First-principles computational discovery of materials for hydrogen storage

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Abstract. Hydrogen-fuelled vehicles require a cost-effective, lightweight material with precisely targeted thermodynamics and fast kinetics of hydrogen release. Since none of the conventional metal hydrides satisfy the multitude of requirements for a practical \( \text{H}_2 \) storage system, recent research efforts have turned to advanced multicomponent systems based on complex hydrides. We show that first-principles density-functional theory (DFT) calculations have become a valuable tool for understanding and predicting novel hydrogen storage materials and understanding the atomic-scale kinetics of hydrogen release. Recent studies have used DFT calculations to (i) predict crystal structures of new solid-state hydrides, (ii) determine phase diagrams and thermodynamically favoured reaction pathways in multinary hydrides, and (iii) study microscopic kinetics of diffusion, phase transformations, and hydrogen release.

1. Introduction

General adoption of hydrogen as a vehicular fuel depends on the ability to store hydrogen at high volumetric and gravimetric densities, as well as on the ability to extract it at sufficiently rapid rates. Since practical requirements for on-board hydrogen storage systems are very challenging and cannot be met with existing technologies, significant effort has been invested in searching for new materials that could efficiently store hydrogen at near ambient conditions [1]. Among the various storage options (such as compressed gas, sorbents and metal-organic frameworks [2,3], chemical hydrides [4]), solid-state hydrogen storage in complex hydrides has attracted particular attention due to very high volumetric storage densities and favorable thermodynamics [5-7]. Interest in complex hydrides was sparked by the discovery [8] that sodium alanate, NaAlH\(_4\), reversibly releases approximately 4.5 wt. % hydrogen at relatively low temperatures (around 120 °C) when doped with small amounts of titanium:

\[ \text{NaAlH}_4 \leftrightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 . \]  (1)
The discovery of reaction (1) instantly doubled the reversible capacity of inexpensive hydrides and pointed to the intriguing possibility that many other complex hydrides, such as alanates, borohydrides and amides, may be used for energy storage. Subsequently, high-density hydrogen storage has been demonstrated in several complex hydride systems, including amides [9,10], borohydrides [11], and others [12]. Nevertheless, achieving the right combination of structural, thermodynamic, kinetic and economic factors remains elusive. Trial-and-error experimentation or high-throughput searches for new materials are often hampered by experimental difficulties, such as small sample sizes and slow (de)hydrogenation kinetics. Thus, it is highly desirable to accurately estimate the thermodynamic properties of new materials before substantial resources are expended on their synthesis and characterization. First-principles calculations of the total crystal binding energies using the density-functional theory (DFT) have been shown to yield sufficiently accurate thermodynamic properties to be useful in predicting new hydrogen storage reactions [13,14]. Since these calculations are parameter-free and require only the atomic numbers and crystal structures as input, they represent an attractive alternative to expensive and time-consuming experimentation.

We review here our recent work towards a systematic, rational approach to designing novel hydrogen storage materials using state-of-the-art scientific computing. We show how the accurate predictive power of first-principles DFT modeling can be used to understand the thermodynamic and kinetic factors involved in hydrogen release and uptake and design new materials systems with improved properties. Our review is organized into three main areas: (1) predicting crystal structures of new materials, (2) predicting thermodynamics of hydrogen storage reactions and identifying favored reaction pathways, and (3) studies of microscopic kinetic mechanisms, rate-limiting steps and activation energies for hydrogen release and absorption reactions.

2. Computational methods
For all calculations presented here, the first-principles density-functional theory (DFT) method of electronic structure calculations has been used to calculate the total binding energies and vibrational free energies. Structural energies and vibrational frequencies were obtained using the ab-initio total-energy and molecular dynamics code VASP [15,16]. Electronic exchange and correlation were treated within the generalized gradient approximation (GGA) of Perdew and Wang [17], and the projected augmented wave (PAW) approach [18,19] was used to represent the interactions between the nuclei and valence electrons. The phonon frequencies were determined using the dynamical matrix approach where the symmetry-inequivalent rows of the dynamical matrix were calculated by displacing ions for a few steps around their equilibrium positions (further details of our implementation are given in Ref. [13]). The vibrational entropies and enthalpies were obtained by summing over the directly calculated normal mode frequencies.

The free energy of the hydrogen molecule is given by:

\[ F[H_2] = E_0[H_2] + \frac{7}{2} k_B T - TS_{H_2} \]  

where \( k_B \) is the Boltzmann constant and \( E_0(H_2) \) is the static DFT energy of an isolated \( H_2 \) molecule at \( T = 0 \) K; it is obtained by placing \( H_2 \) in a periodic cell with edge lengths of 10 Å. \( S_{H_2} \) represents the well-known expression for the entropy of an ideal diatomic gas in the high-temperature limit:

\[ S_{H_2} = k_B \left( \frac{7}{2} \ln(T) - \ln(p) + C_0 \right), \]  

where \( p \) is the pressure and \( C_0 = -4.22 \) is a dimensionless constant chosen to reproduce experimental data [20]. Equations (2) and (3) account for corrections to the free energy of gaseous \( H_2 \), which has to be treated separately from static and vibrational free energy contributions.

3. Predicting crystal structures
Determining the crystal structures of new compounds is the first step required by any first-principles materials discovery effort. However, predicting the ground state crystal structure of a compound with
a given chemical formula remains one of the most challenging problems in the field of computational materials science. Perhaps the most popular method is to choose “reasonable” crystal structure types (so-called “usual suspects”) and calculate their total energies with first-principles techniques. The structure with the lowest total energy (or free energy in finite-temperature studies) is then declared to be the ground state, or at least one that can provide a reasonable approximation to the thermodynamics of the true ground state. This approach has been widely used in studies of intermetallic compounds [21] and pressure-induced phase transformations [22]. With the increase in the available computer power, very large sets of trial structures have become practical, and the use of the so-called database searching approach, has exploded in popularity.

In database searching, candidate crystal structures are obtained from chemically similar compounds in published databases, such as the Inorganic Crystal Structures Database (ICSD) [23]. Next, DFT calculations are performed for all database matches to find the lowest-energy structure. Phonon calculations are then used to verify the dynamic stability of the structure. If the compound has imaginary phonon frequencies, ab initio molecular dynamics (AIMD) simulations or frozen phonon calculations for finite displacements along the unstable mode eigenvectors are used to search for stable geometries with lower energies [24]. For common stoichiometries, ICSD usually has a large set of candidate structures (from many tens to hundreds or even thousands), which constitute a large trial pool to sample the configuration space of competing crystal structure types. The database searching approach has been used with considerable success in numerous studies of complex hydrides [24-29]. The data mining technique introduced by Curtarolo et al. [30] offers an efficient way to narrow down database searching by using probabilistic concepts that guide the choice of the likely candidate ground states. Data mining offers significant efficiencies at common compositions where the number of trial structures can be very large.

All database methods rely heavily on the existence of an extensive catalog of “good” trial structures and have limited use if crystallographic information on chemically similar compounds is not available, as is the case for many novel hydrides. Furthermore, we will show below that even for some common chemical formulae the database searching approach may fail to predict energetically competitive structures because the database entries are too dissimilar in their bonding properties from the target hydride. This shows that there is a strong need for methods that can predict entirely new ground state structure types, i.e. those that are not isostructural with compounds already observed in other systems. There are few first-principles methods that can generate new ground state crystal structures “from scratch” (e.g., genetic algorithms [31] or simulated annealing [32]), but they presently require large computational effort and are efficient only for relatively small unit cells. In this section, we describe two methods that take advantage of special complex hydride bonding properties to generate entirely new crystal structure types with only a moderate computational cost.

3.1. Lattice algebra enumeration

In many materials it has been difficult to determine exactly the location of the hydrogen atoms, while the positions of the heavier ions are well known or can be guessed with a high degree of certainty. For instance, when hydrogen is covalently bonded to anions such as N or O there is often considerable freedom in the bond orientation, making the determination of the structure difficult. To predict the crystal structures in such cases of partial information, we have developed a computational search method, which provides the means for a systematic enumeration of the possible configurations for the unresolved degrees of freedom.

A typical case is presented by the structure of lithium imide, Li₂NH, which is a decomposition product in the famous lithium amide – lithium hydride reaction [9]:

\[ \text{LiNH}_2 + \text{LiH} \leftrightarrow \text{Li}_2\text{NH} + \text{H}_2. \] (4)

All experimental investigations of Li₂NH consistently point to a room temperature structure with Li and N ions occupying the positions of an antifluorite structure (see figure 1). However, there are conflicting reports on the H positions. Some reports suggest that hydrogen is distributed in a disordered manner across various Wyckoff positions within the fluorite framework [33-35], while
recent studies by Herbst and Hector [36] and Balogh et al. [37] propose an ordered arrangement of H positions, resulting in an orthorhombic structure of Ima2 symmetry.

Another interesting case is presented by the crystal structures of mixed Li-Mg imides, such as Li$_2$Mg(NH)$_2$ and Li$_3$Mg(NH)$_3$ [38], which may form as the decomposition products in thermodynamically optimized reactions between lithium amide and magnesium hydride [10]:

\[
2\text{LiNH}_2 + \text{MgH}_2 \rightarrow 2\text{LiH} + \text{Mg(NH)}_2 \leftrightarrow \text{Li}_2\text{Mg(NH)}_2 + 2\text{H}_2.
\]

The ion exchange in the first step of reaction (5) is exothermic and non-reversible, while the second step is endothermic and reversible. In comparison with the original lithium amide – lithium hydride reaction (4), addition of magnesium hydride in reaction (5) lowers the dehydrogenation enthalpy and hydrogen release temperature due to the formation of the strongly bound Li$_2$Mg(NH)$_2$ compound [39]. Experimentally, the structure of Li$_2$Mg(NH)$_2$ is known to belong to the Iba2 space group [40] and contain substitutional disorder on cation (Li and Mg) sites. Site-disordered phases present a challenge to conventional DFT calculations since they require the use of elaborate alloy-theoretical tools, such as the cluster expansion [41] to evaluate finite-temperature energetics. Screening for favorable hydrogen storage thermodynamics usually allows uncertainties of 5-10 kJ/(mol H$_2$) in the calculated reaction enthalpies, comparable to the physical accuracy of the DFT itself [13,14]. Within these accuracy requirements, it is usually sufficient to find the T=0 K ground state with an ordered arrangement of ions and then use its free energy to evaluate the thermodynamic properties of finite-temperature configurationally disordered phases.

The enumeration method is based on the observation that the N-H orientational ordering problem may be mapped onto a multicomponent alloy problem, which allows us to utilize well-established lattice algebra methods developed in the alloy theory community. For Li imide, we consider small unit cell input structures where all N–H dimers are aligned along one of the principle orientations (e.g., [100], [110], [111]). For a given orientational axis, the problem of listing different N–H dimer orientations can be viewed as formally identical to a binary alloy problem on a fixed fcc lattice: by placing Li and N atoms on the sites of the cubic fluorite lattice, N forms a fcc sublattice (see figure 1). We then associate different N–H alignments with ‘atoms’ of certain type and use symmetry to reduce the number of distinct trial structures, followed by DFT total energy calculations to relax all structural degrees of freedom and find the lowest-energy structures [42]. For mixed Li-Mg imides, we generate candidate structures with ordered arrangements of Li$^+$ and Mg$^{2+}$ ions on the cation sites of the antifluorite lattice, leaving some of the sites vacant to satisfy charge neutrality. The procedure of forming a mixed imide from the cubic antifluorite structure is illustrated in figure 1 for the case of Li$_2$Mg(NH)$_2$. Li$^+$ and Mg$^{2+}$ ions are placed on the cation sites of Li$_2$NH and the excess charge due to magnesium ions is accommodated through the introduction of vacancies on the lithium sites. The chemical composition in this family of compounds is given by Li$_{4-2x}$Mg$_x$(NH)$_2$, where $x$ represents the vacant cation sites. To satisfy steric constraints, N-H bonds are oriented towards the neighboring vacant sites whenever possible. Our procedure not only enumerates all possible orientations of N-H dimers and orderings of Li$^+$ and Mg$^{2+}$ within a chosen shape of the unit cell, but also searches through all possible choices of lattice vectors with a given number of atoms in the unit cell. Since the number of distinct symmetry-inequivalent structures increases geometrically with the number of atoms in the
unit cell, the enumeration method is limited to relatively small unit cells, e.g. one formula unit in the case of Li$_4$Mg(NH)$_3$.

For Li$_2$NH, this method yields several new low-energy ordered structures that were found to be lower in energy than all previously proposed ones [42]. An even more sophisticated alloy-theory approach, the so-called continuous cluster expansion, was used by Mueller and Ceder to model the energy of Li$_2$NH in terms of the relative N-H bond orientations and suggest a ground state structure of orthorhombic Pca$_2$1 symmetry [43].

For the mixed-cation imide, Li$_2$Mg(NH)$_2$, we find a new, previously unsuspected structure of Pca$_2$1 symmetry (see figure 2), which is 4.4 kJ/mol lower in energy than the site-ordered Iba$_2$ phase proposed in Ref. [44]. We also predict the existence of a Li$_4$Mg(NH)$_3$ phase, for which we predict an orthorhombic structure of Imm2 symmetry, shown in figure 2. With respect to the antifluorite structure from which these are derived, the rows of vacancies occur in the [100] direction for Li$_2$Mg(NH)$_2$ and in the [110] direction for Li$_4$Mg(NH)$_3$. In both compounds, all N-H bonds are oriented towards the vacancies, pointing to the important role that the hydrogen size constraints play in stabilizing these mixed-cation ordered-vacancy structures.

3.2. Prototype electrostatic ground state search

In many cases, the database searching method fails to predict stable structure types either because the database contains too few entries or the material under consideration is too different from the prototype compounds in the ICSD. For instance, in the case of Mg(BH$_4$)$_2$, the lowest-energy structure predicted by the database searching method using as many as 93 ICSD entries is dynamically unstable [24,45]. We have developed a method, which can predict entirely new, unsuspected ground state structure types for complex ionic crystals [46]. Physically, this approach is based on the observation that complex hydrides are characterized by an arrangement of positively charged cations (e.g., Mg$^{2+}$) and negatively charged complex anions (e.g., BH$_4^-$), with strong covalent bonds within each complex anion and predominantly electrostatic interactions between the cations and the anions [47,48]. These considerations suggest that the choice of the ground state crystal structure is predominantly influenced by the electrostatic energy, with secondary bonding interactions paying a minor role. Accordingly, the PEGS method is based on the assumption that the topology and symmetry (but not the total cohesive energy) of the ground state crystal structure can be determined by minimizing the total electrostatic energy for a set of charged complex anions and cations with soft-sphere repulsion between the ions. The resulting structures, henceforth referred to as prototype electrostatic ground states (PEGS), are then fully relaxed using first-principles DFT calculations to obtain accurate total energies and structural parameters. The PEGS Hamiltonian includes electrostatic and soft-core interionic repulsion terms.
\[ H_{\text{PEGS}} = \sum_{i<j} \left( \frac{Z_i Z_j}{r_{ij}} + \frac{1}{r_{ij}^{12}} \right), \]

where the sums run over all ions, \( r_{ij} \) is the separation between ions \( i \) and \( j \), \( Z_i \) is the ionic charge, and the second term (soft-core repulsion) is zero for non-overlapping ions. Monte Carlo simulated annealing in conjunction with distance scaling potential energy surface smoothing techniques [49] are used to minimize the electrostatic energy given by equation (6). For each compound, many runs are executed in parallel for several different values of a starting random number seed, which initializes the cell contents. The resulting candidate ground states are then used as input to DFT calculations to relax all structural parameters and obtain accurate total energies. The success of our approach does not depend on the precise values of the ionic radii and charges, since the PEGS can be determined for a range of parameters, spanning the parametric regions near the compound under consideration.

We have applied the PEGS method to predict the crystal structure of \( \text{Mg(BH}_4\text{)}_2 \) [24]. The PEGS search easily outperforms database searching [45] and simulated annealing AIMD methods and unexpectedly finds a new tetragonal ground state structure of \( \text{i} \bar{4}m2 \) symmetry (shown in figure 3), which is 5 kJ/mol lower than the \( P6_1 \) low-temperature (LT) structure observed in solution-grown crystals [50,51]. The primitive unit cell of the \( \text{i} \bar{4}m2 \) structure contains only two formula units (22 atoms), compared with 30 formula units (330 atoms) for the experimental \( P6_1 \) structure. Interestingly, both the predicted and experimental structures have very similar near-neighbor environments, but dramatically different densities, suggesting that coordination with solvent molecules and the associated steric factors may play an important role in promoting the growth of the higher-energy LT crystal structure. To the best of our knowledge, the \( \text{i} \bar{4}m2 \) structure has not been observed in any other compounds and represents a completely new type of crystal structure. This demonstrates the usefulness of our approach for rapidly generating new crystal structure types and accurately predicting thermodynamic properties of new materials. Using the derived structure, we obtain a room-temperature decomposition enthalpy of 29.5 kJ/(mol H\(_2\)), corresponding to hydrogen release at \( T=20^\circ \text{C} \) and \( p=1 \) bar (see table 1). Our results indicate that magnesium borohydride might be one of the most promising candidates among all known complex hydrides for high-capacity, near-ambient storage, and that the experimentally observed high H\(_2\) release temperatures and lack of reversibility are due to poor kinetics.

Recently, we used the PEGS search to predict the unknown ground state crystal structures of \( X_n\text{B}_{12}\text{H}_{12} \) compounds involving the icosahedral \( [\text{B}_{12}\text{H}_{12}]^{2-} \) complex, which have been suggested as products during hydrogen release from borohydrides by recent experiments [52-54]. We conducted ground state crystal structure searches using one- and two-formula unit primitive cells for \( \text{Li}_2\text{B}_{12}\text{H}_{12}, \text{MgB}_{12}\text{H}_{12}, \) and \( \text{CaB}_{12}\text{H}_{12} \). The lowest-energy structures found in this search are shown graphically in figure 4. For \( \text{Li}_2\text{B}_{12}\text{H}_{12} \), our structure is \( \sim 7 \) kJ/mol (or \( \sim 70 \) meV per formula unit) lower than the \( P2_1/n \) structure proposed by Ohba \textit{et al.} [55], which was obtained by database searching using candidate structures from the ICSD. Interestingly, it is also 7 kJ/mol lower than the \( \text{P}a\bar{3} \) structure in solution-grown samples obtained in Ref. [56]. There are no existing theoretical predictions or experimental data for the crystal structures of \( \text{MgB}_{12}\text{H}_{12} \) and \( \text{CaB}_{12}\text{H}_{12} \), and our work constitutes the first available study of the crystal structures and thermodynamics of these compounds. All the monoclinic structures found by PEGS have no known prototypes in the ICSD and represent completely new structure types that could not have been predicted using methods based on database searching. It is also worth noting that many borohydrides exhibit structural polymorphism and high-temperature entropically stabilized phases. PEGS results should provide highly accurate reaction

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{Tetragonal \( \text{i} \bar{4}m2 \) structure of \( \text{Mg(BH}_4\text{)}_2 \) predicted using the PEGS search.}
\end{figure}
enthalpies even in these cases, since the predicted energetics are expected to be within a few kJ/mol to the energies of the structural polymorphs. For instance, using the predicted PEGS $\Gamma_4 m 2$ ground state structure instead of the solution-synthesized LT phase of Mg(BH$_4$)$_2$ results in a negligible effect on the reaction enthalpy (less than 2 kJ/mol H$_2$) [24].

The PEGS method has also been successfully used to predict the ground state structures of LiSc(BH$_4$)$_4$, Sc(BH$_4$)$_3$, and Sc$_c$(B$_c$H$_{12}$)$_3$ [57] and high-temperature polymorphs of Ca(BH$_4$)$_2$ [58,59].

4. Predicting thermodynamics and favored hydrogen storage reactions

4.1. Basic thermodynamic considerations

Hydrogen uptake/release from materials is governed by a combination of thermodynamic and kinetic factors. The temperature at which the desorption of H$_2$ becomes thermodynamically possible is determined by the famous van’t Hoff equation,

$$\ln(p) = \frac{\Delta H}{RT} + \frac{\Delta S}{R},$$

where $\Delta H$ and $\Delta S$ are the enthalpy and entropy of the dehydriding reaction, respectively. $\Delta H$ is related to the bond strength between H and the storage material, while $\Delta S$ is dominated by the gas-phase entropy of H$_2$; $\Delta S^0 = 130.68$ J/(K mol H$_2$) at T=20 °C and p=1 bar [20]. The practical constraints of on-board storage place limitations on the accessible temperatures and pressures, and hence may be translated into constraints on the desired values of $\Delta H$. Assuming that $\Delta S$ is dominated by the entropy of H$_2$ gas and requiring hydrogen release at ambient pressures below the operating temperature of proton exchange membrane (PEM) fuel cells (80 °C) leads to the upper enthalpy limit of ~45 kJ/(mol H$_2$), while requiring rehydrogenation at ambient temperatures and pressures of a few hundred bar or lower gives the lower enthalpy limit of ~20 kJ/(mol H$_2$).

Figure 4. Predicted crystal structures of $X_n$B$_{12}$H$_{12}$ borohydrides. Counter-clockwise from top left: C2/m Li$_2$B$_{12}$H$_{12}$, C2/m MgB$_{12}$H$_{12}$, and C2/c CaB$_{12}$H$_{12}$.
4.2. Grand-canonical linear programming

The grand-canonical linear programming (GCLP) method provides a robust framework for automatically predicting new storage reactions in multicomponent systems, where the preferred reaction pathways are often complex and difficult to intuit [62,63]. GCLP was introduced in Ref. [64], where it was used to determine thermodynamically reversible hydrogen storage reactions in the Li-Mg-N-H system. Consider a multi-phase solid containing a certain fixed ratio of non-hydrogen species, which can exchange hydrogen with a reservoir of H₂ gas at a chemical potential \( \mu_{\text{H}_2}(T, p) \); the latter is a function of temperature \( T \) and pressure \( p \). The grand-canonical Gibbs free energy is given by the following expression:

\[
\Xi(p, T) = \sum_i x_i F_i(T) - \frac{1}{2} \sum_i x_i n_i^H \mu_{n_i^H}(p, T),
\]

where \( F_i(T) \) is the free energy of phase “\( i \)” (we neglect the pressure dependence of the free energies of solid phases), \( n_i^H \) is the number of hydrogen ions in one formula unit of phase “\( i \)”, and \( x_i \) are the unknown variable molar fractions of phases coexisting at a given composition, temperature, and pressure. The molar fractions are determined by minimizing Eq. (8), subject to the mass-conservation constraints for non-hydrogen species:

\[
f_i = \sum_i x_i n_i^s = \text{const}.
\]

4.3. Entropy-optimized reactions in the Li-Mg-Ca-B-H system

Armed with the first-principles thermodynamics of the predicted PEGS crystal structures of Mg(BH₄)₂ and \( X_{B_4}H_{12} \) phases, we have used the GCLP approach to identify all thermodynamically favored reactions in the quinary Li-Mg-Ca-B-H system [65]. We have discovered two new, previously unsuspected reactions belonging to a qualitatively new class of entropically optimized reactions that use fully hydrogenated high-entropy borohydrides as reactants and lead to the formation of low-entropy \( X_{B_4}H_{12} \) phases as end products. These reactions are given in table 1 and the corresponding van’t Hoff curves are shown in figure 5, which demonstrates that they both pass through the target window for on-board storage. Two of these reactions exhibit nearly ideal thermodynamics. The first

| Reaction | Wt. % (kg H₂/kg) | Vol. density (g H₂/l) | ΔH | ΔS | Tₜ (°C) |
|----------|------------------|----------------------|----|----|---------|
| 6Mg(BH₄)₂ → MgB₁₂H₁₂+5MgH₂+13H₂ | 8.1 | 63 | 29.3 | 99.8 | 20 |
| 5Mg(BH₄)₂+2LiBH₄ → Li₂B₁₂H₁₂+5MgH₂+13H₂ | 8.4 | 46 | 24.4 | 100.0 | -29 |
| 5Mg(BH₄)₂+CaBH₄ → CaB₁₂H₁₂+5MgH₂+13H₂ | 7.7 | 51 | 25.7 | 100.5 | -18 |
one uses a 5:2 molar mixture of Mg and Li borohydrides, leading to the formation of Li₂B₁₂H₁₂ and MgH₂, accompanied by the release of 8.4 wt. % H₂ at T=−29 °C and p=1 bar. The second reaction involves a 5:1 molar mixture of Mg and Ca borohydrides, leading to the formation CaB₁₂H₁₂ and MgH₂, releasing 7.7 wt. % H₂ at T=−18 °C. All the reactions in table 1 have low enthalpies [~25 kJ/(mol H₂)], which should significantly simplify heat management during on-board recharging.

Even though the enthalpy values in table 1 are at the lower limit of the commonly accepted 20-45 kJ/(mol H₂) range, they are compatible with excellent thermodynamics due to the low vibrational entropies of the Li₂B₁₂H₁₂ and CaB₁₂H₁₂ product phases. Indeed, the calculated reaction entropies are near 100 J/(K mol H₂), approximately 25% below the standard state entropy of gaseous hydrogen. Therefore, hydrogen release occurs at temperatures that are substantially higher than those expected by considering reaction enthalpies only. Low reaction entropies can have a highly beneficial effect since they allow the use of materials with low reaction enthalpies while maintaining the same equilibrium H₂ pressure. Other things being equal, lower enthalpy reactions are always better due to smaller amount of heat released during exothermic regeneration of these hydrides. Formation of the new XnB₁₂H₁₂ compounds is found to be particularly interesting, since the entropy of the tightly bound [B₁₂H₁₂]²⁻ anion is significantly lower than the entropy of the [BH₄]⁻ anion due to the smaller number of low-energy rotational and translational modes on a per-atom basis. A rule of thumb for designing new complex hydride reactions with low entropies suggests using reactants that have complex anions constituted by a small number of atoms (such as NH₂, BH₄, etc., resulting in a high number of low frequency phonon modes per atom) and products that are either tightly bound bulk phases or materials with large complex anions (e.g., B₁₂H₁₂), exhibiting few low-frequency phonon branches [65].

These results demonstrate the power of the combined theoretical framework for structure prediction and GCLP-based reaction prediction, showing that previously unsuspected reactions can be found even in extensively studied materials systems. Practical usefulness of these and other [66-68] theoretically predicted reactions will be determined not only by their thermodynamics, but also by the rate of hydrogen release, i.e., by their kinetics. Indeed, the dehydrogenation kinetics of Mg(BH₄)₂ have been measured: hydrogen desorption does not occur until very high temperatures, and the material has not been successfully rehydrated [54]. One needs to differentiate this type of thermodynamically preferred, but kinetically limited reaction from the type that is thermodynamically limited. The former is an excellent candidate for enhanced reactivity via catalysis, whereas the latter is a dead-end and should be abandoned in the search for reversible solid-state storage systems. It is interesting to note here that even though the reversibility of Mg(BH₄)₂ has not been observed, Ca(BH₄)₂ is reversible and an understanding of its reaction pathways and kinetics may lead to progress with other borohydrides.

5. Kinetics

Preceding discussion shows that recent experimental and theoretical studies have identified promising complex hydride systems with thermodynamic properties and hydrogen storage capacities approaching practical levels. However, most of the predicted reactions suffer from unacceptably poor kinetics, so that achieving fast reversible (de)hydrogenation should now be considered the central challenge in the field. Addressing this challenge requires a sustained focus on gaining a fundamental understanding of reaction mechanisms and rates. Several strategies have been proposed to improve the kinetics of borohydride systems, including the use of catalysts, the design of new reaction pathways, and the optimization of materials properties. These approaches hold promise for achieving reversible solid-state hydrogen storage on practical time scales.
understanding of the detailed atomic-scale kinetic mechanisms involved in the hydrogen release and uptake reactions. First-principles DFT calculations have only recently started to address these important issues, and a complete picture of the hydrogen release process does not exist even for the most extensively studied materials, such as MgH\textsubscript{2} or NaAlH\textsubscript{4}. Researchers have studied select aspects of the complete chain of the microscopic kinetic events that are involved in the hydrogen release process, such as hydrogen dissociation and diffusion [69-71], and direct hydrogen release [72]. Below we give an example relating to mass transport in hydrogen storage materials, which is emerging as the main candidate for the role of the rate-limiting step in the complex hydride reaction kinetics [73,74].

In the prototypical reversible complex hydride, Ti-doped sodium alanate NaAlH\textsubscript{4}, hydrogen release according to reaction (1) is accompanied by long-range diffusion of metal species (Na or Al). Recently, hydrogen-deuterium scrambling experiments suggested that mass transport of the metal species might be the rate limiting step or the dehydrogenation of NaAlH\textsubscript{4} [75]. In Ref. [74], we carried out a first-principles molecular dynamics study of the kinetics of bulk diffusion in NaAlH\textsubscript{4} using the umbrella sampling weighted histogram analysis method [76] to obtain the activation free energies for the bulk diffusion of neutral vacancies in pure NaAlH\textsubscript{4}. This activation energy provides the lower bound on the total activation energy of all bulk diffusion assisted decomposition mechanisms, unaffected by Ti doping in view of the fact that significant bulk substitution of Ti in NaAlH\textsubscript{4} is highly unfavorable [77] and has not been observed [47,78].

We begin by considering the structure of the simplest low-energy charge-neutral defects in NaAlH\textsubscript{4}. Figure 6 shows the calculated structure of neutral AlH\textsubscript{3} and NaH vacancy complexes. It is seen that the introduction of a metal ion vacancy leads to a rearrangement of the coordination of the neighboring AlH\textsubscript{4}\textsuperscript{-} complex anions. Introducing a neutral AlH\textsubscript{3} vacancy results in the formation of an AlH\textsubscript{5}\textsuperscript{2-} moiety in NaAlH\textsubscript{4}, bound to the vacant site by Coulomb attraction due to local excess of Na\textsuperscript{+} ions. Existence of a strong Columbic attraction between the AlH\textsubscript{5}\textsuperscript{2-} complex and the vacancy implies that these defects must diffuse together, which requires a mechanism of changing the orientation of the vacancy-AlH\textsubscript{5}\textsuperscript{2-} pair. According to our AIMD simulations, the extra hydrogen of the AlH\textsubscript{5}\textsuperscript{2-} moiety is very mobile and gets exchanged with the AlH\textsubscript{4}\textsuperscript{-} units surrounding the AlH\textsubscript{3} vacancy about once in every 1 picosecond of simulation at 400 K. This observation implies that the hydrogen ion easily diffuses around the vacancy site, facilitating the re-orientation mechanism required for long-range diffusion of this complex. For the case of a NaH vacancy, two neighboring AlH\textsubscript{4}\textsuperscript{-} tetrahedra start to share a vertex, forming an Al\textsubscript{3}H\textsubscript{7} complex to compensate for the missing H ion (see figure 1 in Ref. [74]). Again, there is a Coulombic attraction between the Al\textsubscript{3}H\textsubscript{7} complex and the Na\textsuperscript{+} vacancy.
requiring that a dynamic process allowing for the shared H ion to travel with the vacancy must accompany the vacancy-mediated diffusion of the Na+ species. The umbrella sampling technique [76] was used to obtain the free energy profiles for the diffusion of both types of neutral defects. The free energy profile for the diffusion of an AlH3 vacancy is shown in figure 6. We find that the free energy barrier for AlH3 vacancy diffusion (12 ± 2 kJ/mol) is in excellent agreement with the anelastic energy loss results of Ref. [79]. The total activation energy for Al mass transport via neutral AlH3 vacancies, which is a sum of vacancy formation and migration energies, is found to be Q=85 kJ/mol H2 [74], in excellent agreement with the experimentally measured activation energies in Ti-catalyzed NaAlH4 of around 80 kJ/(mol H2) [80]. The activation energy for the bulk diffusion via NaH vacancies is found to be significantly higher, Q=112 kJ/(mol H2), and therefore not favored. Our results suggest that bulk diffusion of Al species is the rate-limiting step in the dehydrogenation of Ti-doped samples of NaAlH4. The calculated diffusion coefficient and vacancy concentration at typical decomposition temperatures (D=4×10^-4 cm²/s and C=0.01% at T=400 K) are consistent with the observed dehydrogenation times of minutes to hours in ball-milled Ti-doped powders consisting of micron-sized grains. This study shows that Ti doping is not needed to obtain bulk mass transport at rates that are consistent with the observed dehydrogenation kinetics, and therefore the catalytic effect of Ti is not related to increased concentration of bulk defects and accelerated bulk diffusion [70].

6. Summary
We have demonstrated how a comprehensive first-principles framework involving DFT calculations of total energies and vibrational thermodynamics, efficient algorithms for crystal structure prediction, and thermodynamics-based determination of preferred reaction pathways can be used to discover new materials with superior hydrogen storage thermodynamics. In contrast to earlier studies, which only use information on known compounds [66-68], our methods allow to include new phases with crystal structures that are not yet experimentally measured. This dramatically expands the range of these studies by extending the realm of predictions from reactions with known compounds to reactions with yet-to-be-synthesized ones. Our framework, possibly complemented with other methods for structure prediction (data mining [30], genetic algorithms [31], etc.) should prove very useful for predicting new materials for other methods of energy storage (e.g., electrochemical) that are based on phase transformations between different solid state phases. Kinetics is emerging as the key area where further advances are needed both in methodology and applications. In spite of considerable progress, we do not yet have the ability to determine the microscopic mechanisms and rate-limiting steps in an unbiased and reliable manner without significant input from both the experiment and physical intuition.

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