

## compmatphys.org : project topic 1 (2022-2023)

One of driving forces behind materials research is finding materials by which our society can save energy. Some obvious examples are the materials that are needed to build solar cells or LEDs. But saving energy can be hidden in other corners as well. Electric applications such as motors, transformers or generators all have a magnetic material in the core of their electromagnetic coil. Almost always, this is a so-called [electrical steel](#): a Fe-Si alloy with about 3 wt.% Si. It is known since decades that using a steel with 6.5 wt.% Si would be very much advantageous. Such a steel would reduce energy losses in the application, which would make all electric machines lighter and more energy efficient. Estimates come up with a saving of several billions of euro worth of electricity every year, if every electric machine would use a 6.5 wt.% Si steel.

Why don't we simply use that ideal electrical steel? In contrast to 3 wt.% Si, the 6.5 wt.% Si steel is brittle: you can't press or roll or otherwise form it into the size and shape needed to build the electric application. It would just break apart when trying to do so. Finding an electrical steel with 6.5 wt.% Si that is *not* brittle is since quite a while the holy grail in electrical steel research.

There is a hypothesis about why the brittleness appears. Crystals with long range order are usually more brittle than crystals in which the atoms are more disordered. It is assumed that when increasing the silicon content, there is a stronger tendency for the atoms to develop short-range order.

In this project, you will hunt for ordered crystal structures that may be stable, and that would explain the brittleness. You will do this by exploiting the advantage that ab initio simulations give you full control over defining the crystal: you will tell exactly where you want to have every atom, and quantum chemistry will tell you what is the internal energy that corresponds to such crystal. By modifying the positions of the atoms, and by monitoring the corresponding internal energy, you may find ordered crystals that are thermodynamically stable.

Experimentalists have a hard time doing the same studies in the lab, as the thermodynamically stable ordered crystals that you may find may need a long time (days, months, years, even centuries) to develop. The atoms may need to overcome large energy barriers before they settle in their lowest-energy positions. That is why probably only a small fraction of a sample may show this type of order, enough to cause the brittleness, but too small to be easily detected by experimental characterization methods.

There is an infinite number of ways to distribute the atoms. Who knows, maybe you will be lucky enough to find the particular distribution that is energetically favourable, and that has been missed by all previous researchers. Let's give it a try!

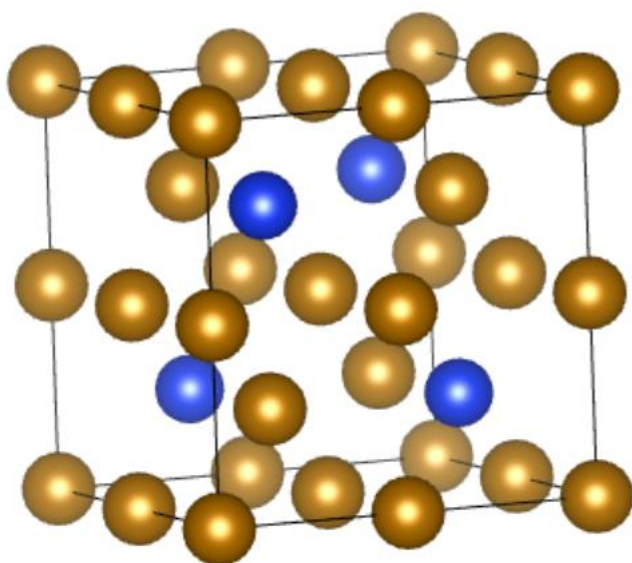
### Task 1: convergence testing

In the relevant region of the phase diagram, all atoms – whether they are Fe or Si – are distributed over an underlying bcc lattice. For a given concentration, this distribution can be random or ordered.

You will first focus on the two crystals that are the limiting cases for your study: bcc-Fe and DO<sub>3</sub>-Fe<sub>3</sub>Si. Let us look what these names mean:

- bcc-Fe is the ground state phase of an iron crystal. All positions on the bcc lattice are entirely occupied by iron atoms. In other words: the silicon concentration is 0%.
- DO3-Fe<sub>3</sub>Si is the name for a crystal of which the unit cell looks like this:
  - The unit cell is built from 8 unit cells of bcc-Fe. These are stacked in a 2x2x2 way, to make a cube with as edge length twice the length of the bcc cube.
  - Of the 8 atoms that are in the body center of the 8 small cubes, 4 will be replaced by Si atoms, in such a way that these 4 atoms form a tetrahedron. (try to recognize this in the picture that is given hereafter)

The unit cell of DO3-Fe<sub>3</sub>Si contains 16 atoms (do you understand the way in which this is counted?). As 4 of them are Si, the Si concentration is 25 at.% (how much would that be in wt.%?).



For these two crystals, you have to run DFT calculations and convince yourself about the proper settings for basis set and k-mesh (see the “let’s play” tile on convergence testing).

Some things to keep in mind:

- All these materials are magnetic. Therefore, the `nspin=2` keyword must be set (see the help section in week 1 of the “let’s play” tile for more info).
- Recommended pseudopotentials: the [SSSP Efficiency](#) library
- For convergence testing, you don’t necessarily need a geometry-optimized crystal. Having a crystal that is reasonably close to the ground state is sufficient. You could take, for instance, the experimental cells, or the cells from Materials Project.
- K-mesh difference between both cells: if you double the cell size in one direction, the number of k-points you need in that direction can be halved, and you still have the same numerical precision (can you figure out why?). That means that a 10x10x10 mesh for bcc-Fe is equivalent to a 5x5x5 mesh for DO3-Fe<sub>3</sub>Si. Be aware of that when deciding which mesh is the minimal one that leads to good results for both crystals simultaneously.

## Task 2 : energies of the end points

Having obtained good numerical settings from task 1, you can now calculate reliable total energies for this type of crystal. Do a full geometry-optimization for your bcc-Fe and DO3-Fe<sub>3</sub>Si crystal, and

note the energy of their ground states. These will be the energies to which you will refer all subsequent calculations.

### Task 3: sanity check

Before embarking on your grand search, let's do a sanity check. Take the DO3-Fe<sub>3</sub>Si crystal, and replace 1 silicon atom by iron. What is the silicon concentration in this new crystal, in at.% and in wt.%?

Do a geometry optimization for this new crystal, and take note of the total energy. If you decompose that crystal into a weighted sum of bcc-Fe and DO3-Fe<sub>3</sub>Si, where on the axis that goes from bcc-Fe to DO3-Fe<sub>3</sub>Si is your new crystal positioned? And is its energy higher or lower than the weighted sum of the energies of bcc-Fe and DO3-Fe<sub>3</sub>Si? In other words: can this new crystal lower its energy by decomposing into bcc-Fe and DO3-Fe<sub>3</sub>Si, or will the energy be lower when it does not decompose? Make a drawing of this, which is equivalent to a convex hull construction for a binary phase diagram (here only limited to the region from pure iron to Fe<sub>3</sub>Si).

### Task 4: the grand search

Now the field is open to let your imagination work. Would there exist a crystal somewhere on the line between bcc-Fe and DO3-Fe<sub>3</sub>Si that is stable, i.e. that cannot lower its energy by decomposing? (where would such a crystal be on your drawing?)

In order to find such a crystal, you can play with two degrees of freedom:

- The concentration of Si atoms in the unit cell. It should be between 0 at.% and 25 at.%. If you stick to a cell with 16 atoms, you can have only 0, 1, 2, 3 or 4 Si atoms (concentration steps of 6.125 at.%). But you can make cells with 32 atoms, in which you can put 0 to 8 Si atoms (concentration steps of 3.0625 at.%). Or cells of 64 atoms, or 128 atoms,... The larger the number of atoms in the cell, the closer you can get to any concentration you want. But remember: the longer your computation time will be.
- The position of the Si atoms in the unit cell. Imagine you have a cell with 32 atoms, and 4 of them are Si. You can put these 4 Si in a tetrahedron as for DO3-Fe<sub>3</sub>Si, in a cube made of 16 atoms, while the next cube with 16 atoms contains only Fe. Or you can put 2 Si atoms in each cube, making a zigzag-line, or in any other configuration.

Construct your own crystals, of a concentration and a choice of positions you want, geometry-optimize them, note the total energy, and put it on your drawing. Maybe you'll see after an initial broad scanning some trends, which will inspire you to construct crystals that have lower and lower energies. Or maybe no crystals with low energies exist. Nobody knows. Try and find out!

### Speculation

I'm particularly curious about the following 'fractal' crystal geometry (fractal, in the sense of self-similarity): take 8 cubes of DO3-Fe<sub>3</sub>Si, and replace in 4 of them all silicon by iron, but in such a way that the remaining cubes form a tetrahedron similar to the tetrahedron of Si-atoms in DO3-Fe<sub>3</sub>Si. This would be a crystal with 16 out of 128 atoms being Si.

### Some additional hints:

If your calculation crashes, complaining about not being able to allocate sufficient memory, then this is what you can do :

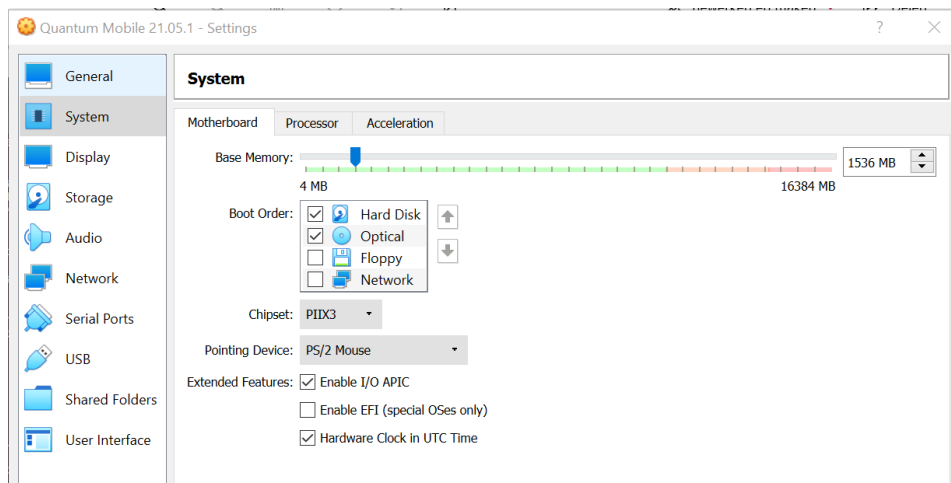
If you open the output file by a text editor (nano, full command is “nano name.out”), you’ll see somewhere in the initial part an estimation of the memory that will be used. Does that make sense for your laptop or not?

You can play with the k-mesh (go down to as small as 1x1x1) and basis set size (encut, even a small value of 5 or 10 Ry is useful to see whether the calculation can run), and inspect how that affects the predicted memory use.

The virtual machine has a built-in max memory use, in order not to crash your laptop. You can change this by clicking the gear symbol before launching Quantum Mobile, then system/motherboard, and use the slider to increase the amount of memory it is allowed to use (compare that with the estimate from the out file, and you’ll see whether or not you have a chance it will run). See screenshot underneath.

If you select the ‘processor’ tab next to ‘motherboard’, you can use more cpu’s of your laptop. You can test on a smaller case whether or not this has any effect. (I did not try this with Quantum Mobile yet, it may be you’ll need to launch the calculation via “mpirun -np 4 pw.x ....” in order to use 4 cpus, or a different number.)

If you cannot get anything running, or in case you hit the ceiling for a given basis set size or kmesh, consider continuing on the HPC (access instructions available in the “let’s play” tile, first week)



### How to install the pseudopotential library once and for all

Go to <https://www.materialscloud.org/discover/sssp/table/efficiency> and click the 'Pseudo' button to download the library. It will download a tar.gz file with a long name, here abbreviated as SSSP.tar.gz.

Bring this file via the shared folder to Quantum Mobile, and copy it from there to the top folder where you have your subfolders with calculations. Unzip and unfold the file there by the commands:

```
gunzip SSSP.tar.gz
```

```
tar -xvf SSSP.tar
```

Now you'll have a folder with one pseudopotential file per element. Take note of the name of the files for the elements you need (UPF files).

In your calculation folder, where you have your Quantum Espresso input file, set the pseudo\_dir variable to the location of this pseudopotential folder, for instance:

```
pseudo_dir='/home/max/work/my-pseudo-library',
```

Now you can list under the ATOMIC\_SPECIES block the name of the UPF files you have take note of.