



Novel Nano Composites for  
Hydrogen Storage Applications

Project acronym: NANOHy

EC contract #210092

Theme 5

Energy

Collaborative project

## **Report on Deliverable D 2.2**

Start date of Project: 1.1.2008

Duration: 45 months

Date of preparation: 15.12.2009

## Deliverable D 2.2

### Documented theoretical approach for predicting size and interface effects on complex hydrides with high hydrogen content (M 24)

#### Abstract

Phase stability and chemical bonding of  $\beta$ -NaBH<sub>4</sub> and  $\beta$ -KBH<sub>4</sub> derived nano-structures and possible low energy surfaces of them from thin film geometry have been investigated using *ab initio* projected augmented plane wave method. Structural optimizations based on total energy calculations predicted that, for  $\beta$ -NaBH<sub>4</sub> and  $\beta$ -KBH<sub>4</sub> phases, the surfaces (011) and (101), respectively are more stable among the possible low energy surfaces. The predicted critical size of the nano-cluster for  $\beta$ -NaBH<sub>4</sub> and  $\beta$ -KBH<sub>4</sub> is 1.35 and 1.8 nm, respectively. The corresponding critical diameter for the nano-whisker is 2.6 and 2.8 nm, respectively, for  $\beta$ -NaBH<sub>4</sub> and  $\beta$ -KBH<sub>4</sub>. 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 nano-confined and destabilized complex hydrides. From the theoretical simulation we have found that most of the complex hydrides have the critical particle size around 2 nm. Calculations show that, if one inserts a small MgH<sub>2</sub> nano-dot/cluster/layer in the carbon scaffolds, the structure of the nano-dot/cluster/layer is completely rearranged and the calculated bond overlap population clearly indicates that the Mg-H bond strength is considerably weakened.

#### I . Nono-phases of NaBH<sub>4</sub> and KBH<sub>4</sub> - a theoretical study

##### i) Active low energy surfaces

For the surface calculations the unrelaxed slabs have been cleaved from the optimized bulk crystal in different possible low indexes, where bulk structures have been fully relaxed with respect to stress and strain. Sufficient numbers of vacuum layers were created and the convergence of total energy with respect to vacuum layers was studied. All atoms in such created slabs have been allowed to relax using the minimization of forces acting on them. For the considered surface models we have included an integer number of Na/KBH<sub>4</sub> formula units and are thus stoichiometric. 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  $\beta$ -Na/KBH<sub>4</sub> system containing the same number of molecular units as that in the slab. Since the constructed super cell of the slab has two surfaces, the energy difference is normalized by twice the area of each surface in Eq.1. From the calculated surface energy as a function of layer thickness in all the studied thin film geometries we have found that super cell with 8 to 9 layers (depending upon the surface) is sufficient to achieve well converged surface energy. From our theoretical investigation we have 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.

Direction	NaBH <sub>4</sub>	KBH <sub>4</sub>	Mg(AlH <sub>4</sub> ) <sub>2</sub>	Ca(BH <sub>4</sub> ) <sub>2</sub>
(001)	1.89	1.64	2.67	0.23
(010)	1.36	1.29	1.56	0.26
(011)	0.24	0.30	1.07	0.19
(100)	1.36	1.29	1.56	0.21
(101)	0.24	0.31	2.00	1.76
(110)	1.75	1.67	0.83	0.21
(111)	0.82	0.73	0.94	0.23

Table 1: Calculated surface energy (in J/m<sup>2</sup>) for  $\beta$ -NaBH<sub>4</sub>,  $\beta$ -KBH<sub>4</sub>,  $\alpha$ -Mg(AlH<sub>4</sub>)<sub>2</sub>, and  $\alpha$ -Ca(BH<sub>4</sub>)<sub>2</sub> in different possible low energy surfaces.

The calculated surface energies for the studied compounds in this phase (year 2009) are listed in the Table 1. In  $\beta$ -NaBH<sub>4</sub> surface energies vary from 0.24 to 1.89 J/m<sup>2</sup> (depending upon the surface) and for the  $\beta$ -KBH<sub>4</sub> surfaces the surface energies are between 0.3 and 1.67 J/m<sup>2</sup> (see Table.1). In both phases the (011) and (101) surfaces having same or almost the same surface energy. The possible reason is that in  $\beta$ -KBH<sub>4</sub> both (011) and (101) surfaces have almost a similar atomic arrangement. In (011) and (101) surfaces K and BH<sub>4</sub> tetrahedral units are arranged as an alternative layers and within the BH<sub>4</sub> layers the tetrahedra are arranged alternatively in an up and down manner. The low surface energy value for these surfaces indicates that the energy costs will be smaller to create these surfaces through only breaking H-Na/K bonds in bulk Na/KBH<sub>4</sub> and are much lesser than  $\alpha$ -MgH<sub>2</sub> [Ref.1] These values are much closure to the corresponding surface energy for the  $\alpha$ -LiBH<sub>4</sub> surfaces [Ref.2] and one could expect a similar value for the other polymorphs of Li/Na/KBH<sub>4</sub> systems. One may also expect a similar value for RbBH<sub>4</sub> and CsBH<sub>4</sub> in the rest of the ABH<sub>4</sub> (A is any one of the alkali element) series and for them such studies are under investigation.

## ii) Critical particle size

If one reduce the particle size beyond certain range (called critical size), most of the atoms will be exposed to the surface. It is at this region where the properties of the material begin to differ drastically from that of the bulk materials. In order to identify the critical particle size we have calculated the total energy as a function of the cluster size and that are shown in Fig.1. From Fig.1 it is evident that 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 1.35 and 1.8 nm for NaBH<sub>4</sub> and KBH<sub>4</sub>, respectively. Similarly, the calculated total energy as a function of nano-whisker diameter shows that (Ref. 3) when one reduce the diameter below certain critical value (2.6 nm for NaBH<sub>4</sub>; the corresponding value for KBH<sub>4</sub> is 2.9 nm) the total energy increase drastically. If one further reduce the cluster size and nano-whisker diameter, the relative energy of the clusters/nano-whiskers becomes drastically changes, which indicates the destabilization of small particles. This also suggests that the thermodynamical properties and in particular the hydrogen sorption temperature is expected to reduce in nanophases compared with that in bulk materials. This is a good indication for reducing the

decomposition temperature which is desired to utilize complex hydrides for energy storage applications. Further, 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.

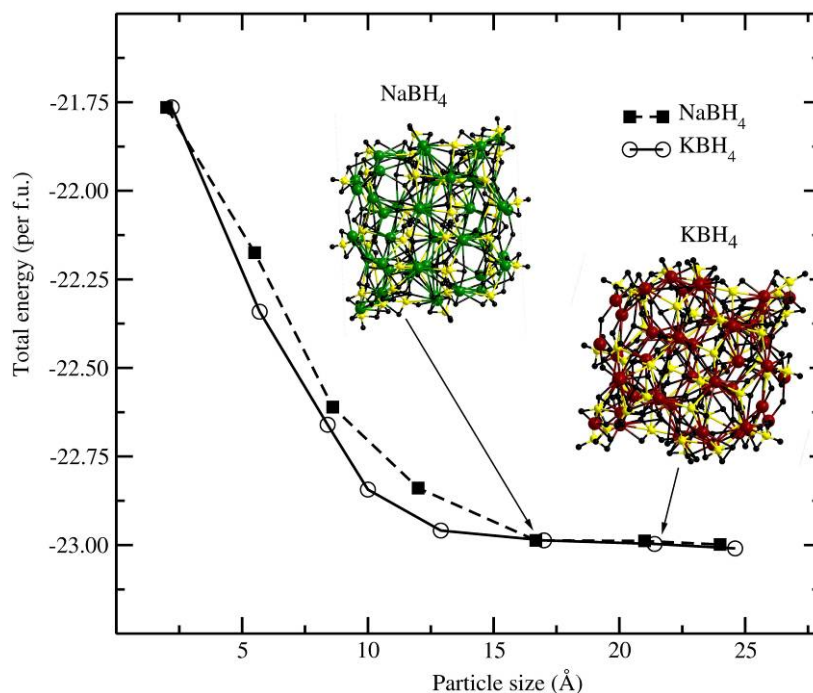


Fig.1: Calculated total energy (in eV/f.u.) as a function of cluster size for NaBH<sub>4</sub> and KBH<sub>4</sub>.

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.2) 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.

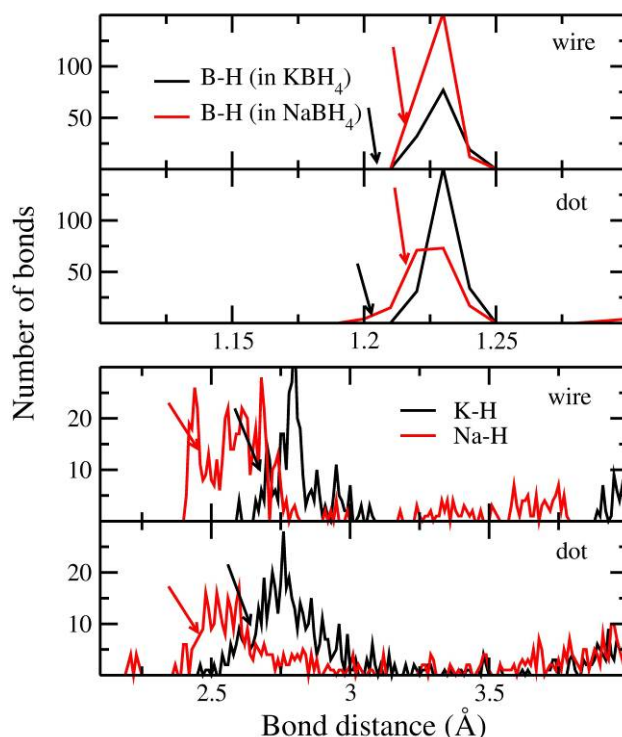


Fig. 3: Calculated inter-atomic distances between B-H, K/Na-H in the optimized Na/KBH<sub>4</sub> nano-clusters and whiskers. Arrow mark indicates the theoretical B-H and K/Na-H (red arrow mark corresponds to NaBH<sub>4</sub> and black corresponds to KBH<sub>4</sub> cluster/whisker) distance for the bulk NaBH<sub>4</sub> and KBH<sub>4</sub> phase.

System	Critical particle size (nm)
LiBH <sub>4</sub>	1.75 (Ref. 2)
NaBH <sub>4</sub>	1.35 (Ref. 3)
KBH <sub>4</sub>	1.80 (Ref. 3)
LiAlH <sub>4</sub>	1.68
Mg(AlH <sub>4</sub> ) <sub>2</sub>	1.98
Ca(BH <sub>4</sub> ) <sub>2</sub>	2.15
Al(BH <sub>4</sub> ) <sub>3</sub>	1.85

Table 2: Calculated critical particle size of the selected hydrides.

### iii) Chemical Bonding

For the bulk phases the theoretical charge-density maps clearly demonstrated the striking ionic character between Na/K and H with noticeable covalent bond within the BH<sub>4</sub> units. In order to gain further understanding about the bonding situation in nano objects of β-Na/KBH<sub>4</sub>, we turn our attention to the charge density analysis. According to the charge-density distribution at the Na and K sites in the center of the nano-phases (Fig.4 a-f), it is evident that the highest charge density resides in the immediate vicinity of the nuclei. The

spherical charge distribution at the Na and K sites (Fig.4 b, c, e, and f) clearly reflects the ionic character. On the other hand, due to the covalent interaction a finite charge density was present in between B and H. In order to have more insight into the chemical bonding we have visualized the charge density with the iso-surface value of  $0.6 e$ , which clearly shows the sharing of electrons in between B and H (see Fig.4b and e). From the Fig.4, it is evident that the charge density distribution in clusters and whiskers are almost similar to that in the bulk phase.

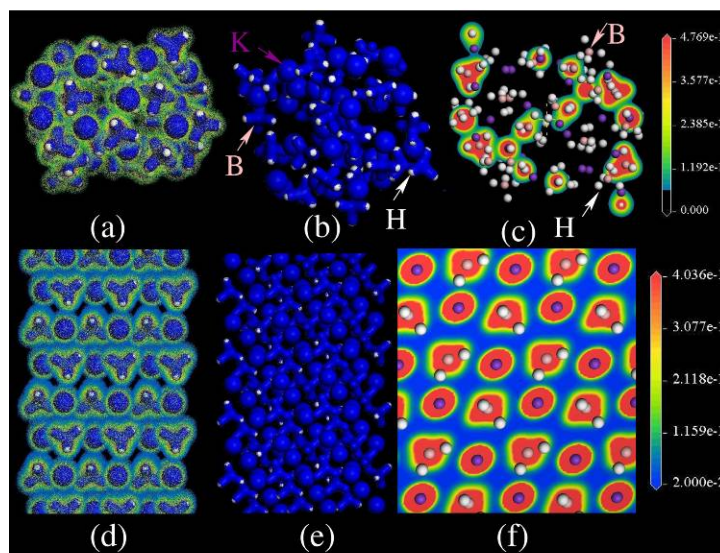


Fig. 4: Charge density distribution in  $\beta$ - $\text{KBH}_4$  derived nano-clusters, and nano-whiskers. Charge distribution in volumetric data view with iso-surface value of  $0.6 e$  [(a) for dot and (d) for whiskers], only the iso-surfaces with value of  $0.6 e$  [(b) for dot and (e) for whiskers], and two dimensional view [(c) for dot and (f) for whiskers].

#### iv) Hydrogen site energy

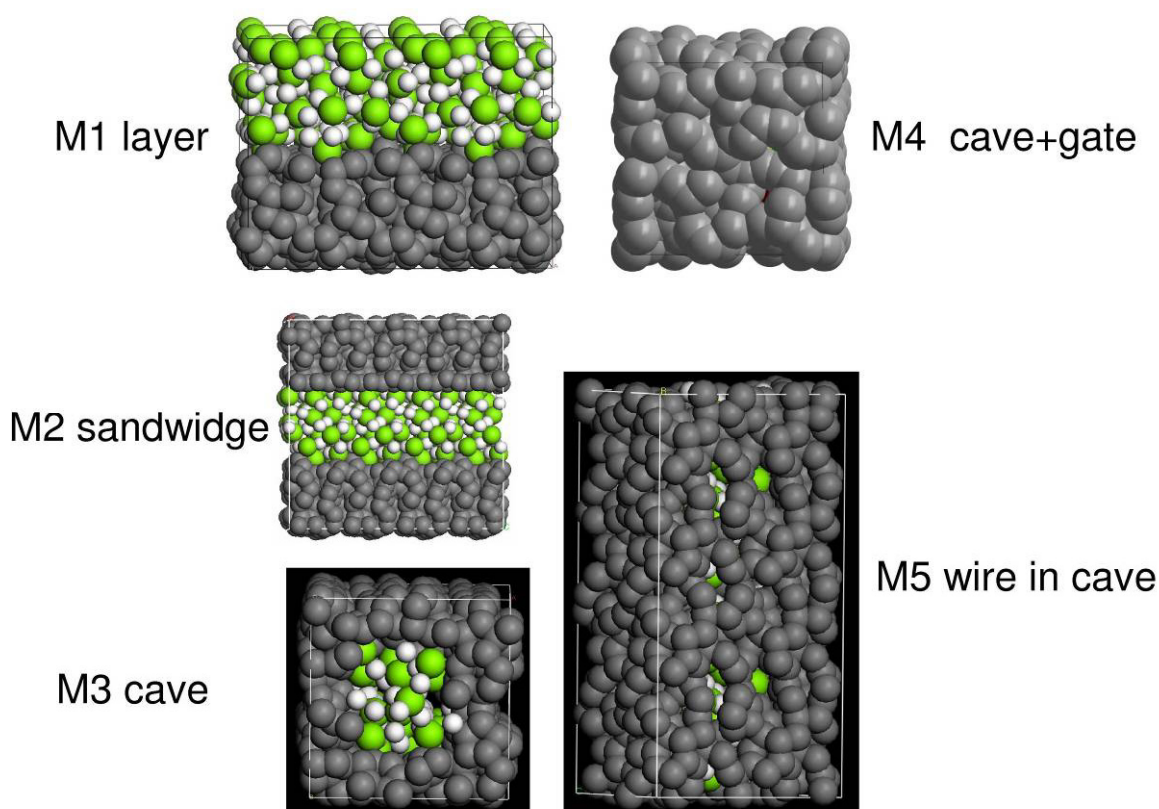
It should be noted that when one increase the cluster/nano-whisker size beyond the critical size these nano objects have core bulk-like Na/ $\text{KBH}_4$  structural units that makes these systems become quite stable. Hence, one must reduce the particle size beyond the critical size to easily remove the H from the Na/ $\text{KBH}_4$  particles. In order to strengthen this argument we have calculated the H site energy (HSE;  $\Delta E$ ) in these particles. In nano-clusters/whiskers the H is situated in four different configurations such as H1 (in between Na/K), H2 (in between Na/K and B), H3 (H is connected with B) and H4 (center of the cluster). The H site energy is calculated in the following manner;

$$\Delta E = EH_{vac} - (E_{nano} + 1/2 E_{Hmol.}) \quad (2)$$

where  $EH_{vac}$  and  $E_{nano}$  refer to the energy of the nano object with and without H vacancy and  $E_{Hmol.}$  is the total energy of a free  $\text{H}_2$  molecule calculated in a large box (the calculated energy is  $-6.789$  eV). The calculated HSE for  $\beta$ - $\text{NaBH}_4$  and  $\beta$ - $\text{KBH}_4$  derived clusters/whiskers are scattered in a wide energy range; which is highly depending upon the environment of the H sites. The calculated H1, H2, H3 and H4 site energy values are 0.65, 0.82, 1.30, and 2.2 eV, for  $\beta$ - $\text{NaBH}_4$  and 0.73, 0.90, 1.32, and 2.31 eV for  $\beta$ - $\text{KBH}_4$  derived clusters. Similarly, for nano-whiskers, the calculated HSE value in  $\beta$ - $\text{NaBH}_4$  is 0.78, 1.09, 1.38 and 2.19 and that in  $\beta$ - $\text{KBH}_4$  whiskers 0.68, 1.14, 1.33, and 2.30 eV for H1, H2, H3 and H4 sites, respectively.

The corresponding HSE value for the bulk phases are 2.21 and 2.32 eV for  $\beta$ -NaBH<sub>4</sub> and  $\beta$ -KBH<sub>4</sub>, respectively. This finding clearly indicates that the required energy to remove H from the center of the nano objects (nano-clusters/nano-whisker) will be similar to that of bulk phase. A substantial reduction in hydrogen removal energy is expected in nano-phases below their critical size. Further, the requirement of only small energy to remove hydrogen from the surface layers of complex hydrides indicates that the nano-phases of hydrogen storage materials will be more advantageous to use for practical applications since they reduce the hydrogen sorption temperature and improve the kinetics.

## II) MgH<sub>2</sub> in Carbon Scaffolds



*Fig. 5: Considered structure models in this study; M1: Over layers of MgH<sub>2</sub> in amorphous carbon (AC) substrate; M2: AC-MgH<sub>2</sub>-AC(sandwich /multilayer) model; M3: MgH<sub>2</sub> in the carbon scaffold; M4: MgH<sub>2</sub> nano dot is placed in the closed scaffolds and M5: MgH<sub>2</sub> nano wire in the carbon scaffolds.*

Magnesium is an attractive material for hydrogen-storage applications because of its light weight, low manufacture cost, and high hydrogen-storage capacity (7.66 wt. %). Unfortunately, the use of magnesium hydride is hampered by relatively slow kinetics for hydrogen release and uptake, and also the thermodynamics,  $\Delta H_f = -75$  kJ/mol H<sub>2</sub>, is rather unfavourable (*i.e.*, MgH<sub>2</sub> must be heated to *ca.* 300 °C in order to release hydrogen at  $p(\text{H}_2) = 1$  bar). Nanoscience may provide novel ideas and solutions to these issues, as suggested in this study. Several factors hinder the rate of hydrogenation and dehydrogenation of the Mg/MgH<sub>2</sub> system. In order to use MgH<sub>2</sub> as an energy carrier in mobile applications one has to find the possible ways to decrease the hydrogen desorption temperature. Numerous studies have been focused on improving the problematic sorption kinetics, including mechanical ball milling and chemical alloying. However, it is found that these methods can only improve the

absorption and not the desorption kinetics, possibly because even the smallest particle sizes (20 nm) obtainable by these methods still primarily display bulk desorption characteristics.

From our theoretical simulation we have found that most of the nanophases having the critical particle size  $\sim 2$  nm (see Table 2). It is much harder to make such nano particles from the available experimental techniques (like ball milling, etc.). Alternatively one can make/isolate such type of particle in scaffolds/in porous structures. For example, recently Nielsen *et al.* [Ref.4] synthesised nanoparticles of magnesium hydride through embedding them in nanoporous carbon aerogel scaffold materials in order to explore the kinetic properties of hydrogen uptake and release. The hydrogen storage properties of nanoconfined  $\text{MgH}_2$  were studied by Sieverts' measurements and thermal desorption spectroscopy, which clearly demonstrated that the dehydrogenation kinetics of the confined hydride depends on the pore size distribution of the scaffold material; that is, smaller pores mediated faster desorption rates possibly due to a size reduction of the confined magnesium hydride. [Ref.4] So, for the theoretical study we have constructed different types of amorphous carbon (AC) models with respect to density (that is corresponding to the pore size). From the optimized AC we have constructed different types of model named M1 (over layers of  $\text{MgH}_2$  in AC substrate layers), M2 ( $\text{MgH}_2$  layers are arranged in between two AC layers, it is also called sandwich/multilayer model), M3 ( $\text{MgH}_2$  nano particle is inserted into a carbon scaffold), M4 (similar to the M3 model but the cave is also closed by AC layers;  $\text{MgH}_2$  nano dot is placed in the closed scaffolds) and M5 ( $\text{MgH}_2$  nano wire in the carbon scaffolds). [Ref. 5]

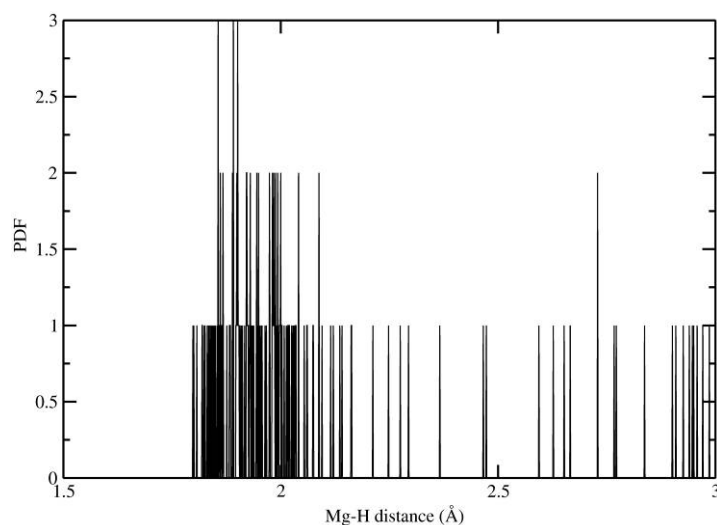


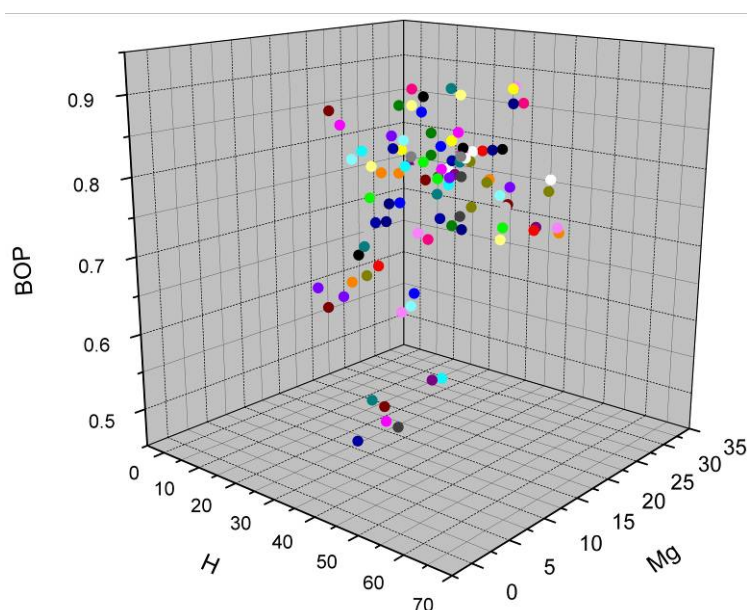
Fig.6: Calculated inter-atomic distances between Mg-H in the optimized M2 model. The corresponding Mg-H distance in the bulk phase is  $1.95\text{Å}$ .

In all these structure models, the calculated Mg-H distances versus number of bonds (e.g., see Fig.6) for the biggest clusters/whiskers indicate that the values were scattered compared with that in the corresponding bulk phase. Especially most of the Mg-H bonds have longer bond distances than that in the bulk. It should be noted that in all these structure models the initial  $\text{MgH}_2$  structure is completely rearranged. This type of structural arrangement is expected in nano- and amorphous-phases with no three dimensional crystallinity owing to reduction in coordination number of atoms.

In order to have a better understanding about the bonding interaction between the constituents the bond overlap population (BOP) values are calculated on the basis of Mulliken population analysis. The BOP values can provide useful information about the bonding property between



atoms. A high BOP value indicates a strong covalent bond, while a low BOP value indicates an ionic interaction. The calculated BOP values for the Mg-H bonds in M2 structure module is shown in Figure 7. The BOP values in Figure 7 clearly shows that the Mg-H bonds are considerably weakened compared with bulk material and it is varying from 0.38 to 0.9 in the nano-phases. This finding is consistent with the HSE study, where the HSE values are vary from 20 to 108.4 kJ/mol. It should be noted that the calculated HSE values in the M2 structure model in different locations [H1: center of the sandwich (20 kJ/mol); H2: near to the center (43.10 kJ/mol.); H3: near to the interface (80.43 kJ/mol.); H4: at the interface (108.4 kJ/mol.)] indicates that the H removal from the center of the system is energetically more favourable than that at the interface. This study clearly indicates that the interfaces have significant role in the hydrogen desorption process. The role of particle and pore sizes on the changes in the hydrogen desorption process in the carbon scaffolds are under investigation.



*Fig.7: Calculated bond overlap population between Mg-H in the optimized M2 model vary from 0.38 to 0.9. The corresponding value in the bulk  $MgH_2$  phase is 0.89.*

## References

- [1] P. Vajeeston, P. Ravindran, H. Fjellvåg, *Nanotechnology* 19, 275704 (2008).
- [2] P. Vajeeston, P. Ravindran, H. Fjellvåg, *Nanotechnology* 20, 275704 (2009).
- [3] P. Vajeeston, P. Ravindran, H. Fjellvåg, (submitted for publication in *Physical Review B*)
- [4] T. K. Nielsen, K. Manickam, M. Hirscher, F. Besenbacher, and T. R. Jensen (*ACS Nano* in press)
- [5] P. Vajeeston, P. Ravindran, H. Fjellvåg, M. Fichtner manuscript under preparation (2009)