarized in Fig. 1 and discussed in detail below. The major steps consist of the following: (a),(b) high-throughput sampling and first-principles calculations of solid solution configurations are used to fit equation-of-state parameters, (c) GNN training to predict these configuration-dependent parameters using the idealized starting structure as input, (d) Monte Carlo simulations of pressure-dependent enthalpies, (e) calculation of Gibbs energies and phase diagrams.

A. High-throughput sampling of Lu-N-H system

First we generate 1179 $2 \times 2 \times 2$ ideal FCC supercell configurations, $\mathbf{X}_{\text{FCC}}$, of $\text{Lu}(\text{H}, \text{N}, \text{Va})_3$. Each initial configuration, consisting only of Lu at each packing site, differs only by the identity (N, H, or Va) of the octahedral and tetrahedral interstitials. For each initial configuration, energy-volume calculations are performed by calculating the energy of the relaxed structure at multiple volumes. The volume sampling is a two-stage procedure. First, several initial volumes with a spacing of 2% volume change are sampled, generating an initial equation of state (EOS). Then, guided by the initial EOS, the rest of the volumes are sampled to ensure the pressure range from 0 to approximately 10 GPa is covered. In each relaxation, atomic positions and the cell shape were allowed to change, but the cell volume was fixed. The resulted energy-volume data are used to fit the Rose-Vinet EOS [37] and obtain $E_{f,0}$, v_0 , bulk modulus B , and pressure derivative of bulk modulus B' . In addition, from the energy-volume data, pressure-dependent enthalpy for each configuration at a series of pressures from 0 to 2 GPa at a step of 0.01 GPa is calculated. The brute-force DFT-sampled potential energy landscape from the approximately 1200 configuration training data is shown in Fig. 2(a) as a function of x_H and x_{Lu} . To construct Fig. 2(b), we compute the standard deviation, σ , of a configuration's nearest-neighbor Lu-Lu interatomic distances, then summarize the data as a box-and-whisker plot, grouping configurations by x_N . This indicates that, as expected, higher N concentrations are more likely than higher H concentrations to introduce larger structural distortions to the idealized FCC lattice where $\sigma = 0$.

B. GNN surrogate model validation

We seek a surrogate model, parameterized by θ , that can utilize an *unrelaxed* and idealized representation of

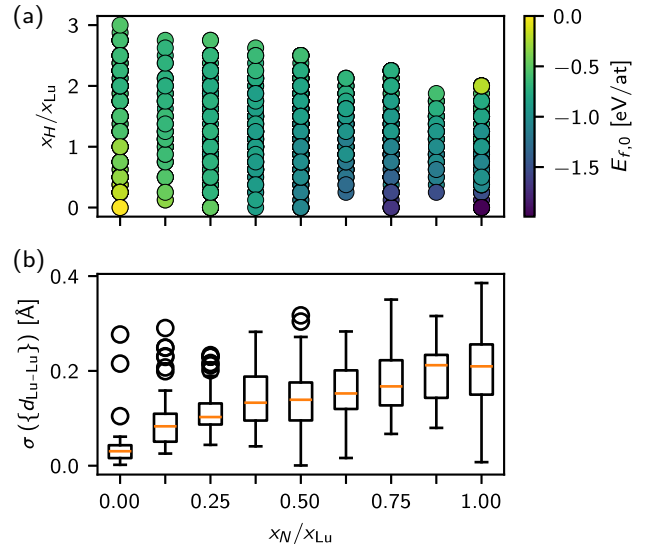


FIG. 2. (a) The DFT calculated formation energies of training configurations as a function of x_H/x_{Lu} and x_N/x_{Lu} . (b) For each configuration, the standard deviation of all nearest-neighbor Lu-Lu interatomic distances, $\sigma(\{d_{\text{Lu-Lu}}\})$, is computed and summarized as a box and whisker by grouping configurations for a given x_N/x_{Lu} .

an alloy and its interstitial site occupations (denoted here $\mathbf{X}_{\text{FCC}}$) to predict the *relaxed* formation energies and specific volumes,

$$\{E_{f,0}, v_0\} = f_{\text{GNN}}(\mathbf{X}_{\text{FCC}}; \theta). \quad (1)$$

We adopted a graph neural-network (GNN) approach (see Sec. IV for more details), but we note that this problem can equivalently be formulated for a more traditional cluster-expansion (CE) approach [36,38,39]. We therefore quantified a CE models' performance in the Supplemental Material [40] (including Refs. [17,23,36,38,39,41–49]) to confirm that our selected GNN approach delivers improved accuracy. Finally, it is worth noting that this approach explicitly bypasses the force calculations needed to directly optimize structures and obtain $E_{f,0}$, which could in principle be performed if one were to utilize more recent and advanced equivariant models [50,51]. However, these approaches and potentially more complicated model architectures can require orders of magnitude larger training datasets than the one considered here and were not required to achieve the desired accuracy in relaxed $E_{f,0}$ predictions, as discussed next.

Figure 3's top and bottom rows summarize the performance of our trained GNN models on the $E_{f,0}$ and v_0 prediction tasks, respectively. For each prediction target, three versions of parity plot for the combined $K = 10$ -fold test set predictions are differentiated by color coding either H content (x_H/x_{Lu}), N content (x_N/x_{Lu}) or the data density. The parity plots immediately reveal that low $E_{f,0}$ is

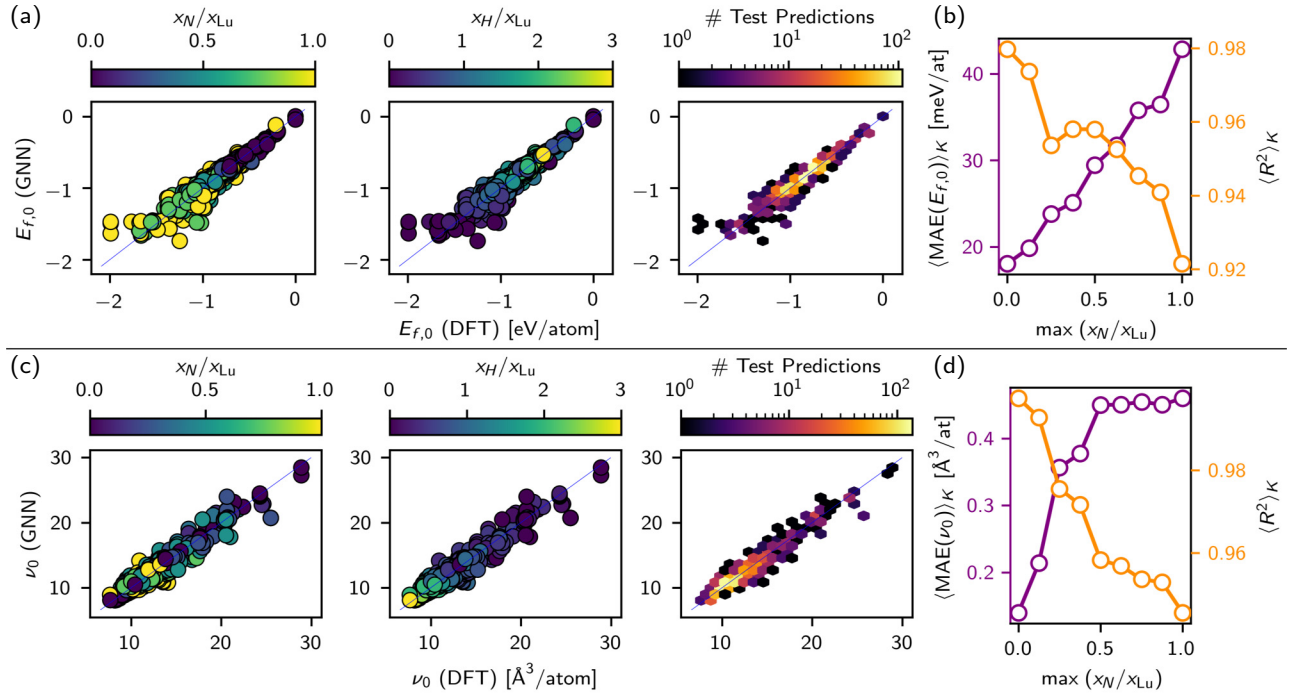


FIG. 3. Model validation for (a),(b) $E_{f,0}$ and (c),(d) ν_0 predictions. Parity plots (a),(c) correspond to the combined $K = 10$ -fold test set predictions, differentiated by color coding H content (x_H/x_{Lu}), N content (x_N/x_{Lu}), or the data density. (b),(d) show expected (K-fold averaged test set) MAE R^2 in purple and orange, respectively, as a function of the maximum x_N/x_{Lu} considered.

correlated with high N content. Additionally, we plot the expectation mean absolute error (MAE) and coefficient of determination (R^2) across K-fold test sets, $\langle \text{MAE} \rangle_K$ and $\langle R^2 \rangle_K$, respectively, as a function of x_N/x_{Lu} , where any configurations with a higher N content are excluded from the performance metric. This reveals critical insight into model performance: for $x_N/x_{Lu} < 1$ we can achieve expected MAE, depending on x_N , of 20–40 meV/atom and $R^2 \geq 0.9$. Considering the errors of 96 meV/atom that have been observed for DFT with respect to experimental formation energies [52,53], the additional MAE introduced by the GNN model can be considered marginal. Therefore, the overall expected performance is quite good and outperforms a traditional CE approach (see Supplemental Material [40]), but performance indeed starts to deteriorate for $x_N/x_{Lu} \geq 1$ where MAE increases are driven by a small number (note the data density's log scale) of difficult-to-predict configurations. This generally arises because high N content configurations undergo significant distortion from the ideal FCC lattice and interstitial geometry [Fig. 2(b)], meaning the actual structure deviates further from the idealized lattice that must be used as input to the ML model. Note that increasing MAE with increasing x_N/x_{Lu} is due to a relative error increase as well since R^2 also begins to drop for higher N content configurations. This insight bounds the expected accuracy of the subsequent phase diagram predictions as a function of N content. As discussed next, for the material system and

conditions of interest here, a high-accuracy approximation of the dependence of enthalpy on pressure for an individual configuration only requires accurate GNN predictions for $E_{f,0}$ and ν_0 . Although not necessary for the current study, it is nonetheless noteworthy that more advanced recent (equivariant) GNN architectures [54] can predict even more complex mechanical properties (e.g., elasticity tensors) and could be integrated into this workflow, likely at the cost of needing to significantly expand our training dataset size.

C. Gibbs energies and phase equilibria of cubic $\text{Lu}(\text{H}, \text{N}, \text{Va})_3$

The Monte Carlo (MC) simulations were employed to calculate Gibbs energies at a fixed chemical composition, temperature and pressure. The enthalpy is obtained by

$$H = \sum_{\alpha} H_{\alpha} \rho_{\alpha} = \sum_{\alpha} (c_{0,\alpha} + c_{1,\alpha} P + \dots) \rho_{\alpha}, \quad (2)$$

where H_{α} is enthalpy of a sampled configuration α , P is pressure, and ρ_{α} is the frequency of the configuration α appearing in the simulation. As a function of P , H_{α} is expanded as a series, with $c_{0,\alpha}, c_{1,\alpha}, \dots$ as coefficients. As discussed in the Supplemental Material [40], a linear approximation is sufficiently accurate by making the truncation error less than 1 meV/atom within the pressure range

studied (0–2 GPa):

$$H = \sum_{\alpha} (c_{0,\alpha} + c_{1,\alpha}P) \rho_{\alpha}, \quad (3)$$

where $c_{0,\alpha} = H_{\alpha}|_{P=0} = E_{0,\alpha}$ and $c_{1,\alpha} = \partial H_{\alpha}/\partial P|_{P=0} = V_{0,\alpha}$, which are predicted by the present lattice GNN model. We have the exact differential

$$d(\beta G) = d(\beta(H - TS)) = H d\beta + \beta V dP, \quad (4)$$

where G is the Gibbs energy, $\beta = (k_B T)^{-1}$, k_B is Boltzmann constant, and T is temperature. Using $\lim_{\beta \rightarrow 0} \beta G = \sum y_i \ln y_i$, where y_i is the site fraction of species i ($i = \text{H, N, Va}$) in the interstitial sites, the Gibbs energy at temperature T , pressure P , and compositions x_H and x_N can be calculated as

$$\beta G(T, P, x_H, x_N) = n \sum y_i \ln y_i + \int_0^{\beta} H(\beta', P, x_H, x_N) d\beta'. \quad (5)$$

The number of interstitial sites n is three per Lu atom. The site fractions and compositions are related by $y_H = x_H/(3x_{\text{Lu}})$ and $y_N = x_N/(3x_{\text{Lu}})$. Gibbs energies of

the cubic $\text{Lu}(\text{H,N,Va})_3$ solid solution under three pressures (0, 1, 2 GPa) and two temperatures (273, 1273 K) are shown in Fig. 4. More details including site occupancies of each species in each of the interstitial sites, the MC-sampled distribution of enthalpies of configurations and plots of Gibbs energies as functions of temperature can be found in the Supplemental Material [40]. The Gibbs energies are most sensitive with respect to y_N , most negative when $y_N \sim 1/3$, i.e., $x_N/x_{\text{Lu}} \sim 1$, and increase drastically when y_N further increases. Notably, the Gibbs energy surfaces are nonconvex, with multiple local minima, indicating immiscibility between the three constituents H, N, and vacancy within the interstitial sites. The temperature and pressure up to 2 GPa have an effect on, but do not majorly alter, the features of the Gibbs energy surfaces fundamentally.

Based on the calculated Gibbs energies, the ternary phase equilibria of cubic $\text{Lu}(\text{H,N,Va})_3$ are computed and shown in Fig. 5 for different combinations of temperatures and pressures. Instead of compositions, chemical potentials (μ_H and μ_N) are chosen as the diagram axes since they are control variables for H and N more frequently in experiments and can be tuned via temperature and partial pressure when these components are in a vapor state. However, it should be noted that here the phase equilibria

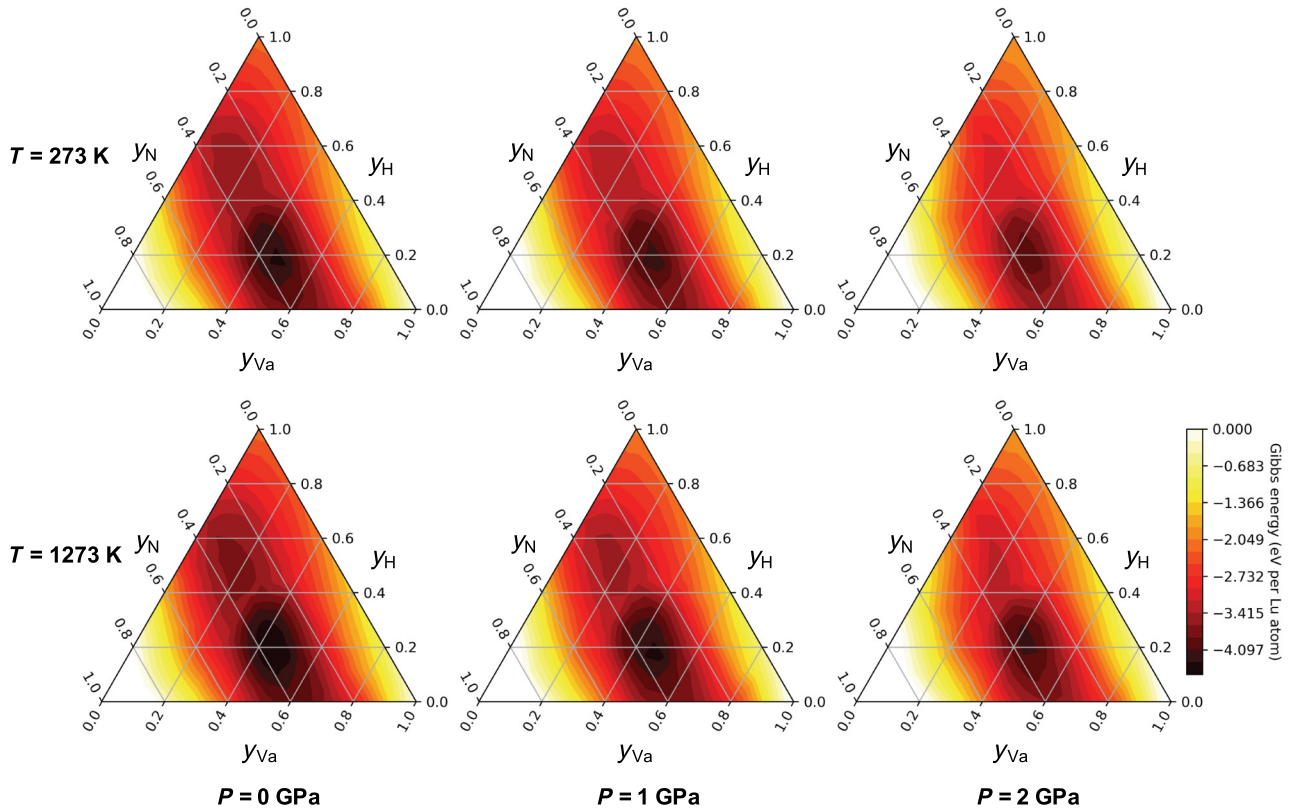


FIG. 4. Gibbs energies of the cubic $\text{Lu}(\text{H,N,Va})_3$ solid solution under different pressures and temperatures. The reference states are the elements at their standard states.

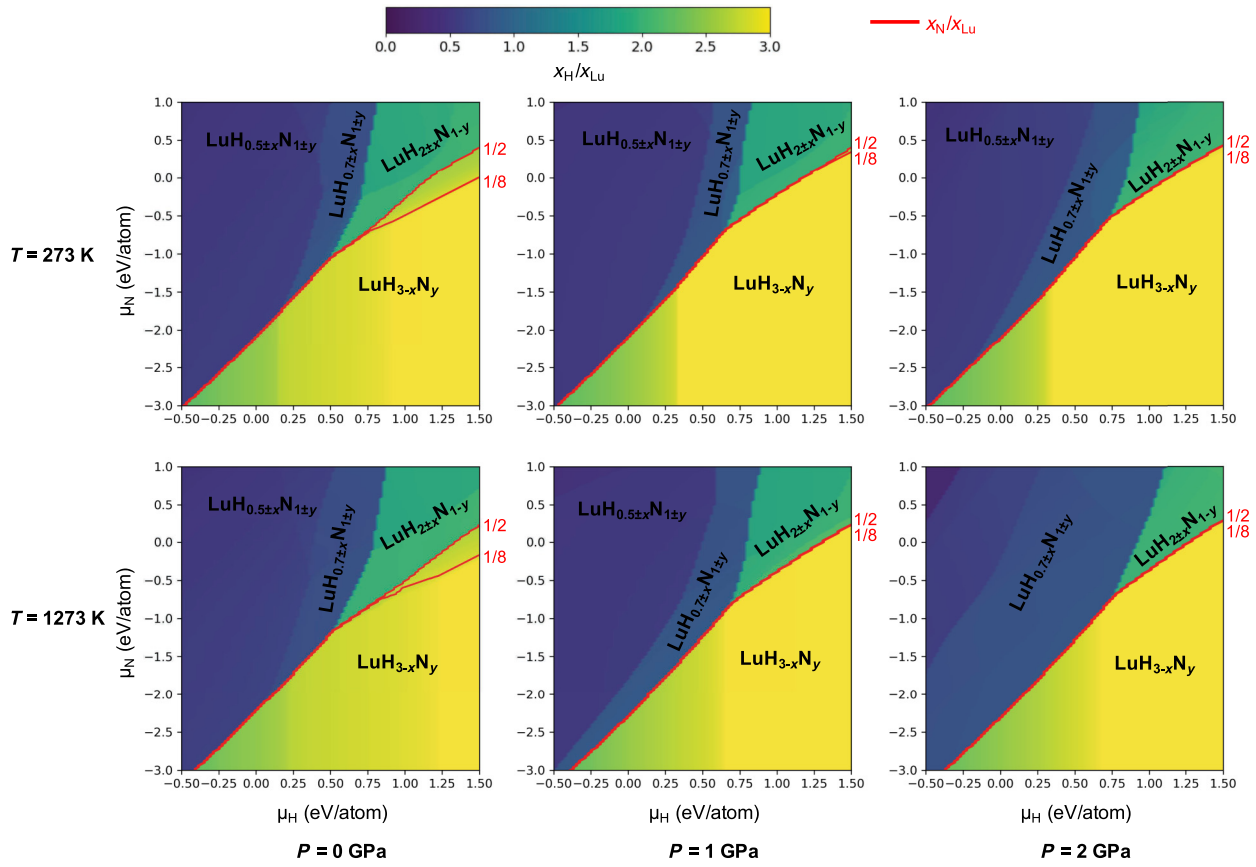


FIG. 5. Equilibrium phase diagrams of the cubic $\text{Lu}(\text{H,N,Va})_3$ solid solution under different pressures and temperatures.

are calculated for the cubic Lu-H-N phases only without assuming a solid-vapor equilibrium, otherwise the total four conditions (T , P , μ_H , and μ_N) cannot be varied independently according to the phase rule. Within the range of conditions shown in the figures, there are four phase regions, i.e., $\text{LuH}_{3-x}\text{N}_y$, $\text{LuH}_{2\pm x}\text{N}_{1-y}$, $\text{LuH}_{0.7\pm x}\text{N}_{1\pm y}$, and $\text{LuH}_{0.5\pm x}\text{N}_{1\pm y}$. The composition changes discontinuously across the phase boundaries, while it changes gradually within each single-phase region. Due to the fact that the GNN energy model has increasing errors when $x_N/x_{\text{Lu}} > 1$ and the high sensitivity of calculated phase boundaries with respect to Gibbs energy errors, it is possible that the relatively small composition discontinuity between the two H-poor phases $\text{LuH}_{0.7\pm x}\text{N}_{1\pm y}$ and $\text{LuH}_{0.5\pm x}\text{N}_{1\pm y}$ may be artifacts and they belong to the same continuous solid solution. With temperature increasing, $\text{LuH}_{0.7\pm x}\text{N}_{1\pm y}$ has a larger phase region, mainly due to its larger configurational entropy since it has more equal fractions of H, N, and vacancy compared with the other phases. A decreasing H stoichiometry with increasing temperature is observed for the $\text{LuH}_{3-x}\text{N}_y$ phase, similarly due to the entropy effect. With pressure increasing, both H-rich $\text{LuH}_{3-x}\text{N}_y$ and N-rich $\text{LuH}_{0.7\pm x}\text{N}_{1\pm y}$ have expanded phase regions, while the $\text{LuH}_{2\pm x}\text{N}_{1-y}$ phase with significant fractions of both H and

N shrinks, indicating the larger immiscibility between H and N under pressure.

An important conclusion from Fig. 5 is that it is difficult to achieve significant N-doping levels in the $\text{LuH}_{3-x}\text{N}_y$ phase under thermodynamic equilibrium, which agrees with some experimental works where no or low N content ($x_N/x_{\text{Lu}} \leq 0.02$) were detected [25,55]. Evidently, equilibrium N concentration in $\text{LuH}_{3-x}\text{N}_y$ is significant only at near-ambient pressures with $\mu_H > 0.7$ eV and $\mu_N > -0.7$ eV and μ_H much larger than μ_N , a region close to the $\text{LuH}_{3-x}\text{N}_y/\text{LuH}_{2\pm x}\text{N}_{1-y}$ phase boundary. However, providing such a high H chemical potential at near-ambient pressures is quite difficult using conventional methods, although nonconventional methods such as the pressure-potential approach introducing electrochemical driving force have been proposed for this purpose [13,14]. For H_2 in equilibrium with the hydrides, increasing pressure can increase μ_H , but lower equilibrium N solubility in $\text{LuH}_{3-x}\text{N}_y$ at the same time. Despite this, it is noted that there have been other experimental studies reporting successful synthesis of Lu hydrides with a significant N content under high pressures [18,19]. In the work by Xing *et al.* [19], the averaged nitrogen content was 0.84 wt.%, i.e., $x_N/x_{\text{Lu}} \sim 0.11$. Li *et al.* reported a sample with an

average nitrogen content of 1.3 wt.% ($x_N/x_{Lu} \sim 0.17$), where nitrogen was widespread homogeneously, though they attributed this phenomenon to the presence of LuN [56]. The large discrepancy in the reported N contents from different studies indicates the need for more detailed characterization of distribution of H and N to determine whether a homogeneous solid solution forms or phase separation occurs. If the presence of N is not due to secondary phases, then it is very likely that the reported samples are nonequilibrium phases with supersaturated N solutes, based on the present calculations.

In addition to phase equilibria and compositions, site occupancies are also of interests in some applications. For example, theoretical investigations show that N in the octahedral interstitial sites may be key for the special electronic properties of N-doped Lu hydrides [24,57]. In the present study, it is found that for low N contents, N prefers the first nearest-neighbor interstitial sites of Lu, i.e., the tetrahedral interstitial sites (Fig. S2), which is consistent with a previous calculation [17]. When the N content is high enough, N prefers the octahedral interstitial sites, similar with LuN. For low N contents, a small but non-negligible portion of N in the octahedral interstitial sites may be obtained if quenched from a very high temperature (Fig. S2).

D. Paraequilibrium of cubic Lu(H,N,Va)₃ at fixed N-doping levels

When there is a large difference in mobility of different components in a solid solution, instead of a full equilibrium, a temporary paraequilibrium state may occur, where rapidly diffusing elements reach equilibrium while slowly diffusing elements are treated as immobile [58]. In a paraequilibrium, the ratios of molar fractions of immobile components are the same in all phases. The concept of paraequilibrium has been applied in hydrogenation of alloys, where metal atoms were treated as immobile and H atoms were treated as mobile [59]. Here, based on the

fact that the diffusivity of H in metals is much higher than that of heavy interstitials like O and N [60], we calculate paraequilibrium of the cubic Lu(H,N,Va)₃ solid solution by assuming: (1) the diffusion of N atoms can be ignored and (2) H atoms are mobile enough to reach equilibrium between different phases. Such paraequilibrium can be obtained from minimization of Gibbs energies at fixed N-doping levels. In addition, we assume the Lu-H-N solids are in equilibrium with a H₂/N₂ fluid phase, thus we can include partial pressures as condition variables. We are most interested in low N compositions, which indicates that μ_H needs to be much larger than μ_N based on Fig. 5 and therefore the fluid phase pressure is dominated by H₂ with $P \approx P_{H_2}$, where P_{H_2} is partial pressure of H₂. The following equation is used to correlate chemical potential and partial pressure of H₂:

$$\mu_{H_2}(T, P_{H_2}) = \mu_{H_2}(T, P_0) + k_B T \ln \left(\frac{P_{H_2}}{P_0} \right) + k_B T \ln \gamma_{H_2}. \quad (6)$$

We choose 1 bar (0.1 MPa) for the reference hydrogen partial pressure P_0 , and k_B is the Boltzmann constant. γ_{H_2} is the fugacity coefficient of H₂, and is calculated using the model of Joubert [47]. $\mu_{H_2}(T, P_0)$ can be written as

$$\mu_{H_2}(T, P_0) = E_{H_2}(P_0) + \Delta\mu_{H_2}(T, P_0), \quad (7)$$

where $E_{H_2}(P_0)$ is the DFT-computed energy of a H₂ molecule at reference pressure, while $\Delta\mu_{H_2}(T, P_0)$ is the finite-temperature contribution. In the present work, lattice vibration of solid phases is not explicitly calculated, since its treatment needs expensive calculations like SSCHA due to anharmonic phonons of Lu hydrides [23]. Alternatively, for $\Delta\mu_{H_2}(T, P_0)$, an effective value $\Delta\mu_{H_2}^{\text{eff}}(T, P_0) \approx 136 * T \text{ J/mol}$ (T in K) based on the literature [48] is used to implicitly consider the vibrational contributions to Gibbs energies of solids in a simple approximate way (detailed

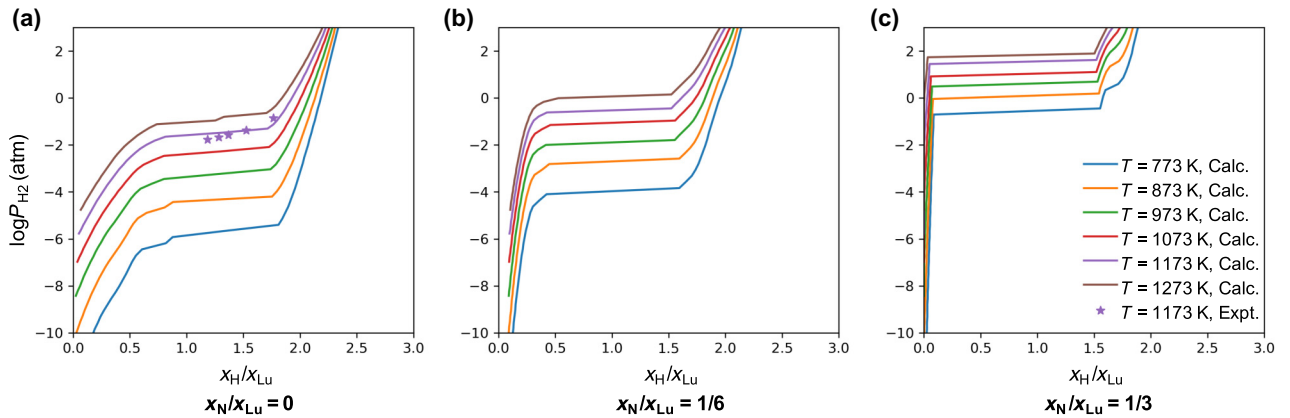


FIG. 6. Paraequilibrium pressure-composition-temperature isotherms of the cubic Lu(H,N,Va)₃ solid solution at fixed N-doping levels under near-ambient pressures.

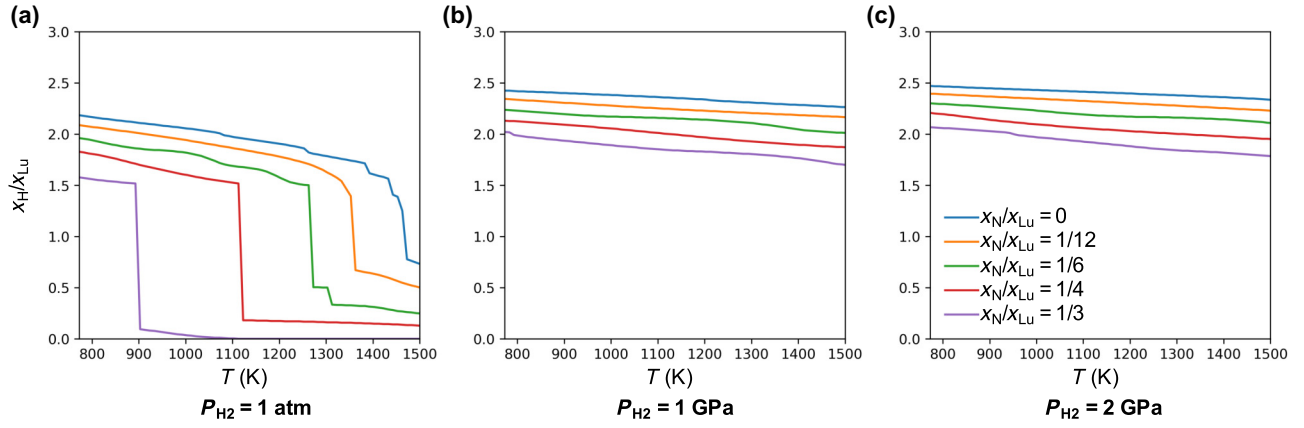


FIG. 7. Temperature-dependent paraequilibrium H composition of the cubic $\text{Lu}(\text{H},\text{N},\text{Va})_3$ solid solution at fixed N-doping levels under different pressures.

discussions can be found in the Supplemental Material [40]). By using $\Delta\mu_{\text{H}_2}^{\text{eff}}(T, P_0)$ for $\Delta\mu_{\text{H}_2}(T, P_0)$ in Eqs. (6) and (7), P_{H_2} can be solved from a given $\mu_{\text{H}_2}(T, P_{\text{H}_2})$.

The paraequilibrium PCT isotherms of the cubic $\text{Lu}(\text{H},\text{N},\text{Va})_3$ solid solution at several fixed N-doping levels under near-ambient pressures are shown in Fig. 6. These PCT isotherms all show plateau pressures within certain composition ranges due to equilibrium between an H-poor phase and an H-rich phase, which is a usual feature of metal-hydrogen systems. To our best knowledge, the only available experimental PCT data within the whole Lu-H-N system are those measured for the binary Lu-H system in the temperature range 824–950 °C [48]. The agreement between the present calculations and the experimental data is quite good, demonstrating the validity of our approach. It is evident that, regardless of the N-doping level and within near-ambient pressures (< 1000 atm), synthesizing a cubic $\text{Lu}(\text{H},\text{N},\text{Va})_3$ phase with $x_{\text{H}}/x_{\text{Lu}} \gtrsim 2.5$ by pure chemical hydrogenation using fluid H_2 is quite challenging, which necessitates introducing pressures in the GPa level or other driving forces [13,14]. Remarkably, the N-doping level can significantly change the PCT isotherms. A higher N-doping level leads to orders of magnitude higher plateau pressures, only slightly smaller maximum H capacities, and steeper shapes of the PCT isotherms.

The temperature-dependent paraequilibrium H compositions of the cubic $\text{Lu}(\text{H},\text{N},\text{Va})_3$ solid solution at several fixed N-doping levels are shown in Fig. 7. The general trend under different pressures is the decrease of H composition with increasing temperature, regardless of the N-doping level. At $P_{\text{H}_2} = 1$ atm, a phase transition between H-rich and H-poor occurs at a critical temperature T_{dehyd} , which corresponds to the hydrogenation and dehydrogenation temperature. Clearly, T_{dehyd} is very sensitive with respect to the N-doping level. Compared with the undoped Lu-H phase, a N-doping concentration of $x_{\text{N}}/x_{\text{Lu}} = 1/3$ can lower T_{dehyd} by near 600 K, although

the maximum H capacity also simultaneously decreases. At $P_{\text{H}_2} = 1$ GPa and $P_{\text{H}_2} = 2$ GPa, no transition to a H-poor phase is observed up to 1473 K within the studied temperature range.

The remarkable effects of the N-doping level on the PCT isotherms and T_{dehyd} imply an anion-doping strategy to optimize thermodynamic behaviors of metal hydrides. A major problem for some of the highest capacity hydrogen-storage alloys, such as Mg-based alloys [61] or refractory metal-based high entropy alloys [62,63], is their high T_{dehyd} . Doping is well known to destabilize metal hydrides [64], but previous efforts mainly focused on cation-doping, which may be subjected to some limitations like cost of the dopants and weight increase. If this strategy can be generalized to those materials systems, i.e., a moderate anion doping can significantly lower T_{dehyd} with a small trade-off in maximum H capacity, superior hydrogen-storage alloys can be made. We note that the complex hydrides also feature incorporation of N or B, but in a much larger amount. One disadvantage of complex hydrides is the great difficulties in reversing the hydrogen release reaction, while the anion-doping strategy may circumvent such drawback. Although one possible hurdle for applying the new strategy may be synthesizing a hydrogen-storage alloy and hydride with supersaturated N solutes without N-rich secondary phases, some experimental studies have reported successful high-pressure synthesis of Lu hydrides with significant N doping [18,19]. Experimental explorations are desirable for verifying the anion-doping strategy, which may lead to hydrogen-storage alloys with superior performance.

III. CONCLUSIONS

In conclusion, we developed an *ab initio* thermodynamic approach by combining Monte Carlo simulation and GNN models trained on first-principles data. This

approach can be used to predict pressure-dependent thermodynamics and phase equilibria of multicomponent solid solutions, as exemplified by the cubic Lu-H-N phases. An integral expression is formulated to calculate pressure-dependent Gibbs energies from enthalpies, which can be obtained from MC simulations. The MC simulations use surrogate models based on a GNN (instead of the conventional CE approach), which, respectively, achieve approximately 20–40 meV/atom and approximately 0.1–0.4 Å³/atom MAE's in cross-validated relaxed formation energy and volume per atom test set predictions using the idealized FCC lattice structure as input. In the future, we anticipate building separate datasets and models for the same target quantities in different lattice types (e.g., BCC, HCP, etc.), in order to predict phase equilibria beyond composition, temperature, and pressure, i.e., account for the possible decomposition and phase-coexistence between multiple lattice types.

Based on the calculated Gibbs energies, phase equilibria of cubic Lu-H-N phases are predicted under different pressures and temperatures. Under full thermodynamic equilibrium, N solubility in LuH_{3-x}N_y is quite small, which leads to a hypothesis that the experimentally reported N-doped Lu hydride samples are likely to be nonequilibrium phases with supersaturated N solutes or contain secondary N-rich phases. Considering the large difference between interstitial H and N mobilities, paraequilibrium of cubic Lu(H,N,Va)₃ at fixed N-doping levels are calculated, showing good agreement with experimental data. N-doping levels can significantly modify thermodynamic properties, such as the dehydrogenation temperature, indicating a potential anion-doping strategy to optimize performance of hydrogen-storage alloys.

We expect this work to provide a general approach to model thermodynamics of multicomponent solid solutions efficiently, which will be especially useful for compositionally complex materials such as high-entropy alloys, high-entropy ceramics, and mixed-anion compounds. It also offers a first-principles method that can be integrated into semiempirical frameworks of thermodynamic modeling like CALPHAD (CALculation of PHase Diagrams) [49,65–67] and its deep learning counterpart [68]. The approach can be further extended to systems with lower dimension like surfaces, with applications in high-entropy catalysts [69,70]. The approach can be also further improved by introducing other machine learning techniques such as active learning [71,72] for acquiring the data needed to more efficiently train the GNN model. Additionally, at the cost of requiring much larger amounts of training data than we acquired in this study, machine learning interatomic potentials [73] and more recently developed equivariant models [51] could potentially serve as a DFT forces surrogate model to explicitly relax each lattice structure sampled within the Monte

Carlo simulations, rather than relying on our prediction of relaxed formation energy from an unrelaxed representation.

IV. METHODOLOGY

A. First-principles calculations

All DFT calculations were done with the Perdew-Burke-Ernzerhof (PBE) [74] exchange correlation functional using the Quantum Espresso software [75]. The employed pseudopotentials of the PAW (projector augmented wave) type [76] were taken from the PSLibrary (version 1.0.0) [77]. The 5s, 6s, 5p, 6p, and 5d electrons of Lu atoms, 1s electrons of H atoms, and 2s and 2p electrons of N atoms were treated as valence electrons. The kinetic-energy cutoff for the plane-wave basis of electronic wave functions and the charge density cutoff were chosen as 42 and 333 Ry, respectively. A 4 × 4 × 4 mesh of Monkhorst-Pack *k* points [78] was adopted for sampling the Brillouin zone. For each structure, the geometry was relaxed to satisfy the convergence criterion that all components of all forces are smaller than 0.001 Ry/Bohr and the total energy changes less than 0.0001 Ry. For the solid phases, the Gibbs energies include 0 K total energies and contributions from pressure, while the finite-temperature vibrational contributions are not explicitly calculated. For each pressure, a Vinet EOS was fitted to find the equilibrium volume that minimizes the Gibbs energy, and the corresponding Gibbs energy was also determined simultaneously.

B. Graph neural network models

We train a GNN, parameterized by model weights, θ , to predict DFT-computed Vinet EOS parameters, $\mathcal{P}$, for a given solid solution configuration from its ideal (unrelaxed) FCC crystal structure representation, $\mathbf{X}_{\text{FCC}}$,

$$\{\mathcal{P}\} = f_{\text{GNN}}(\mathbf{X}_{\text{FCC}}; \theta). \quad (8)$$

Any input structure therefore has identical lattice vectors and metal and interstitial site coordinates, while the only difference between them is the population or absence of N or H at the possible octahedral or tetrahedral interstitial sites. Here, the fitted parameters we wish to predict are $\mathcal{P} = \{E_0, V_0, B, B'\}$, which correspond to the energy at zero pressure, the volume at zero pressure, the equilibrium bulk modulus, and its pressure derivative. To aid in model training we convert E_0 to the formation energy at zero pressure, $E_{f,0}$ and convert V_0 to the volume per atom at zero pressure v_0 .

While a plethora of increasingly complex and accurate GNN methodologies [31–33] have been proposed for materials science applications in recent years, we utilize here the crystal graph convolutional neural-network (CGCNN) formalism [31] since it facilitates training in low data regimes (approximately 10³ or less training examples)

by maintaining sufficiently expressive models with low parameter complexity. The method is resummarized here with the minor modifications made for the GNNs trained in this work.

- (1) The idealized crystal structure $\mathbf{X}_{\text{FCC}}$ is constructed as a graph with nodes corresponding to atoms and edges representing connections between neighboring atoms with distance less than a cutoff radius, $r_c = 4.5 \text{ \AA}$. Lattice vectors for $\mathbf{X}_{\text{FCC}}$ are set such that the distance between nearest-neighbor Lu atoms is $3.53 \text{ \AA}$ (i.e., a_0 of the FCC lattice is $3.53 \text{ \AA}$).
- (2) The initial node feature vector of atomic site i , $\mathbf{v}_i^{(t=0)}$, is generated by one-hot encoding its atomic number. Initial edge features between neighbors i and j , $\mathbf{b}_{ij}$, are encoded by two-body symmetry functions [73] of the bond distance according to a set of Gaussian widths (η), centers (R_s), r_c , and a cutoff function, f_c :

$$\mathbf{b}_{ij} = \{\exp[-\eta(r_{ij} - R_s)^2]f_c(r_{ij})\}. \quad (9)$$

Here we use $\eta = \{0.5, 1.0, 1.5\}$, $R_s = \{1.0, 2.0, 3.0, 4.0, 5.0\}$, and

$$f_c(r_{ij}) = \begin{cases} \left(\cos\left(\frac{\pi r_{ij}}{r_c}\right) + 1\right)/2, & \text{for } r_{ij} \leq r_c, \\ 0, & \text{for } r_{ij} > r_c. \end{cases} \quad (10)$$

- (3) At each convolution layer, t , node feature vectors are updated according to the following filter:

$$\mathbf{v}_i^{(t+1)} = g\left(\mathbf{v}_i^{(t)} + \sum_j \sigma\left(\mathbf{z}_{ij}^{(t)} \mathbf{W}_1^{(t)} + \mathbf{b}_1^{(t)}\right) \odot g\left(\mathbf{z}_{ij}^{(t)} \mathbf{W}_2^{(t)} + \mathbf{b}_2^{(t)}\right)\right). \quad (11)$$

Here $\mathbf{z}_{ij} = \mathbf{v}_i \oplus \mathbf{v}_j \oplus \mathbf{b}_{ij}$ is the concatenation of features between connected nodes in the graph, $\mathbf{W}_1, \mathbf{W}_2$ and b_1, b_2 represent weights and biases of different learnable weight matrices (i.e., fully connected neural network layers), σ denotes a sigmoid activation function, g denotes a softplus activation, and $\odot$ denotes element-wise multiplication.

- (4) Following t' convolution layers, node feature vectors for all N atoms in the crystal are pooled to compute a global crystal feature vector, $\mathbf{v}_c = \text{Pool}(\mathbf{v}_0^{(t')}, \mathbf{v}_1^{(t')}, \dots, \mathbf{v}_N^{(t')})$.
- (5) Finally, n_h fully connected hidden layers are utilized to predict target properties, $\{\mathcal{P}\}$.

All GNN models were constructed and trained with the architecture and hyperparameters in Table I. Note that

TABLE I. Architecture and training hyperparameters used for all models in this study.

Hyperparameter	Value
Node feature vector dimensionality	$\mathbf{v}_i^{(t)} \in \mathbb{R}^8$
Number of convolution steps	$t' = 3$
Crystal feature vector dimensionality	$\mathbf{v}_c \in \mathbb{R}^8$
Number of feed forward layers postconvolutions	$n_h = 2$
Training epochs	1000
Learning rate	0.05
Optimizer	Adam

the selection of $t' = 3$ allows for site interactions [e.g., Eq. (11)] beyond r_c .

C. Monte Carlo simulations

The isothermal-isobaric (NPT) Monte Carlo method was employed to simulate the $\text{Lu}(\text{H}, \text{N}, \text{Va})_3$ solid solution, where the number of each species, pressure and temperature are constant in each simulation. In each MC move, a new configuration is proposed by swapping the positions of a randomly chosen pair of species and changing the volume with all the positions of species rescaled. The Metropolis acceptance probability for the move is given by Ref. [79]:

$$P_{\text{acc}} = \min(1, e^{-\beta \Delta \tilde{H}}), \quad (12)$$

with

$$\Delta \tilde{H} = E(\mathbf{r}') - E(\mathbf{r}) + P(V' - V) - \beta^{-1} N \ln \frac{V'}{V}, \quad (13)$$

where $\mathbf{r}$, N is the number of atoms, V and $E(\mathbf{r})$ are species coordinates, volume and energy of the old configuration, and $\mathbf{r}'$, V' and $E(\mathbf{r}')$ are the corresponding variables of the new configuration. For simplicity, the volume fluctuation around the equilibrium value for each configuration at a given pressure is neglected, and only the equilibrium volume V_0 and energy E_0 are sampled, which can be readily obtained from the present lattice GNN model.

The MC simulations were implemented based on the ASAP code (<https://gitlab.com/asap/asap>), at a series of temperatures $5000/i \text{ K}$ ($i = 1, 2, 3, \dots$) and at three pressures 0, 1 and 2 GPa. A supercell containing $3 \times 3 \times 3$ FCC conventional unit cells was used for simulations, which has 108 Lu atoms, 108 octahedral interstitial sites, and 216 tetrahedral interstitial sites. To sample the composition triangle of $\text{Lu}(\text{H}, \text{N}, \text{Va})_3$, the sampling step along the site fraction of each species (H, N, or Va) is $1/18$, which leads to 190 sampled compositions in total. The average energy in each MC simulation is converged to 0.001 eV. The enthalpy of the solid solution phase can then be calculated from the ensemble average using Eq. (3), which can be used to calculate Gibbs energy based on Eq. (5).

ACKNOWLEDGMENTS

The authors gratefully acknowledge research support from the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration (DOE/NNSA) under Contract No. DE-NA0003525. This written work is authored by an employee of NTESS. The employee, not NTESS, owns the right, title, and interest in and to the written work and is responsible for its contents. Any subjective views or opinions that might be expressed in the written work do not necessarily represent the views of the U.S. Government. The publisher acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this written work or allow others to do so, for U.S. Government purposes. The DOE will provide public access to results of federally sponsored research in accordance with the DOE Public Access Plan. We also acknowledge Dr Roman Lucrezi and Dr Christoph Heil at Graz University of Technology, and Adam Denchfield and Dr Russell J. Hemley at University of Illinois Chicago for their discussions.

DATA AVAILABILITY

The data that support the findings of this article are openly available [80].

- [1] H. Liu, I. I. Naumov, R. Hoffmann, N. W. Ashcroft, and R. J. Hemley, Potential high- T_c superconducting lanthanum and yttrium hydrides at high pressure, *Proc. Natl. Acad. Sci. U.S.A.* **114**, 6990 (2017).
- [2] F. Peng, Y. Sun, C. J. Pickard, R. J. Needs, Q. Wu, and Y. Ma, Hydrogen clathrate structures in rare earth hydrides at high pressures: Possible route to room-temperature superconductivity, *Phys. Rev. Lett.* **119**, 107001 (2017).
- [3] Z. M. Geballe, H. Liu, A. K. Mishra, M. Ahart, M. Somayazulu, Y. Meng, M. Baldini, and R. J. Hemley, Synthesis and stability of lanthanum superhydrides, *Angew. Chem. Int. Ed.* **57**, 688 (2018).
- [4] M. Somayazulu, M. Ahart, A. K. Mishra, Z. M. Geballe, M. Baldini, Y. Meng, V. V. Struzhkin, and R. J. Hemley, Evidence for superconductivity above 260 K in lanthanum superhydride at megabar pressures, *Phys. Rev. Lett.* **122**, 027001 (2019).
- [5] A. P. Drozdov, P. P. Kong, V. S. Minkov, S. P. Besedin, M. A. Kuzovnikov, S. Mozaffari, L. Balicas, F. F. Balakirev, D. E. Graf, V. B. Prakapenka, E. Greenberg, D. A. Knyazev, M. Tkacz, and M. I. Erements, Superconductivity at 250 K in lanthanum hydride under high pressures, *Nature* **569**, 528 (2019).
- [6] Y. Sun, J. Lv, Y. Xie, H. Liu, and Y. Ma, Route to a superconducting phase above room temperature in electron-doped hydride compounds under high pressure, *Phys. Rev. Lett.* **123**, 097001 (2019).
- [7] J. Lv, Y. Sun, H. Liu, and Y. Ma, Theory-orientated discovery of high-temperature superconductors in superhydrides stabilized under high pressure, *Matter Radiat. Extremes* **5**, 068101 (2020).
- [8] K. P. Hilleke and E. Zurek, Rational design of superconducting metal hydrides via chemical pressure tuning, *Angew. Chem. Int. Ed.* **61**, e202207589 (2022).
- [9] S. Di Cataldo, C. Heil, W. von der Linden, and L. Boeri, LaBH_8 : Towards high- T_c low-pressure superconductivity in ternary superhydrides, *Phys. Rev. B* **104**, L020511 (2021).
- [10] X. Liang, A. Bergara, X. Wei, X. Song, L. Wang, R. Sun, H. Liu, R. J. Hemley, L. Wang, G. Gao, *et al.*, Prediction of high- T_c superconductivity in ternary lanthanum borohydrides, *Phys. Rev. B* **104**, 134501 (2021).
- [11] R. Lucrezi, S. Di Cataldo, W. von der Linden, L. Boeri, and C. Heil, In-silico synthesis of lowest-pressure high- T_c ternary superhydrides, *npj Comput. Mater.* **8**, 119 (2022).
- [12] S. Di Cataldo and L. Boeri, Metal borohydrides as ambient-pressure high- T_c superconductors, *Phys. Rev. B* **107**, L060501 (2023).
- [13] P.-W. Guan, R. J. Hemley, and V. Viswanathan, Combining pressure and electrochemistry to synthesize superhydrides, *Proc. Natl. Acad. Sci. U.S.A.* **118**, e2110470118 (2021).
- [14] P.-W. Guan, Y. Sun, R. J. Hemley, H. Liu, Y. Ma, and V. Viswanathan, Low-pressure electrochemical synthesis of complex high-pressure superconducting superhydrides, *Phys. Rev. Lett.* **128**, 186001 (2022).
- [15] N. Dasenbrock-Gammon, E. Snider, R. McBride, H. Pasan, D. Durkee, N. Khalvashi-Sutter, S. Munasinghe, S. E. Disanayake, K. V. Lawler, A. Salamat, *et al.*, Retracted article: Evidence of near-ambient superconductivity in a N-doped lutetium hydride, *Nature* **615**, 244 (2023).
- [16] Z. Huo, D. Duan, T. Ma, Z. Zhang, Q. Jiang, D. An, H. Song, F. Tian, and T. Cui, First-principles study on the conventional superconductivity of N-doped fcc- LuH_3 , *Matter Radiat. Extremes* **8**, 038402 (2023).
- [17] Y. Sun, F. Zhang, S. Wu, V. Antropov, and K.-M. Ho, Effect of nitrogen doping and pressure on the stability of LuH_3 , *Phys. Rev. B* **108**, L020101 (2023).
- [18] X. Ming, Y.-J. Zhang, X. Zhu, Q. Li, C. He, Y. Liu, T. Huang, G. Liu, B. Zheng, H. Yang, *et al.*, Absence of near-ambient superconductivity in $\text{LuH}_{2\pm x}\text{N}_y$, *Nature* **620**, 72 (2023).
- [19] X. Xing, C. Wang, L. Yu, J. Xu, C. Zhang, M. Zhang, S. Huang, X. Zhang, Y. Liu, B. Yang, *et al.*, Observation of non-superconducting phase changes in nitrogen doped lutetium hydrides, *Nat. Commun.* **14**, 5991 (2023).
- [20] K. P. Hilleke, X. Wang, D. Luo, N. Geng, B. Wang, F. Belli, and E. Zurek, Structure, stability, and superconductivity of N-doped lutetium hydrides at kbar pressures, *Phys. Rev. B* **108**, 014511 (2023).
- [21] P. P. Ferreira, L. J. Conway, A. Cucciari, S. Di Cataldo, F. Giannessi, E. Kogler, L. T. Eleno, C. J. Pickard, C. Heil, and L. Boeri, Search for ambient superconductivity in the Lu-N-H system, *Nat. Commun.* **14**, 5367 (2023).

- [22] F. Xie, T. Lu, Z. Yu, Y. Wang, Z. Wang, S. Meng, and M. Liu, Lu–H–N phase diagram from first-principles calculations, *Chin. Phys. Lett.* **40**, 057401 (2023).
- [23] R. Lucrezi, P. P. Ferreira, M. Aichhorn, and C. Heil, Temperature and quantum anharmonic lattice effects on stability and superconductivity in lutetium trihydride, *Nat. Commun.* **15**, 441 (2024).
- [24] A. Denchfield, H. Park, and R. J. Hemley, Electronic structure of nitrogen-doped lutetium hydrides, *Phys. Rev. Mater.* **8**, L021801 (2024).
- [25] Y. Han, Y. Ou, H. Sun, J. Kopaczek, G. J. Leonel, X. Guo, B. L. Brugman, K. Leinenweber, H. Xu, M. Wang, *et al.*, Thermodynamic properties and enhancement of diamagnetism in nitrogen doped lutetium hydride synthesized at high pressure, *Proc. Natl. Acad. Sci.* **121**, e2321540121 (2024).
- [26] R. G. Mullen and N. Goldman, Quantum accurate prediction of plutonium–plutonium dihydride phase equilibrium using a lattice gas model, *J. Phys. Chem. C* **124**, 20881 (2020).
- [27] G. Zepón, B. H. Silva, C. Zlotea, W. J. Botta, and Y. Champion, Thermodynamic modelling of hydrogen-multicomponent alloy systems: Calculating pressure-composition-temperature diagrams, *Acta Mater.* **215**, 117070 (2021).
- [28] J. B. Ponsoni, V. Aranda, T. da Silva Nascimento, R. B. Strozi, W. J. Botta, and G. Zepón, Design of multicomponent alloys with C14 laves phase structure for hydrogen storage assisted by computational thermodynamic, *Acta Mater.* **240**, 118317 (2022).
- [29] M. D. Witman, N. C. Bartelt, S. Ling, P.-W. Guan, L. Way, M. D. Allendorf, and V. Stavila, Phase diagrams of alloys and their hydrides via on-lattice graph neural networks and limited training data, *J. Phys. Chem. Lett.* **15**, 1500 (2024).
- [30] E. Weinan, Machine learning and computational mathematics, [arXiv:2009.14596](https://arxiv.org/abs/2009.14596).
- [31] T. Xie and J. C. Grossman, Crystal graph convolutional neural networks for an accurate and interpretable prediction of material properties, *Phys. Rev. Lett.* **120**, 145301 (2018).
- [32] K. Choudhary and B. DeCost, Atomistic line graph neural network for improved materials property predictions, *npj Comput. Mater.* **7**, 185 (2021).
- [33] O. T. Unke, S. Chmiela, M. Gastegger, K. T. Schütt, H. E. Sauceda, and K.-R. Müller, Spookynet: Learning force fields with electronic degrees of freedom and nonlocal effects, *Nat. Commun.* **12**, 7273 (2021).
- [34] J. Gibson, A. Hire, and R. G. Hennig, Data-augmentation for graph neural network learning of the relaxed energies of unrelaxed structures, *npj Comput. Mater.* **8**, 211 (2022).
- [35] M. D. Witman, A. Goyal, T. Ogitsu, A. H. McDaniel, and S. Lany, Defect graph neural networks for materials discovery in high-temperature clean-energy applications, *Nat. Comput. Sci.* **3**, 675 (2023).
- [36] J. M. Sanchez, F. Ducastelle, and D. Gratias, Generalized cluster description of multicomponent systems, *Physica A* **128**, 334 (1984).
- [37] P. Vinet, J. Ferrante, J. H. Rose, and J. R. Smith, Compressibility of solids, *J. Geophys. Res. Solid Earth* **92**, 9319 (1987).
- [38] C. Wolverton and D. de Fontaine, Cluster expansions of alloy energetics in ternary intermetallics, *Phys. Rev. B* **49**, 8627 (1994).
- [39] C. D. Spataru, M. D. Witman, and R. E. Jones, Tuning the critical Li intercalation concentrations for MoX₂ (X = S, Se, or Te) bilayer phase transitions, *Phys. Rev. Mater.* **5**, 084005 (2021).
- [40] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/bsxd-qtpb> for the crystal structure of cubic LuH₃; validity of a linear approximation for pressure-dependent enthalpy of individual configuration; graph neural-network comparison with cluster expansion; temperature-dependent site fractions of H and N in the nearest-neighbor interstitial sites of Lu under different pressures and compositions; fugacity coefficient of H₂; approximate consideration for the vibrational contributions; histogram of enthalpies of sampled configurations; Gibbs energy as a function of H composition for cubic Lu–H solid solutions for pressures of 0, 1 and 2 GPa and temperatures of 273, 573, 873, 1173 and 1473 K; and temperature-dependent Gibbs energies of cubic Lu–H–N solid solutions in N-poor regime at 0, 1 and 2 GPa.
- [41] M. Asta, C. Wolverton, D. De Fontaine, and H. Dreyssé, Effective cluster interactions from cluster-variation formalism. I, *Phys. Rev. B* **44**, 4907 (1991).
- [42] H. Y. Geng, M. H. F. Sluiter, and N. X. Chen, Cluster expansion of electronic excitations: Application to fcc Ni–Al alloys, *J. Chem. Phys.* **122**, 214706 (2005).
- [43] R. Feng, P. K. Liaw, M. C. Gao, and M. Widom, First-principles prediction of high-entropy-alloy stability, *npj Comput. Mater.* **3**, 50 (2017).
- [44] T. Rehman, M. Jaipal, and A. Chatterjee, A cluster expansion model for predicting activation barrier of atomic processes, *J. Comput. Phys.* **243**, 244 (2013).
- [45] P. Das, K. Thekkepat, Y.-S. Lee, S.-C. Lee, and S. Bhattacharjee, Computational design of novel MAX phase alloys as potential hydrogen storage media combining first principles and cluster expansion methods, *Phys. Chem. Chem. Phys.* **25**, 5203 (2023).
- [46] Z. Lun, B. Ouyang, D.-H. Kwon, Y. Ha, E. E. Foley, T.-Y. Huang, Z. Cai, H. Kim, M. Balasubramanian, Y. Sun, J. Huang, Y. Tian, H. Kim, B. D. McCloskey, W. Yang, R. J. Clément, H. Ji, and G. Ceder, Cation-disordered rocksalt-type high-entropy cathodes for Li-ion batteries, *Nat. Mater.* **20**, 214 (2021).
- [47] J.-M. Joubert, A calphad-type equation of state for hydrogen gas and its application to the assessment of Rh–H system, *Int. J. Hydrogen Energy* **35**, 2104 (2010).
- [48] P. Subramanian and J. Smith, Hydrogen vapor pressure measurements over a portion of the Lu–H system, *J. Less Common Met.* **87**, 205 (1982).
- [49] H. Lukas, S. G. Fries, and B. Sundman, *Computational Thermodynamics: the Calphad Method* (Cambridge University Press, Cambridge, England, 2007).
- [50] J. P. Darby, D. P. Kovács, I. Batatia, M. A. Caro, G. L. W. Hart, C. Ortner, and G. Csányi, Tensor-reduced atomic density representations, *Phys. Rev. Lett.* **131**, 028001 (2023).
- [51] I. Batatia *et al.*, A foundation model for atomistic materials chemistry, [arXiv:2401.00096](https://arxiv.org/abs/2401.00096).

- [52] J.-H. Pöhls, M. Heyberger, and A. Mar, Comparison of computational and experimental inorganic crystal structures, *J. Solid State Chem.* **290**, 121557 (2020).
- [53] S. Kirklin, J. E. Saal, B. Meredig, A. Thompson, J. W. Doak, M. Aykol, S. Rühl, and C. Wolverton, The open quantum materials database (OQMD): Assessing the accuracy of DFT formation energies, *npj Comput. Mater.* **1**, 15010 EP (2015).
- [54] M. Wen, M. K. Horton, J. M. Munro, P. Huck, and K. A. Persson, An equivariant graph neural network for the elasticity tensors of all seven crystal systems, *Digit. Discov.* **3**, 869 (2024).
- [55] S. Cai, J. Guo, H. Shu, L. Yang, P. Wang, Y. Zhou, J. Zhao, J. Han, Q. Wu, W. Yang, *et al.*, No evidence of superconductivity in a compressed sample prepared from lutetium foil and H_2/N_2 gas mixture, *Matter Radiat. Extremes* **8**, 048001 (2023).
- [56] X. Li, Y. Wang, Y. Fu, S. A. Redfern, S. Jiang, P. Zhu, and T. Cui, Stabilization of high-pressure phase of face-centered cubic lutetium trihydride at ambient conditions, *Adv. Sci.* **11**, 2401642 (2024).
- [57] A. Denchfield, F. Belli, E. Zurek, H. Park, and R. J. Hemley, Quantum stabilization and flat hydrogen-based bands of nitrogen-doped lutetium hydride, *Phys. Rev. B* **110**, 174110 (2024).
- [58] M. Hillert, *Phase Equilibria, Phase Diagrams and Phase Transformations: Their Thermodynamic Basis* (Cambridge University Press, Cambridge, England, 2007).
- [59] E. Alvares, P. Jerabek, Y. Shang, A. Santhosh, C. Pistidda, T. W. Heo, B. Sundman, and M. Dornheim, Modeling the thermodynamics of the FeTi hydrogenation under para-equilibrium: An ab-initio and experimental study, *Calphad* **77**, 102426 (2022).
- [60] J. Völkl and G. Alefeld, in *Hydrogen in Metals I: Basic Properties* (Springer Berlin, Heidelberg, 2005).
- [61] L. Pasquini *et al.*, Magnesium- and intermetallic alloys-based hydrides for energy storage: Modelling, synthesis and properties, *Prog. Energy* **4**, 032007 (2022).
- [62] M. Sahlberg, D. Karlsson, C. Zlotea, and U. Jansson, Superior hydrogen storage in high entropy alloys, *Sci. Rep.* **6**, 36770 (2016).
- [63] M. D. Witman, S. Ling, M. Wadge, A. Bouzidi, N. Pineda-Romero, R. Clulow, G. Ek, J. M. Chames, E. J. Allendorf, S. Agarwal, M. D. Allendorf, G. S. Walker, D. M. Grant, M. Sahlberg, C. Zlotea, and V. Stavila, Towards Pareto optimal high entropy hydrides via data-driven materials discovery, *J. Mater. Chem. A* **11**, 15878 (2023).
- [64] M. D. Allendorf, V. Stavila, J. L. Snider, M. Witman, M. E. Bowden, K. Brooks, B. L. Tran, and T. Autrey, Challenges to developing materials for the transport and storage of hydrogen, *Nat. Chem.* **14**, 1214 (2022).
- [65] Z.-K. Liu, First-principles calculations and calphad modeling of thermodynamics, *J. Phase Equilib. Diffus.* **30**, 517 (2009).
- [66] M. Palumbo, E. Dematteis, L. Fenocchio, G. Cacciamani, and M. Baricco, Advances in calphad methodology for modeling hydrides: A comprehensive review, *J. Phase Equilib. Diffus.* **45**, 273 (2024).
- [67] W. Yi, J. Gao, and L. Zhang, A CALPHAD thermodynamic model for multicomponent alloys under pressure and its application in pressurized solidified Al–Si–Mg alloys, *Adv. Powder Mater.* **3**, 100182 (2024).
- [68] P.-W. Guan, Differentiable thermodynamic modeling, *Scr. Mater.* **207**, 114217 (2022).
- [69] T. A. Batchelor, J. K. Pedersen, S. H. Winther, I. E. Castelli, K. W. Jacobsen, and J. Rossmeisl, High-entropy alloys as a discovery platform for electrocatalysis, *Joule* **3**, 834 (2019).
- [70] Y. Sun and S. Dai, High-entropy materials for catalysis: A new frontier, *Sci. Adv.* **7**, eabg1600 (2021).
- [71] T. Lookman, P. V. Balachandran, D. Xue, and R. Yuan, Active learning in materials science with emphasis on adaptive sampling using uncertainties for targeted design, *npj Comput. Mater.* **5**, 21 (2019).
- [72] K. Gubaev, E. V. Podryabinkin, G. L. Hart, and A. V. Shapeev, Accelerating high-throughput searches for new alloys with active learning of interatomic potentials, *Comput. Mater. Sci.* **156**, 148 (2019).
- [73] J. Behler and M. Parrinello, Generalized neural-network representation of high-dimensional potential-energy surfaces, *Phys. Rev. Lett.* **98**, 1 (2007).
- [74] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [75] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, *et al.*, Quantum espresso: a modular and open-source software project for quantum simulations of materials, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- [76] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* **50**, 17953 (1994).
- [77] A. Dal Corso, Pseudopotentials periodic table: From h to pu, *Comput. Mater. Sci.* **95**, 337 (2014).
- [78] H. J. Monkhorst and J. D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B* **13**, 5188 (1976).
- [79] M. E. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (Oxford University Press, Oxford, England, 2023).
- [80] P.-W. Guan, C. Spataru, V. Stavila, R. Jones, P. Sharma, and M. Witman, “Thermodynamic modeling of complex solid solutions in the Lu–H–N system via graph neural network accelerated Monte Carlo simulations, ChemRxiv” (2024).