

Competing hydrogenation pathways to metastable CaH_6 revealed by machine learning potential molecular dynamics

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The synthesis of the high- T_c superhydride CaH_6 has stimulated significant interest in understanding synthesis pathways for metastable hydrides. However, the microscopic mechanisms governing such hydrogenation reactions remain poorly understood. Here, we show that machine-learning potential molecular dynamics simulations can reproduce and distinguish competing reaction pathways leading to metastable and stable hydrides. By simulating hydrogenation reactions at CaH_2/H_2 and CaH_4/H_2 interfaces, we identify two distinct pathways that produce clathrate-type CaH_6 and A15-type $\text{CaH}_{5.75}$, respectively. $\text{CaH}_{5.75}$ lies on the convex hull but requires extensive Ca sublattice rearrangement and therefore forms only at elevated temperatures. In contrast, CaH_6 becomes kinetically accessible when CaH_2 is used as the precursor. The crystallographic compatibility between the Ca sublattice of CaH_2 and the body-centered cubic framework of CaH_6 enables a martensitic-like topotactic transformation that bypasses the reconstructive pathway leading to $\text{CaH}_{5.75}$. These results reveal how precursor structure and thermodynamic stability compete to determine superhydride formation pathways and demonstrate that machine-learning molecular dynamics can directly capture the kinetic selection of metastable phases in reactive materials systems.

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I. INTRODUCTION

Since the discovery of superconductivity in mercury by Onnes in 1911 [1], achieving superconductivity at room temperature has remained a central challenge in condensed-matter physics. While superconductors underpin technologies such as quantum computing and magnetic resonance imaging, all known materials operate far below room temperature, limiting their widespread practical use.

Among known superconducting materials, superhydrides [2,3] exhibit the highest superconducting transition temperatures (T_c) and are regarded as promising candidates for realizing room-temperature superconductivity. For example, CaH_6 [4–6] has been reported to exhibit a T_c of approximately 210 K at 160 GPa. Although such high T_c values have been achieved in binary hydride systems [7–12], room-temperature superconductivity has not yet been realized, motivating the exploration of multicomponent hydride systems [13–16]. Indeed, while independent experimental verification is still required, reports of room-temperature superconductivity have

emerged in ultrahigh-pressure ternary systems such as La–Sc–H, with T_c of 271–298 K at pressures of 195–266 GPa [17]. However, such extreme pressures pose significant challenges for practical applications, prompting growing interest in multicomponent polyhydrides that may exhibit high T_c at more moderate pressures [18–20].

Advances in crystal-structure prediction, driven by the development of machine-learning workflows [21,22] and universal machine-learning potentials [23], have dramatically accelerated the discovery of candidate superconducting hydrides. Nevertheless, substantial challenges remain in assessing whether predicted structures are experimentally synthesizable, and more importantly, in identifying viable synthesis pathways. For instance, theoretical studies on metastable Mg_2IrH_6 proposed a synthesis route via Mg_2IrH_7 based on thermodynamic stability and structure prediction [18]. Subsequent experiments, however, reported the formation of a disordered Mg_2IrH_5 phase instead [19], highlighting the difficulty of predicting synthesis pathways based solely on thermodynamic considerations. In our previous work, we successfully reproduced hydrogenation reactions leading to polyhydrides such as CaH_4 using machine-learning-potential molecular dynamics (MLP-MD) simulations [24]. In principle, such simulations enable the direct observation of reaction pathways and kinetic competition between multiple products under extreme conditions. However, there are currently no clear guidelines for the targeted synthesis of metastable phases (i.e., thermodynamically unstable phases with respect to the 0 K convex hull). Although stable polyhydrides are

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expected to be readily obtained at high pressures due to reduced activation energies, as suggested in our previous study, metastable phases remain difficult to access in a controlled manner. Such metastable phases have attracted increasing attention because some of them are associated with high superconducting transition temperatures.

In this study, we focus on possible synthesis pathways of CaH_6 , a superhydride whose synthesis required nearly a decade [5] after its theoretical prediction [4]. This long interval highlights the difficulty of experimentally realizing theoretically predicted superhydrides. To examine how the precursor structure and temperature affect the formation of metastable CaH_6 , we performed high-temperature and high-pressure MLP-MD simulations of CaH_x/H_2 interfaces using CaH_2 and CaH_4 as different Ca–H precursors.

Analysis of the simulated reactions revealed the formation of two structurally distinct superhydrides depending on the precursor and temperature: metastable clathrate CaH_6 with a bcc Ca sublattice and A15-type $\text{CaH}_{5.75}$ with a markedly different Ca arrangement. The latter is thermodynamically favored over CaH_6 under the conditions considered here, making $\text{CaH}_{5.75}$ a plausible competing product. Distinguishing the formation pathways of these two phases is important for controlling phase selectivity and for interpreting experimental structural and superconducting signatures. Based on the elucidated reaction mechanisms of $\text{CaH}_{5.75}$ and CaH_6 synthesis, we discuss the physicochemical factors governing the formation of metastable superhydrides and propose insights into practical synthesis strategies.

II. METHODS

A. Training data collection by DFT calculation

Approximately 0.15 million density functional theory-based molecular dynamics simulation (DFT-MD) atomic configurations were employed as the training dataset as summarized in the Supplemental Material Table S1 [25]. The dataset was curated to ensure transferability across the wide range of atomic environments that occur along the synthesis pathway. First, we collected the DFT-MD data for Ca, CaH_2 , CaH_4 , CaH_6 , CaH_{24} , and H_2 so that structures with various stoichiometry during the hydrogenation reactions are explicitly included, meaning that all dynamics occurs in an interpolated region of the constructed MLP. DFT-MD data at high temperatures (3000–10 000 K) ensure the sampling of unstable structures, such as the liquid phase, under high pressure. This also enables the MLP to accurately reproduce hydrogenation reactions that occur via the liquid phase (i.e., surface melting-driven hydrogenation reaction [24]).

Additionally, DFT-MD simulations of heterogeneous cells for $\text{CaH}_2(100)/\text{H}_2$, $\text{CaH}_4(001)/\text{H}_2$, and $\text{CaH}_6(100)/\text{H}_2$ under high pressure were included to improve the accuracy of atomic behavior near the interface. The DFT-MD data of metallic hydrogen under 600 GPa was also included, to account for possible molecular-atomic decomposition of H_2 under HT and HP conditions, as is known to occur at 2000 K and 100 GPa [26].

To efficiently learn short-range interatomic repulsion [27], additional datasets were included consisting of geometry opti-

mizations of systems compressed by 20% from the most stable structures. Finally, to enable the MLP to capture pressure-dependent behavior, DFT calculations of optimized structures of Ca, CaH_2 , CaH_4 , CaH_6 , CaH_{24} , and H_2 at pressures ranging from 0 to 300 GPa were also incorporated into the training dataset in addition to those listed in the Supplemental Material Table S1 [25]. These additional structures consist of DFT-relaxed structures at 0 K and do not include finite-temperature or intentionally generated off-equilibrium configurations. For each selected composition and polymorph, one relaxed structure was included at each pressure. The calculations were performed at 10 GPa intervals from 0 to 200 GPa and at 20 GPa intervals from 200 to 300 GPa, while CaH_6 and CaH_{24} structures were included only at pressures of 50 GPa and above.

All these DFT calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) [28–30] with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [31]. Standard PBE projector augmented wave (PAW) potentials [32] were used to represent the core states, whereas the valence states (Ca $3p^6 4s^2$, and H: $1s^1$) were treated explicitly by the plane-wave basis set with an energy cutoff of 400 eV. We employed $2 \times 2 \times 2$ Gamma-centered k -point meshes were employed for the Brillouin zone sampling in the calculations listed in the Supplemental Material Table S1 [25], except for the 32-atom H_2 system.

B. Machine learning potential construction

The MLP was trained using the deep potential-smooth edition scheme as implemented in the deepmd-kit package [33–36]. We chose an embedding network with three hidden layers and (25, 50, 100) nodes per layer. The size of the embedding matrix was set to 16. Three hidden layers with (240, 240, 240) nodes per layer were used in the fitting network. The cutoff radius was set to 6.0 Å and the descriptors decay smoothly from 0.35 to 6.0 Å.

The mean absolute error (MAE) of atomic forces between DFT and MLP calculations is around 0.2 eV/Å for training and testing data below 3000 K and 150 GPa, which is comparable to previous studies of MLP for finite temperature and high pressure simulations [24,37,38]. The constructed MLP also reproduces atomic forces during MLP-MD simulations for $\text{CaH}_{5.75}$ and CaH_{12} with comparable accuracy, despite no DFT data for either of these structures being present in the training dataset, demonstrating the robustness and transferability of the constructed MLP.

C. Molecular dynamics simulation

The large-scale atomic/molecular massively parallel simulator (LAMMPS [39]) was used for MD simulations. A Nose-Hoover thermostat [40] and a Parrinello-Rahman barostat [41] were used for the NPT-MD simulations. The timestep was set to 1 fs and the mass of deuterium (D) was used instead of that of hydrogen. Note that the same hydrogenation reactions were reproduced during MLP-MD simulations from same atomic configurations with H mass, as summarized in the Supplemental Material Fig. S1 [25].

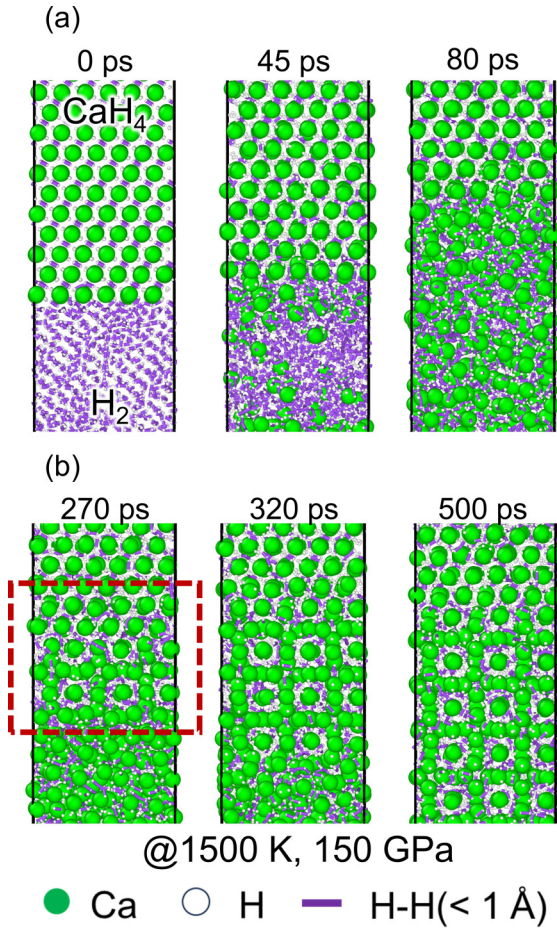


FIG. 1. Snapshots of the atomic configurations of CaH_4/H_2 interface during MLP-MD simulations at 1500 K and 150 GPa. (a) The initial Ca dissolution into H_2 layers. (b) $\text{CaH}_{5.75}$ formation near the interface after Ca supersaturation. The corresponding snapshots of the whole simulation cell are shown in the Supplemental Material Fig. S5 [25].

In this study, we use two different CaH_x/H_2 interfaces for hydrogenation reactions (see Fig. S2 in the Supplemental Material [25] for the snapshots). One is the $\text{CaH}_4(101)/\text{H}_2$ interface containing about 8000 atoms (Ca, 1152 atoms; H, 7008 atoms). The other is $\text{CaH}_2(100)/\text{H}_2$ with 5000 atoms (Ca, 576 atoms; H, 4596 atoms). The initial cell parameters are $16.9 \times 16.8 \times 95.6 \text{ \AA}^3$ and $11.3 \times 16.1 \times 88.9 \text{ \AA}^3$, which are sufficiently large compared with the MLP cutoff radius ($6 \text{ \AA}$). For these interface systems, we initialized MLP-MD simulations at 300 K and heated for about 50 ps until the system reaches the specific temperature under fixed pressure (150 GPa), as shown in the Supplemental Material Fig. S3 [25]. OVITO [42] was used for visualization of the MLP-MD simulation results.

III. RESULTS

A. A15-type $\text{CaH}_{5.75}$ superhydride synthesis

Figure 1 shows the snapshots of the atomic configurations during MLP-MD simulations of the CaH_4/H_2 interface at 1500 K and 150 GPa. After approximately 40 ps, Ca atoms start to dissolve into the H_2 high-pressure phase, forming

a solid solution [referred to as $\text{H}_2(\text{Ca})$]. Notably, the local structure around Ca atoms in this phase resembles a CaH_{12} phase, a phase composed of Ca coordinated by H_2 dimers, which has been reported to be stable above 100 GPa [4].

The radial distribution functions (RDFs) of the Ca-dissolved H_2 phase are shown in Fig. S4. The observed RDF peaks coincide with those of $\text{CaH}_{5.75}$ and CaH_{12} . This indicates that the H_2 phase accommodates Ca atoms and forms a liquid-like Ca-H environment characterized by local structural motifs similar to these phases.

The recurrence of similar structural motifs in both a molten phase and CaH_x phases (i.e., $\text{CaH}_{5.75}$ and CaH_{12}) that are not included in the training data is noteworthy for two reasons. First, as we have explicitly validated the structural description of the $\text{CaH}_{5.75}$ and CaH_{12} phases using DFT-MD as an independent reference for our MLP, it is likely that the appearance of these motifs in the molten phase is also valid and physically sensible. Second, the similarity in structural motifs hints at possible kinetically favored pathways for crystallization from the melt.

After the H_2 phase becomes saturated with Ca and sufficient time has elapsed, a new bulk CaH_x phase nucleates at the interface, as highlighted by the red dashed box at $t = 270 \text{ ps}$ in Fig. 1. This CaH_x region subsequently grows with time and becomes the dominant phase within the simulation cell ($t = 500 \text{ ps}$). Since the system forms a liquid-like phase [$\text{H}_2(\text{Ca})$] as an intermediate state before forming a new superhydride, this hydrogenation reaction is successfully explained by surface-melting-driven hydrogen absorption—our previous thermodynamic model for polyhydrides [24]. We also examined the robustness of the CaH_x formation pathway by performing additional MLP-MD simulations of CaH_4/H_2 cells with different interface orientations and overall H:Ca ratios. These simulations also produced the same CaH_x phase as shown in Figs. S6 and S7, indicating that this superhydride formation pathway is not specific to the $\text{CaH}_4(101)/\text{H}_2$ interface or to a single overall composition. The product yield, however, depends on the overall H:Ca ratio due to the coexistence of other stable phases like CaH_4 and Ca-dissolved H_2 layers like liquid CaH_{12} .

Figure 2(a) shows a snapshot after 1 ns of MLP-MD at 150 GPa and 1500 K, along with the resulting atomic structure, and the corresponding XRD diffraction pattern compared to that calculated for A15-type $\text{CaH}_{5.75}$. After 1 ns of simulation, all Ca atoms in the MLP-MD calculation shown in Fig. 1 aggregate to form a bulk phase with an A15-type framework. As confirmed by the XRD diffraction pattern, this structure is consistent with that of $\text{CaH}_{5.75}$. Note that some XRD peaks appear below $\sim 10^\circ$ ($\text{Cu K}\alpha$) in the MLP-MD simulation result. These low-angle peaks originate from hydrogen-enriched grain-boundary regions in the simulation cell. This is a consequence of a fixed overall H:Ca ratio of 6:1 in the MLP-MD cell of CaH_4/H_2 interface for $\text{CaH}_{5.75}$ synthesis. Nevertheless, the RDF obtained from $\text{CaH}_{5.75}/\text{H}_2$ interface agrees well with that of $\text{CaH}_{5.75}$ [Fig. 2(c)], indicating that the hydrogen content within the bulk phase is essentially equivalent to that of $\text{CaH}_{5.75}$.

This result appears to contradict previous experimental work [5], which suggested that the CaH_6 phase was synthesized under similar conditions, namely, 160–190 GPa with

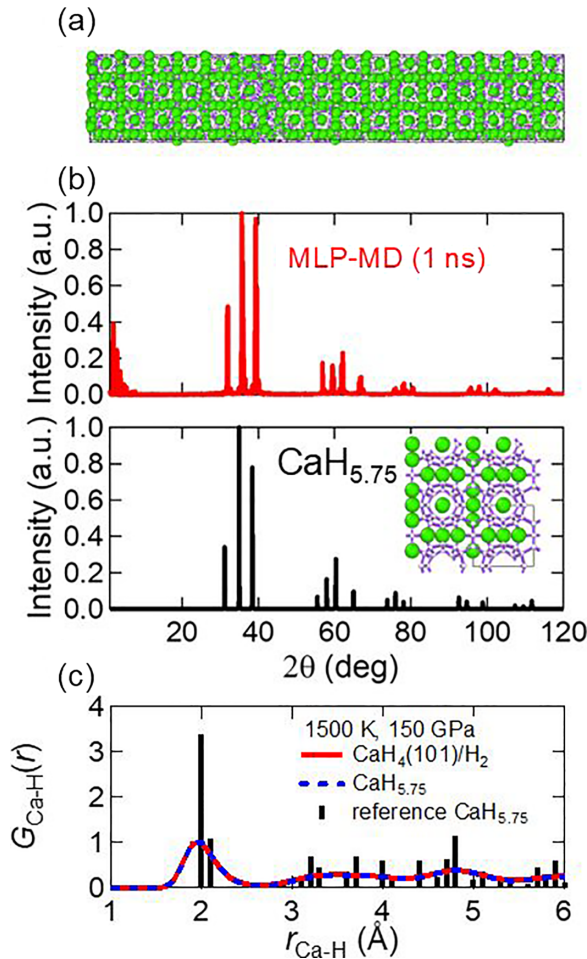


FIG. 2. (a) Snapshots of atomic configurations of the whole simulation cell for the CaH₄/H₂ interface obtained from 1 ns MLP-MD simulations at 1500 K and 150 GPa. (b) Calculated XRD patterns of (top) the structure obtained from the MLP-MD simulation and (bottom) the reference A15-type CaH_{5.75} structure ($a = 5.53$ Å) optimized by DFT at 150 GPa. Note that the CaH_{5.75} reference structure was constructed by referring to the BaH_{5.75} structure reported in a previous study [42]. The atomic coordinates of the CaH_{5.75} reference structure are provided in the Supplemental Material Table S2 [25]. (c) Time-averaged radial distribution functions (RDFs) of H atoms around Ca atoms obtained from the MLP-MD simulation of the CaH₄/H₂ interface after CaH_{5.75} formation (0.9–1.0 ns). The black solid line represents the RDF of the reference CaH_{5.75} structure, while the blue dashed line corresponds to the MLP-MD simulation of bulk CaH_{5.75} at 1500 K and 150 GPa.

YAG laser heating to approximately 2000 K. However, reanalysis of the obtained XRD patterns suggests that CaH_{5.75} was also present in the final product. Figure 3 qualitatively compares the experimental XRD pattern of CaH_x at 173 GPa reported by Ma *et al.* [5] with that calculated for CaH_{5.75} after structural optimization at 160 GPa using DFT. Diffraction peaks observed near $\theta = 13^\circ$ and 16° that were previously assigned to an unknown phase are found to coincide well with the calculated peak positions of CaH_{5.75}.

In addition, the formation energy of CaH₆ from CaH_{5.75} (i.e., $\text{CaH}_{5.75} + \text{H}_2 \rightarrow \text{CaH}_6$) is calculated to be +0.29 eV per formula unit. Therefore, from a thermodynamic point of view,

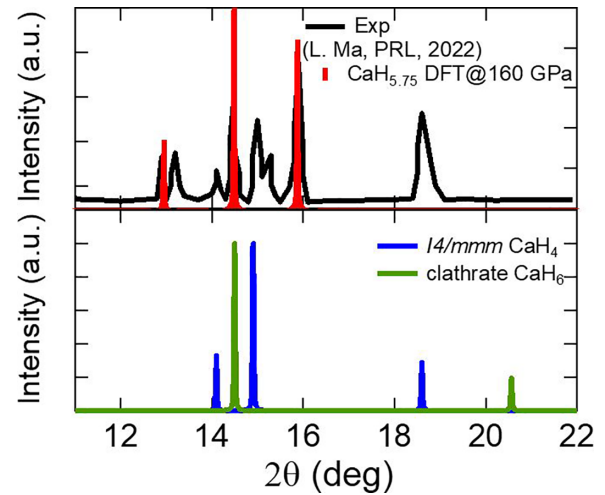


FIG. 3. Calculated XRD patterns of A15-type CaH_{5.75} structure ($a = 5.50$ Å) optimized by DFT at 160 GPa. The black line is the experimental XRD pattern taken from the Supplemental Material (Fig. S2) of the previous report by Ma *et al.* [5], while the blue and green lines are XRD patterns for 14/mmm CaH₄ ($a = 2.71$ Å, $c = 5.05$ Å) and clathrate CaH₆ ($a = 3.47$ Å), respectively.

CaH_{5.75} is more stable than CaH₆ under these conditions. Moreover, A15-type superhydrides similar to CaH_{5.75} have been reported to be stable in other systems [43–45] such as Ba and La, suggesting that the appearance of an A15 structure in the Ca system is not unexpected.

B. CaH₆ superhydride synthesis

Despite having a positive formation enthalpy with respect to CaH_{5.75} and H₂, in this section we demonstrate that CaH₆ becomes kinetically accessible by selecting appropriate precursor and temperature conditions. Figure 4 shows snapshots from the MLP-MD simulations of the CaH₂(100)/H₂ interface at 1000 K and 150 GPa. Under these conditions, CaH_x phases other than CaH_{5.75} are formed after 1 ns, as illustrated in Fig. 4(a). Figure 4(b) shows a magnified view of this new CaH_x bulk. As shown in the snapshot at 1000 ps, a hydrogen network similar to that of the clathrate CaH₆ is formed in this new CaH_x bulk.

During this hydrogenation process, Ca atoms undergo small in-plane rearrangements, accompanied by a hexagonal close packed (hcp)-like to body-centered cubic (bcc)-like transformation of the Ca sublattice. Figures 4(c) and 4(d) show the Ca displacement vectors between 300 and 700 ps, corresponding to the structural change before and after the transformation. As shown in these figures, the Ca sublattice transforms from an hcp-like arrangement to a bcc-like arrangement through an elongation along the CaH₂[100] direction. The Ca displacements remain relatively small, approximately on the order of single CaH₂ layer, rather than showing long-range diffusive rearrangement. This result supports the interpretation that the CaH₂-to-CaH₆ transformation proceeds through a martensitic-like transformation with only limited rearrangement of the Ca sublattice. The Ca(100) plane of the *Pnma* CaH₂ structure corresponds to the (11–20) plane of *hcp* Ca, when considering only the Ca sublattice. The observed Ca rearrangement satisfies the orientation relationship

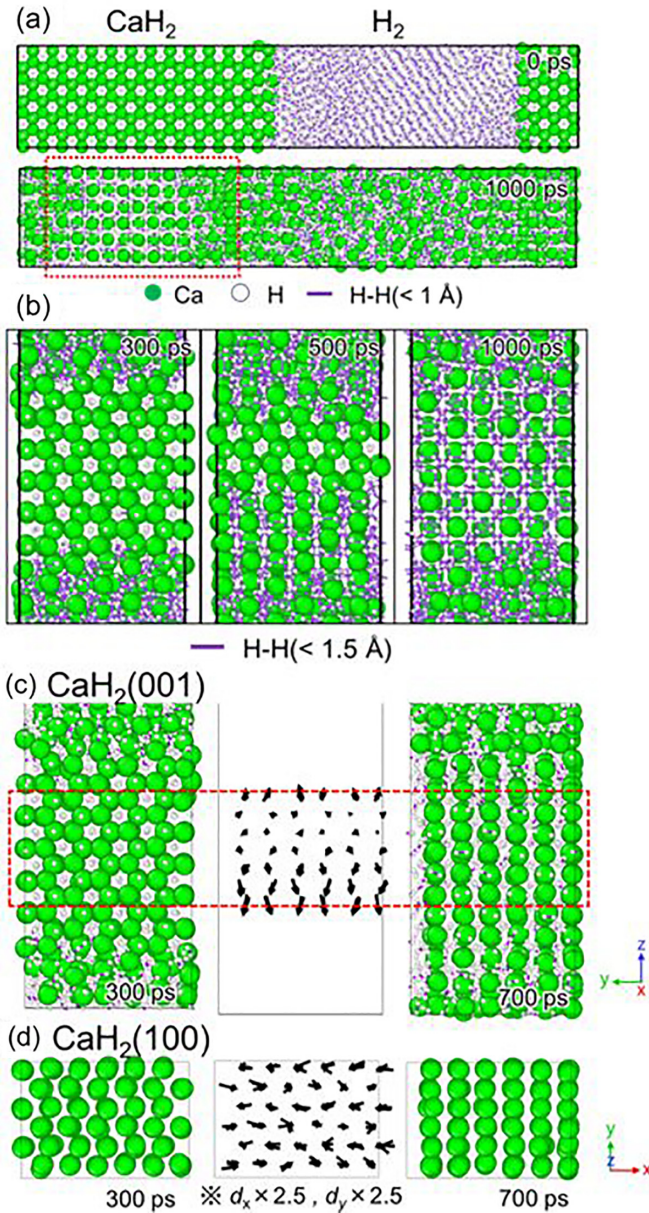


FIG. 4. (a) Snapshots of the atomic configurations during MLP-MD simulation of $\text{CaH}_2(100)/\text{H}_2$ interface at 1000 K and 150 GPa. (b) Magnified figures for the obtained new CaH_x inside the slab. Longer H-H bonds ($1.5 \text{ \AA}$) were used for the clarity of hydrogen network in the clathrate CaH_6 . (c), (d) Snapshots of the atomic configuration at the $\text{CaH}_2(100)/\text{H}_2$ interface with Ca displacement vectors between 300 and 700 ps. For clarity, only the displacement vectors of Ca atoms within the region enclosed by the red dashed square are shown. H atoms are also omitted in Fig. 4(d) for ease of viewing.

$(11-20)_{\text{hcp}}// (101)_{\text{bcc}}$. This indicates that the hydrogenation reaction proceeds via a diffusionless transformation analogous to a martensitic-like phase transition.

The RDF of the obtained CaH_x bulk was comparable to that of the CaH_6 clathrate during MLP-MD simulation at 1000 K and 150 GPa as shown in the Supplemental Material Fig. S9 [25]. This demonstrates that both metastable CaH_6 and stable $\text{CaH}_{5.75}$ phases can be synthesized via high-pressure

hydrogenation through appropriately designing the precursor and temperature conditions.

We note that, even in the MLP-MD simulations of the $\text{CaH}_2(100)/\text{H}_2$ interface at 1000 K, structures similar to $\text{CaH}_{5.75}$ are formed near the interface. A possible reason is that Ca atoms dissolve into the H_2 region, thereby enhancing Ca mobility near the interface.

This observation suggests that the obtained CaH_x phase can be strongly affected by the overall composition of the system and the method by which hydrogen is supplied to the precursor. For example, under hydrogen-rich conditions such as those assumed in our MLP-MD simulations, $\text{CaH}_{5.75}$ may preferentially form. In contrast, when hydrogenation proceeds via hydrogen diffusion through polycrystalline grain boundaries of Ca metal or CaH_x , the space available for Ca diffusion and rearrangement is likely to be more restricted. Under such conditions, Ca rearrangement may be suppressed, and in combination with hydrogen deficiency (when compared to the CaH_x/H_2 interface), reaction pathways leading to the formation of CaH_6 may be relatively favored.

These results indicate that the superhydride phase obtained can be sensitive to experimental conditions, with different reaction pathways being favored depending on the hydrogen supply and local structural environment. Accordingly, careful consideration is required when interpreting CaH_x phases observed in the vicinity of interfaces.

IV. DISCUSSION

The origin of these two competing hydrogenation pathways can be attributed to a combination of the thermodynamic stability of CaH_x phases, temperature-dependent Ca mobility, and the structure of the Ca matrix in the precursor. Figure 5(a) shows the pressure dependence of the formation enthalpy of CaH_x phases. Here, the formation enthalpy ΔH_{hyd} is defined with respect to CaH_2 and H_2 ; a negative value of ΔH_{hyd} indicates that the corresponding phase is more stable than CaH_2 . At each pressure, the phase with the lowest ΔH_{hyd} is therefore thermodynamically favored. Although the results shown in Fig. 5(a) are obtained from DFT calculations, MLP employed in this study reproduces the same qualitative trends with good accuracy, as demonstrated in Supplemental Material Fig. S8 [25].

$\text{CaH}_{5.75}$ becomes thermodynamically more stable than CaH_4 above 100 GPa [Fig. 5(a)]. In contrast, CaH_6 exhibits a higher formation enthalpy than other CaH_x phases over the entire pressure range considered and is therefore a metastable phase. From a purely thermodynamic equilibrium perspective, the synthesis of CaH_6 is thus intrinsically unfavorable.

However, $\text{CaH}_{5.75}$ formation is kinetically suppressed. As illustrated in Fig. 5(b), the A15-type $\text{CaH}_{5.75}$ phase possesses a complex Ca atomic arrangement that differs significantly from typical bcc, face-centered cubic (fcc), or hcp crystal structures. Consequently, the formation of $\text{CaH}_{5.75}$ from CaH_4 with a bcc-type Ca matrix requires substantial rearrangement of Ca atoms, which requires high temperatures to enable sufficient Ca diffusion.

By contrast, the Ca sublattice of CaH_6 is bcc and exhibits high structural similarity to those of CaH_2 (hcp) and CaH_4 (bcc). As a result, CaH_6 can form without large Ca rear-

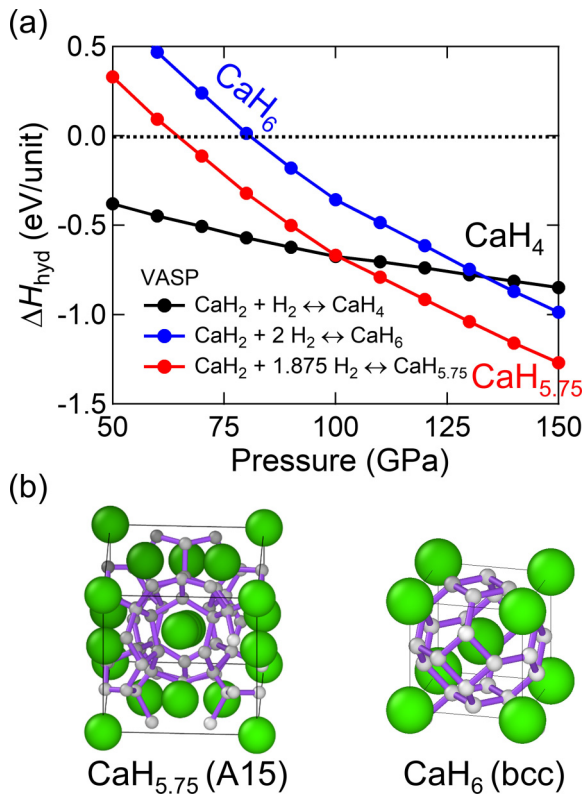


FIG. 5. (a) Hydrogenation enthalpy at 0 K of CaH_4 , $\text{CaH}_{5.75}$, and CaH_6 obtained from DFT calculation as a function of pressure. The same trends were obtained in MLP as summarized in the Supplemental Material Fig. S8 [25]. (b) Structure of A15- $\text{CaH}_{5.75}$ and of clathrate CaH_6 .

range. Nevertheless, the formation-enthalpy difference between CaH_4 and CaH_6 is very small [Fig. 5(a)], which limits the thermodynamic driving force to overcome the activation barrier for the hydrogenation reaction. Consistently, our MLP-MD simulations show that CaH_6 does not form at $\text{CaH}_4(101)/\text{H}_2$ interfaces under relatively low-temperature conditions around 1000 K. In the experimental study [5] (see Fig. 3 for the corresponding XRD pattern), CaH_4 and $\text{CaH}_{5.75}$ were reported to coexist in the probed regions. While the spatial distribution of these phases within the x-ray-irradiated region cannot be resolved, the XRD pattern measured in those regions does not show a clear reflection near $\sim 20^\circ$, where CaH_6 is expected to exhibit a characteristic peak. This suggests that the contribution of CaH_6 in the probed region may be limited. Such an interpretation is compatible with our MLP-MD results, which indicate that CaH_6 formation from CaH_4 is kinetically hindered at moderate temperatures.

In the case of a CaH_2 precursor, the formation-enthalpy difference of approximately 1 eV/unit exists at 150 GPa, providing a sufficient thermodynamic driving force for hydrogenation. Owing to the combination of this large driving force and the high structural similarity of the Ca matrix, CaH_6 formation is observed at $\text{CaH}_2(100)/\text{H}_2$ interfaces even under low-temperature conditions where the formation of $\text{CaH}_{5.75}$ is kinetically suppressed.

Experimentally, both CaH_6 and $\text{CaH}_{5.75}$ have been reported to form under nominally similar conditions around 2000 K

and 173–190 GPa, as evidenced by Fig. 1 and Fig. S2 in Ma *et al.* [5]. This suggests that, even experimentally, the observed phase formation is influenced not only by thermodynamic equilibrium but also by kinetic constraints.

In previous experiments, CaH_x phases were synthesized under laser heating at temperatures of approximately 2000 K [5]. In our MLP-MD simulations, as summarized in the Supplemental Material Sec. S1 and Fig. S10, CaH_6 loses its crystalline order and enters a liquid-like state at around 1750 K within 1 ns simulation. At lower temperatures, such as 1500 K, CaH_6 does not maintain its bcc structure but instead undergoes a structural transformation toward a different phase, likely related to $\text{CaH}_{5.75}$, as illustrated by the snapshots in Fig. S7. $\text{CaH}_{5.75}$ also exhibits liquid-like behavior upon heating to around 2000 K. The higher melting temperature of $\text{CaH}_{5.75}$ compared with CaH_6 in these MLP-MD simulations is consistent with the greater thermodynamic stability of $\text{CaH}_{5.75}$ relative to CaH_6 .

These observations suggest that laser heating is likely to generate a transient liquid-like Ca–H environment in the vicinity of the heated region, rather than stabilizing well-defined crystalline CaH_x phases at high temperature. It is also noteworthy that, in the high-temperature limit (~ 2000 K), the stability of CaH_6 and $\text{CaH}_{5.75}$ becomes effectively equivalent, since both systems evolve into a liquid-like state with an H:Ca ratio close to 6:1.

Consequently, it may be necessary to consider hydrogenation reactions occurring at heterogeneous interfaces under conditions with significant temperature gradients, as well as bulk crystallization processes during rapid thermal quenching after laser irradiation. Detailed information of the temperature history of the sample, particularly in regions where XRD diffraction patterns are measured, would facilitate a much more definitive discussion.

A recent study also discussed the stability of $\text{CaH}_{5.75}$ and CaH_6 [46]. $\text{CaH}_{5.75}$ lies on the convex hull, whereas CaH_6 is metastable at 0 K. Based on the harmonic approximation, it is suggested that CaH_6 becomes thermodynamically stable above approximately 1800 K; however, the transition to a liquid state was not explicitly considered. In our MLP-MD simulations, both $\text{CaH}_{5.75}$ and CaH_6 transform into liquid-like states at approximately 1500–2000 K. As both systems approach similar liquid-like states at high temperatures, the free-energy difference between them is expected to diminish in the high-temperature limit.

Experimentally, $\text{CaH}_{5.75}$ has been reported to be synthesized at relatively low temperature [46], consistent with our MLP-MD results where $\text{CaH}_{5.75}$ emerges at around 1500 K. In the previous CaH_6 study [5], both CaH_6 and $\text{CaH}_{5.75}$ were observed after the synthesis under laser heating at around 2000 K. Although the interpretation differs from previous work [46], our results suggest that the reported formation of CaH_6 cannot be explained solely by thermodynamic stabilization; instead, kinetic factors—particularly Ca diffusion and precursor lattice compatibility—play a central role in selecting the reaction pathway. The precursor-dependent synthesis pathway presented here is consistent with all currently available experimental results, considering the thermodynamic stability of $\text{CaH}_{5.75}$ and CaH_6 .

V. CONCLUSION

In this study, we investigated the hydrogenation reactions leading to CaH_6 using machine-learning-potential molecular dynamics (MLP-MD) simulations. MD simulations at CaH_x/H_2 interfaces under 150 GPa revealed two competing hydrogenation pathways depending on the precursor phase. One pathway corresponds to the formation of A15-type $\text{CaH}_{5.75}$ at the CaH_4/H_2 interface. While this reaction is thermodynamically plausible, it requires substantial rearrangement of Ca atoms and therefore proceeds only at relatively high temperatures. The other pathway involves the formation of clathrate-type CaH_6 at the CaH_2/H_2 interface. Although CaH_6 is metastable, its Ca sublattice is closely related to those of other CaH_x phases like CaH_2 , enabling its formation even at lower temperatures where $\text{CaH}_{5.75}$ is kinetically inaccessible, through a diffusionless transformation reminiscent of a martensitic-like process.

A more quantitative discussion will require detailed experimental information on the local variation of temperature, sample morphology, and the location of the dominant reaction centers—for example, to determine whether hydrogenation occurs at bulk/ H_2 interfaces or via hydrogen diffusion along polycrystalline grain boundaries. Reconciling these experimental conditions with the assumptions inherent in atomistic simulations will be essential for establishing practical synthesis guidelines. Nevertheless, the present results demonstrate that metastable superhydrides such as CaH_6 can be synthesized in practice by appropriately designing the precursor structural similarity, the H/M ratio, and temperature condi-

tions. We expect that these insights will contribute to the rational design and experimental synthesis of new predicted superhydride materials.

More generally, this work demonstrates that machine-learning potential molecular dynamics simulations can be used to directly investigate competing reaction pathways and kinetic selection processes in complex materials systems under extreme conditions. This opens a new avenue for the use of machine-learning potentials, extending their applications beyond structure prediction to the exploration of synthesis pathways for realizing new materials.

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DATA AVAILABILITY

There are no publicly available research data or software supporting this article. Requests for further information or data should be sent to the authors.

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