
First-Principles Studies of Phase Stability and Reaction Dynamics in Complex Metal Hydrides

Mei-Yin Chou

School of Physics, Georgia Institute of Technology
Atlanta, GA 30332-0430, meiyin.chou@physics.gatech.edu

Program Scope

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 create 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

- 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;
- to facilitate materials design and improvement; and
- to explore novel hydrides with various compositions.

We aim to identify and explore materials that have favorable and improved thermodynamic properties by modifications such as alloying and substitution, as well as investigate and understand the mechanisms that improve the kinetics of hydrogen desorption and absorption, such as doping and reduction of the particle size. With the simulations, we will explore and screen the possibilities of forming new complex hydrides with high hydrogen contents from various lightweight metals.

Recent Progress

Lattice dynamics and thermodynamic properties of NaAlH₄

We have performed detailed studies on the lattice dynamics and thermodynamic properties of NaAlH₄ within the density functional theory and pseudopotential methods. The optimal ground-state structure is investigated within the LDA and GGA approaches. The zero-point motion has a considerable effect on the calculated lattice parameters, giving rise to a volume expansion of $\sim 4.4\%$ for both LDA and GGA.

Born effective charges and dielectric permittivities are calculated within the linear response approach. NaAlH₄ exhibits complex vibrational properties at the Γ point. The normal modes are characterized with appropriate assignments within a point group of crystal (4/m). These assignments are related to the mode characters of the T_d point group of individual AlH₄⁻. The four group of normal modes can be identified as: low-frequency

translational modes, librational modes, hydrogen bending modes, and hydrogen stretching modes. The calculated frequencies are in reasonable agreement with the experiment. The phonon dispersion and phonon density of state also show four separate groups of normal modes. The projected phonon density of states indicates that Na and Al atoms are predominantly involved in the low-energy oscillations, while hydrogen motion dominates the three high-energy groups of modes. The total and projected phonon densities of states are shown in Fig. 1.

A number of thermodynamical properties have been calculated. We have used the quasi-harmonic approach estimate the changes of lattice parameters with temperature and the results indicate an expanding lattice on heating. The expansion is anisotropic, and the crystal expands more along axis c than in the perpendicular direction along axes a . The extent of expansion seems to be correlated with the amount of deviation of the c/a ratio from the ideal value of 2.

We have evaluated the mode Grüneisen parameters, an anharmonicity coefficient for individual normal modes, at a grid of \mathbf{k} points in the Brillouin zone. The largest anharmonicity is detected among the low-energy vibrations, while very small values are found for

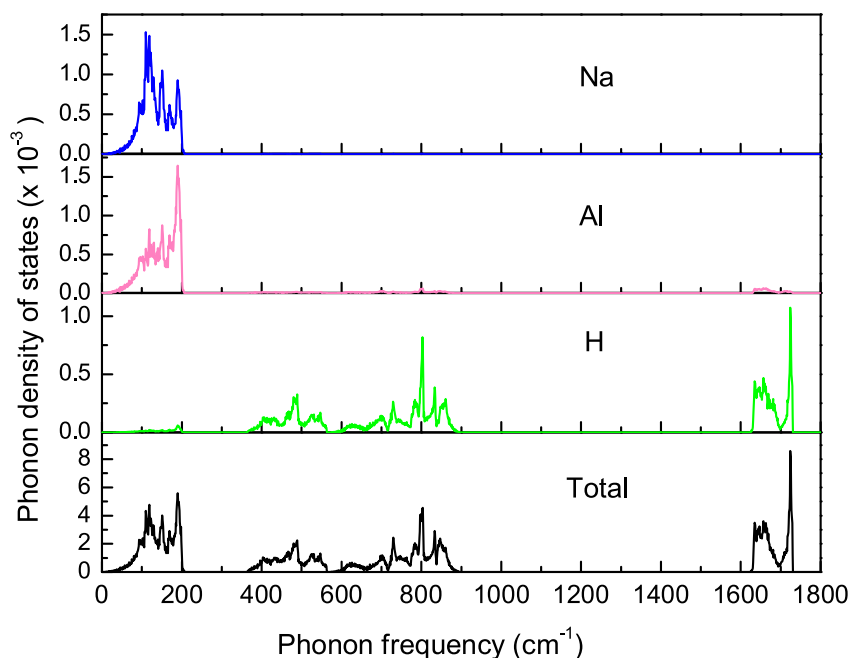


Figure 1: Total and projected phonon density of states calculated using GGA at the theoretical volume.

highest frequency modes. We have also calculated the anharmonic correction to the constant volume specific heat due to thermal expansion. The resulting C_P values for NaAlH_4 up to 300 K compare well with the experiment.

The “mobility” of the species in NaAlH_4 has been studied through the temperature dependence of the atomic mean-square displacements in the NaAlH_4 about their equilibrium position. The results are shown in Fig. 2. A good agreement of Debye-Waller factors with scattering experiments is found. The Lindemann empirical criterion is used to predict a melting temperature, which agrees very well with the observed value. Even at a temperature close to the melting temperature, the thermal energy ($k_B T_m$) is sufficient to excite only the low-energy vibrations involving the translational motion between Na^+ and the AlH_4^- complex. These vibrations are found to be the most anharmonic among all normal modes. This suggests that the melting of NaAlH_4 involves the breakup of lattice periodicity by large displacements of Na^+ and AlH_4^- , while Al remains in a tetrahedral coordination with hydrogen, and the Al-H bond is not broken.

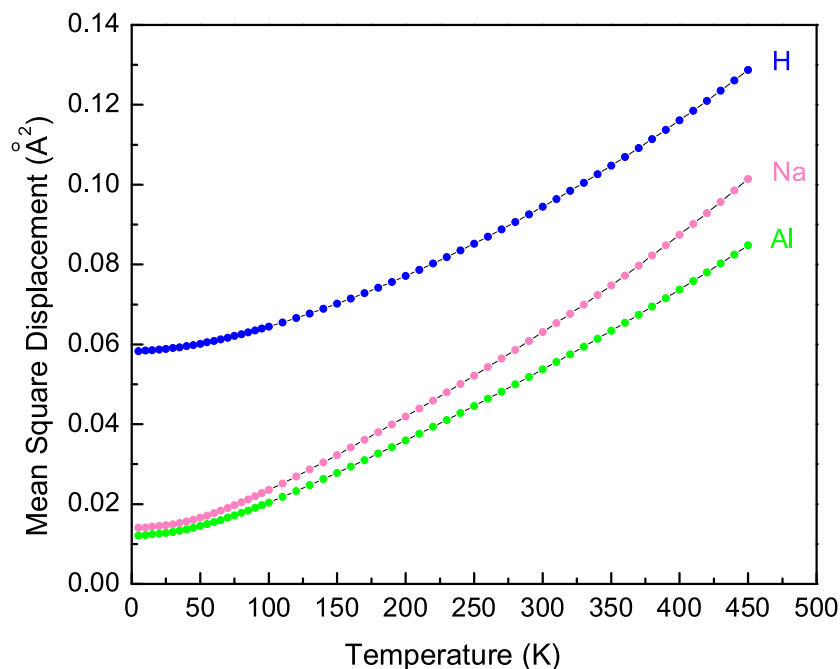


Figure 2: Temperature dependence of the mean square displacements of atoms about their equilibrium positions calculated using LDA.

Future Plans

Although possible mechanisms for the catalyst-assisted desorption process have been proposed in the literature, no definitive experimental conclusion has been drawn despite extensive efforts in the past few years. In general two possibilities exist. The first one is that the catalyst enters the bulk as a dopant and stimulates phase separation and crystal growth inside the material. The second one is that the catalyst does not enter the bulk, but acts as a hydrogen dissociation-recombination site near the surface, and at the same time helps the nucleation of the Al phase. The latter scenario involves a long-range diffusion of certain metal species (possibly in the form of AlH_3) through the alanate to the catalyst near the surface. Our unpublished results do not support the first scenario; therefore, our future plans focus on the surface effects.

Using first-principles simulations, we plan to answer the following questions that will shed light on the mechanism of the catalytic reaction:

1. *If Ti is deposited onto Al surfaces, what is the surface structure and composition ?*
2. *Does this surface facilitate the dissociation of a hydrogen molecule?*
3. *Is the formation of alane oligomers affected by the existence of Ti on the surface?*

Publications

Amra Peles and M. Y. Chou, "Lattice dynamics and thermodynamic properties of NaAlH_4 : Density-functional calculations using a linear response theory," Phys. Rev. B (in press).