crystals for hydrogen storage

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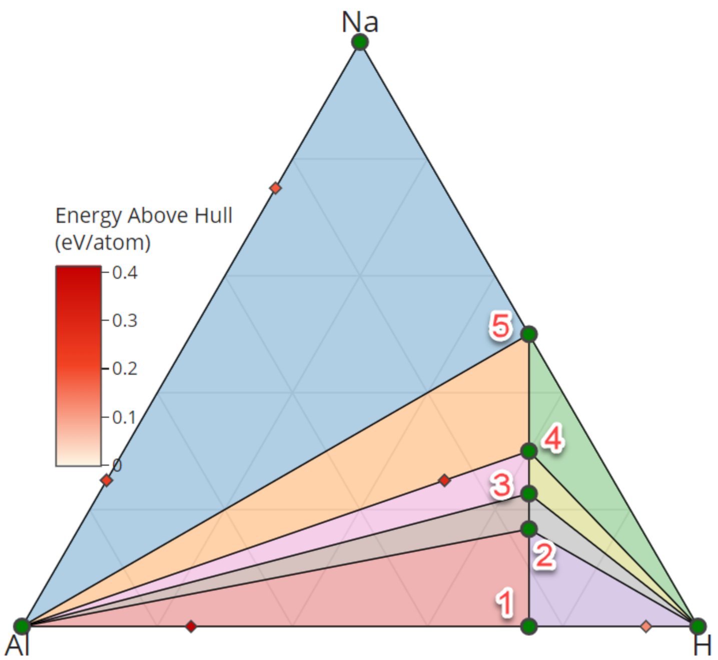
Hydrogen is likely to play an important role in the energy economy of the coming decades. It can be used in a fuel cell to generate electricity, for instance to power an electric motor that is not connected to the grid but to a hydrogen tank. The hydrogen itself can be produced by adding excess electric energy from wind turbines or solar cells to a source material like water (electrolysis of H_2O in an electrolyser).

An important question is: how to store the hydrogen between its production and use? A tank with compressed H_2 gas is an option, but a high pressure is required to store a meaningful amount of hydrogen. Having a highly flammable (not to say: explosive) gas under high pressure in a metal container that is often degenerating when being in contact with hydrogen (hydrogen embrittlement of steel) is not very attractive.

Chemical storage of hydrogen in a crystal that naturally contains a large fraction of hydrogen is an alternative. This calls for the study of phase diagrams of hydrogen with one or more other elements, in search for stable phases with various hydrogen contents. The Na-Al-H phase diagram is an example of this. You find the picture here (taken from Materials Project), and we will focus on the line that connects AlH3 (nr. 1 on the picture) with NaH (nr. 5 on the picture). There are three ternary crystals on that line.



1 : AlH_3 (mp-1106356)

2 : $NaAlH_4$ (mp-23704)

3 : $Na_5Al_3H_{14}$ (mp-24822)

4 : Na_3AlH_6 (mp-23705)

5: NaH (mp-23870)

Step 1: preparation

Search in crystallographic databases for cif files of these 5 crystals.

- How many geometrical degrees of freedom does every crystal have?
- How many atoms are there in a primitive cell of each crystal?
- How many pairs of hydrogen atoms are there per volume in each of these crystals? To which H2-pressure in a gas tank would this correspond? (consider H_2 as an ideal gas)
- You can consider these 5 crystals as being part of a binary phase diagram, with nrs. 1 and 5 as the end members, and nrs. 2, 3 and 4 as linear combinations of the end members. For nrs. 2, 3 and 4: write the chemical reaction (with the proper coefficients) for their decomposition into the two end members.

Step 2: convergence testing

Among the three crystals that contain all 3 elements (i.e. either nr. 2, 3 or 4), pick the one that you expect will require the shortest computation time with DFT. Vary the k-mesh, ecutwfc and ecutrho in order to find settings that give you a precision of about 3 mRy/au in forces and 3 kbar for any component of the stress tensor. Use the pseudopotentials from the SSSP library.

Step 3: phase diagram and geometry optimization

With the k-mesh, ecutwfc and ecutrho you found, calculate the total energy for those 5 cif files. Use them to draw a 2D binary phase diagram, with crystals nrs. 1 and 5 as end members. Now do a full geometry optimization for all five crystals, and make the phase diagram again for the new energies you found. Discuss the differences. Which of those crystals would you prefer for hydrogen storage, and why?

Step 4: exploration

So far you looked at (a section of) the Na-Al-H phase diagram. Now extend the scope to X-Al-H phased diagrams, where X is an alkali element (H, Li, [Na], K, Rb, Cs). Take one of these phase diagrams, and see which binary and ternary phases are documented. For instance, in Rb-Al-X crystals 3 and 4 are not documented in the Materials Project database. Maybe they don't exist and were therefore not plot. Or maybe they were never calculated so far. For the X-Al-H of your choice, calculate the crystal structures that appear in this section of Na-Al-H but do not appear in X-Al-H (or the other way around, if there are crystals that appear in this section of X-Al-H but not in Na-Al-H). Are these missing crystals stable or not? Would they be interesting as candidates for hydrogen storage? … Maybe you discover this way new candidate materials for this purpose, materials that may not have been prepared experimentally yet?

You can go as far as you want in step 4: you can do more than one other phase diagram. You can apply all structures you meet across all phase diagrams to each of the phase diagrams. You can replace not only the alkali element, but also the Al atom (would B or Ga be more useful? Or what about replacing Al by an element from an entirely different group) …