Ex 5-6: Exercise in Rietveld refinements

The crystal structure of Th_2AlD_x was reported in 1961 (Bergsma et al.) as

a = b = 7.629 Å c = 6.517 Å α = β = γ = 90° space group *I4/mcm*

Th:	0.162	0.662	0
Al:	0	0	¼
D:	0.368	0.868	0.137

- What is the Wyckoff position for the deuterium site that Bergsma et al. reports? Use the information for space group I4/mcm in International Tables. What is the composition of the Th_2Al deuteride if that site is fully occupied by hydrogen?

The file *Th2AlDx_saturated_RT.xy* contains the neutron diffraction pattern (PUS, Kjeller, Norway) for Th2AlDx, prepared by exposing Th2Al alloy to 1 bar D2 gas at room temperature.

The wavelength is 1.5554 Å.

- Use Fullprof to compare the structure model reported by Bergsma et al. with the PND data. Take the supplied pcr-file from the Al2O3 demonstration refinement as a starting point.
  TIPS:
  - Remember to lock all parameters except the scale factor before you run Fullprof :-)
  - The space group is written I 4/M C M in the pcr file.
  - Nat (number of atoms) must be increased to 3.
  - Increase the "Current global Chi2" at line two in the pcr file to a large number. The fit will initially be much worse than the Al2O3 refinement and a low Chi2 in the header of the pcr file will cause Fullprof to not update the file.
  - Remember that Fullprof takes occupancies (Occ) as
  - $\frac{site\ multiplcity}{general\ multiplicity} * site\ occupancy$
    - Example. A fully occupied 8-fold site in space group *I*4/*mcm* (where the general multiplicity is 32) should have Occ 0.25.

- Do you think Bergsma et al. obtained an approximately correct structure model back in 1961?

- Check if the deuterium atoms contribute significantly to the PND signal by rerunning the refinement with occ 0 for D.

- Plot the structure model with Vesta (*.vesta file is generated by Fullprof).
  - Measure the shortest distances between the deuterium atoms to confirm that they are in conflict with the "Rule of 2 Å" (click the "Distance" button or press 'd' and then click on two atoms to measure the distance between them.
  - Do you manage to make a simple mathematical expression for the D-D distance?
    - Hint1: You only need two structural parameters in the expression.

        - Hint2: It is easier to see if you plot two unit cells in the z-direction. Go to Objects > Boundary… and chance z(min) from -0.1 to -1.
    - Do Rietveld refinements of the structure model to make it fit better with the experimental data.
        - Hint1: Don't refine too may parameters too suddenly. Try to make good choices of the order you refine the parameters and make frequent backups of the pcr file.
        - Hint2: You can assume that the Th2Al alloy is stochiometric, but the hydrogen (deuterium) content in intermetallic hydrides is often non-stochiometric.
        - You should be able to get a Globle chi2 around 3.
        - What are the most significant changes in the refined structure model compared to the starting model?
- Simulate the X-ray diffraction pattern from the Th2AlDx model (set Job to 2 instead of 1 in the pcr file). Repeat the simulation (with a different prc file name) for the same structure model but without deuterium. The simulated patterns are saved in *.sim files which can be viewed in WinPlotr from File>Open pattern file>Instrm=0.
    - Evaluate the possibilities of extracting information about the hydrogen (deuterium) positions with X-ray diffraction.

Some of the deuterium was desorbed from the material by heating it to 170°C under dynamic vacuum. The neutron diffraction data (PUS) for this sample is in the file *Th2AlDx_des170C_RT.xy*.

- Use Rietveld refinements to obtain a structure model for sample.
  Hints:
    - You should use the pcr file for previous refinement as starting point. The structure is still tetragonal, but the unit cell parameters have changed too much to refine with the values from the saturated deuteride as the starting point. You must adjust them a bit manually first. The a-axis has actually expanded after deuterium desorption, while the c-axis has contracted. You can use the 400 reflection (2theta ~ 47.6) and the 002 reflection (2theta ~ 28.6) to find a and c. You can either calculate “by hand” from Braggs law or by adjust the unit cell parameters in the pcr file to move the calculated 400 and 002 to approximately the right positions.
    - Some deuterium has migrated to the site 0 ½ ¼, so this must be included to get a good fit.
    - What is the composition?
    - What is the distance between the D-positions?
    - How does this fit with the "2Å rule"? What kind of measurements could be made to get a better estimate of the D-D separation in this material?

Bonus question (only if the stuff above is not enough):
Another sample was made where deuterium was desorbed from the saturated material at 115°C, thus yielding a material with deuterium content intermediate of the first two. The PND data for the material is in the file *Th2AlDx_des115C_RT.xy*.

- Compare the PND data for data for the material desorbed at 115°C with the other data sets. What could be the reason for the differences?

- Make an estimate of the unit cell. Use LeBail fits to check your estimate (jbt = 2).