# Evolutionary search for superconducting phases in the lanthanum-nitrogen-hydrogen system with universal neural network potential

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Recently, Grockowiak *et al.* reported "hot superconductivity" in ternary or multinary compounds based on lanthanum hydride [A. D. Grockowiak *et al.*, Front. Electron. Mater. **2**, 837651 (2022)]. In this paper, we explored thermodynamically stable phases and superconducting phases in the lanthanum-nitrogen-hydrogen system (La<sub>x</sub>N<sub>y</sub>H<sub>1-x-y</sub>,  $0 \le x \le 1$ ,  $0 \le y \le 1$ ) at a pressure of 20 GPa. We rapidly and accurately constructed the formation-enthalpy convex hull using an evolutionary construction scheme based on density functional theory calculations, extracting the candidates for stable and moderately metastable compounds by the universal neural network potential calculations. The convex hull diagram shows that more than 50 compounds emerge as stable and moderately metastable phases in the region of  $\Delta H \le 4.4$  mRy/atom. In particular, the compounds are concentrated on the line of x = 0.5 connecting between LaH and LaN. We found that the superconductivity is gradually enhanced due to N doping for LaH and the superconducting critical temperature  $T_c$  reaches 8.77 K in La<sub>2</sub>NH with y = 0.25. In addition, we predicted that metastable La<sub>2</sub>NH<sub>2</sub> shows the highest  $T_c$  value, 14.41 K, of all the ternary compounds predicted in this study. These results suggest that it is difficult to obtain the hot superconductivity in the La-H compounds with N at 20 GPa.

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### I. INTRODUCTION

Metallic hydrides have attracted much attention as potential candidates for room-temperature superconductors [1,2]. In 2015, Drozdov et al. performed electric resistivity measurements on hydrogen sulfide in diamond anvil cells to verify high-temperature superconductivity predicted in sulfur hydrides under high pressure [3,4] and observed the superconductivity at 203 K at a pressure of 155 GPa [5]. This discovery has led to further experimental and theoretical studies on stoichiometry, crystal structure, and superconductivity in sulfur hydrides under high pressure [6-11], and x-ray diffraction measurements have clarified that sulfur hydride takes cubic  $H_3S$  in the high-temperature superconducting phase [12]. In 2018 and 2019, Somayazulu et al. and Drozdov et al. observed that lanthanum hydride (LaH<sub>10</sub>) shows the superconductivity at 250–260 K in the pressure region of 170–190 GPa [13,14], which exceeds the superconducting critical temperature  $(T_c)$ in H<sub>3</sub>S and is close to room temperature. In addition to these hydrides, first-principles calculations have predicted the superconductivity in binary hydrides under high pressure with respect to more than 60 elements [15], in which YH<sub>10</sub> [16],  $MgH_6$  [17],  $CaH_{12}$  [18], and  $AcH_{10}$  [19] are predicted to show T<sub>c</sub> values over 200 K.

As the next stage of the exploration, recently, ternary hydrides have been gathering attention as the candidate for higher  $T_c$  superconductivity. In 2019, Sun *et al.* predicted from first-principles calculations that Li<sub>2</sub>MgH<sub>16</sub> shows a  $T_c$  of 475 K at 250 GPa [20]. In 2020, Sun et al. and Cui et al. predicted that the insertion of CH<sub>4</sub> into H<sub>3</sub>S causes the dynamical stabilization of the high- $T_c$  phase at lower pressures and CSH<sub>7</sub> shows  $T_c$  values of 100–190 K in a pressure range of 100-200 GPa [21,22]. Inspired by these theoretical results, experimentalists have explored novel ternary or multinary hydrides showing higher  $T_c$  at lower pressures. In 2020, Snider et al. observed that carbonaceous sulfur hydride, i.e., the C-S-H system, shows a room-temperature superconductivity of  $T_c = 288$  K at 267 GPa [23]. However, in 2022, the article was retracted owing to a lot of questions about the data and results [24,25]. In 2022, Grockowiak et al. reported "hot superconductivity" in ternary or multinary compounds based on lanthanum hydride [26]. The authors claim that  $T_c$  is increased to 556 K by subsequent thermal excursion to high temperatures, which might be induced by the reaction of La-H with other materials existing in the sample chamber of the diamond anvil cell (DAC). In 2023, Dasenbrock-Gammon et al. observed a room-temperature superconductivity near ambient pressure, i.e.,  $T_c = 294$  K at 1 GPa, in nitrogen-doped lutetium hydride (Lu-N-H) [27], whereas the room-temperature superconductivity has not been reproduced by first-principles calculations [28] and other experiments [29]. Finally, the article was retracted at the request of the coauthors eight months later [30].

In the experiments shown in Ref. [27], ammonia borane,  $NH_3BH_3$ , was used as a hydrogen source material for the synthesis of La-H. We assumed that La-H is reacted with N included in the sample chamber of DAC and searched for thermodynamically stable and metastable phases and superconducting phases in the La-N-H ternary system using

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first-principles calculations and our originally developed algorithm for stable composition search, which is based on an evolutionary construction of a formation-enthalpy convex hull combined with the universal neural network potential. Stable and superconducting phases of this ternary system in a high-pressure region above 100 GPa have already been explored using first-principles calculations and structure search algorithms [31,32]. However, the hot superconductivity has not been obtained in the calculations, and further validation at not only high but also low pressures is required to confirm the hot superconductivity. Experimental synthesis of ternary hydrides strongly depends on pressure and temperature path for it even if they are predicted to be thermodynamically stable, and it is particularly difficult to control the synthesis under high-pressure conditions above 100 GPa. Thus, in this study, we focus on the La-N-H system at a low pressure of 20 GPa. The pressure value of 20 GPa is easily generated by a multianvil apparatus which has widely been used in the field of materials science. Since the multianvil apparatus can accommodate much larger samples than DAC, synthesis of hydrides, x-ray diffraction measurements, superconductivity measurements (zero resistance and the Meissner effect), and data analysis are much easier than those in DAC. In other words, calculated results can immediately be validated by many experimental groups.

## **II. COMPUTATIONAL DETAILS**

The experimental findings of the metallic hydrides with high  $T_{\rm c}$  have all been motivated by theoretical crystal structure predictions [33–36]. Since the search for thermodynamically stable phases in ternary systems is computationally expensive, we combined an evolutionary construction scheme (ECS) of a formation-enthalpy convex hull [37] with an atomic simulator using the universal neural network potential, MATLANTIS [38]. In the ECS, compositions and structures with high probability of being stable are created by random applications of "mating," "mutation," and "adaptive mutation" to the compounds whose enthalpy difference  $(\Delta H)$  to the convex hull is small (see Figs. 2 and 3 in Ref. [37]). All the created structures are optimized and the convex hull is updated, which is defined as one generation. The stable and moderately metastable compounds are efficiently explored due to a data-driven approach based on the structural information of stable compounds [39], where "moderately metastable" means "small  $\Delta H$ ." In MATLANTIS, the potentials for more than 70 elements are being created using 10<sup>7</sup> training data obtained by the density functional theory (DFT) calculations and a graph neural network and can universally be applied to a wide variety of systems including high-pressure conditions. The universal neural network potential is called the "preferred potential (PFP)" [40]. Figure 1 shows the flowchart of our algorithm. At each generation, a few thousand structures created by the ECS are optimized using the PFP and the convex hull is updated within MATLANTIS. Thanks to the PFP, the optimization is rapidly and accurately accomplished with small calculation resources. The calculation speed and accuracy of MATLANTIS is compared with those of DFT in Table S1 and Figs. S1 and S2 in the Supplemental Material (SM) [41]. Then, the candidates for thermodynamically stable and



FIG. 1. Flowchart of the evolutionary construction scheme (ECS) of a formation-energy convex hull (FECH) combined with density functional theory (DFT) calculations and the universal neural network potential (preferred potential, PFP) calculations. The PFP calculation is implemented in an atomic simulator, MATLANTIS.  $N_{\rm str}$  represents the number of crystal structures.

moderately metastable compounds are extracted based on  $\Delta H$  for the convex hull diagram, where the number of structures is significantly decreased to a few tens. Then, only the extracted structures are optimized using the DFT calculations and the convex hull is updated.

In our search, we used the QUANTUM ESPRESSO (QE) code [42] for the DFT part. According to a large-scale datamining study of the Materials Project in Ref. [43], metastable materials with  $\Delta H < 70 \text{ meV/atom} = 5.15 \text{ mRy/atom}$  predicted by DFT calculations are promising candidates to be synthesized by experimental techniques. Hence, we set the upper limit of  $\Delta H$  in the ECS at 4.4 mRy/atom for QE. We used the generalized gradient approximation by Perdew, Burke, and Ernzerhof [44] for the exchange-correlation functional, and we used the Rabe-Rappe-Kaxiras-Joannopoulos ultrasoft pseudopotential [45]. The energy cutoff was set at 80 Ry for the wave function and 640 Ry for the charge density. We adopted Marzari-Vanderbilt cold smearing of width 0.01 Ry [46]. We tested whether the smearing method changes the stability of insulating phases using ordinary Gaussian smearing and Methfessel-Paxton smearing in addition to the Marzari-Vanderbilt smearing. The enthalpy differences among them are much smaller than 0.1 mRy/atom, which suggests that the thermodynamical stability of not only metallic but also insulating structures is accurately predicted by the Marzari-Vanderbilt smearing method only. We increased the number of the k-point samplings in the Brillouin zone for the optimization until the formation enthalpy was sufficiently converged. We used v.3.0.0 for the version of the PFP and the L-BFGS algorithm [47] for the optimization. Preparing for unexpected errors of the PFP, we used  $\Delta H \leq 11$ mRy/atom as a condition for the candidate extraction by

MATLANTIS, which is approximately twice as large as the tolerance mentioned above. We performed the constant-pressure variable-cell optimization at 20 GPa for the created structures.

The superconducting  $T_c$  was calculated using the Allen-Dynes-modified McMillan formula [48],

$$T_{\rm c} = \frac{f_1 f_2 \omega_{\rm log}}{1.2} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right].$$
 (1)

The parameters  $\lambda$  and  $\omega_{\log}$  are electron-phonon coupling constant and logarithmic-averaged phonon frequency, respectively, which represent a set of characters for the phonon-mediated superconductivity.  $f_1$  and  $f_2$  are correlation factors for the systems showing large  $\lambda$ . These parameters are defined as follows, using Eliashberg function  $\alpha^2 F(\omega)$ :

$$\lambda = 2 \int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega},\tag{2}$$

$$\omega_{\log} = \exp\left[\frac{2}{\lambda} \int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega} \log \omega\right],\tag{3}$$

$$f_1 = \left\{ 1 + \left[ \frac{\lambda}{2.46(1+3.8\mu^*)} \right]^{3/2} \right\}^{1/3}, \tag{4}$$

$$f_2 = 1 + \frac{(\omega_2/\omega_{\log} - 1)\lambda^2}{\lambda^2 + [1.82(1 + 6.3\mu^*)(\omega_2/\omega_{\log})]^2},$$
 (5)

where

$$\omega_2 = \left[\frac{2}{\lambda} \int_0^\infty d\omega \alpha^2 F(\omega)\omega\right]^{1/2}.$$
 (6)

To obtain these parameters, we performed the phonon calculations implemented in the QE code. The effective screened Coulomb repulsion constant  $\mu^*$  was assumed to be 0.10, which has been considered to be a reasonable value for hydrides. The *k*- and *q*-point grids for the calculations are listed in Table S2 in the SM [41].

## **III. RESULTS**

Figure 2 shows the convex hull diagram of the formation enthalpy for the La-N-H system (La<sub>x</sub>N<sub>y</sub>H<sub>1-x-y</sub>,  $0 \le x \le 1$ ,  $0 \leq y \leq 1$ ) at the 20th generation obtained by MATLANTIS, at which the convex hull is sufficiently converged. In Fig. 2(a), the convex hull is projected on the xy plane, viewed along the z axis showing the formation enthalpy. The lines and their intersections show the edges and vertices of the convex hull, respectively: the vertices correspond to thermodynamically stable compounds at 20 GPa. The dots other than the intersections are compositions created by the ECS. We obtained 13 thermodynamically stable compounds as follows: LaH<sub>3</sub> and LaH on the La-H line; NH<sub>4</sub> and N<sub>7</sub>H<sub>3</sub> on the N-H line; LaN<sub>4</sub>, LaN<sub>2</sub>, La<sub>2</sub>N<sub>3</sub>, and LaN on the La-N line; and LaNH<sub>2</sub>, La<sub>2</sub>NH<sub>3</sub>, La<sub>2</sub>N<sub>3</sub>H, La<sub>5</sub>N<sub>4</sub>H, and La<sub>2</sub>NH in the triangle. In Fig. 2(b), the moderately metastable compounds with  $\Delta H$  less than 4.4 mRy/atom are extracted. The compounds are concentrated on the line connecting between LaH and LaN, i.e., the line of x = 0.5; on the line connecting between LaN and  $La_2N_3H$ ; and near the line connecting between  $La_2NH$  and LaH<sub>3</sub>. Figure 3 shows a similar convex hull diagram obtained by the QE optimization after the screening by MATLANTIS. The



FIG. 2. Formation-enthalpy convex hull diagram of the La-N-H system  $(La_xN_yH_{1-x-y})$  at 20 GPa, obtained by MATLANTIS. The convex hull is projected on the *xy* plane, and the vertices (the intersections of the lines) correspond to thermodynamically stable compounds. Panel (a) shows all the compounds investigated in this study and panel (b) shows the moderately metastable compounds with  $\Delta H$  less than 4.4 mRy/atom.

stable and metastable compounds are compared with those obtained by MATLANTIS in Table I. Eight out of 26 compounds were obtained as the stable compounds by both MATLANTIS and QE: LaH<sub>3</sub>, LaH, LaN<sub>4</sub>, LaN<sub>2</sub>, LaN, LaNH<sub>2</sub>, La<sub>2</sub>NH<sub>3</sub>, and La<sub>2</sub>N<sub>3</sub>H. Out of the other 18 compounds, 16 compounds are predicted to be stable by MATLANTIS or QE and moderately metastable ( $\Delta H \leq 4.4 \text{ mRy/atom}$ ) by the other. These results suggest that MATLANTIS has high predictability for thermodynamically stable compounds and is a competent precursor for QE. In contrast, MATLANTIS shows a low predictability for the compounds on the N-H line; NH3 and N7H3 were predicted as quite unstable and stable compounds by MATLANTIS, respectively. See also two data largely deviated from the tendency of the other data in Fig. S2 in SM, which correspond to NH<sub>4</sub> and N<sub>7</sub>H<sub>3</sub> [41]. The inaccuracy of MATLANTIS for the N-H system seems to occur due to insufficient training data of the N-H compounds under high-pressure conditions. Thus, careful attention should be paid to the use of MATLANTIS for the N-H system at high pressures.

In experimental studies on the La-H system, LaH<sub>2</sub> with the fluorite structure emerges as a stable phase at ambient pressure [49] and decomposes into LaH with the rock salt structure and LaH<sub>2+ $\delta$ </sub> with  $\delta$  = 0.3 at 11 GPa [50,51]. LaH<sub>2+ $\delta$ </sub>



FIG. 3. Formation-enthalpy convex hull diagram of the La-N-H system  $(La_xN_yH_{1-x-y})$  at 20 GPa, obtained by QE. The convex hull is projected on the *xy* plane, and the vertices (the intersections of the lines) correspond to thermodynamically stable compounds. Panel (a) shows all the compounds investigated in this study and panel (b) shows the moderately metastable compounds with  $\Delta H$  less than 4.4 mRy/atom.

has an intermediate structure between LaH<sub>2</sub> and LaH<sub>3</sub> with the bismuth trifluoride structure and the  $\delta$  value increases toward 1.0 with further increase of pressure [52]. Our QE results show that LaH<sub>2</sub> is an unstable compound with  $\Delta H$ of 6.9 mRy/atom and decomposes into LaH with the rock salt structure and LaH<sub>3</sub> with the bismuth trifluoride structure at 20 GPa. In addition, the compounds with the  $\delta$  values of 0.40–0.83 were obtained as the moderately metastable phases with  $\Delta H < 4.4$  mRy/atom. These results suggest that the calculated results are consistent with the experimental ones. Next, we investigate the superconductivity of the La-N-H system following the convex hull diagram (Fig. 4). First we focus on the compounds existing on the line of x = 0.5. Figure 5 shows the density of states (DOS) for LaH (y = 0),  $La_2NH$  (y = 0.25), and LaN (y = 0.5). LaH has a large dip at around the Fermi level in the DOS and shows weak superconductivity:  $\lambda$  is 0.2195 and  $T_c$  is less than 5 mK. The DOS at the Fermi level gradually increases with the increase of N doping in LaH, and the  $\lambda$  and  $T_c$  values increase to 0.5848 and 4.13 K in La<sub>5</sub>NH<sub>4</sub> (y = 0.1) and reach 0.7492 and 8.77 K in La<sub>2</sub>NH. The DOS data show that the 5dstates of La, which are defined as La(5d) here, dominantly contribute to the electronic states at the Fermi level. La<sub>2</sub>NH

TABLE I. Comparison of thermodynamically stable and metastable phases between MATLANTIS and QE. The stable and moderately metastable ( $\Delta H \leq 4.4$  mRy/atom) phases are indicated by circles and triangles, respectively. Unstable compounds appearing in the region of  $\Delta H > 4.4$  mRy/atom are indicated by a cross.

System		Compounds	MATLANTIS	QE
La-H		LaH <sub>3</sub>	0	0
		LaH	0	0
N-H		$NH_4$	0	$\triangle$
		NH <sub>3</sub>	×	0
		$N_7H_3$	0	×
La-N		LaN <sub>6</sub>	$\bigtriangleup$	0
		$LaN_4$	0	0
		$LaN_2$	0	0
		$La_2N_3$	0	$\triangle$
		LaN	0	0
		$La_{11}N_{10}$	$\bigtriangleup$	0
		$La_4N_3$	$\bigtriangleup$	0
La-N-H	x = 0.5	$La_5N_2H_3$	$\bigtriangleup$	0
		La <sub>2</sub> NH	0	$\triangle$
		$La_3N_2H$	$\bigtriangleup$	0
		$La_4N_3H$	$\bigtriangleup$	0
		$La_5N_4H$	0	$\triangle$
		$La_{11}N_9H_2$	$\bigtriangleup$	0
		La <sub>7</sub> N <sub>6</sub> H	$\bigtriangleup$	0
	Others	$LaNH_2$	0	0
		$La_2NH_3$	0	0
		$La_2N_3H$	0	0
		$La_4N_5H$	$\bigtriangleup$	0
		$LaN_2H_3$	$\bigtriangleup$	0
		$La_2N_5H_9$	$\bigtriangleup$	0
		La <sub>3</sub> NH <sub>6</sub>	$\bigtriangleup$	0

takes a monoclinic C2/m structure, which is assigned using FYNDSYM [54] (Fig. 6). The superconductivity, however, is weakened by further N doping and the  $T_c$  values are less than 2.90 K, and finally, LaN is an insulator with a band gap of 0.6 eV. The superconductivity data and the space groups of the structures are listed in Table II. Apart from the compounds on the line of x = 0.5, we explored other compounds showing higher  $T_c$  than that of La<sub>2</sub>NH. We found that La<sub>2</sub>NH<sub>2</sub> shows  $\lambda = 0.9337$  and  $T_c = 14.41$  K. La<sub>2</sub>NH<sub>2</sub> takes a trigonal P3m1 structure. In this structure, the triangular lattice is formed in the plane parallel to the *ab* plane and is stacked along the c axis with the order of A(La)-B(N)-C(La)-A(H)-B(H), as shown on the right side of Fig. 7(a). Note that A, B, and C are the same as the layer positions describing the hexagonal close-packed structure (A-B) or the face-centered-cubic structure (A-B-C). Figure 7(b) shows the DOS for La<sub>2</sub>NH<sub>2</sub>. The DOS has a large peak at around the Fermi level due to a dominant contribution of the 5d states of La, which results in the enhancement of the superconductivity. The top of the peak emerges at 0.1 eV from the Fermi level, and the superconductivity is expected to be further enhanced by electron doping. In hydrides based on lanthanides, the contribution of the 4f electrons to the superconductivity has been discussed [55,56]. For example, the earlier predicted high- $T_c$  superconductor, LaH<sub>10</sub>, shows the dominant contribution of the La(4f) states to the



FIG. 4. Superconducting  $T_c$  data for the La-N-H system at 20 GPa. The superconducting and insulating phases are indicated as closed circles and open squares, respectively. The color of the circle represents the magnitude of the  $T_c$  value.

electronic states at the Fermi level due to high pressurization [16]. Also, the Lu-N-H compounds, in which Lu has a completely filled 4f shell, are predicted to show  $T_c$  values above 100 K at ambient pressure due to the Hubbard U correction on the 4f electrons (U = 5 eV) [57]. In sharp contrast with these systems, La<sub>2</sub>NH<sub>2</sub> shows that the La(4f) states contribute less to the electronic states at the Fermi level. We also predicted that La<sub>4</sub>N<sub>6</sub>H shows  $\lambda = 0.9353$  and  $T_c = 14.12$  K, which are comparable to the values of La<sub>2</sub>NH<sub>2</sub>. Unlike La<sub>2</sub>NH<sub>2</sub>, the 2p states of N dominantly contribute to the electronic states at the Fermi level. La<sub>2</sub>N<sub>5</sub>H<sub>2</sub> and La<sub>3</sub>N<sub>4</sub>H show  $T_c$  values of 12.08 and 11.95 K, respectively:  $\lambda = 0.7592$  and



FIG. 5. Density of states (DOS) for LaH, La<sub>2</sub>NH, and LaN at 20 GPa. La(5*d*), La(4*f*), N(2*p*), and H(1*s*) represent the 5*d* states of La, the 4*f* states of La, the 2*p* states of N, and the 1*s* states of H, respectively. The Fermi level is set to 0.





FIG. 6. Crystal structure of  $La_2NH$ , assigned as a monoclinic C2/m. The right shows the structure viewed along the *b* axis. The structure was drawn with VESTA [53].

 $\omega_{\text{log}} = 274.2 \text{ K}$  for La<sub>2</sub>N<sub>5</sub>H<sub>2</sub> and  $\lambda = 0.7492$  and  $\omega_{\text{log}} = 280.0 \text{ K}$  for La<sub>3</sub>N<sub>4</sub>H. The  $\lambda$  values are smaller than those of La<sub>2</sub>NH<sub>2</sub> and La<sub>4</sub>N<sub>6</sub>H and are approximately the same as the  $\lambda$  values of La<sub>2</sub>NH on the line of x = 0.5, whereas the  $\omega_{\text{log}}$  values are larger than those of the three compounds, which results in  $T_c$  values of about 12 K. In addition to these compounds, we predicted more than 20 compounds showing the superconductivity. Their superconductivity data are shown in Table S3 in SM [41].

Although La<sub>4</sub>NH<sub>13</sub> with x = 0.2222 and y = 0.0556 has the largest hydrogen concentration of all the stable and moderately metastable ternary compounds predicted by our search, this compound is the insulator with a band gap of 0.45 eV. In addition, ternary compounds with  $x \le 0.3$  and  $y \le 0.4$  are all insulating phases (see Fig. 4), which are listed in Table S4 in SM [41]. These results suggest that superhydrides such as LaH<sub>10</sub> observed in a megabar region [13,14] are not expected to be obtained at 20 GPa in the La-N-H ternary system.

TABLE II. Superconductivity data of ternary compounds in the La-N-H system, predicted by the evolutionary construction scheme of a formation-enthalpy convex hull.  $\Delta H$ ,  $\lambda$ ,  $\omega_{log}$ , and  $T_c$  are the enthalpy difference to the convex hull in the unit of mRy/atom, the electron-phonon coupling constant, the logarithmic-averaged phonon frequency in the unit of K, and the superconducting critical temperature in the unit of K, respectively.

	Compound	Structure	$\Delta H$	λ	$\omega_{ m log}$	$T_{\rm c}$
x = 0.5	La <sub>5</sub> NH <sub>4</sub>	C2/m	2.12	0.5848	189.2	4.13
	$La_2NH$	C2/m	3.51	0.7492	205.2	8.77
	La <sub>5</sub> N <sub>3</sub> H <sub>2</sub>	C2/m	1.05	0.4916	226.2	2.63
	$La_3N_2H$	$P\bar{6}m2$	0	0.2802	279.6	0.07
	$La_4N_3H$	C2/m	0	0.4127	280.1	1.42
	La <sub>5</sub> N <sub>4</sub> H	C2/m	0.14	0.3852	300.0	1.03
	$La_{11}N_9H_2$	$P\overline{1}$	0	0.3886	309.1	1.11
	La <sub>6</sub> N <sub>5</sub> H	C2/m	0.59	0.4614	294.2	2.60
	La <sub>7</sub> N <sub>6</sub> H	RĪ	0	0.3761	320.0	0.94
	$La_8N_7H$	P2/m	0.33	0.3541	251.1	0.49
Others	La <sub>2</sub> NH <sub>2</sub>	P3m1	4.12	0.9337	215.6	14.41
	$La_4N_6H$	<i>P</i> 1	2.99	0.9353	210.8	14.12
	$La_2N_5H_2$	Cm	4.28	0.7592	274.2	12.08
	$La_3N_4H$	<i>P</i> 1	1.61	0.7492	280.0	11.95



FIG. 7. (a) Crystal structure of La<sub>2</sub>NH<sub>2</sub>, assigned as a trigonal P3m1, viewed along the *c* axis (left) and the *b* axis (right). The stacking order A(La)-B(N)-C(La)-A(H)-B(H) is formed along the *c* axis. The structure was drawn with VESTA [53]. (b) Density of states (DOS) for La<sub>2</sub>NH<sub>2</sub> at 20 GPa. La(5*d*), La(4*f*), N(2*p*), and H(1*s*) represent the 5*d* states of La, the 4*f* states of La, the 2*p* states of N, and the 1*s* states of H, respectively. The Fermi level is set to 0.

#### IV. CONCLUSIONS AND DISCUSSION

To predict novel hydride superconductors, we explored thermodynamically stable and metastable phases at 20 GPa in the La-N-H ternary system ( $\text{La}_x \text{N}_y \text{H}_{1-x-y}$ ,  $0 \le x \le 1$ ,  $0 \le y \le 1$ ), integrating the evolutionary construction scheme of a formation-enthalpy convex hull, the universal neural network potential (PFP) calculations implemented in MATLANTIS, and the DFT calculations implemented in QE. Thanks to the

screening by the PFP calculations, we quickly and accurately obtained stable and moderately metastable phases. The convex hull diagram shows that more than 50 compounds emerge as stable and moderately metastable phases in the region of  $\Delta H \leq 4.4$  mRy/atom, which can be obtained experimentally by high-pressure and high-temperature synthesis techniques. In particular, they are concentrated on the line connecting between LaH and LaN, i.e., the line of x = 0.5. Following the convex hull diagram, we investigated the superconductivity in the La-N-H system at 20 GPa. For the compounds on the line of x = 0.5, we found that the superconductivity is gradually enhanced due to N doping for LaH and the  $T_c$  value reaches 8.77 K in La<sub>2</sub>NH with y = 0.25. In addition, we predicted that metastable La<sub>2</sub>NH<sub>2</sub> shows the highest  $T_c$  value, 14.41 K, of all the ternary compounds predicted in this study. Ternary compounds with  $x \leq 0.3$  and  $y \leq 0.4$  are all insulating phases. These results suggest that it is difficult to obtain high- $T_c$  superconductivity in the La-N-H system at 20 GPa. In addition, further investigations, e.g., changing the third element from N or changing the pressure condition, are required to prove the hot superconductivity previously observed in the La-H-based system by the electric resistivity measurements.

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- [1] N. W. Ashcroft, Phys. Rev. Lett. 21, 1748 (1968).
- [2] N. W. Ashcroft, Phys. Rev. Lett. 92, 187002 (2004).
- [3] Y. Li, J. Hao, H. Liu, Y. Li, and Y. Ma, J. Chem. Phys. 140, 174712 (2014).
- [4] D. Duan, Y. Liu, F. Tian, D. Li, X. Huang, Z. Zhao, H. Yu, B. Liu, W. Tian, and T. Cui, Sci. Rep. 4, 6968 (2014).
- [5] A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov, and S. I. Shylin, Nature (London) 525, 73 (2015).
- [6] D. Duan, X. Huang, F. Tian, D. Li, H. Yu, Y. Liu, Y. Ma, B. Liu, and T. Cui, Phys. Rev. B 91, 180502(R) (2015).
- [7] I. Errea, M. Calandra, C. J. Pickard, J. Nelson, R. J. Needs, Y. Li, H. Liu, Y. Zhang, Y. Ma, and F. Mauri, Phys. Rev. Lett. 114, 157004 (2015).
- [8] R. Akashi, M. Kawamura, S. Tsuneyuki, Y. Nomura, and R. Arita, Phys. Rev. B 91, 224513 (2015).
- [9] I. Errea, M. Calandra, C. J. Pickard, J. R. Nelson, R. J. Needs, Y. Li, H. Liu, Y. Zhang, Y. Ma, and F. Mauri, Nature (London) 532, 81 (2016).

- [10] T. Ishikawa, A. Nakanishi, K. Shimizu, H. Katayama-Yoshida, T. Oda, and N. Suzuki, Sci. Rep. 6, 23160 (2016).
- [11] R. Akashi, W. Sano, R. Arita, and S. Tsuneyuki, Phys. Rev. Lett. 117, 075503 (2016).
- [12] M. Einaga, M. Sakata, T. Ishikawa, K. Shimizu, M. I. Eremets, A. P. Drozdov, I. A. Troyan, N. Hirao, and Y. Ohishi, Nat. Phys. 12, 835 (2016).
- [13] M. Somayazulu, M. Ahart, A. K. Mishra, Z. M. Geballe, M. Baldini, Y. Meng, V. V. Struzhkin, and R. J. Hemley, Phys. Rev. Lett. 122, 027001 (2019).
- [14] 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. Eremets, Nature (London) 569, 528 (2019).
- [15] T. Ishikawa, T. Miyake, and K. Shimizu, Phys. Rev. B 100, 174506 (2019).
- [16] H. Liu, I. I. Naumov, R. Hoffmann, N. W. Ashcroft, and R. J. Hemley, Proc. Natl. Acad. Sci. USA 114, 6990 (2017).

- [17] X. Feng, J. Zhang, G. Gao, H. Liu, and H. Wang, RSC Adv. 5, 59292 (2015).
- [18] D. V. Semenok, I. A. Kruglov, I. A. Savkin, A. G. Kvashnin, and A. R. Oganov, Curr. Opin. Solid State Mater. Sci. 24, 100808 (2020).
- [19] D. V. Semenok, A. G. Kvashnin, I. A. Kruglov, and A. R. Oganov, J. Phys. Chem. Lett. 9, 1920 (2018).
- [20] Y. Sun, J. Lv, Y. Xie, H. Liu, and Y. Ma, Phys. Rev. Lett. 123, 097001 (2019).
- [21] Y. Sun, Y. Tian, B. Jiang, X. Li, H. Li, T. Iitaka, X. Zhong, and Y. Xie, Phys. Rev. B 101, 174102 (2020).
- [22] W. Cui, T. Bi, J. Shi, Y. Li, H. Liu, E. Zurek, and R. J. Hemley, Phys. Rev. B 101, 134504 (2020).
- [23] E. Snider, N. Dasenbrock-Gammon, R. McBride, M. Debessai, H. Vindana, K. Vencatasamy, K. V. Lawler, A. Salamat, and R. P. Dias, Nature (London) 586, 373 (2020).
- [24] T. Wang, M. Hirayama, T. Nomoto, T. Koretsune, R. Arita, and J. A. Flores-Livas, Phys. Rev. B 104, 064510 (2021).
- [25] E. Snider, N. Dasenbrock-Gammon, R. McBride, M. Debessai, H. Vindana, K. Vencatasamy, K. V. Lawler, A. Salamat, and R. P. Dias, Nature (London) 610, 804 (2022).
- [26] A. D. Grockowiak, M. Ahart, T. Helm, W. A. Coniglio, R. Kumar, K. Glazyrin, G. Garbarino, Y. Meng, M. Oliff, V. Williams, N. W. Ashcroft, R. J. Hemley, M. Somayazulu, and S. W. Tozer, Front. Electron. Mater. 2, 837651 (2022).
- [27] N. Dasenbrock-Gammon, E. Snider, R. McBride, H. Pasan, D. Durkee, N. Khalvashi-Sutter, S. Munasinghe, S. E. Dissanayake, K. V. Lawler, A. Salamat, and R. P. Dias, Nature (London) 615, 244 (2023).
- [28] Y. Sun, F. Zhang, S. Wu, V. Antropov, and K.-M. Ho, Phys. Rev. B 108, L020101 (2023).
- [29] X. Ming, Y.-J. Zhang, X. Zhu, Q. Li, C. He, Y. Liu, T. Huang, G. Liu, B. Zheng, H. Yang, J. Sun, X. Xi, and H.-H. Wen, Nature (London) 620, 72 (2023).
- [30] N. Dasenbrock-Gammon, E. Snider, R. McBride, H. Pasan, D. Durkee, N. Khalvashi-Sutter, S. Munasinghe, S. E. Dissanayake, K. V. Lawler, A. Salamat, and R. P. Dias, Nature (London) 624, 460 (2023).
- [31] Y. Ge, F. Zhang, and R. J. Hemley, Phys. Rev. B 104, 214505 (2021).
- [32] S. Di Cataldo, W. von der Linden, and L. Boeri, npj Comput. Mater. 8, 2 (2022).
- [33] A. R. Oganov and C. W. Glass, J. Chem. Phys. 124, 244704 (2006).
- [34] A. R. Oganov, Y. Ma, A. O. Lyakhov, M. Valle, and C. Gatti, Rev. Mineral. Geochem. **71**, 271 (2010).
- [35] Y. Wang, J. Lv, L. Zhu, and Y. Ma, Phys. Rev. B 82, 094116 (2010).
- [36] C. J. Pickard and R. J. Needs, J. Phys.: Condens. Matter 23, 053201 (2011).

- [37] T. Ishikawa and T. Miyake, Phys. Rev. B 101, 214106 (2020).
- [38] MATLANTIS (https://matlantis.com/), software as a service style material discovery tool.
- [39] T. Ishikawa, T. Fukazawa, G. Xing, T. Tadano, and T. Miyake, Phys. Rev. Mater. 5, 054408 (2021).
- [40] S. Takamoto, C. Shinagawa, D. Motoki, K. Nakago, W. Li, I. Kurata, T. Watanabe, Y. Yayama, H. Iriguchi, Y. Asano, T. Onodera, T. Ishii, T. Kudo, H. Ono, R. Sawada, R. Ishitani, M. Ong, T. Yamaguchi, T. Kataoka, A. Hayashi *et al.*, Nat. Commun. **13**, 2991 (2022).
- [41] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevB.109.094106 for calculation speed and accuracy of MATLANTIS and calculation conditions and superconductivity data for stable and moderately metastable compounds in the La-N-H system at 20 GPa.
- [42] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Cereso, G. L. Chiarott, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos *et al.*, J. Phys.: Condens. Matter **21**, 395502 (2009).
- [43] W. Sun, S. T. Dacek, S. P. Ong, G. Hautier, A. Jain, W. D. Richards, A. C. Gamst, K. A. Persson, and G. Ceder, Sci. Adv. 2, e1600225 (2016).
- [44] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- [45] A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, Phys. Rev. B 41, 1227 (1990).
- [46] N. Marzari, D. Vanderbilt, A. De Vita, and M. C. Payne, Phys. Rev. Lett. 82, 3296 (1999).
- [47] D. C. Liu and J. Nocedal, Math. Program. B 45, 503 (1989).
- [48] P. B. Allen and R. C. Dynes, Phys. Rev. B 12, 905 (1975).
- [49] C. E. Holley Jr., R. N. R. Mulford, F. H. Ellinger, W. C. Koehier, and W. H. Zachariasen, J. Phys. Chem. 59, 1226 (1955).
- [50] A. Machida, T. Watanuki, D. Kawana, and K. Aoki, Phys. Rev. B 83, 054103 (2011).
- [51] A. Machida, M. Honda, T. Hattori, A. Sano-Furukawa, T. Watanuki, Y. Katayama, K. Aoki, K. Komatsu, H. Arima, H. Ohshita, K. Ikeda, K. Suzuya, T. Otomo, M. Tsubota, K. Doi, T. Ichikawa, Y. Kojima, and D. Y. Kim, Phys. Rev. Lett. 108, 205501 (2012).
- [52] Y. Sakurai, A. Machida, and K. Aoki, Solid State Commun. 151, 815 (2011).
- [53] K. Momma and F. Izumi, J. Appl. Cryst. 44, 1272 (2011).
- [54] H. T. Stokes and D. M. Hatch, J. Appl. Cryst. 38, 237 (2005).
- [55] E. Plekhanov, Z. Zhao, F. Macheda, Y. Wei, N. Bonini, and C. Weber, Phys. Rev. Res. 4, 013248 (2022).
- [56] W. Wu, Z. Zeng, and X. Wang, J. Phys. Chem. C 127, 20121 (2023).
- [57] N. S. Pavlov, I. R. Shein, K. S. Pervakov, V. M. Pudalov, and I. A. Nekrasov, JETP Lett. 118, 693 (2023).