compmatphys.org : project topic 2020-2021

The project for this year is based on the following paper:

Spontaneous magnetization-induced phonons stability in γ'-Fe_4N crystalline alloys and high-pressure new phase

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In this paper, the authors examine by DFT the crystal γ'-Fe_4N under pressure, and more specifically how the symmetry of the crystal is broken by pressure. In this project, you will verify some of their results and elaborate upon them, in order to get a more complete view on the behavior of this crystal under pressure.

The first part of the task description focusses on calculations that are computationally not very demanding, such that everybody -- including people with no access to large computing resources -- can perform them and make a meaningful project. Near the end, there are a few steps that can be computationally more demanding. They can be done by those people in a project team who have access to larger computers (if any).

task 1 : structure building and convergence testing

Create a cif file for γ'-Fe_4N (search databases or create it yourself based on the information in Tab. 2 of the paper), and do a proper convergence testing procedure in order to determine good computational settings. Your convergence target should be to predict reliable hydrostatic pressures. Compare the settings you determined with what the paper reports in Sec. 2 (using a different DFT code).

All calculations should be spin-polarized (magnetic), using the PBE XC-functional.

You have the necessary background for this task as soon as you have completed the hands-on parts on 'a basic calculation' (week 2) and 'convergence testing' (week 3).

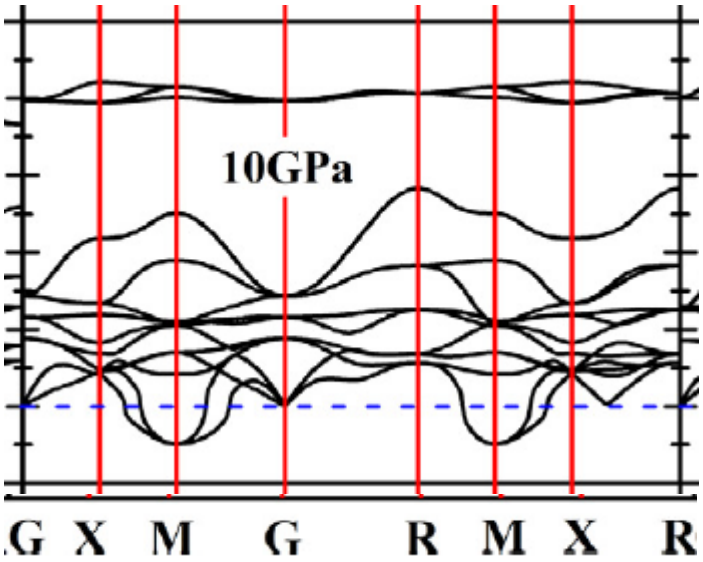
task 2 : E(V)-curve for γ'-Fe4N

Having determined good settings, calculate the total energy of γ'-Fe_4N as a function of volume, and use that to predict the equilibrium volume and bulk modulus of this crystal. Determine the pressure that corresponds to each volume (you should go to a pressure of about 40 GPa). Make a E(V)-plot (with the energy expressed per volume or per formula unit) and indicate the volumes at which the

pressures of 10 and 30 GPa have been reached. By how much percent has the volume been reduced at a pressure of 10 GPa? And of 30 GPa? Compare this with what was predicted in the paper, using a different DFT code.

This task makes use of topics discussed in week 5 and 6 on geometry optimization, but only the most basic ones of them (there are no free coordinates in this crystal, and the shape of the unit cell remains cubic throughout). Therefore it is sufficiently intuitive, and a quick glance on the hands-on document for week 5 will be sufficient to get you going.

task 3 : the M-instability



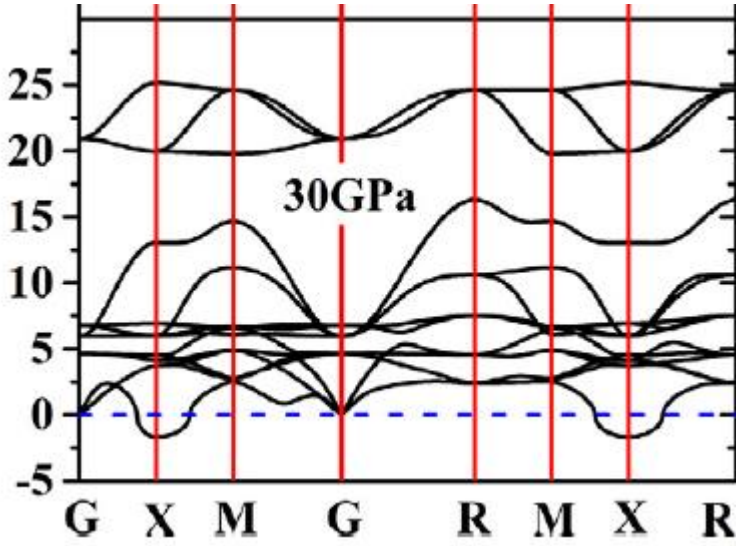
In Fig. 6 (part of which is duplicated here), the authors report a phonon spectrum of γ'-Fe_4N under a pressure of 10 GPa. The 'negative' (imaginary) frequencies at the M-point – a so-called "soft mode" – indicate that this crystal becomes unstable at this pressure, and will make a phase transition to a less symmetric structure.

In Tab. 2 of the paper, the unit cell of the low-symmetry crystal structure is given. You should try to understand how the authors could find this (see next paragraph), but for a while you can consider this as given information. Do a full geometry optimization (volume, shape and internal positions) to determine the equilibrium geometry of γ'-Fe_4N in this crystal structure, and then determine the total energy as a function of volume (down to about 40 GPa). Plot the total energy of this crystal (expressed per atom or per formula unit) on the same E(V)-graph as you did for γ'-Fe_4N. Indicate the volumes where a pressure of 10 GPa and of 30 GPa is reached. Which of both crystal structures will nature prefer in the different pressure ranges ?

If you did not learn about phonons before, it is advised you scan through the 'phonon' chapter in part B of www.compmatphys.org (will become available around October 2020). And/or you can discuss the basics with members of your team who know more about phonons, and teach each other. Having grasped the phonon basics, you can examine in that same phonon chapter how information about a soft mode can be used to find a candidate low-symmetry crystal structure for the phase transition. Try to understand how the low-symmetry structure from Tab. 2 emerged as the result of such a reasoning. You will need this later.

The calculations for this task can be completed after having digested the hands-on tasks for week 5 and week 6 (geometry optimization). For understanding how the (given) low-symmetry structure is obtained, you should learn about phonons (a chapter in the optional part B of www.compmatphys.org).

task 4: the X-instability



Also in Fig. 6 of the paper, another instability in γ'-Fe_4N (not in the low-symmetry crystal) emerges at 30 GPa. The corresponding low-symmetry crystal is <u>not</u> given in the paper. Use your knowledge about phonons and the soft mode procedure to find a candidate for this low-symmetry crystal (there might be multiple possibilities). Do a geometry optimization for this crystal, and determine its E(V)-curve. Plot it on the same graph as where you have put your previous two crystals. What are now your conclusions about the crystal structure that is most stable beyond 30 GPa? Will it be the one you determined now (which should be more stable than γ'-Fe_4N), or is the crystal you found after the 10 GPa transition more stable?

That is an aspect that has not been discussed in this paper, and which you can answer via this project.

If you are short in computing time, you may skip these calculations. Proposing this second low-symmetry crystal, however, does not require computing time. This, at least, you can do.

(reflection)

Once you reached this stage, it is meaningful to reflect on what you have achieved. You could predict what happens to the individual atoms of a piece of material you never had in your hands. You could predict what these atoms do when subject to high pressure, without you having access to the special equipment that is needed to apply such pressures on actual samples. All you had was your brains and your computer, and still you predict how matter is behaving in uncommon circumstances. Isn't that cool…?

elaborations

There are many ways in which you can add more results, predictions or insight to this project. Some of them are straightforward, some of them require a bit or a lot of extra work. Some suggestions are given here as inspiration. To be used by those teams that want to do something extra.

- Plot the total magnetization of the different structures (expressed per formula unit) as a function of pressure. Would you notice a change in magnetization at the pressure(s) where a phase transition occurs?

- Plot the bulk modulus of the different structures as a function of pressure. Would you notice a change in bulk modulus at the pressure(s) where a phase transition occurs?
- Calculate the elastic constants and/or some elastic moduli for one or more of the crystal structures, in their respective equilibrium state. Are the differences between the structures large or small?
- Maybe there are other observable properties, listed by Quantum Espresso in the output, or to be computed with some extra work, which you want to plot as a function of pressure. Perhaps you find one that makes a particularly large jump at the phase transition?
- In Fig. 8 of the paper, there are other soft modes visible at even higher pressures. To which structures would these correspond, and would those structures be more or less stable than the two low-symmetry crystals you have determined hereabove?
- Use the frozen phonon method to determine the frequency of an optical phonon of γ'-Fe_4N, at the equilibrium geometry.
- Idem, but study this phonon frequency as a function of pressure, up to the phase transition. What is the grüneisen parameter of this phonon?
- Install and use the Phonopy code to determine the full phonon band structure of γ'-Fe_4N at its equilibrium geometry, and compare with what was reported in the paper. An example for this will appear in the phonon topic in part B early in October. (Warning: a lot of calculations required for this).
- Use the Phonopy code to determine the full phonon band structure of the low-symmetry structure at 10 GPa, to verify whether or not the soft mode has disappeared from the phonon band structure after the transition to a lower symmetry. (Warning: a lot of calculations required for this).
- … (up to your imagination)