Periodic band calculation on low index surfaces of crystalline LiAlH$_4$

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Abstract

The low-index surfaces (001), (010), (100) and (101) of crystalline LiAlH$_4$ have been studied by periodic density functional calculations within the generalized gradient approximation. The most stable surfaces have been identified by calculating the surface energy; the results show that there are several different surfaces that are equally stable, with both Li, Al, and a mixture at the surface. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

The search for lightweight metal hydrides for reversible hydrogen storage entered a new stage when Bogdanovic et al. found that the hydrogenation of NaAlH$_4$ can be made reversible by addition of small amounts of Ti, making more than 5 wt.% hydrogen reversibly available [1]. The theoretical capacity of LiAlH$_4$ is even larger, with 7.9 wt.% hydrogen available below 200 °C. The addition of Ti as a catalyst has made it possible to extract up to 2 wt.% reversibly from Li$_3$AlH$_6$ [2], but it still remains to be shown that reversibility may be achieved from LiAlH$_4$.

A scanning electron microscopy study has shown significant elemental segregation on the surface of the fully desorbed material when starting from NaAlH$_4$, and the same study also found that the catalyst (Ti) was clearly chemically associated with Al at the surface. No corresponding studies have to our knowledge characterized the surface of LiAlH$_4$ before or after hydrogen desorption, and not very much is known about the phase transformations and microscopic properties of the material.

The bulk structure of LiAlH$_4$ has recently been thoroughly studied by XPD and NPD, and the space group has been determined to be $P2_1/c$ with $a = 481.74$, $b = 780.20$, $c = 782.14$ pm and $\beta = 112.228°$ at 8 K [3]. The bulk unit

cell consists of four formula units of LiALH$_4$, that is 24 atoms. The AlH$_4$ units form slightly deformed tetrahedra, which are linked via the Li atoms.

2. Method

Our calculations are performed using ADF-BAND [4,5], employing the generalized gradient approximation (GGA) due to Becke [6] and Perdew [7]. The one-electron basis sets representing the electron density consist of both Herman–Skillman numerical atomic orbitals (NAO) and Slater-type orbitals (STO), with a frozen core. Scalar relativistic corrections have been included through the zeroth order regular approximation [8]. Our slab calculations use two-dimensional translational symmetry. All important numerical parameters have been checked, and the overall convergence is well within 0.1 eV in all our results.

We have studied the four low-index surfaces (001), (010), (100) and (101), shown in Fig. 1. They form together a representative choice of surfaces, from the most close-packed surface of this compound (101) to one of the most open surfaces (010). The (001) and (010) surfaces only contain one metal atom per surface unit cell, while the (100) surface contains two atoms of the same kind. The close-packed (101) surface contains four metal atoms, two of each kind. This gives the possibility of making three different slabs of the three primary faces: one with two

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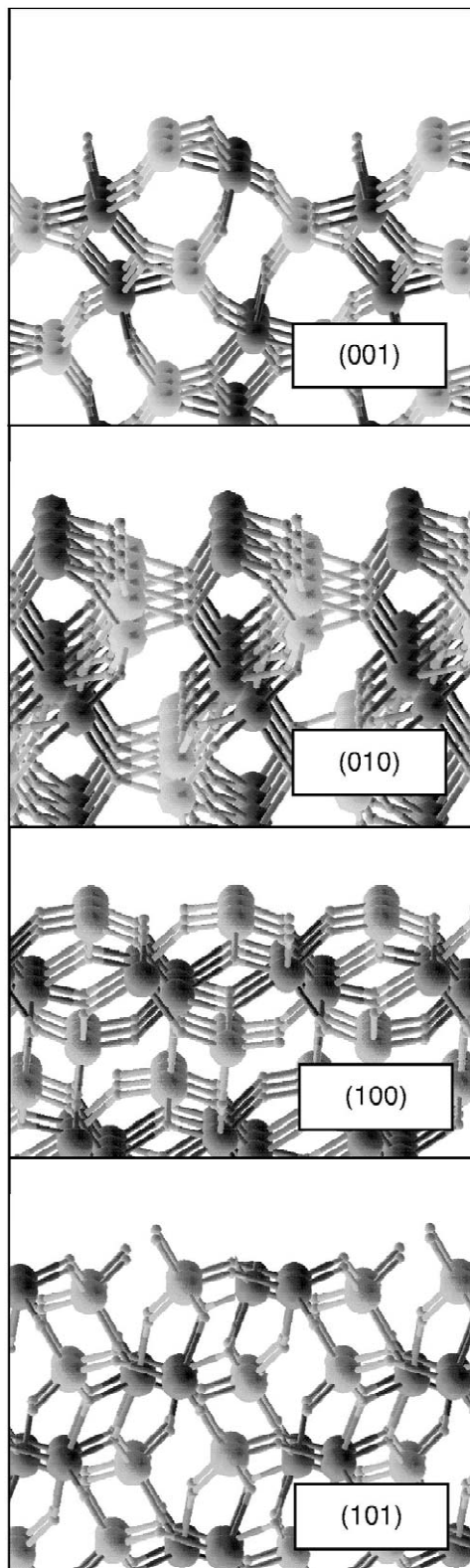*E-mail address:* o.m.lovvik@fys.uio.no (O.M. Løvvik).

Al-rich surfaces, one with two Li-rich surfaces, and a slab with one surface being Al-rich and the other Li-rich. The (101) slabs, on the other hand, only have surfaces consisting of both Al and Li. When forming the slabs, we have kept the AlH_4 tetrahedra intact, so that the only bonds being broken are Li–H bonds. We have performed tests showing that breaking Al–H bonds is much more difficult, and gives consistently less stable geometries.

3. Results

The surface energy of a crystal may be calculated by the following formula:

$$E_{surf} = \frac{1}{2}(E_{slab} - N_{layers}E_{bulk}) \quad (1)$$

where E_{slab} is the cohesive (or total) energy of a slab with N_{layers} layers, and E_{bulk} is the corresponding energy in bulk of a surface layer unit. To be consistent, we define one layer to consist of one formula unit, so that some layers may contain more than one physical layer.

It is well known that the formula above diverges linearly as the number of layers increases if the true bulk energy is used, so it is usually more safe to represent the bulk energy by a linear fit to the difference in energy between two successive layers $E_{diff}(N_{layers})$ [9,10]. However, the surfaces being built in this study are much more complex than the simple metallic surfaces of Refs. [9,10], and E_{diff} does not converge rapidly towards a distinct value. An example of this is E_{diff} for the (010) surface, which is plotted in Fig. 2. We have therefore chosen to use the bulk energy in Eq. (1). To be sure that we have not been affected by the linear divergence that is possible when using this method, we

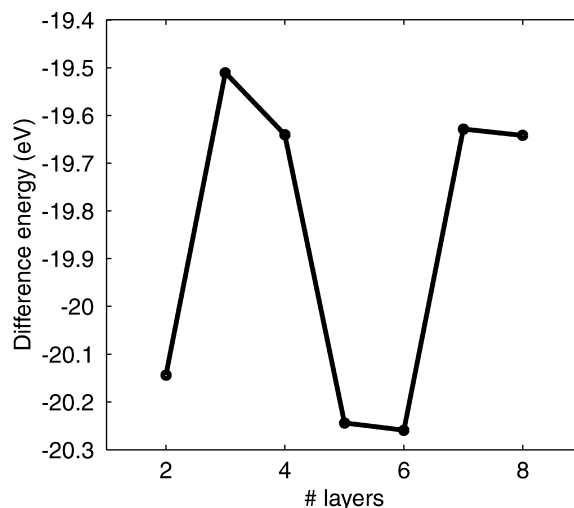Fig. 1. Sideview of the four surfaces being studied: (001), (010), (100) and (101).

Fig. 2. Difference in cohesive energy between two successive layers for the (001) slabs with both an Al- and a Li-rich surface as a function of the number of layers of the largest slab.
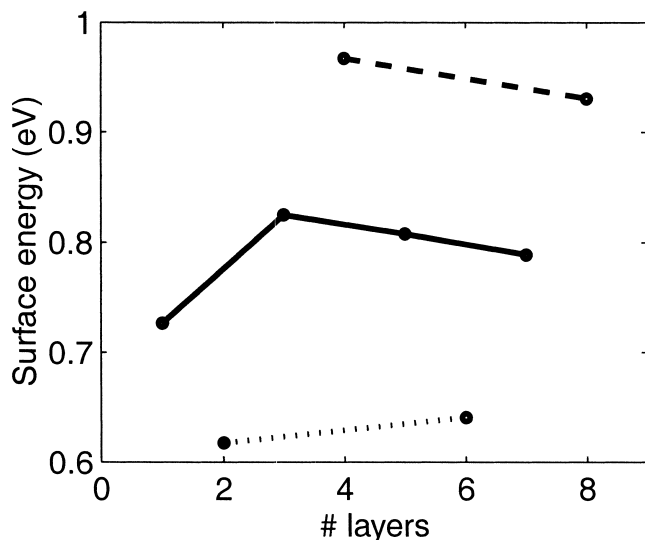
Fig. 3. Calculated surface energy for the (001) slabs with both an Al- and a Li-rich surface as a function of the number of layers.

have checked our results towards other methods for all the slabs, and no sign of linear divergence was found.

When the resulting surface energy from the above method is plotted, however, we find that it is strongly oscillating, as shown for the (001) slabs with both Al- and Li-rich surfaces in Fig. 3. The reason for these oscillations is the relatively large unit cell of $LiAlH_4$, giving three different ways of creating slabs with both kinds of surfaces. The first is by using the full unit cell, which gives any whole multiple of four layers. The second is by using a half unit cell in addition to full ones, which gives 2, 6, 10, etc. layers. The last possibility is to use single layers in addition to the above possibilities, giving an odd number of layers. We have connected these three possibilities by a dashed, solid, and dotted line, respectively, in Fig. 3, and then we see that the surface energy behaves quite smoothly for each of the possibilities. We have in what follows included the lowest surface energy for each of the different surfaces.

The resulting surface energies are shown in Table 1. We see that the three most stable surfaces (with the lowest surface energy) are the Li-rich (010) surface, the Al-rich (100) surface, and the (101) surface with both Al and Li.

Table 1
Calculated surface energy (J/m^2) for the various surfaces studied in this work

Surface	001	010	100	101
Al-rich	0.292	0.544	0.205	
Li-rich	0.292	0.195	0.680	
Al+Li	0.428	0.285		0.267

This is quite surprising; no clear trend is found, and the three most stable surfaces represent almost all possible different surfaces—from open to close-packed, and from Al- to Li-rich via the intermediate surfaces. It is nevertheless possible to understand the most important parts of the trend by a simple count of the number of Li–H bonds that are broken upon formation of the different surfaces. For instance, at the (010) surface, the minimal number of broken bonds is 8, 9 and 10 for the Li-rich, mixed, and Al-rich surface, respectively. Thus it is not surprising that the Li-rich surface is the most stable of the three possible (010) surfaces.

4. Conclusions

Various surfaces of $LiAlH_4$ have been studied by the density functional theory within the generalized gradient approximation. The surface energy has been calculated for each surface by varying the number of layers of the slabs representing the surfaces. It was found that the three most stable surfaces represent a wide variety of the possibilities present in this system: the open and Li-rich (010) surface, the medium packed and Al-rich (100) surface, and the close-packed (101) surface with both Al and Li at the surface. This was most readily explained by the number of broken Li–H bonds upon formation of the different surfaces.

Acknowledgements

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