Crystals for Hydrogen Storage

Sarang Gosavi,[1, a)] A.T. Ezhil Vilian,[2, b)] and F. Hiba Kunnath[3, c)]
[1)] *NA*
[2)] *Department of Energy and Materials Engineering, Dongguk University-Seoul, Seoul 100-715, Republic of Korea*
[3)] *NA*

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Hydrogen is the most abundant element in the universe. Needless to say, there is ongoing research to make use of this gas for various purposes, that mainly include energy generation. Unfortunately, this is not an easy task, as the gas is highly flammable and extremely difficult to store in compressed form at high pressures. In this paper, we investigate various crystals that could have the potential to store this gas safely. We examine these crystals using the Quantum ESPRESSO software for the DFT calculations.

Keywords: DFT, Quantum ESPRESSO, lattice, phase diagrams

I. INTRODUCTION:

Hydrogen is the most abundant element in the universe. Due to its single valence electron structure and a relatively small nucleus consisting of only a single proton it can bind with elements easily. H_2O (water) is one such useful example.Apart from this it has also the potential to be used as a fuel source. Hydrogen fuel cells is one such example. Making use of Hydrogen requires us to store the gas for a longer duration of time, be it for its use as a fuel source or for research purposes. Storing Hydrogen in metal cylinder needs to be compressed. Compressing a flammable gas can be dangerous and needs extra care while handling.

Evidently, there exists another method to achieve the successful storage of Hydrogen. This involves storage in crystals formed with alkaline earth metals, i.e. metals from the s-block of the periodic table. With the help of DFT we show how it might possible to store Hydrogen in these crystals. For this task we use the Quantum ESPRESSO software to perform the DFT calculations. For our calculations we use the Perdew-Burke-Enzerhof(PBE) functional.

II. CONVERGENCE TESTING

For convergence testing we selected $NaAlH_4$. Using Quantum ESPRESSO we found the optimum value for the k-mesh, the minimum cut-off values for wave-function and the charge density, *ecutwfc* and *ecutrho*. The pseudo-potential files were taken from the SSSP library[1].

For the convergence testing, we selected the crystal that would contain all the elements and would require the least amount of runtime. $NaAlH_4$ fit that criteria.[2]

$NaAlH_4 \rightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2$

$NaH \rightarrow Na + \frac{1}{2}H_2$

[a)] Electronic mail: chakrawal24@gmail.com
[b)] Electronic mail: ezhil2040@gmail.com
[c)] Electronic mail: fhibakunnath@gmail.com

TABLE I. To determine the appropriate values of *ecutwfc* and *ecutrho* for $NaAlH_4$ crystal with $5x5x5$ k-mesh.

ecutwfc (Ry)	**ecutrho (Ry)**	**Total energy**	Δe	**Hydrostatic Pressure (kbar)**
36	180	-306.70969614	-0.187810430	-166.12
46	230	-306.89750657	-0.008106129	15.65
56	280	-306.9056127	-0.006862269	26.84
66	330	-306.91247497	-0.005006059	24.53
76	380	-306.91748103	-0.001726210	26.86
86	430	-306.91920724	-0.000392739	28.83
96	480	-306.91959998	-0.000719110	29.45
200	800	-306.92031909	0	29.62

TABLE II. Optimised crystals[3]

Crystal	**Space Group**	**Total Energy (Ry)**	**Crystal System**
LiH	Fm3m	-65.08733803	Cubic
NaH	Fm3m	-441.55041067	Cubic
KH	Fm3m	-456.82968521	Cubic
NaAlH4	$I4_1/a$	-306.96057111	Tetragonal

II

Table I above shows the values of cut-off wave-function and charge density compared with Hydrostatic pressure and total energy. The values for the crystal were chosen for sodium[Na] considering those were the highest for the crystal. The actual values were 66 Ry and 323 Ry for *ecutwfc* and *ecutrho* respectively. the charge density value was rounded off to 330 to make it a factor of 5 larger than the wave-function value.

From Table I we can deduce that the Hydrostatic pressure stabilizes at cut-off wave-function value of 96 Ry and charge density value of 480 Ry. Hence we rounded of the same value to 100 and 500 respectively. These values also obey the relation where the charge density value is five times the wave-function value. We have maintained this value throughout the calculation for all crystals.

To determine the k-mesh we used a similar methodology where the Hydrostatic Pressure maintains at a certain value. This k-mesh value was determined to be 7x7x7 as is evident from the table below.

III. GEOMETRIC OPTIMIZATION

With the k-mesh set at $7x7x7$ and $7x7x4$ for the $NaAlH4$ considering the reciprocal space of the 1st Brilllouin Zone (BZ). We used the *vc-relax* feature of the Quantum ESPRESSO. We ran the full optimization of the crystals given in Table II using the BFGS method.
II

IV. FIGURES AND TABLES

Below we show the Phase diagrams of the various crystal systems with the general formula $X - Al - H$. Where X represents the Alkali earth metal Na, K, and Li.

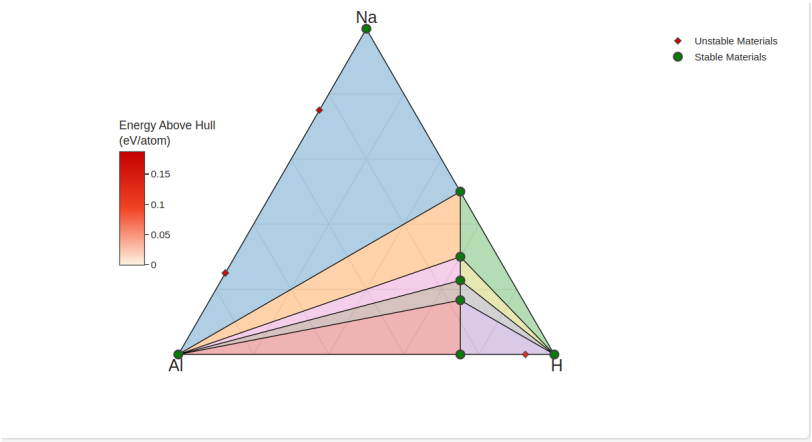

FIG. 1. Na-Al-H Phase Diagram.

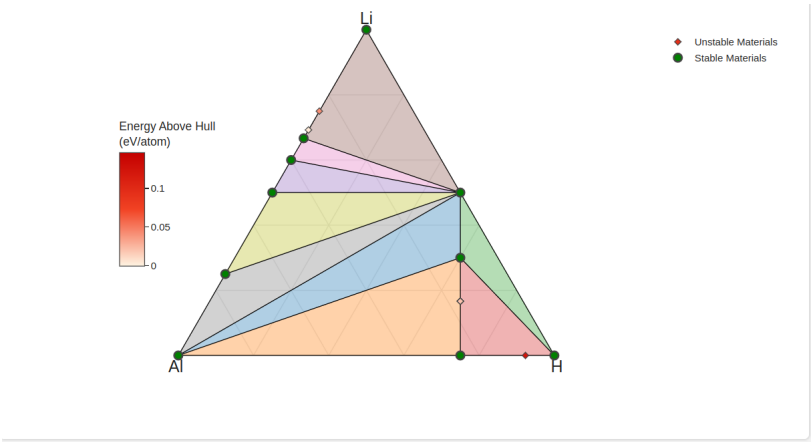

FIG. 2. Li-Al-H Phase Diagram.

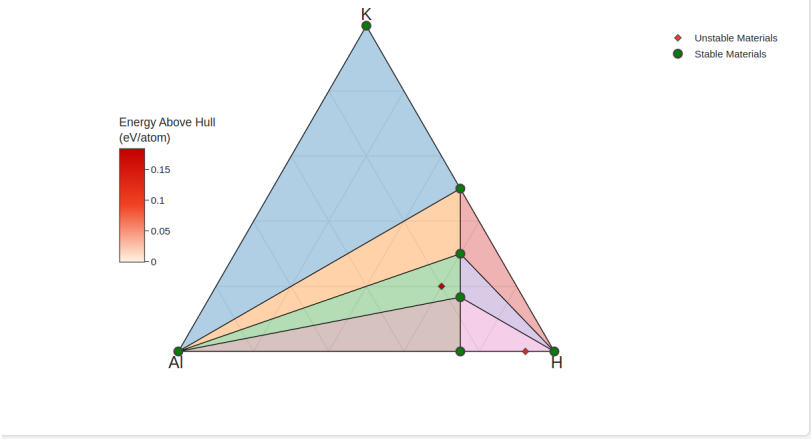

FIG. 3. K-Al-H Phase Diagram.

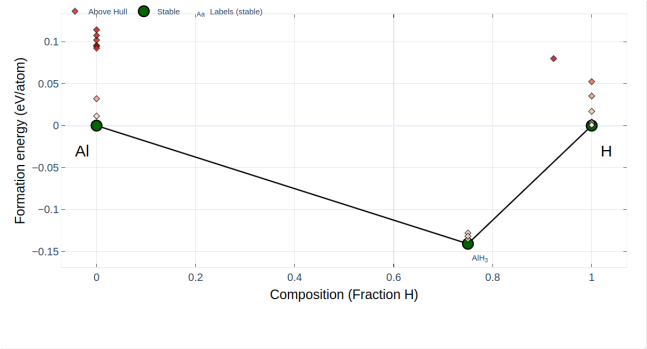

FIG. 4. Al-H Phase Diagram

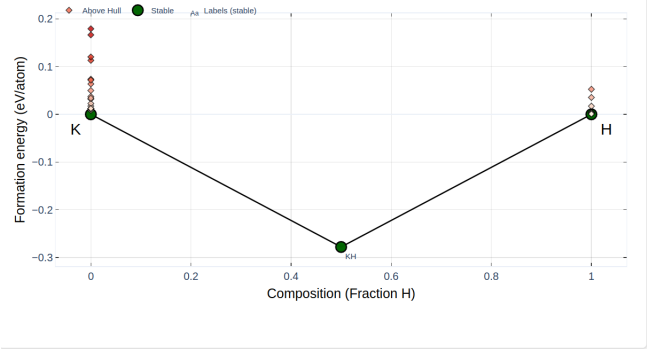

FIG. 5. K-H Phase Diagram

V. LIMITATIONS

There are many crystals in the alkali group and and the p-block periodic table, that can potentially be explored, but due to low computation power we had to limit our study to the above four materials. To further study the remaining materials we believe it will require some powerful computing equipment that is currently inaccessible to us.

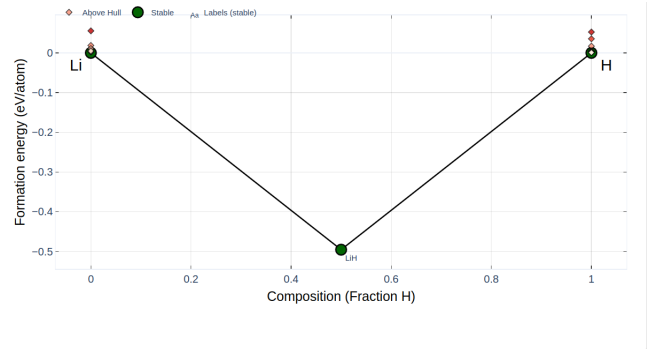

FIG. 6. Li-H Phase Diagram

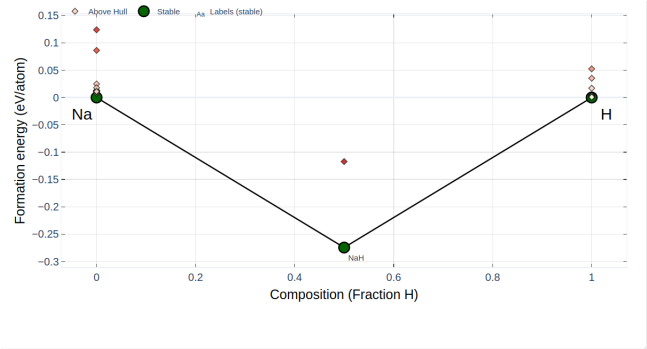

FIG. 7. Na-H Phase Diagram

VI. CONCLUSION

From the information we get from Table II we can say that LiH crystal is the most stable. But Li atom is very small compared to that of the other tested alkali metals. This could result in high density which in turn world increase pressure in the crystal. This compression does not seem feasible for the Hydrogen storage. But there happens to be another crystals which has comparatively lower energy and has a relatively larger volume that might store the Hydrogen efficiently. It is $NaAlH4$. This appears to be the ideal candidate for the crystal storage of the optmised materials.

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Appendix A: Reactions

$$KH \rightarrow K + \tfrac{1}{2}H_2$$

$$LiH \rightarrow Li + \tfrac{1}{2}H_2$$

Appendix B: Bibliography

[1] G. Prandini, A. Marrazzo, I. E. Castelli, N. Mounet, and N. Marzari, "Precision and efficiency in solid-state pseudopotential calculations," npj Computational Materials **4**, 72 (2018), http://materialscloud.org/sssp.

[2] X. Ke and I. Tanaka, "Decomposition reactions for $NaAlh_4$, na_3Alh_6, and nah: First-principles study," Phys. Rev. B **71**, 024117 (2005).

[3] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, and K. A. Persson, "Commentary: The Materials Project: A materials genome approach to accelerating materials innovation," APL Materials **1**, 011002 (2013), https://pubs.aip.org/aip/apm/article-pdf/doi/10.1063/1.4812323/13163869/011002_1_online.pdf.