hydrogen storage in Ti-Fe-Hf alloys

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TiFe-alloys are a (cheap) candidate for a hydrogen storage material. You can read some background about it in the (introductory parts of) the two papers that are added to the project.

A research group at the AGH University of Krakow is investigating this material with an experimental technique called "Mössbauer spectroscopy" (what this method is about does not matter much for this project, but if you're curious you can find more information in a module of www.hyperfinecourse.org).

What is interesting in their approach is that they have many of their experiments done as practical sessions for master students. Following the philosophy that students should be exposed to actual research. I like that, and I would like to organize a computational counterpart to this – whence this project, to investigate computationally some aspects of these very same crystals.

Before you start, mind that several of these crystals are magnetic (ferro- or ferri-magnetic, Materials Project mentions this per case). That means your calculations have te be done with magnetism present. That is not the case for most of the examples in the course. In the "let's play module" there are specific explanations for magnetic calculations.

Step 1

Do a convergence study (basis set size, k-mesh) for a TiFe crystal, until the pressure is converged within a few kbar. Keep these settings for all your future calculations (mind to adjust the k-mesh based on cell size). Convergence testing is explained in the "let's play module" (DFT part 2).

Step 2

Construct a E(V) curve for TiFe, fit the equation of state, report the equilibrium volume and bulk modulus. Then do a full geometry optimization for this same crystal, and compare the equilibrium volume with what you got from a E(V) fit. Discuss how much the volume changes if you would be able to apply a pressure of 10 GPa (=100 kbar). The E(V) curve and how to fit it is explained in the module "geometry optimization".

Step 3

Do full geometry optimizations for all 6 Ti-Fe and Hf-Fe crystals, as well as for elemental crystals of Fe, Ni and Hf (search their cif files in Materials Project). Find in this way the formation energies of these 6 crystals. Which ones do you predict should appear in nature? Does that agree with experiment? Full geometry optimization is explained in the module "geometry optimization".

Step 4

Now go back to TiFe, and put 1 hydrogen atom in the unit cell, at an interstitial site (which one?). Check whether your converged settings still hold for a system with hydrogen, and adjust if needed. Do a full geometry optimization for this system, and determine how much energy it

takes to store 1 hydrogen atom per unit cell. What are the implications for hydrogen storage? (this energy cost is similar to a formation energy, as discussed for phase diagrams in the module on geometry optimization)

Step 5 – the creative phase

Proceed with further calculations as you like to make a (small yet) meaningful story. A good target could be to hunt for the crystal/site that has the smallest energy cost per hydrogen atom to insert hydrogen in that crystal/site. You may consider any of the 9 crystas listed elsewhere in this text. Or you may create supercells in order to make mixed (Hf,Ti)(Fe,Ni) crystals. Or you can introduce a vacancy or even other simple defects and put the hydrogen at or near these defects. Or … (any other thing you feel useful). If you see opportunities for other/different stories, go ahead – everything listed in this paragraph is a suggestion, not a must.

Step 6 – the optional and challenging phase

The paper reports Mössbauer data, in particular the electric-field gradient or quadrupole splitting. This is a property that can be experimentally determined, and that serves as a fingerprint for the very local environment of a Fe atom. This property will be different if Fe is in a different crystal structure, if it has a Hf rather than a Ti nearest neigbhour, if there is a hydrogen atom or a vacancy nearby,… You can calculate this property with the GIPAW extension of Quantum Espresso (https://github.com/dceresoli/qe-gipaw). You may try to do that, and explore how the electric-field gradient changes depending on the environment. Perhaps you can even check the site-assignments that have been made in the paper of Komedera et al.

The results and interpretation of your calculations should be discussed in a paper and a video, as explained in more detail in the Project tile at www.compmatphys.org. Information about (intermediate) due dates can be found in the Quick Start tile.

Additional information

In the 'geometry optimization' module of this course, we will mention the MaterialsProject website: www.materialsproject.org. It contains a few cif files (discussed in the 'crystallography' module) that will be relevant for this project:

- TiFe in space group Pm-3m : https://next-gen.materialsproject.org/materials/mp-305
- $TiFe_2$ in space group P63/mmc (hexagonal Laves phase) : https://next-gen.materialsproject.org/materials/mp-2454
- $TiFe_2$ in space group Fd-3m (cubic Laves phase): not available, but you can construct it yourself based upon the corresponding Hf-Fe or Ti-Ni crystals.
- HfFe in space group Pm-3m :): not available, but you can construct it yourself based upon the corresponding Ti-Fe or Ti-Ni crystals.
- $HfFe_2$ in space group $P6_3/mmc$ (hexagonal Laves phase) : https://next-gen.materialsproject.org/materials/mp-956096
- $HfFe_2$ in space group Fd-3m (cubic Laves Phase) : https://next-gen.materialsproject.org/materials/mp-333
- TiNi in space group Pm-3m : not available, you can construct it yourself

- $TiNi_2$ in space group Fd-3m (cubic Laves Phase): not available, you can construct it yourself
- $TiNi_2$ in space group P63/mmc (hexagonal Laves phase) : not available, but you can construct it yourself