

IV.I.22 Computational Studies of Hydrogen Interactions with Storage Materials

Chris G. Van de Walle
University of California, Santa Barbara

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Brief Description of Accomplishments

During our second year we have continued to make substantial progress in all areas of the project: interstitial hydrogen in metals, diffusion in metal hydrides, and kinetics of complex hydrides. The overall goal is to elucidate the physics and chemistry of hydrogen interactions with hydrogen storage materials by performing first-principles calculations based on density functional theory (DFT). By specifically addressing the behavior of hydrogen-related and other point defects, we are able to investigate the kinetics of hydrogen uptake and release, the decomposition of complex hydrides, and the effect of adding impurities to the system. Our approach takes into account that defects and impurities in non-metallic systems can occur in charge states other than the neutral state; this important aspect of the problem had not been addressed in previous computational studies performed to date, and our investigations show that it has extremely important consequences for defect concentration and diffusion. Other groups are now starting to apply the same methodology.

Structural optimization, total energy and electronic structure calculations are performed based on DFT using the generalized-gradient approximation (GGA) and the projector-augmented wave (PAW) method as implemented in the VASP code.

Below, we briefly summarize results in each of the main topical areas of the project.

1. Metals: Hydrogen and Vacancies in Al and Mg

Al-based and Mg-based hydrides have great potential as reversible hydrogen storage materials. It is essential to understand the structure and stability of hydrogen as an impurity in the bulk of these materials. Recent theoretical [1,2] and experimental studies [3] indicate that trapping of H at vacancies in Al significantly slows down the diffusion through

the crystal. It has been also suggested that multiple H atoms might be trapped in an Al vacancy, which overcompensates the energy cost to form the defect and could induce superabundant vacancy concentrations and vacancy clustering [4]; this process could potentially play an important role in hydride formation. In the case of Mg, much less is known about H as an impurity and the H-vacancy interaction; a recently published experimental study reports that H have much lower formation energies than vacancies in Mg [5].

The differences between Al and Mg motivated us to investigate and compare the properties of H impurities in Al and Mg. Our calculations build on investigations of isolated interstitial hydrogen, interstitial H_2 molecules, and isolated vacancies in the material. We find that in both materials individual vacancies can in principle host up to two or eight H atoms, not 12 as previously reported [2,4]. The character of the H-vacancy interaction strongly depends on the amount of hydrogen dissolved in the metal, which in turn is determined by the hydrogen chemical potential. We evaluate the concentrations of the relevant hydrogen-vacancy complexes as a function of hydrogen chemical potential, ranging from normal conditions over high pressures to hydrogen plasma. Our analysis reveals fundamental differences between the characteristics of the H-vacancy interaction in Al and Mg: Al shows significant H trapping for low as well as for very high hydrogen chemical potentials, while Mg shows H trapping only at high chemical potentials. However, in Mg a moderate pressure increase of H_2 gas (on the order of 1 GPa at room temperature) is sufficient to induce H-enhanced superabundant vacancy formation, which in Al is possible only at very high hydrogen chemical potentials (as for example obtained with a hydrogen plasma).

2. Metal Hydrides: Point Defects in MgH_2

We are focusing on MgH_2 , a material that is not a suitable storage material in its own right because of unfavorable kinetics. However, it is a constituent of other compound materials that are currently being investigated, and we also feel it can provide useful insights in the fundamental mechanisms of hydrogen kinetics in hydrides.

We have investigated the possible native point defects in bulk MgH_2 . We find that under H-poor conditions the lowest energy defects are positively and negatively charged vacancies (V_H^+ and V_H^-). Under H-rich conditions, the lowest energy defects are V_H^+ , H_i^- , and V_{Mg}^{2-} . We have also calculated interstitial H_2 , which is stable mainly in the neutral charge state, and Mg

interstitials, which are higher in energy than the other point defects. The behavior of V_{Mg} is unusual in that it is amphoteric, i.e., it can act either as a donor or an acceptor. Cation vacancies in ionic materials usually act exclusively as acceptors.

The defects are characterized by unusually large local structural rearrangements, which strongly depend on the charge state of the defect. The hydrogen-related defects are also highly mobile, with migration barriers on the order of 0.1 eV or less for H_i^+ , H_i^- and H_{2i} . Vacancies have somewhat higher migration barriers: 0.38 eV for V_{H}^+ and 0.63 eV for V_{H}^- . The migration barrier for V_{Mg}^{2-} is 0.74 eV. By combining the calculated formation energies with migration barriers, we can estimate activation energies for hydrogen self-diffusion, finding a value of 1.48 eV for V_{H}^+ -mediated diffusion under conditions corresponding to hydrogen desorption; this value falls within the experimentally reported range [6].

3. Complex Hydrides: Alanates

In the area of complex hydrides, we have expanded our studies beyond NaAlH_4 to materials such as LiBH_4 , Li_2NH , and LiNH_2 . In addition, we are investigating not just hydrogen-related but also other point defects, with the goal of elucidating decomposition reactions. We have also performed investigations of various transition-metal additives and their effects on diffusion.

3.a. NaAlH_4

In addition to the studies of hydrogen-related point defects that were previously reported [7], we have performed detailed investigations of the atomic structure of the point defects [8] and compared the results with muon spin rotation experiments [9]. We have also completed a comprehensive study of Na- and Al-related defects in NaAlH_4 . Our analysis indicates that the structure and energetics of these defects can be interpreted in terms of elementary building blocks, which include $V_{\text{AlH}_4}^+$, V_{Na}^- , V_{H}^+ , H_i^- , and H_{2i} . Other point defects, such as V_{Al} , Al_i , and Na_i are found to be less important.

We have calculated formation energies as well as migration barriers for the key defects, in order to compare diffusion activation energies to experimentally measured activation energies of desorption. Our results exhibit some key differences from previous studies [10,11]. As previously reported, migration barriers for hydrogen-related defects are very low. For $V_{\text{AlH}_4}^+$ we find a barrier of 0.46 eV; for V_{Na}^- , 0.41 eV. Based on our calculated numbers, we conclude it is highly unlikely that neutral V_{AlH_3} or V_{NaH} entities would play a role. We argue that $V_{\text{AlH}_4}^+$ and/or V_{Na}^- are the key defects responsible for Al and Na transport. Each of these will not occur on its own, but in combination with one or more hydrogen-related defects; in particular, H_i^- and

V_{H}^+ act as charge-carrying defects that will provide the necessary local charge neutrality. The resulting activation energies are in agreement with experimental observations [12].

Finally, we have completed our study of fluorine and chlorine interactions with NaAlH_4 [13], motivated by the fact that TiF_3 and TiCl_3 are frequently used to introduce Ti into NaAlH_4 . Fluorine substitution for hydrogen has been proposed as a means of destabilizing hydrides, but we find this to be unlikely for either NaAlH_4 or Na_3AlH_6 . Fluorine interstitials are most stable as charged defects; however, their concentration will likely be too low to affect the electronic structure or diffusion of point defects. The migration barrier for interstitial fluorine is low enough to easily allow diffusion during cycling through the hydride phases. Chlorine has a large size mismatch with hydrogen and every chlorine-related defect studied was found to have a high formation energy. Chlorine is therefore unlikely to incorporate in NaAlH_4 .

3.b. LiBH_4

Our calculated atomic and electronic structure of bulk LiBH_4 (space group *Pnma*, 24 atoms/unit cell) is in agreement with previous reports [14,15]. The calculated GGA band gap of LiBH_4 is 7.01 eV; the valence-band maximum (VBM) is dominated by bonding states consisting of B *p* and H *s* states, whereas the conduction-band minimum (CBM) consists predominantly of the anti-bonding state of B *p* and H *s* states plus contributions from Li *s* states. The decomposition process in LiBH_4 can proceed as $\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + 3/2 \text{H}_2$. We therefore assume that the chemical potentials of Li, B, and H can be obtained from the equations that express the stability of LiH, B, and LiBH_4 . The lowest-energy hydrogen-related defects are V_{H}^+ and H_i^- .

We have investigated the atomic and electronic structure of various transition metal impurities in LiBH_4 . Some of the impurities induce a substantial shift in the Fermi level, relative to the value in undoped material. Such a shift will lower the formation energy of charged point defects and thereby enhance the kinetics, as proposed in Ref. [7]. Based on this analysis we are able to identify impurities that would be most effective in enhancing kinetics.

3.c. LiNH_2 and Li_2NH

Bulk LiNH_2 has a tetragonal space group $I\bar{4}$ and 32 atoms/unit cell) [16]; our calculated lattice parameters and formation enthalpy (-2.065 eV/f.u.) are in qualitative agreement with previous work [16-19]. Our new results include an examination of the band structure and density of states. The VBM of LiNH_2 consists predominantly of N *p* states, with some contribution from Li *s* and H *s* states; the CBM consists

predominantly of N p states and some contribution from Li s states. The calculated DFT-GGA band gap is 3.17 eV; the band gap is indirect with the VBM at the M point and the CBM at the Γ point. For bulk Li_2NH we assume a hypothetical orthorhombic phase with space group $Pbca$ and 32 atoms/unit cell [20]. Again, calculated structural properties are in good agreement with previous work [20]. The calculated DFT-GGA band gap is direct, with a value of 2.26 eV.

It was observed by Chen *et al.* [21] that a mixture of LiNH_2 and Li_2NH released hydrogen via a two-step reaction: $\text{LiNH}_2 + 2 \text{LiH} \leftrightarrow \text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 \leftrightarrow \text{Li}_3\text{N} + 2\text{H}_2$. We therefore assume that LiNH_2 is in equilibrium with Li_2NH and LiH , and the chemical potentials of Li, N, and H in LiNH_2 can then be obtained from the equations that express the stability of Li_2NH , LiH , and LiNH_2 . Similarly, the chemical potentials of Li, N, and H in Li_2NH can be obtained by assuming equilibrium with LiH and Li_3N .

For LiNH_2 , we find that the dominant H-related defects are H_i^+ and V_H^- . The Fermi-level position where these two defects have equal formation energies is ~ 2.2 eV. H_i^+ corresponds to the formation on an NH_3 unit. We have also examined Li and NH_2 -related point defects, finding $V_{\text{NH}_2}^+$ and V_{Li}^- to be the lowest-energy ones. The results are qualitatively similar in Li_2NH ; now the Fermi-level position where H_i^+ and V_H^- have equal formation energies is at ~ 1.4 eV. The alignment between hydrogen-related levels in the two materials is consistent if we assume a valence-band offset of ~ 0.9 eV in going from LiNH_2 to Li_2NH . In Li_2NH , $V_{\text{NH}_2}^{2+}$ is lower in energy than $V_{\text{NH}_2}^+$ for relevant positions of the Fermi level. All of these defects are instrumental in diffusion of H, Li, and N.

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List of papers acknowledging DOE support

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1. "Atomic and electronic structure of hydrogen-related centers in hydrogen storage materials", C. G. Van de Walle, A. Peles, A. Janotti, and G. B. Wilson-Short, *Physica B* **404**, 793 (2009).

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1. "First-principles investigations of F and Cl impurities in NaAlH_4 ", G. B. Wilson-Short, A. Janotti, A. Peles, and C. G. Van de Walle, *J. Alloys Compd.* (in press, 2009). (DOI: 10.1016/j.jallcom.2009.04.091).

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1. "Formation and migration of charged native point defects in MgH_2 : First-principles calculations, M. S. Park, A. Janotti, and C. G. Van de Walle (Phys. Rev. B).
2. "Hydrogen interactions with vacancies in Al and Mg: A comparative analysis based on density functional theory", M. S. Park, L. Ismer, A. Janotti, and C. G. Van de Walle (Phys. Rev. B).
3. "Formation and migration of native defects in NaAlH_4 ", G. B. Wilson-Short, A. Janotti, K. Hoang, and C. G. Van de Walle (Phys. Rev. B).

List of people working on the project:

Graduate student:

Gareth B. Wilson-Short; full support, through 03/30/2009.

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Visiting Scientist:

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