2025

Introduction to the FAULTS program

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TABLE OF CONTENTS

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1 EXAMPLE 1: STACKING FAULTS IN GRAPHITE

In the graphite structure, the carbon atoms are ordered in 6-membered rings within the layers (see *Figure 1* (a)). The layer stacking periodicity can be every two or three layers (Figure 2 (b, c)). This special form of polymorphism is termed polytypism. In these polytypic structures, the first one (b) results in a hexagonal unit cell while the second one (c) produces a rhombohedral cell. These structures are accordingly referred to as the 2H- and 3R-polytypes of graphite, respectively. However, it is common for these materials to crystallize with a significant presence of stacking faults or intergrowth of both phases. Consequently, traditional refinement models like Rietveld are insufficient for accurately describing the structure. This is where the inclusion of FAULTS becomes necessary.

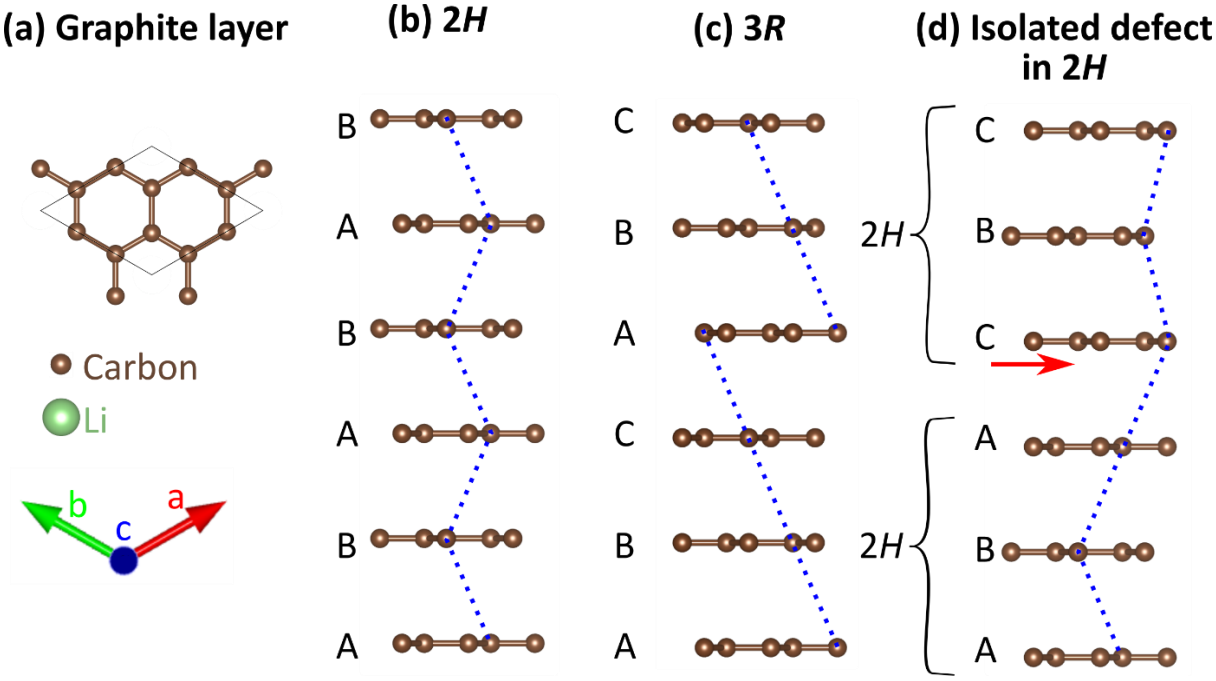

Figure 1. (a) Single layer of graphite view from the top. (b) 2*H* polytype (c) 3*R* polytype (d) example of a single stacking fault in a 2H matrix.

1.1 CRYSTALLOGRAPHIC INFORMATION OF GRAPHITE

2*H* polytype			
Space group: *P*63/*mmc*			
Unit cell parameters:			
a = 2.464 Å	b = 2.464 Å	c = 6.711 Å	γ = 120°
Atomic positions:			
	x / a	y / b	z / c
C1	0	0	0.25

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C2	1/3	2/3	0.25

3R polytype:			
Space group: R-3m			
Unit cell parameters:			
a = 2.464 Å	b = 2.464 Å	c = 10.0665 Å	γ = 120°
Atomic positions:			
	x / a	y / b	z / c
C1	0.25	0.25	0.25

1.2 EXERCISE: GRAPHITE POLYTYPES

a) **Getting familiar with the stacking vectors.** Build the structural model of both polytypes 2*H* and 3*R* using the program VESTA. Visualize the structure using VESTA. Looking at the structures of both polytypes, imagine how they could be described using layers and stacking vectors. Since several descriptions are possible for each polytype, the model will be built with a "unit cell" containing a single layer. Understand (and describe) the stacking vectors occurring in the 2*H* and the 3*R* structures.

b) Build the simulation input file for the 2*H* polytype using only one type of layer (structure described with several transition vectors). Check your FAULTS model using VESTA. Simulate with FAULTS the XRD pattern of the 2*H* graphite and compare it with the XRD pattern of the 2*H* graphite simulated with FullProf. TIP: *you can use the atomic positions that result from transforming the cell to P1 space group. This can be easily done with VESTA: go to the menu Edit → Edit data → Unit cell → remove symmetry and confirm with the buttons Apply and/or OK.*

c) Build the simulation input file for the 3*R* polytype using only one type of layer (structure described with several transition vectors). Check your FAULTS model using VESTA. Simulate with FAULTS the XRD pattern of the 3R graphite and compare it with the XRD pattern of the 3*R* graphite simulated with FullProf.

d) Using the same FAULTS cell, build the input file to describe a 2*H* structure including different degree of stacking faults (e.g., 1%, 2%, 5%, 10%, 20%, 50% 80%, 90%, 95%. 98% 100%) until you get an ideal 3*R* structure. Check your FAULTS model using VESTA and simulate the XRD pattern of this intergrowth of graphite 3*R* and graphite 2*H*. Analyze the effect of stacking faults in the XRD patterns. Are all peaks affected? How are they affected?

2 EXAMPLE 2: STACKING FAULTS IN $LINIO_2$

Lithium nickel oxide has been intensively studied as a positive electrode material in Li-ion batteries. As other lithium transition metal oxides, it crystallizes in an *O*3-type layered

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structure, with an ABCABC oxygen stacking sequence, and lithium ions are located in the octahedral sites of the interlayer spaces (see Figure 2). *O*1 stacking faults that represent a break in the normal stacking sequence of the structure, with a local ABAB oxygen stacking sequence, can appear at low lithium concentrations.

In intermediate states of Li_xNiO_2 where x is between 0 and 1 some *O*1 layers emerge in the *O*3 matrix, and their presence increases as the degree of delithiation is higher. Again, the Rietveld method is not able to model these defects so FAULTS is needed for a proper structural description.

NOTE: For simplicity, we will consider that the lithium interlayer in the O3 motifs is fully occupied while it is empty in the O1 motifs).

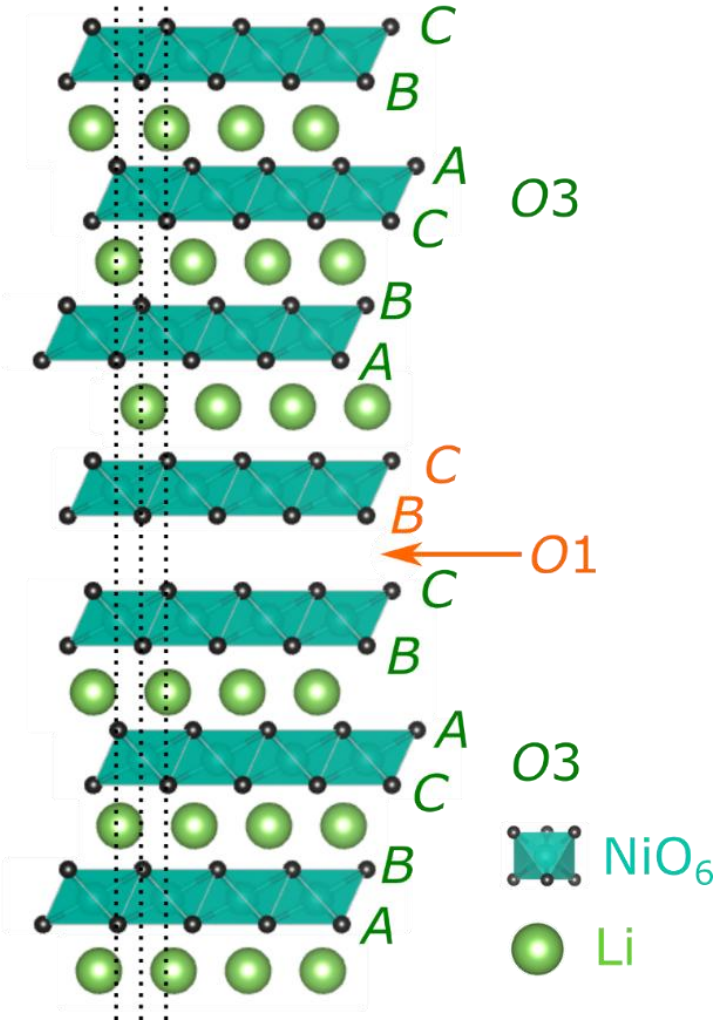

Figure 2. Structure of Li_xNiO_2 where a O1 defect appears in a O3 matrix. The dashed lines are a visual guide to easier follow the ABC stacking sequence.

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2.1 CRYSTALLOGRAPHIC INFORMATION OF $LINIO_2$

$LiNiO_2$			
Space group: $R\bar{3}m$			
Unit cell parameters:			
a = 2.8769 Å	*b = 2.8769 Å*	*c = 14.198 Å*	*γ = 120°*
Atomic positions:			
	x / a	*y / b*	*z / c*
Li	*0.0*	*0.0*	*0.5*
Ni	*0*	*0*	*0*
O	*0*	*0*	*0.2580*

2.2 EXERCISE: LI_XNIO_2

a) **Getting familiar with multiatomic layers.** Build the structural model of $LiNiO_2$. Check your FAULTS model using VESTA. Simulate the XRD pattern of ideal $LiNiO_2$. As for the case of graphite*: you can use the atomic positions that result from transforming the cell to P1 space group. This can be easily done with VESTA: go to the menu Edit → Edit data →Unit cell → remove symmetry and confirm with the buttons Apply and/or OK.*

b) Build a structural model for Li_xNiO_2 with stacking faults. Check your FAULTS model using VESTA. Take into account that the absence of Li modifies the interlayer distance (10% of reduction). Explore the effect of having varying amounts of *O*1-type stacking faults in Li_xNiO_2. Get the obtained stoichiometry from the .out file.

c) **Getting started with refinements.** Build the input file to refine $LiNiO_2$ with stacking faults and NiO impurities. You need to include a regular background, the NiO background file and select the refinable parameters. After the refinement process analyse your results and, if needed, run the refinement again using the FILENAME_new.flts file.

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3 EXAMPLE 03: STACKING FAULTS IN LI_2MNO_3

Li_2MnO_3, which can also be described as $Li[Li_{1/3}Mn_{2/3}]O_2$ to better take into account its layered structure, can be indexed with the *C*2/*m* space group (Figure 3 (a)). As there is an excess of lithium, this accommodates in the transition metal layer, where the Li/Mn atoms are arranged following a "honeycomb" ordering scheme (see Figure 3 (b)).

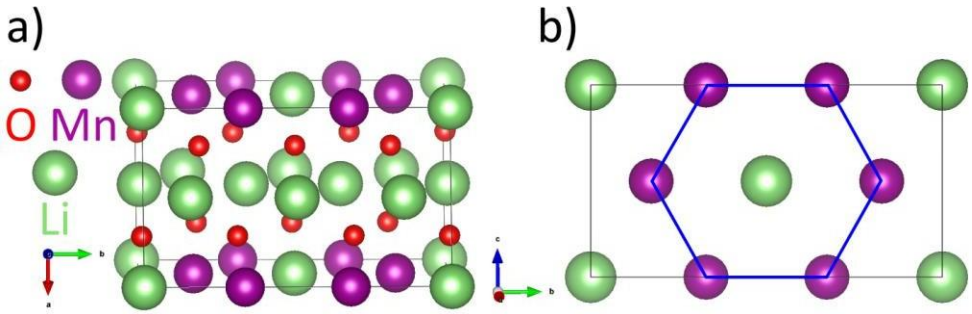

Figure 3. a) Li2MnO3 C2/m unit cell and b) view of the Li/Mn layers where the honeycomb arrangement can be observed.

This extra ordering leads to three stacking possibilities as shown in Figure 4 and therefore this type of material is prone to exhibit stacking faults. The concatenation of such stacking faults generates a characteristic asymmetric peak broadening as a consequence of the ordering loss (Warren fall) in the XRD pattern visible in the range $2\theta_{Cu}$ = 20-35°, where superstructure peaks appear.

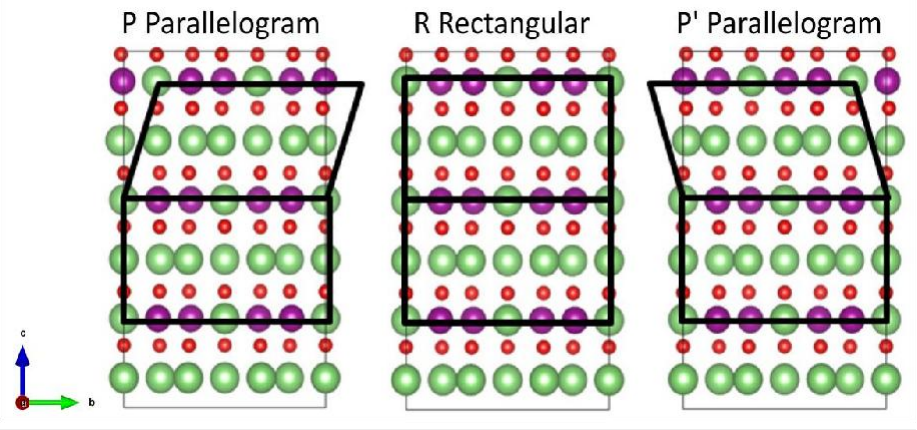

Figure 4. ***Possible layer transitions in the crystal structure of Li_2MnO_3. R shows the ideal stacking while P and P' represent stacking faults.***

In the following exercise we will analyse this peak broadening. Additionally, the effect this disorder causes to the ED patterns will also be evaluated.

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3.1 CRYSTALLOGRAPHIC INFORMATION OF LI_2MNO_3

Li_2MnO_3			
Space group: C 2/m			
Unit cell parameters:			
a = 4.9292 Å	*b = 8.5315 Å*	*c = 5.0250 Å*	*β = 109.337°*
Atomic positions:			
	x / a	*y / b*	*z / c*
Li 2b	0.000	0.000	0.000
Li 2c	0.500	0.000	0.500
Li 4h	0.000	0.847	0.500
Mn 4g	0.000	0.328	0.000
O 8j	0.747	0.811	0.751
O 4i	0.262	0.000	0.755

3.2 EXERCISE:

a) Build the .flts file and simulate the powder diffraction pattern of Li_2MnO_3 using the provided .cif file. NOTE: In FAULTS program the stacking direction must be perpendicular to the *ab* plane, which means that β must be 90° and hence a new cell *c* parameter (perpendicular to both *a* and *b*) has to be calculated. This will affect both the description of atomic positions as well as that of layer transitions.

b) Explore the effect of varying degrees of stacking faults in Li_2MnO_3.

c) Generate ED patterns with samples with different degree of stacking faults. The files created by FAULTS for the simulated ED patterns are unsigned 16-bit images of size 256x256 with a *.sadp extension. They can be opened with a specific software such as ImageJ (available at: https://imagej.nih.gov/ij/download.html)

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4 IMPORTANT REMARKS TO CORRECTLY RUN FAULTS

- Carefully read the messages written by FAULTS in the command window and in the output file .out. Most of the errors can be identified from these messages!

- Like in FullProf, tabs are not allowed in the input files. They can generate unpredictable errors! Only spaces should be used. Working with editors such as Notepad ++ can help us to find these mistakes.

- In Notepad ++ you can select and edit several lines at the same time by pressing alt while selecting with the mouse. This can be helpful when refining the background parameters in FullProf, for example.

- All the non-optional sections and keywords have to be present in the .flts input file.

- Contrary to the .pcr input files used in FullProf, a missing refinement code will be not considered as zero but will produce an error, so all the refinement codes have to be present in the .flts input file.

- The combination of the profile parameters U, V, W, X should not lead to a profile function with negative values (no negative Gaussian and/or Lorentzian FWHM). The user can check this by calculating the Gaussian and Lorentzian FWHM (H2G and HL) with the formula given in page 10 of the FAULTS manual, using the program WinPLOTR (Menu Calculations => I.R.F. (U,V,W,X,Y,Z)) or any spreadsheet.

- The way of working with FAULTS requires especial care of the user. Before starting to do refinements it is advisable to make simulations in order to start with an initial model that is not too far from the experimental diffraction pattern.

- If the structural model is complicated, the first calculations can take time, so the user should make sure that he/she lets the program some minutes before concluding that it is blocked. Keep in mind that the derivatives are calculated numerically by calling two times the total function per free parameter and this calculation may be expensive in CPU-time.

- In refinement mode, at least one parameter should be refined.

- The name of the input files (including the extension) is limited to 29 characters.

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5 OTHER TIPS

- Work with Notepad ++ to find errors easily.
  - In notepad remove Auto-Completion options: Settings → Preferences → Auto- Completion → Un-tick options

- See all file extensions:
  - For Windows 10: Open a folder. Go to View tab. Check File name extensions option.

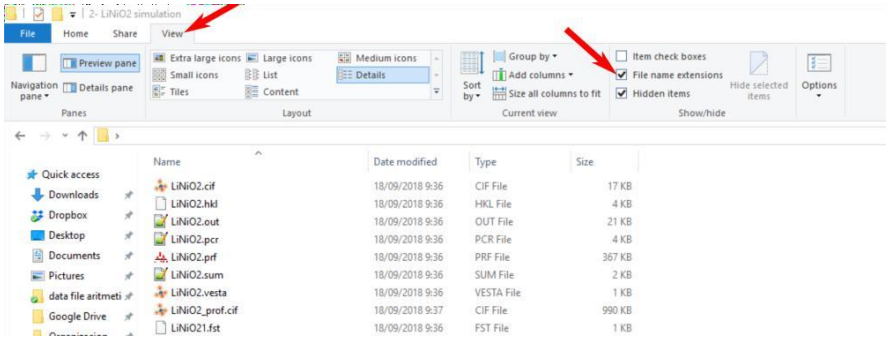

Figure 5. Steps to follow to see all the file extensions.

- To open a console in the desired folder: Shift + right click → Open PowerShell window here.