IV.I.14 First-Principles Studies of Phase Stability and Reaction Dynamics in Complex Metal Hydrides

PI: Mei-Yin Chou
Georgia Institute of Technology

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Project Description

Complex metal hydrides are believed to be among the most promising materials for developing hydrogen storage systems that are suitable for transportation applications. In order to facilitate the much-needed breakthroughs in this field, we plan to perform extensive theoretical studies on various properties of hydrogen in these complex hydrides. The purposes are: (1) to understand the fundamental science associated with the intrinsic materials properties of these hydrides, the hydrogen absorption and desorption dynamics, and the mechanisms of catalytic reactions; (2) to facilitate materials design and improvement; and (3) to explore novel hydrides with various compositions.

Accomplishments in 2008

(a) Phase Stability of Mixed Alkali Alanates

We have performed first-principles calculations to study the possible alloy phases of mixed sodium and lithium alanates and their structural and energetics properties. For the tetrahydrides, the energetics of the alloy $Na_{1-x}Li_xAlH_4$ is calculated and a small, positive mixing energy less than 5 KJ/mol was found for all values of x, indicating that the alloy is not stable with respect to the end compounds. The equilibrium structure undergoes a transition from a tetragonal structure to a monoclinic structure between $x = 0.25$ and 0.5. Within each structure the cell volume decreases with increasing x, which can be explained by Li having a smaller ion size than Na. In contrast, for the hexahydides $Na_{3(1-x)}Li_{3x}AlH_6$, one stable intermediate compound Na_2LiAlH_6 (x=1/3) is found in agreement with experiment. [J. Alloys Compd., in press]

(b) Local Order in a Mixed Lithium-Magnesium Imide

Recently it was discovered that a total of 5.6 wt% H_2 could be released from the 1:2 mixture of lithium amide and magnesium hydride at temperature as low as 150°C. With a reaction enthalpy of 44 KJ/mol-H_2, this system has high potential for on-board hydrogen storage applications. The fully desorbed product is believed to be a mixed lithium-magnesium imide $Li_2Mg(NH)_2$. Rijssenbeek et al. reported that $Li_2Mg(NH)_2$ has disordered cation and vacancy arrangements at room temperature and above. We have performed first-principles calculations to investigate a series of ordered low-energy configurations for this compound. Specific local orderings are found in the cation vacancy arrangement, shedding light on the experimental disordered structure models. A possible ordered phase at low temperature is proposed based on these local orderings. The similarity and difference of local arrangements among hydrogen, cations, and vacancies are also noted for the three amide/imide systems: $LiNH_2$, $Mg(NH_2)_2$, and $Li_2Mg(NH)_2$. [J. Appl. Phys. **104**, 093619 (2008)]

(c) Special Binding Features in γ-AlH_3

Aluminum hydride (alane) AlH_3 is an important material in hydrogen storage applications. It is known that AlH_3 exists in multiple forms of polymorphs, where α-AlH_3 is found to be the most stable with a hexagonal structure. Recent experimental studies on γ-AlH_3 reported an orthorhombic structure with a unique double-bridge bond between certain Al and H atoms. This was not found in α-AlH_3 or other polymorphs. Using density functional theory, we have investigated the energetics, and the structural, electronic, and phonon vibrational properties for the newly reported γ-AlH_3 structure. The calculation concludes that γ-AlH_3 is less stable than αAlH_3 by 1.2 KJ/mol, with the zero-point energy included. Interesting binding features associated with the unique geometry of γ-AlH_3 are identified from the calculated electronic properties and phonon vibrational modes. The binding of H-s with higher energy Al-*p*, *d* orbitals is enhanced within the double-bridge arrangement, giving rise to a higher electronic energy for the system. Distinguishable new features in the vibrational spectrum of γ-AlH_3 were attributed to the double-bridge and hexagonal-ring structures. [Phys. Rev. B **77**, 014101 (2008)]

(d) Catalytic Effect of Near-Surface Titanium on Hydrogen Interaction on the Al(100) Surface

The critical role played by the Ti catalyst in helping hydrogen cycling in alanates remains a challenging question for this hydrogen storage material. In this study we examine the hydrogen related reactions on an Al surface in the presence of Ti by first-principles density-functional calculations. It is found that a stable alloy $TiAl_3$ is formed near the Al surface with Ti occupying subsurface sites. This subsurface Ti arrangement not only enhances H binding with the Al surface layer, but also improves H mobility on the surface. Moreover, the stability of dissociated H is improved and the dissociation energy barrier is reduced. Based on these results and existing experimental data, we propose that for the dehydrogenation process the catalyst kinetically facilitates the release and decomposition of AlH_3 from solid-state alanates, and for the hydrogenation process the catalyst helps the absorption of hydrogen and the formation of AlH_3 on Al surfaces.

Publications

1. Yan Wang and M.Y. Chou, "Electronic and Vibrational Properties of γ-AlH_3," Phys. Rev. B **77**, 014101/1-8 (2008).

2. Zhu Ma and M.Y. Chou,"Low-Energy Ordered Structures of $Li_2Mg(NH)_2$," J. Appl. Phys. **104**, 093619/1-6 (2008).

3. Zhu Ma and M.Y. Chou, "First-Principles Investigation of Sodium and Lithium Alloyed Alanates," J. Alloys Compd. (in press).

Personnel

Zhu Ma (Graduate student, full support)
Pei Lin (Graduate student, partial support, 50%)
Yan Wang (Research scientist, partial support, 25%)
Fen Zhang (Postdoc, full support)