



Novel Nano Composites for  
Hydrogen Storage Applications

Project acronym: NANOHy

EC contract #210092

Theme 5

Energy

Collaborative project

## **Report on Deliverable D 2.1**

Start date of Project: 1.1.2008

Duration: 45 months

Date of preparation: 30.11.2008

Dissemination status: public

Co-ordinator: Maximilian Fichtner, Forschungszentrum Karlsruhe GmbH, Institute for  
Nanotechnology

## Deliverable D 2.1 (M 12)

### Equilibrium geometry of nanophases

Ponniah Vajeeston, Helmer Fjellvåg  
University of Oslo

#### Abstract

The possible low energy surfaces and stability of nano-clusters and nano-whiskers were investigated using *ab initio* total energy calculations. The calculated surface energy of the low-index surfaces shows that the (010) surface is the most stable surface in LiBH<sub>4</sub>. We predicted that the critical size of the nano-cluster and nano-whisker of LiBH<sub>4</sub> is 1.75 and 1.5nm, respectively. If one reduces the diameter below these critical sizes the stability of the cluster/nano-whisker is drastically reduced. This is an important hint for the design of nanoconfined and destabilized complex hydrides.

We have identified that in such objects most of the atoms are exposed to the surface. The bonding interactions in surface layers are considerably weaker than that at the centre of the cluster/whisker. As a result, one can expect that the removal of hydrogen from the surface of the nanophases is much easier than that from the bulk or from the inner part. In order to use LiBH<sub>4</sub> as a hydrogen-storage material, one must reduce the particle size below the critical diameter.

Application of pressure on AlH<sub>3</sub> makes a sequence of phase transitions from  $\beta \rightarrow \alpha' \rightarrow \alpha \rightarrow$  hp1 (P63/m)  $\rightarrow$  hp2 (Pm $\bar{3}$ n) modification, and the estimated transition pressures are 2.4, 4.3, 64, 104 GPa, respectively.

#### 1. Theoretical investigation on nanostructures of LiBH<sub>4</sub>

##### i) Low energy surfaces

At ambient conditions LiBH<sub>4</sub> crystallizes with an orthorhombic structure ( $\alpha$ -LiBH<sub>4</sub>) in which each [BH<sub>4</sub>]<sup>-</sup> anion is surrounded by four lithium Li<sup>+</sup> cations and each Li<sup>+</sup> by four [BH<sub>4</sub>]<sup>-</sup>, both in tetrahedral configurations. In this study we have concentrated on ambient condition  $\alpha$ -LiBH<sub>4</sub> phase. The possible low energy surfaces were identified with the help of Bravais-Friedel Donnay-Harker (BFDH) method implemented in MS Modeling package (version 4.2).

This information has been used to pre-screen the list of faces used as an input to more sophisticated VASP calculations. According to the BFDH calculation (001), (101), (100), (201), and (111) are possible low energy surfaces. In order to validate the BFDH method, we have also cleaved other possible low index (010), (011), and (110) surfaces. The surface energy of a crystal can be calculated using the following equation

$$E_{surf}(n) = [E_{tot}(n) - E_{bulk}(n)]/2A \quad (1)$$

where  $E_{tot}$  and  $A$  are the total energy and total surface area, respectively.  $E_{bulk}$  refers to the energy of the bulk  $\alpha$ -MgH<sub>2</sub> system containing the same number of molecular units in the slab. Since the constructed supercell of slab has two surfaces, the energy difference is normalized by twice the area of each surface. The calculated surface energies vary from 0.11 to 1.2 J/m<sup>2</sup> (depending upon the surface) and the magnitude are in the following sequence: (010) < (101) < (100) < (011) < (111) < (201) < (110) < (001). Further the calculations show that the surface energy is almost the same for (010), (100), and (101) surfaces with the variation with respect to (010) is only 0.005 and 0.002 J/m<sup>2</sup> for (100) and (101) surfaces, respectively. The low surface energy of these surfaces indicates that the energy cost to create these surfaces is much less than that in  $\alpha$ -MgH<sub>2</sub>. [1] From our theoretical investigation, we found that BFDH method is not sufficient to find a correct low energy surface of the materials. In order to identify the correct low energy surfaces one must perform *ab initio* total energy calculations for all possible surfaces.

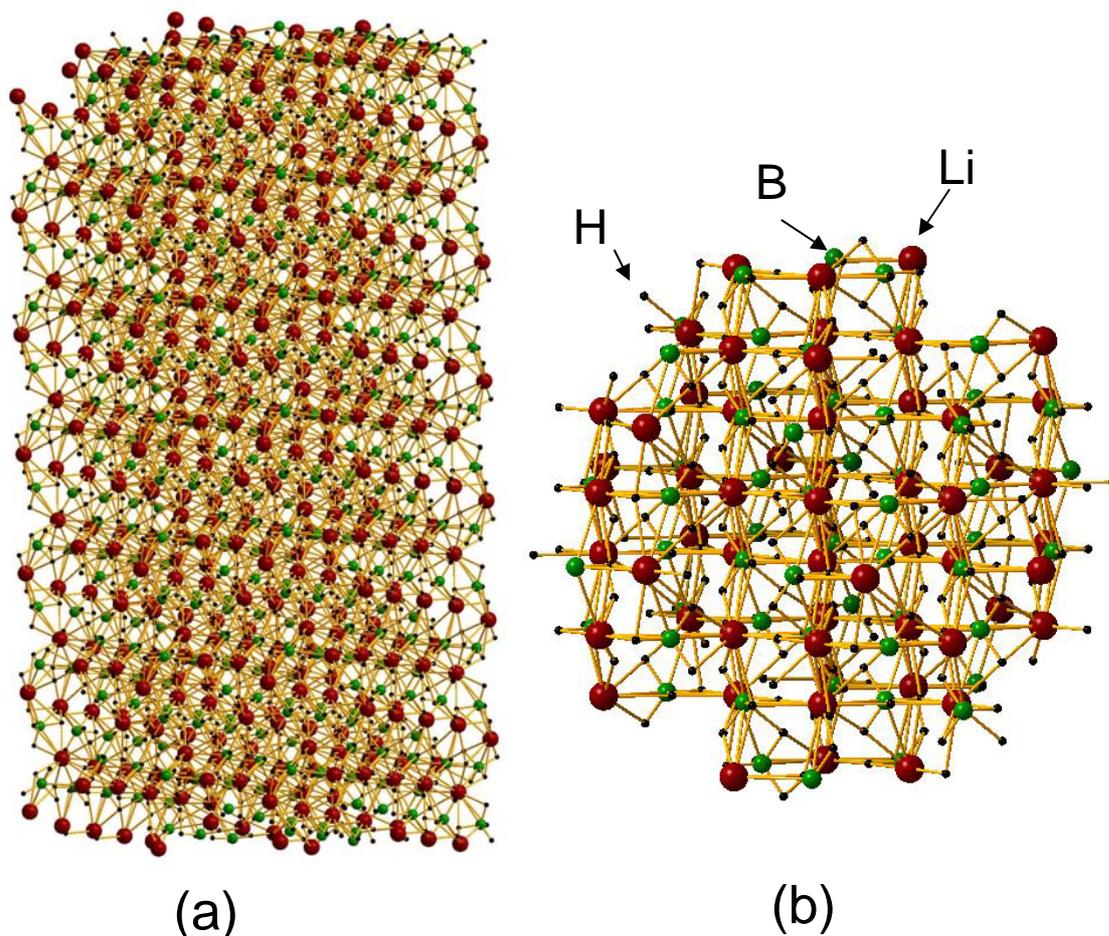


Fig. 1: Optimized stable (a) nano-whiskers and (b) nanocluster of  $\text{LiBH}_4$  derived from  $\alpha\text{-LiBH}_4$  structure.

## ii) Critical particle size

The calculated total energy as a function of the cluster size shows that (see Fig. 2), if the cluster size decreases, the total energy becomes more positive (i.e. the formation energy decreases with decrease of cluster size). In particular there is a steep increase in the total energy when the size of the cluster is below 1.75 nm. Similarly, the calculated total energy as a function of nano-whisker diameter shows that (not shown in figure), when we reduce the diameter below 1.5 nm the nano-whiskers become highly unstable. If one reduces the cluster size and nano-whisker diameter, the formation energy of the clusters/nanowhisker becomes less negative indicating that one can destabilize  $\text{LiBH}_4$  by preparing it in nanophases. This is a good indication for reducing the decomposition temperature which is desired to utilize complex hydrides for energy storage applications. The surface-to-volume ratio increases upon decreasing the cluster/nanowhisker size. Since the surface atoms have a lower coordination, the average number of bonds is lower for smaller clusters.

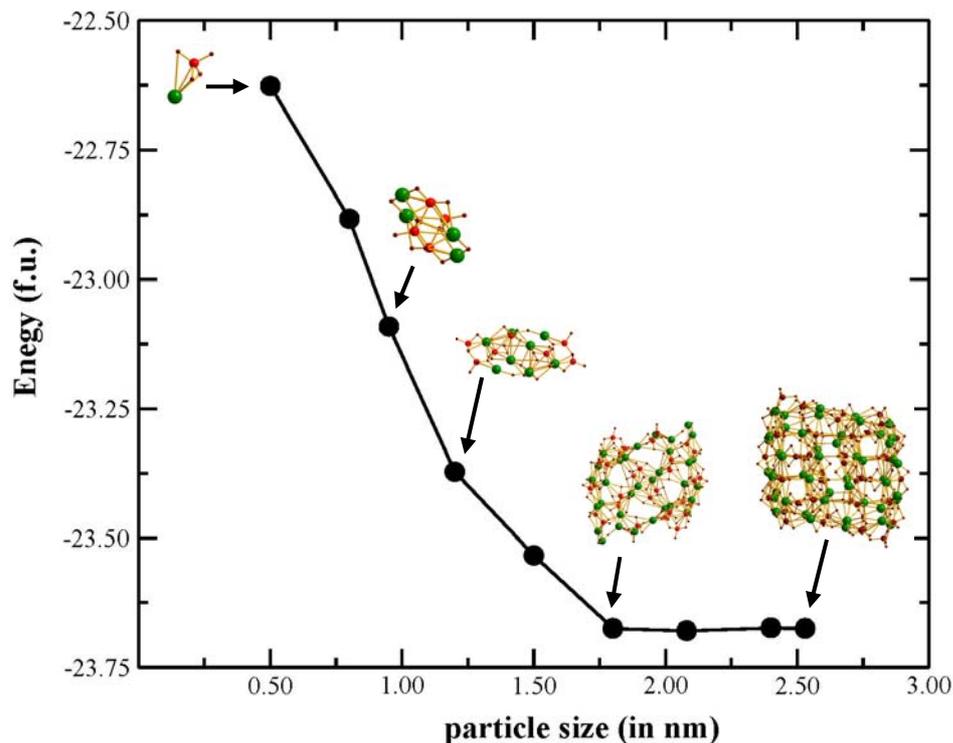


Fig. 2: Calculated total energy (in eV/f.u.) as a function of  $\text{LiBH}_4$  cluster size (in nm).

Moreover, in ultra small clusters and whiskers, the hydrogen atoms are generally found to occupy the less stable top and bridge sites at the surfaces compared to the more stable three-dimensionally coordinated sites commonly found in thicker clusters/whiskers (diameter above 1.75/1.5 nm respectively). The calculated B-H distances versus number of bonds (see Fig.3) for the biggest clusters/whiskers indicate that the values are very scattered compared to that in the bulk phase. Especially several B-H bonds have longer bond distances than that in the bulk.

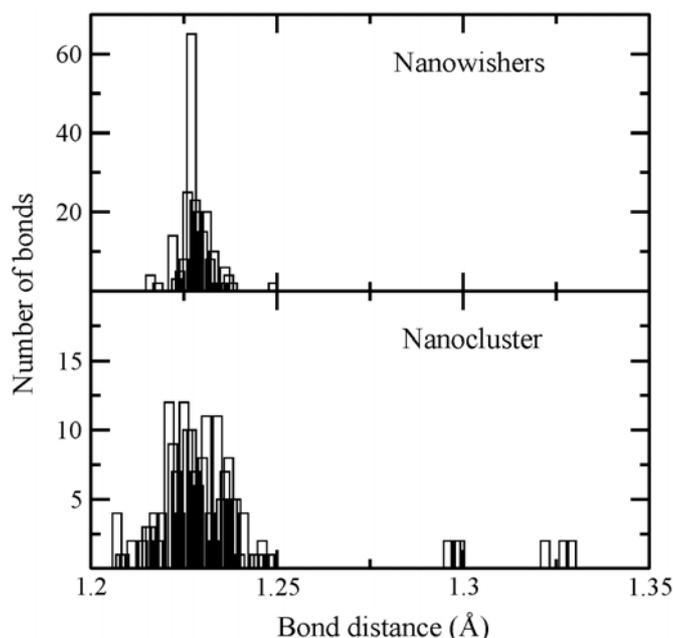


Fig. 3: Calculated interatomic distances between B and H in the optimized  $\text{LiBH}_4$  nano-clusters and whisker. Arrow mark indicates the theoretical B-H distance for the bulk  $\text{LiBH}_4$  phase.

### iii) Hydrogen site energy

Once we increase the cluster or nanowhisker size above the critical size these nano objects will have core  $\text{LiBH}_4$  structural units which makes them quite stable. Hence, one must reduce the particle size beyond the critical size in order to easily remove the H from the  $\text{LiBH}_4$  particles. To substantiate this observation we have calculated the H site energy (HSE;  $\Delta E$ ) in these nanophases. In the nanoclusters/whisker H is situated in four different chemical environments; viz., at the surface: H1 (in between Li); H2 (between Li and B) H3 (H connected with B); and H4 (center of the cluster). The H site energy is calculated in the following manner

$$\Delta E = E_{H_{vac}} - (E_{nano} + 1/2 E_{H_{mol}}) \quad (2)$$

where  $E_{H_{vac}}$  and  $E_{nano}$  refers to the energy of the nano object with and without H vacancy,  $E_{H_{mol}}$  is the total energy of a free  $\text{H}_2$  molecule calculated in a large box. The calculated HSE for clusters/whiskers in H1, H2, H3 and H4 sites are 8.93, 13.10, 30.26, and 52.96 kJ/mol, respectively. The corresponding HSE value in the bulk phase is 54 kJ/mol. This clearly indicates that the energy required to remove H from the centre of the nanophase (cluster/whisker) is similar to that in the bulk material. Moreover the small value of hydrogen

site energy in the surfaces of the nanophases compared to that in bulk material indicates that, one can remove hydrogen relatively easily from the nanophases. Similar to the bulk phase all the studied nanophases and the surfaces also have non-metallic character and the calculated band gap value varies between 4.4 to 7.02 eV (7.07, 6.71, 5.6, and 4.6 eV for bulk, surface, whisker, and cluster, respectively). [2]

## 2. Novel high pressure phases of $\text{AlH}_3$

Using total energy calculations within the generalized-gradient Approximation we demonstrate that application of pressure makes sequence of phase transitions from  $\beta \rightarrow \alpha' \rightarrow \alpha \rightarrow hp1 \rightarrow hp2$  modification and the estimated transition pressures are 2.4, 4.3, 64, 104 GPa respectively. The coordination of Al has been changed from six to nine in the newly identified high pressure hp1 and to twelve in hp2 polymorphs. The electronic structures reveal that  $\alpha$ ,  $\alpha'$ ,  $\beta$ , and  $\gamma$  polymorphs are non-metals with calculated band gaps varying between 1.99 to 3.65eV, whereas the hp1 and hp2 phases possess semiconducting and metallic behavior, respectively. The calculated lattice dynamic properties confirm that the predicted phases are dynamically stable.

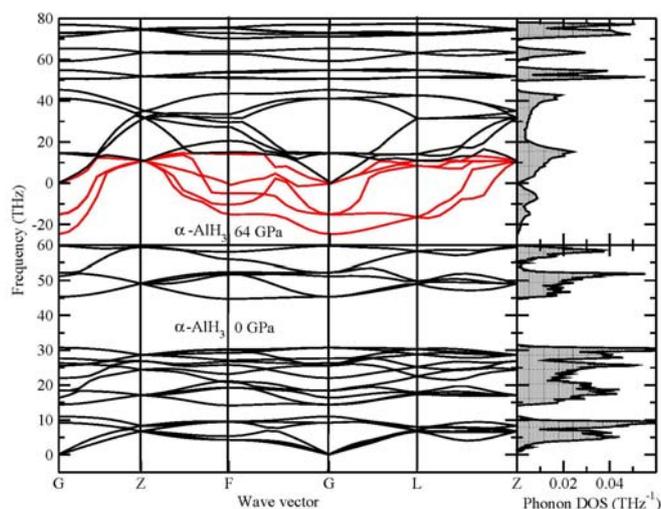


Fig.4: Calculated phonon spectra for the  $\alpha\text{-AlH}_3$  phase at zero pressure (bottom-most panel), at the phase transition point (top-most panel), and the corresponding phonon DOS are given in the right hand side of the figure.

## References

- [1] P. Vajeeston, P. Ravindran, H. Fjellvåg, Nanotechnology 19, 275704 (2008).
- [2] P. Vajeeston, P. Ravindran, H. Fjellvåg, (submitted for publication in ACS-Nano)
- [3] P. Vajeeston, P. Ravindran, H. Fjellvåg, (manuscript under preparation)