Comment on “Structural Stability and Electronic Structure for Li$_3$AlH$_6$”

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Density functional calculations of the electronic structure are used to elucidate the bonding of Li$_3$AlH$_6$. It is found that this material is best described as ionic, and in particular that the [AlH$_6$]$^{3-}$ units are not reasonably viewed as substantially covalent.

Vajeeston and co-workers (VRKF, Ref. 1), recently presented a detailed pioneering study of the electronic structure and structural phase changes under pressure for Li$_3$AlH$_6$. The complex hydrides, $A_x(MH_4)_y$, 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.\cite{2-5} Further, in 1997 Bogdanovic and Schwickardi reported that with certain metal additions, particularly Ti, NaAlH$_4$ can be cycled.\cite{2} However, this has yet to be achieved with other members of this family. Better understanding of the bonding, chemistry and thermodynamics of these hydrides is clearly needed in searching for other cyclable members of this family. Understanding the properties of Li$_3$AlH$_6$ is of importance because of its place as the intermediate product in the decomposition of LiAlH$_4$. In fact, NaAlH$_4$ follows a similar decomposition pathway, with Na$_3$AlH$_6$ as an intermediate product.

Based on their calculations, VRKF conclude that “energetic degeneration of Al-$p$ and H-$s$ states together with the spatially favorable constellation of Al and H favors covalent bonding between Al and H” and that “[AlH$_6$]$^{3-}$ forms distinct covalently bonded units”. Here results of density functional calculations, showing this not to be the case are presented. It is argued instead that Li$_3$AlH$_6$ is best viewed as an ionic solid, nominally Li$_7$Al$_{3+}$H$_6$.\cite{6}

The present calculations were done within the local density approximation (LDA) to density functional theory, using the general potential linearized augmented planewave (LAPW) method with local orbital extensions.\cite{6,7} The convergence was checked by doing calculations with various basis set sizes and Brillouin zone samplings. The LAPW method uses as decomposition of space into atom centered spheres and an interstitial. The sphere radii are constrained by the requirement that they be non-overlapping and that core states do not significantly spill into the interstitial. H LAPW sphere radii ranging from 1.1 $a_0$ to 1.55 $a_0$ were tested and the results were found to be insensitive to this choice.

Combined synchrotron X-ray and neutron diffraction experiments have shown that Li$_3$AlD$_6$ occurs in space-group $R3$, $a=8.07117$ Å, and $c=9.5130$ Å.\cite{8} This structure is near cubic. The rhomboedral setting has $a=5.636$ Å, and rhomboedral angle 91.45°. Experimental and calculated structural coordinates in this setting are given in Table I. As may be seen, these are very close, and in particular the calculated Al-H bond length in good agreement with experiment [1.736 Å and 1.734 Å (the same to within the precision of the calculation) vs. experimental values of 1.754 Å and 1.734 Å, for H1-Al1 and H2-Al2, respectively]. In this setting the Al are at the corner and body centered positions and are octahedrally coordinated by H; the Li occur near the (1/2,0,1/4) positions, and are coordinated by distorted H octahedra. This structure in itself is not particularly suggestive of covalency.

The calculated electronic density of states (DOS) and projections onto the H LAPW spheres for the experimental crystal structure are shown in Fig. 1. The DOS for the LDA atomic positions is practically the same and agrees in its large features with that of VRKF. It shows three distinct manifolds of states. The two occupied manifolds are a group of “split-off” bands, containing a total of 2 electrons per formula unit (4 per cell) at about -7 eV, relative to the valence band maximum and a broader manifold containing 10 electrons per formula unit. This latter manifold is almost split by a pseudogap (at -2 eV) into a lower group of bands containing 6 electrons and an upper group containing 4 electrons per formula unit. These valence bands are in turn separated by a ~ 3 eV band gap from the conduction states. The simplest covalent picture of an [AlH$_6$]$^{3-}$ unit would have 6 H 1s orbitals, 1 Al s orbital and 3 Al $p$ orbitals. The Al $s$ orbital, if weakly hybridized, could form a “split-off” state holding 2 electrons per formula unit. The remaining orbitals, would then form three manifolds of 6 electrons each: a lower bonding group, a non-bonding group, and an upper antibonding group. Since Li$_3$AlH$_6$ has 12 electrons per formula unit, the Fermi energy in this scenario would intersect the non-bonding bands, yielding a metal or perhaps a Mott insulating ground state. This is hardly consistent with the calculated DOS. Furthermore, if the covalency were strong, one would expect H character to be distributed between the three $s$-$p$ manifolds. However, as may be seen from the projections of the DOS, there is very much more H $s$ character in the valence bands than in the conduction bands. Furthermore, the “split-off” manifold has approximately the same proportion of H $s$ character as the main valence band manifold.
The simplest ionic picture would have full H\(^-\) ions stabilized by the Coulomb field. In this picture, one would expect to have occupied H s derived valence bands accommodating the 12 electrons per formula unit, separated by an insulating gap from metal derived conduction bands. Interactions between the 6 hydrogens in the octahedron, which could be direct or via assisted hopping using unoccupied Al s d orbitals, would break the occupied H bands into a symmetric (s) combination (2 electrons), a \(t_{2g}\) combination (6 electrons) and an \(e_g\) combination (4 electrons), consistent with the shape of the DOS. In this case, the valence DOS would be dominated by H s character and the conduction bands would have much less H s character.

To better assess the correspondence between this ionic scenario and the calculated electronic structure, we did atomic calculations in the LDA for H\(^-\) stabilized by a Watson sphere, charge +e and radius 3.06 \(a_0\), which is slightly smaller than the average H-AI distance (3.30 \(a_0\)). The density profile of this ion is shown in Fig. 2. A sphere of radius 1.1 \(a_0\) would contain only 0.45 e for this large ion, while 0.60 e is in a 1.3 \(a_0\) sphere. As mentioned, it is not possible to use a sufficiently small Al LAPW sphere to exclude H character and reflect only the Al states. However, since H has no core electrons, we do use small H spheres. In this case, it may be expected that the s projection in the H sphere would represent primarily the H s contribution. Integrating the H s projection of the DOS over the occupied valence band, it is found that there are 0.54 e per H inside 1.1 \(a_0\) LAPW spheres and 0.71 e per H inside 1.3 \(a_0\) spheres. So the total DOS, the 1.3 \(a_0\) H projection and the 1.1 \(a_0\) projection are in a ratio of 12 : 4.3 : 3.2, which is reasonably close to 12 : 3.6 : 2.7 for six isolated Watson sphere stabilized H\(^-\) ions, and lends support to the present ionic view of the bonding. This is similar to the argument that was used to support an ionic picture of the bonding in NaAlH\(_6\).\(^9\)

In other materials, core level shifts can be used to evaluate the ionic character. This is not generally possible in hydrides because H has no core levels. However, as a further test, we performed a calculation with the position of one Li in the unit cell (6 Li and 12 H total) exchanged with a H. In either a covalent or an ionic picture this would be highly energetically unfavorable, both because of the unfavorable bond length, and because of the breaking of bonds in the covalent case, and the placing of Li on an anion site in the ionic case. Indeed it is found that this is highly unfavorable (by 0.76 Ry, unrelaxed). However, significantly, the 1s core level of the substituted Li is at 4.1 eV higher binding energy (lower energy) than the other five Li ions in the cell. This large shift, which reflects the Coulomb potential, clearly shows that the H site is an anion site.

The reason for the ionic electronic structure of Li\(_3\)AlH\(_6\) 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 \(O2^+\) 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.

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| Atom | x     | y     | z     |
|------|-------|-------|-------|
| Li (EXP) | 0.5595 | 0.0651 | 0.2487 |
| Al1 (EXP) | 0.0000 | 0.0000 | 0.0000 |
| Al2 (EXP) | 0.5000 | 0.5000 | 0.5000 |
| H1 (EXP) | 0.0731 | 0.2950 | 0.9340 |
| H2 (EXP) | 0.4138 | 0.2080 | 0.5482 |
| Li (LDA) | 0.5627 | 0.0695 | 0.2486 |
| Al1 (LDA) | 0.0000 | 0.0000 | 0.0000 |
| Al2 (LDA) | 0.5000 | 0.5000 | 0.5000 |
| H1 (LDA) | 0.0707 | 0.2960 | 0.9323 |
| H2 (LDA) | 0.4118 | 0.2048 | 0.5496 |
FIG. 1. Electronic density of states [solid line] and $s$ projection onto the H LAPW spheres, radius $1.3 \ a_0$ ($1.1 \ a_0$), [dashed (dotted) line] for Li$_3$AlH$_6$, in eV$^{-1}$ on a per formula unit basis using the experimental crystal structure. The valence band maximum is at 0 eV. Note the ionic nature shown by the very different hydrogen $s$ contributions to the valence and conduction bands.

FIG. 2. LDA charge distribution of a H$^-$ ion stabilized by a Watson sphere (see text). The charge is defined as $q(r) = 4\pi r^2 \rho(r)$, where $\rho(r)$ is the density and $r$ is the radius in Bohr.