Electronic Structure of the Complex Hydride NaAlH₄

A. Aguayo and D.J. Singh

Center for Computational Materials Science, Naval Research Laboratory, Washington, DC 20375
1 also at School of Computational Sciences, George Mason University, Fairfax, VA 22030

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Density functional calculations of the electronic structure of the complex hydride NaAlH₄ and the reference systems NaH and AlH₃ are reported. We find a substantially ionic electronic structure for NaAlH₄, which emphasizes the importance of solid state effects in this material. The relaxed hydrogen positions in NaAlH₄ are in good agreement with recent experiment. The electronic structure of AlH₃ is also ionic. Implications for the binding of complex hydrides are discussed.

The complex hydrides, Aₓ(MH₄)ᵧ, with A=Li, Na, K, Mg, Ca, Sr or a mixture of these and M=B or Al seem promising for H storage since they contain very high weight percent H, and much of the H content can be evolved at moderate temperatures. However, hydrogen desorption from these materials is associated with their melts, and they were long viewed intrinsically noncycable. However, in 1997 Bogdanovic and Schwickardi reported that with certain metal additions, particularly Ti, NaAlH₄ can be cycled. This discovery opened the door for consideration of these complex hydrides as cyleable hydrogen storage materials. However, this result has not been reproduced for other related complex hydrides and understanding of the basic materials properties that govern the uptake of H is still not complete. What is known is that hydrogen desorption from NaAlH₄ takes place via a two step process, forming first Na₃AlH₆, Al and hydrogen, and then NaH and Al metal. Desorption is associated with the temperature where melting occurs. While the Ti addition is often referred to as a catalyst or dopant, the actual role of Ti in enabling the cyclability of NaAlH₄ has yet to be established. Possibilities include catalysis as mentioned, modification of the thermodynamics of the decomposition, i.e. the balance between solid state Ti containing NaAlH₄ and the decomposed NaH - Al - Ti mixture, modification of the microstructure of post decomposition NaH + Al mixture, e.g. by keeping the precipitated Al and the NaH from segregating over large distances, e.g. by enhancing the solubility of Al in NaH or by the formation of Ti-Al alloys, like TiAl₃, instead of precipitated Al, and others.

Developing understanding of the various phases involved will likely be important for sorting out the physics of cycable hydrogen storage in this material. Here we start with the simplest of these phases, NaAlH₄, by using density functional calculations of the electronic structure, in comparison with results for NaH and AlH₃. Conventionally, the bonding in NaAlH₄ is viewed as that of a salt made of Na⁺ cations and AlH₄⁻ anions, with the internal bonding of the AlH₄⁻ units being primarily covalent, consistent with the tetrahedral coordination of Al and what is expected in the liquid. We show that the electronic structure of solid NaAlH₄ is better described as mixed ionic, i.e., Na⁺Al³⁺H⁻. Solid NaH is found to be ionic as expected. AlH₃ is also ionic but with a smaller band gap. The ionic nature of solid NaAlH₄ is understood as a result of long range Coulomb interactions, implying a greater sensitivity of the electronic structure and therefore bonding of H in NaAlH₄ to substitutions and defects, than would otherwise be the case. Further this provides an explanation for the association between the hydrogen desorption and melting.

The present calculations were done within the local density approximation (LDA) to density functional theory, using the general potential linearized augmented plane-wave method with local orbital extensions, as implemented in the WIEN2K code. For consistency, the same LAPW sphere radii of 1.7 a₀ and 1.1 a₀ were used for the metal and hydrogen atoms, respectively, in all three compounds. Well converged basis sets consisting of an LAPW cutoff, kₘₐₓ=5.91 a₀⁻¹ plus local orbitals were used (the effective dimensionless values of the basis cutoff were Rₖₘₐₓ = 6.50 for H and Rₖₘₐₓ = 10.05 for the metal atoms. The Brillouin zone samplings were done using the special k-points method, with 21, 38 and 84 points in the irreducible wedge for NaAlH₄, AlH₃ and NaH, respectively. This was found to be well converged for these insulating materials.

NaAlH₄ occurs in a tetragonal structure (space group I₄₁/a) with lattice parameters a=5.021 Å, c=11.346 Å, and its own structure type, which has two formula units per primitive cell. Recent neutron measurements for NaAlD₄ confirm this structure, with slightly lower lattice parameters, but rather different H positions. NaH occurs in the NaCl structure, with lattice parameter a=4.88 Å. AlH₃ occurs in a rhombohedral structure (space group R₃c or possibly R₃), with hexagonal lattice parameters, a=4.451 Å, c=11.766 Å, and two formula units per primitive rhombohedral cell (from neutron and X-ray diffraction). In general, the structures of hydrides, particularly the H positions, are difficult to determine because the H has a very small X-ray scattering factor and samples can differ in H stoichiometry and ordering. Here we fully relaxed the internal structures using LDA total energies and forces, keeping the pre-

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sumably reliable lattice parameters fixed at the reported experimental values. For NaH there was no relaxation to do because both atoms are on high symmetry sites. For NaAlH$_4$ we obtain positions differing from the positions reported in Ref. 16, but in close agreement with very recent neutron results. The relaxed H positions (Wycoff notation, site $16f$) are $x=0.2364$, $y=0.3906$ and $z=0.5451$ as compared to $x=0.2371$, $y=0.3867$ and $z=0.5454$ from neutron scattering. This structure is illustrated in Fig. 1, which clearly shows the AlH$_4$ building blocks. The Al-H bond length in our structure is 1.652 Å. This is only a little bigger than the sum of the covalent radii of Al and H (0.37Å + 1.18 Å = 1.55Å) and would seem to be a reasonable number for covalently bonded AlH$_4^-$ units. For AlH$_3$ we relaxed in the lower symmetry $R3$ spacegroup considered by Zogal et al. Our positions differ somewhat from the X-ray structure of Ref. 21, but are consistent with the assignment of $R3$ in the absence of H disorder. The Al - H nearest neighbor distance in our structure is 1.731 Å, which is longer than in NaAlH$_4$ and is also longer than the sum of the Al and H covalent radii. It should be mentioned that this Al - H bond length is close to the value of 1.715 Å, from the structure of Turley and Rinn. We also considered $R3$, but obtained no further relaxation (see below).

The calculated LDA band structure and corresponding electronic density of states (DOS) for NaAlH$_4$ is shown in Figs. 2 and 3, respectively. The total DOS is similar to that recently reported by Vajeeston and co-workers, and is also similar to that reported for the related compound LiAlH$_4$. The band structure has a large ~4 eV band gap, separating H derived valence bands from metal derived conduction bands. We emphasize that despite the seeming AlH$_4$ units in the structure, and the expected covalency of such chemical units, the calculated electronic structure is very strongly ionic. In particular, it can be seen from Fig. 3 that the valence bands are strongly dominated by H, while the conduction bands have very much less H character. The valence bands consist of two crystal field split manifolds, each ~3 eV in width. The calculated DOS of NaH and AlH$_3$ are shown in Figs. 4 and 5, respectively, along with the projections onto the H LAPW spheres. Since, the 1.1 a$_0$ spheres are not large enough to fully contain the 1s states of H$^-$ ions, the H projection underestimates that H contribution to the electronic structure. However, the ratio between the projections on H from different energy regions, gives a good indication of the ratio of the H contributions to the electronic structure in those energy regions. The band structure of NaH is also strongly ionic, with a band gap slightly smaller than that of NaAlH$_4$, while AlH$_3$ is also ionic, but has a smaller ~2 eV band gap. The valence band width of AlH$_3$ is ~9 eV. It should be noted that Goncharenko and co-workers, had already conjectured that AlH$_3$ is ionicallly bonded based on its crystal structure.

The reason for the ionic electronic structure of NaAlH$_4$ can be understood as due to the long range Coulomb interaction in solids. This Ewald contribution to the energy favors ionic electronic structures, and is well known to stabilize O$^{2-}$ in metal oxides, for example, even though dimers and small molecules with the same metal - O neighbors may be covalent. Here H$^-$ is stabilized in this way. In metal oxides, especially when there is some covalency between the O and nominally unoccupied metal orbitals, the O$^{2-}$ ions are highly polarizable, as may be expected from the fact that O$^{2-}$ outside the Coulomb field of the solid is not a stable ion. Following the arguments of Cohen, which related ferroelectricity in oxide perovskites to ionic electronic structures with weak covalency of this type, and considering the electronic structure of AlH$_3$, it seemed worthwhile to check if ferroelectricity is present. Accordingly, we made small displacements of the atoms away from the relaxed positions within the reduced symmetry non-centrosymmetric spacegroup $R3$ and calculated the restoring forces. However, no ferroelectric instability was found within this symmetry.

Returning to the bonding of NaAlH$_4$, we note some expected consequences of the ionic electronic structure. First of all, since the bonding is stabilized by long range interactions, rather than primarily short range Al-H covalent bonds, it should be more sensitive to stoichiometry, defects, lattice parameter changes and off-site substitutions, than in a salt made of strongly covalent AlH$_4^-$ units. This implies tunability of the hydrogen binding, e.g. by alloying, which in turn would offer tunability of the thermodynamic balance between the solid and the dehydrided NaH + Al mixture. Secondly, it provides a natural explanation of why the hydrogen desorption is strongly connected with melting. Presumably, melting involves disruption of the H lattice and with it a loss of the long range Coulomb stabilization of the H$^-$ ions. The resulting loss of binding at melting then would result in H release from the material. Finally, we note that while our calculations are specific to NaAlH$_4$, the DOS of LiAlH$_4$ is qualitatively similar, suggesting that similar physics may be operative there and in other related complex hydrides.

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In terms of rhombohedral lattice vectors, our relaxed structure for AlH$_3$, has Al at (0,0,0) and (1/2,1/2,1/2) and H at (0.751,0.389,0.111). The lattice vectors are \((\alpha, \beta, \beta)\), \((\beta, \alpha, \beta)\) and \((\beta, \beta, \alpha)\), with \(\alpha=4.3626\,\text{Å}\) and \(\beta=1.2153\,\text{Å}\).

FIG. 1. Crystal structure of tetragonal NaAlH$_4$ with the relaxed atomic positions. The small spheres are H, the large dark spheres are Na and the large light spheres are Al.

FIG. 2. LDA band structure of NaAlH$_4$ with the relaxed crystal structure. The band gap is between a H derived valence band and metal derived conduction bands.
FIG. 3. Electronic density of states and projection onto the H LAPW spheres for NaAlH$_4$, on a per formula unit basis. Note the ionic nature shown by the very different hydrogen contributions to the valence and conduction bands.

FIG. 4. Electronic density of states and projection onto the H LAPW sphere for NaH.

FIG. 5. Electronic density of states and projection onto the H LAPW spheres for AlH$_3$, on a per formula unit basis, using the relaxed crystal structure. Note the smaller band gap but still ionic nature.