

Defects Matter:

A versatile program for modeling X-ray diffraction patterns of defective layered structures

Bruno Lanson, Sylvain Grangeon,
Alain Plançon, Boris A. Sakharov, Victor A. Drits



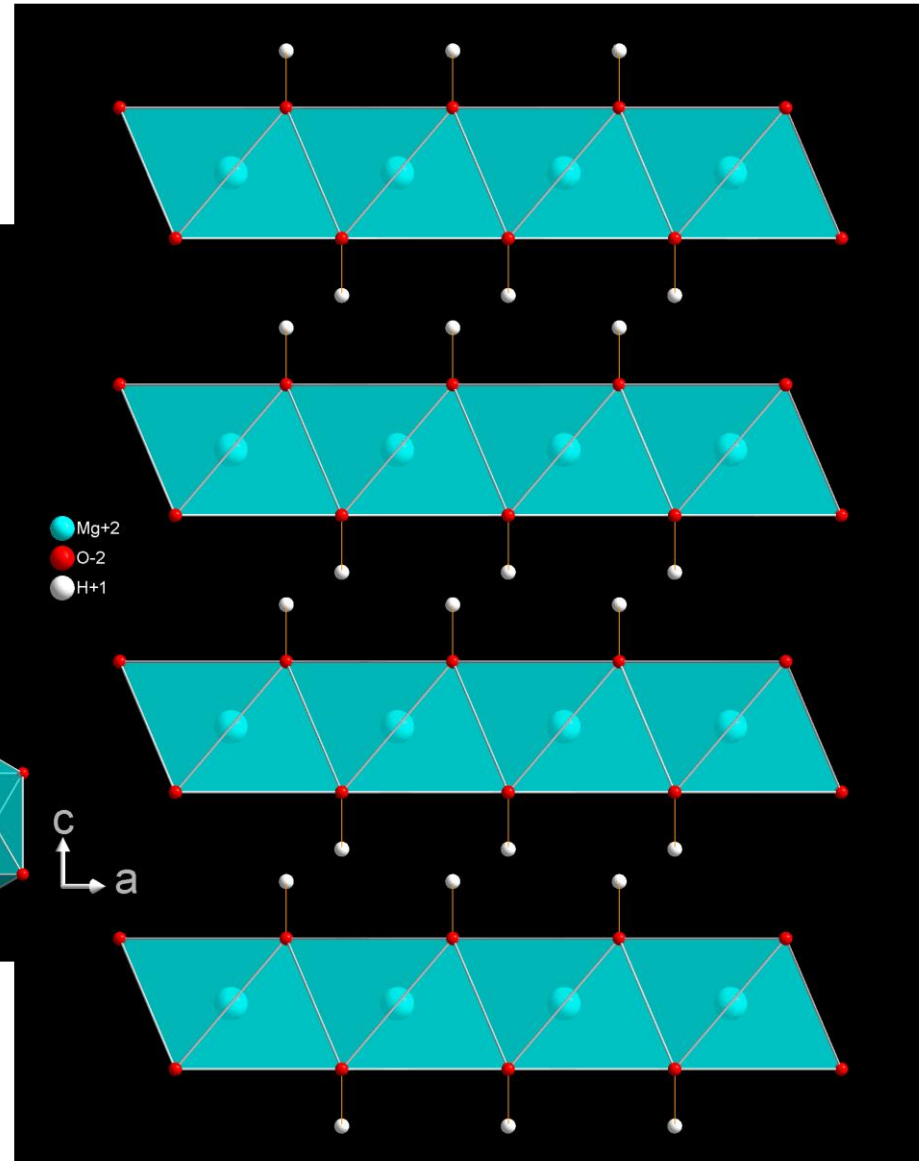
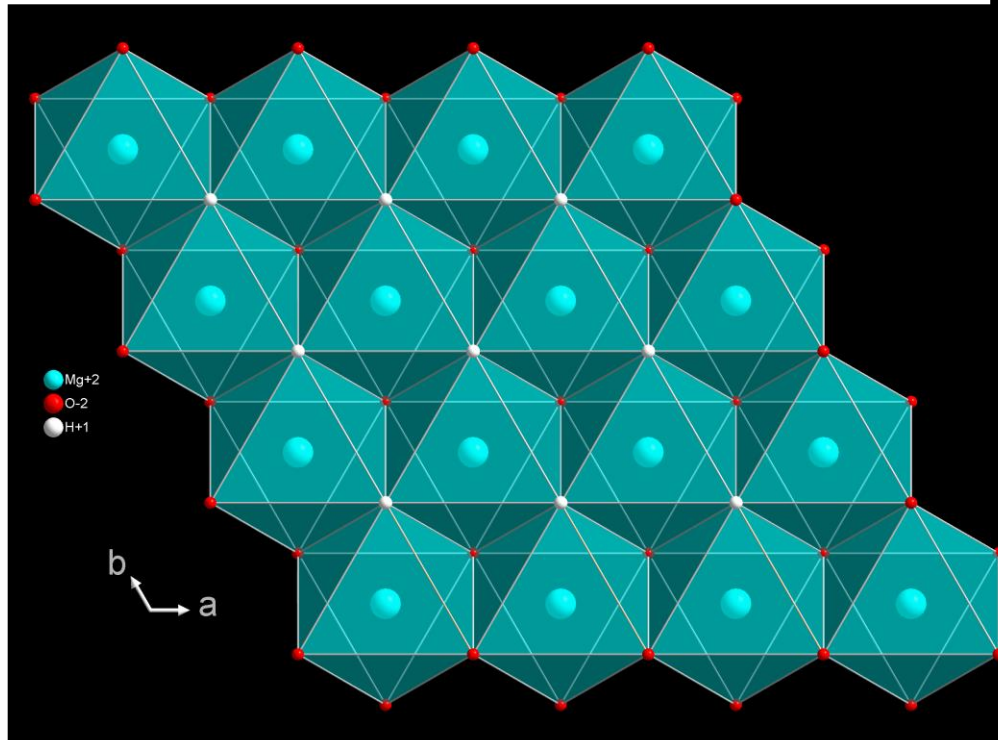
bruno.lanson@univ-grenoble-alpes.fr

Defects Matter:

https://isterre.fr/IMG/zip/lanson_bari_aic_tutorials.zip

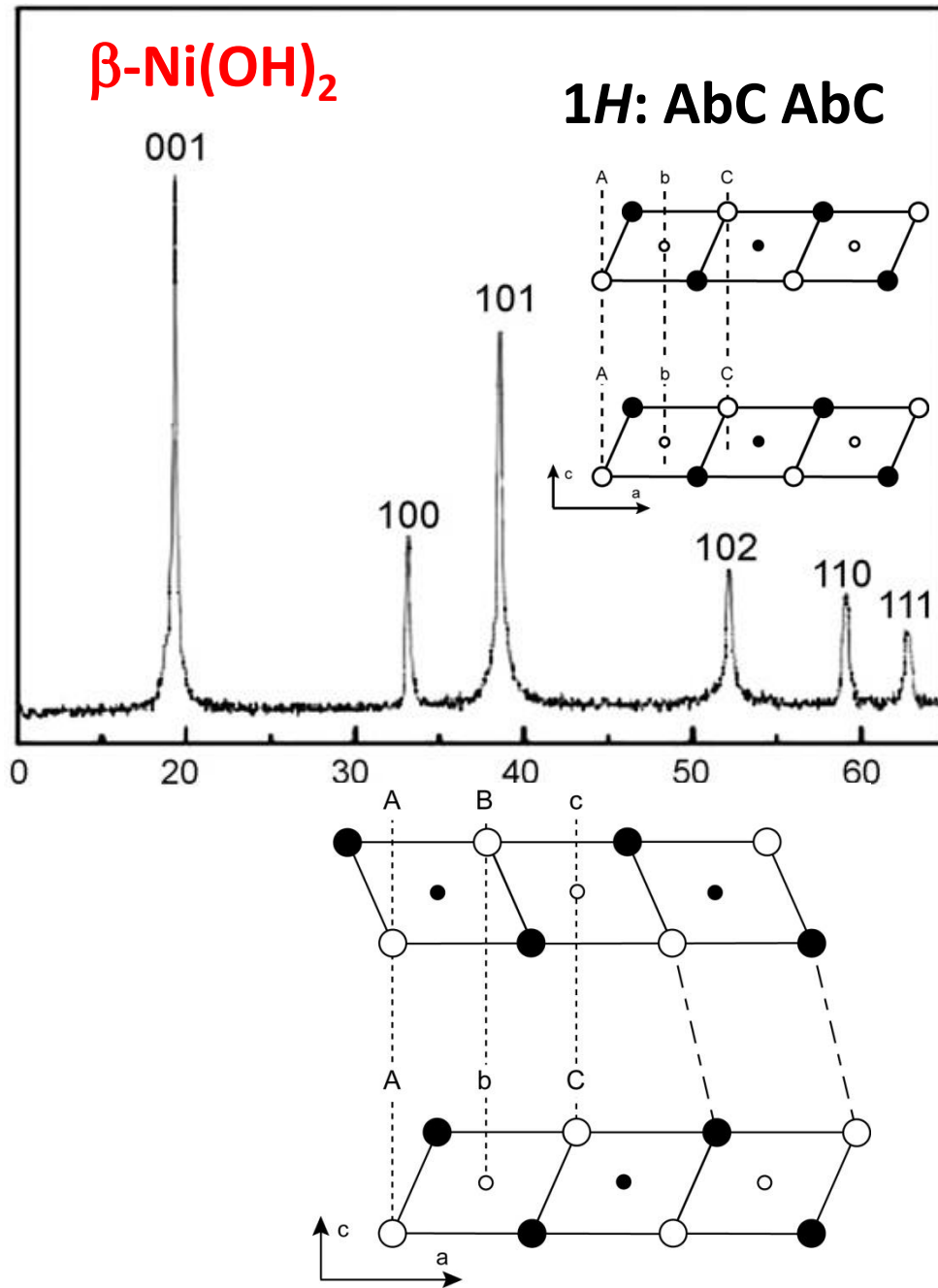
Natural clays and other lamellar structures

2D octahedral layers “building blocks”



Stacking faults in $\text{Ni}(\text{OH})_2$ cathode materials

2 major types of stacking faults

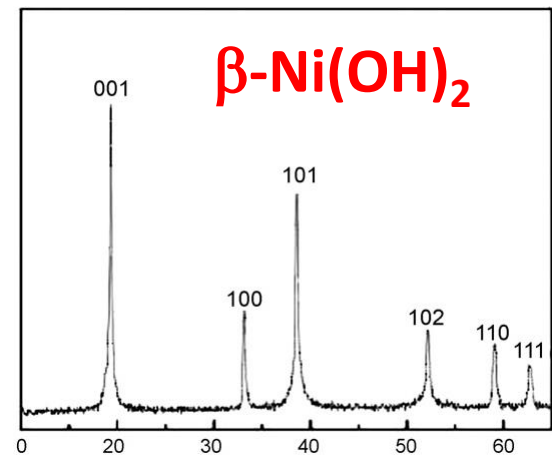
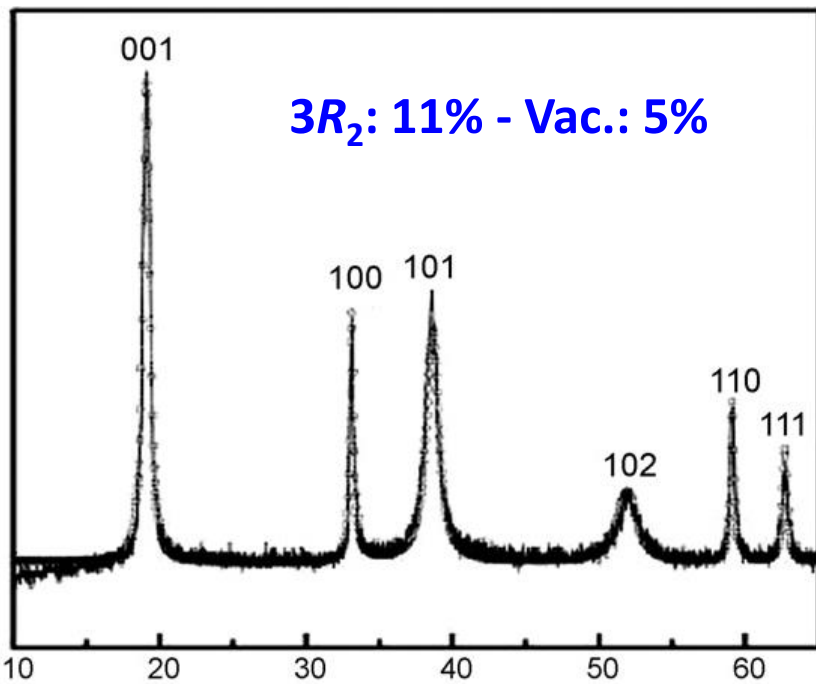
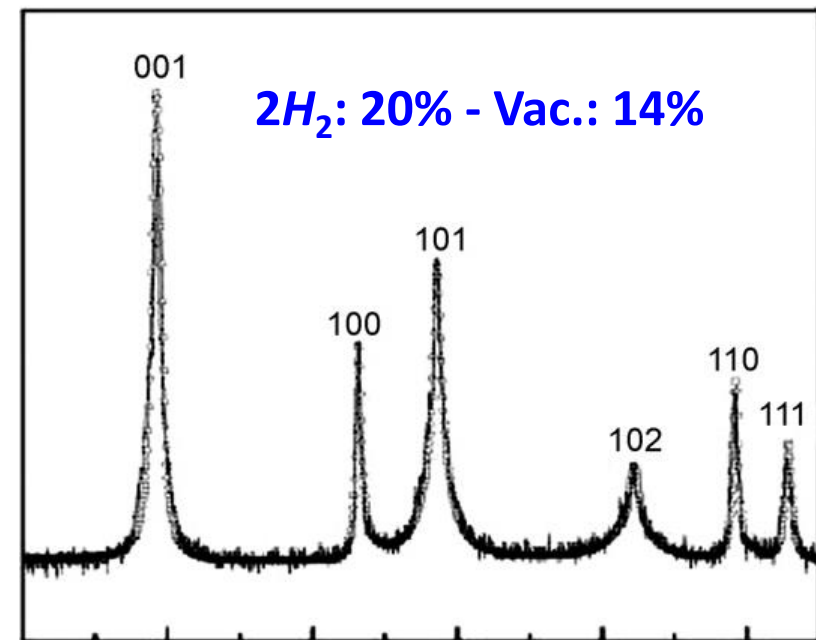


3R₂: AbC BcA CaB AbC
+a/3 layer shift

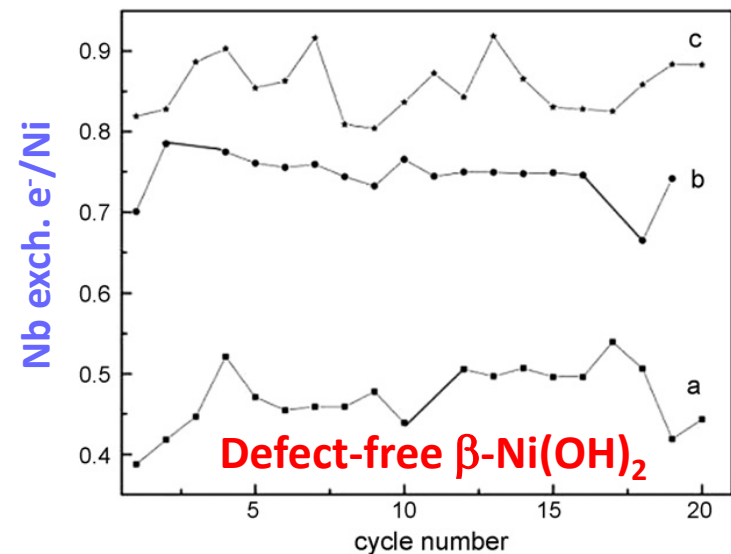
2H₂: AbC AcB AbC
180° rotation

Ramesh & Kamath, 2008
 Mat Res Bull, 43, 2827

Stacking faults in Ni(OH)_2 cathode materials

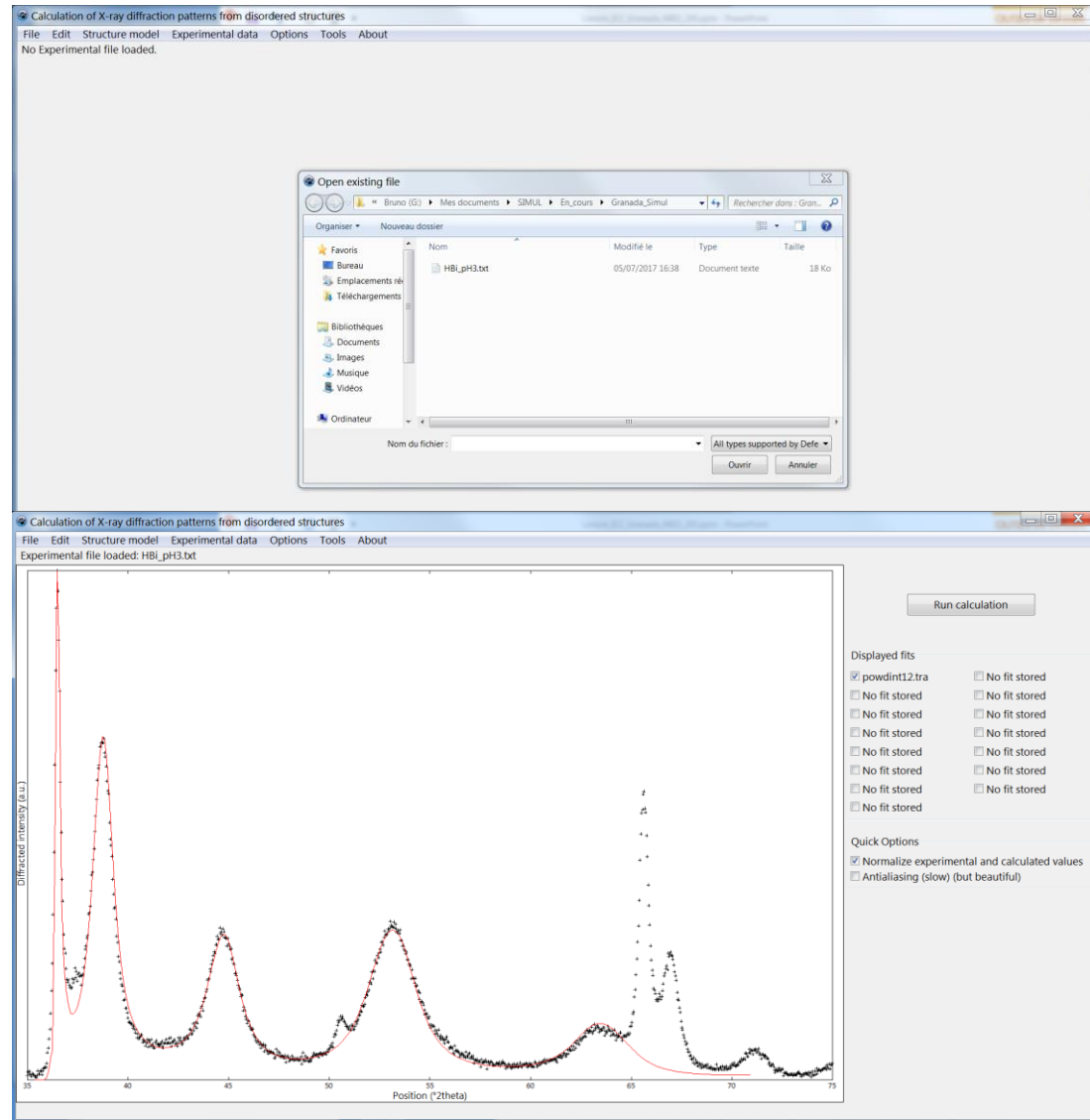


Electrochemical performance increases with the amount of faults and vacancies



Defects Matter - GUI

- Handles xy text files
- Ability to zoom, subtract linear “background”
- Direct comparison with calculated patterns
- Keeps tracks of calculation “history”
- Ability to sum up different contributions



Calculation algorithms are those developed by Plançon and Sakharov/Naumov

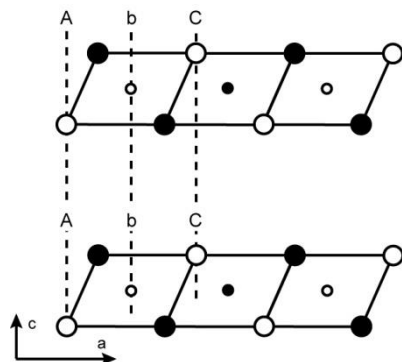
Building the β -Ni(OH)₂ octahedral layer (no H₂O)

Kazimirov et al., 2010 Solid State Ionics, 181, 1764

Table 1

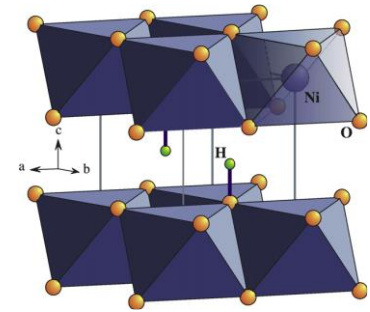
Structural parameters of β -Ni(OH)₂ and Mg(OH)₂ obtained by Rietveld refinement of neutron diffraction data measured at room temperature and calculated through the energy minimization procedure. The refinement implied the space-symmetry group P-3m1 with Ni/Mg and O/H atoms occupying the (0, 0, 0) and (1/3, 2/3, z) positions respectively. Atomic displacement parameters, B, for Ni/Mg and O were fixed at 0.6 and 1.0 Å² respectively.

| Parameter | Ni(OH) ₂ |
|-----------|---------------------|
| | Exp. |
| a, Å | 3.1268(1) |
| c, Å | 4.6060(1) |
| Z(O) | 0.2153(4) |
| Z(H) | 0.4537(10) |



1H: AbC AbC

β -Ni(OH)₂



1 / Type of layer

5.41580 3.1268 90.00 / Unit-cell parameters (a, b, γ)

0.1000 27 / Tabul. param. for scat. fact.

2 / # of atoms

2 'OXYGENES' / # of positions for O atoms

1.00000 / B of O

9.9984 9.5896... / Scat. Fact. for O

0.33300 0.00000 0.992 1.0 'OXYBA1'

x y z (Å) positions, occ.

-.33300 0.00000 -0.992 1.0 'OXYBA1'

1 'Nickel'

0.60000

26.0045 25.7256...

0.00000 0.00000 0.000 1.00 'Ni' [...]

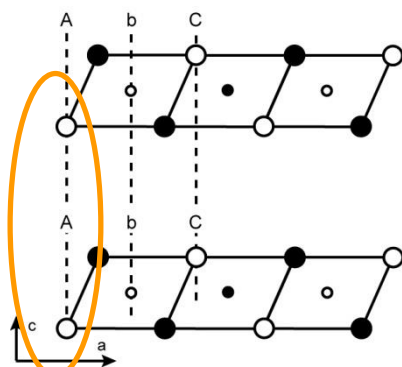
Stacking β -Ni(OH)₂ layers

Kazimirov et al., 2010 Solid State Ionics, 181, 1764

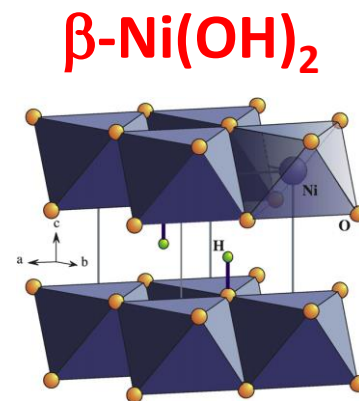
Table 1

Structural parameters of β -Ni(OH)₂ and Mg(OH)₂ obtained by Rietveld refinement of neutron diffraction data measured at room temperature and calculated through the energy minimization procedure. The refinement implied the space symmetry group P-3m1 with Ni/Mg and O/H atoms occupying the (0, 0, 0) and (1/3, 2/3, z) positions respectively. Atomic displacement parameters, B, for Ni/Mg and O were fixed at 0.6 and 1.0 Å² respectively.

| Parameter | Ni(OH) ₂ |
|-----------|---------------------|
| | Exp. |
| a, Å | 3.1268(1) |
| c, Å | 4.6060(1) |
| Z(O) | 0.2153(4) |
| Z(H) | 0.4537(10) |



1H: AbC AbC



1 / Type of layer

5.41580 3.1268 90.00 / Unit-cell parameters (a, b, γ)
[...]

50

500

Average and maximum size of CSDs along c*

0.00 / Abundance of random stacking faults

1.00 / Abundance of this layer

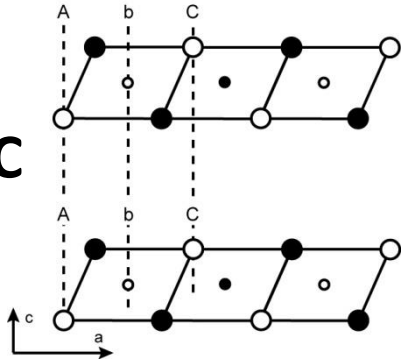
1

1.000 0.00000 0.00 0.00000 0.00 4.6060 0.000

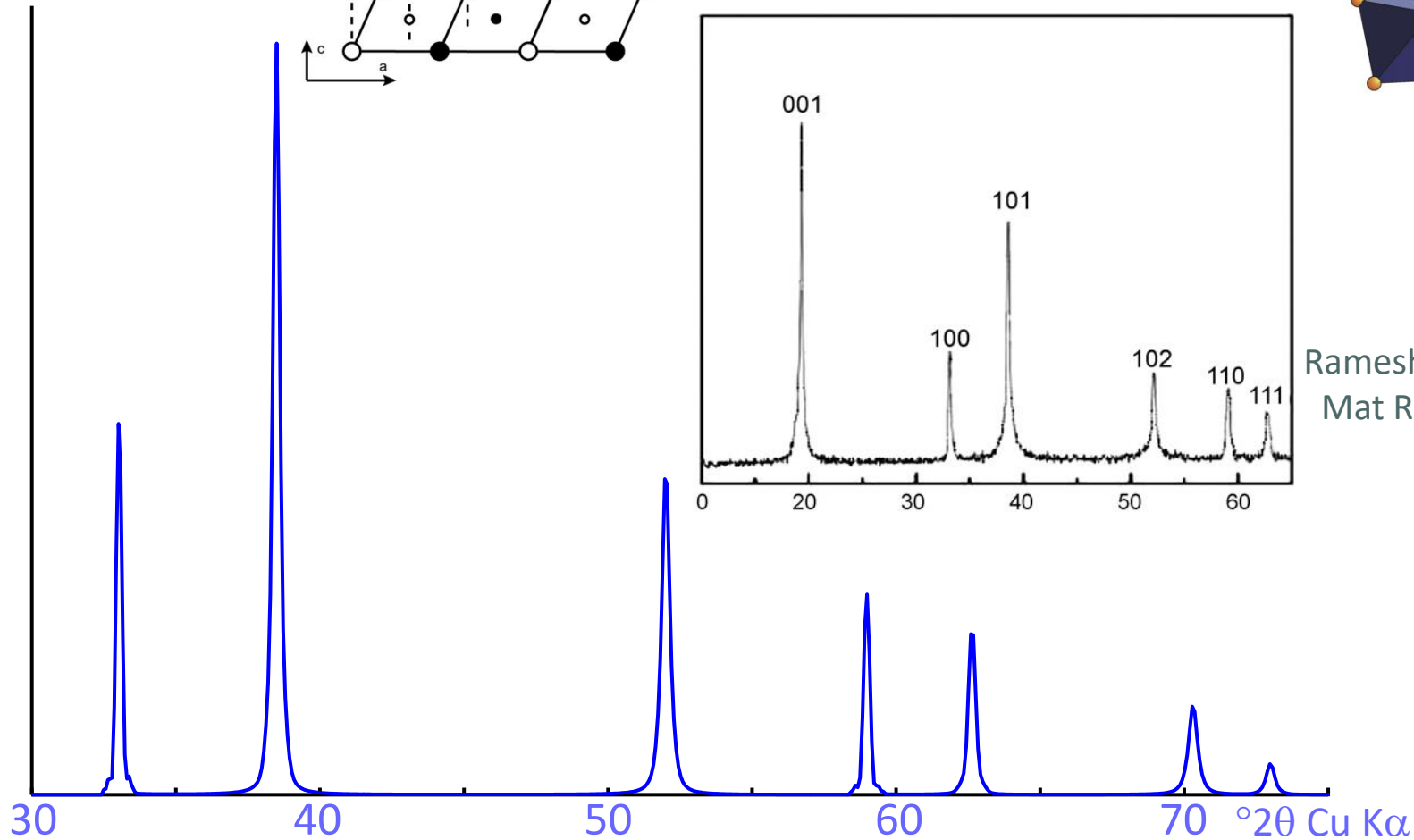
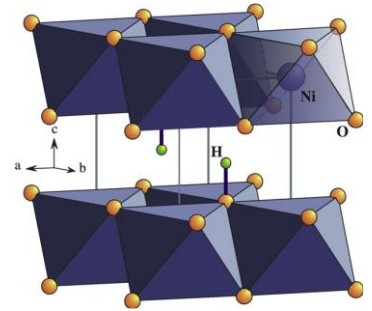
Number, probability, and shift (along a, b, c* axes)

Calculation of periodic 1H β -Ni(OH)₂ polytype

1H: AbC AbC

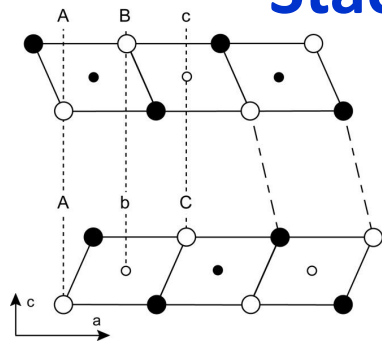


β -Ni(OH)₂



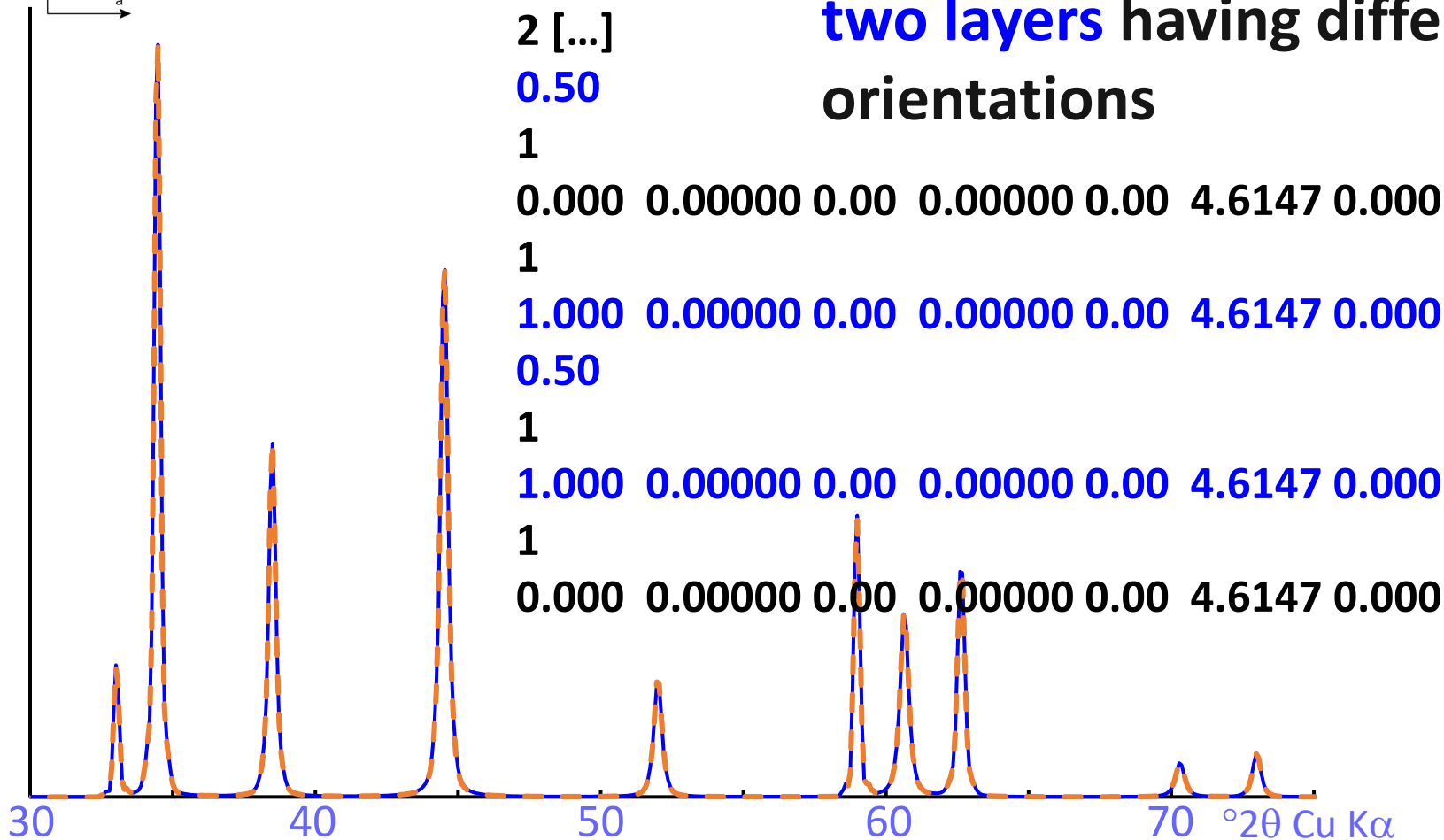
Ramesh & Kamath, 2008
Mat Res Bull, 43, 2827

Stacking octahedral layers different ways



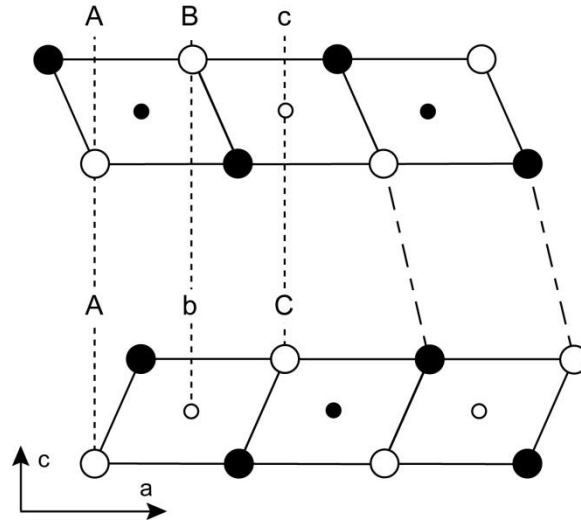
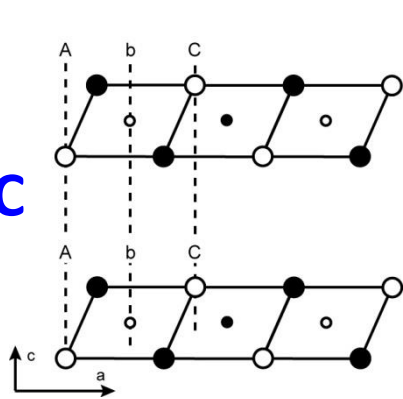
2H₂: AbC AcB AbC

2H₂ polytype can be equally described as a **2 layer polytype** or as the **regular alternation of two layers** having different orientations

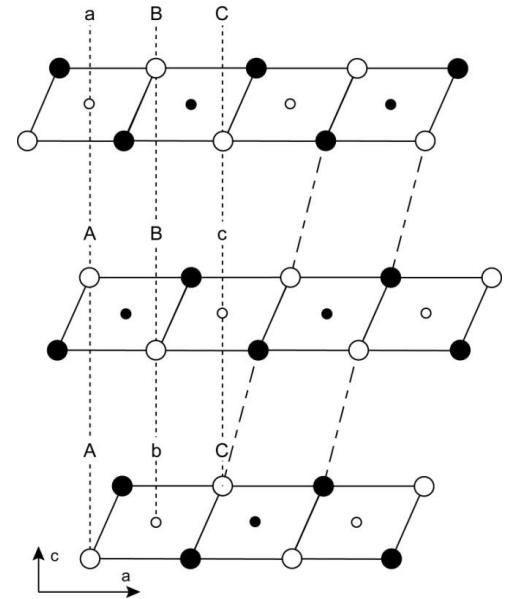


Stacking octahedral layers different ways

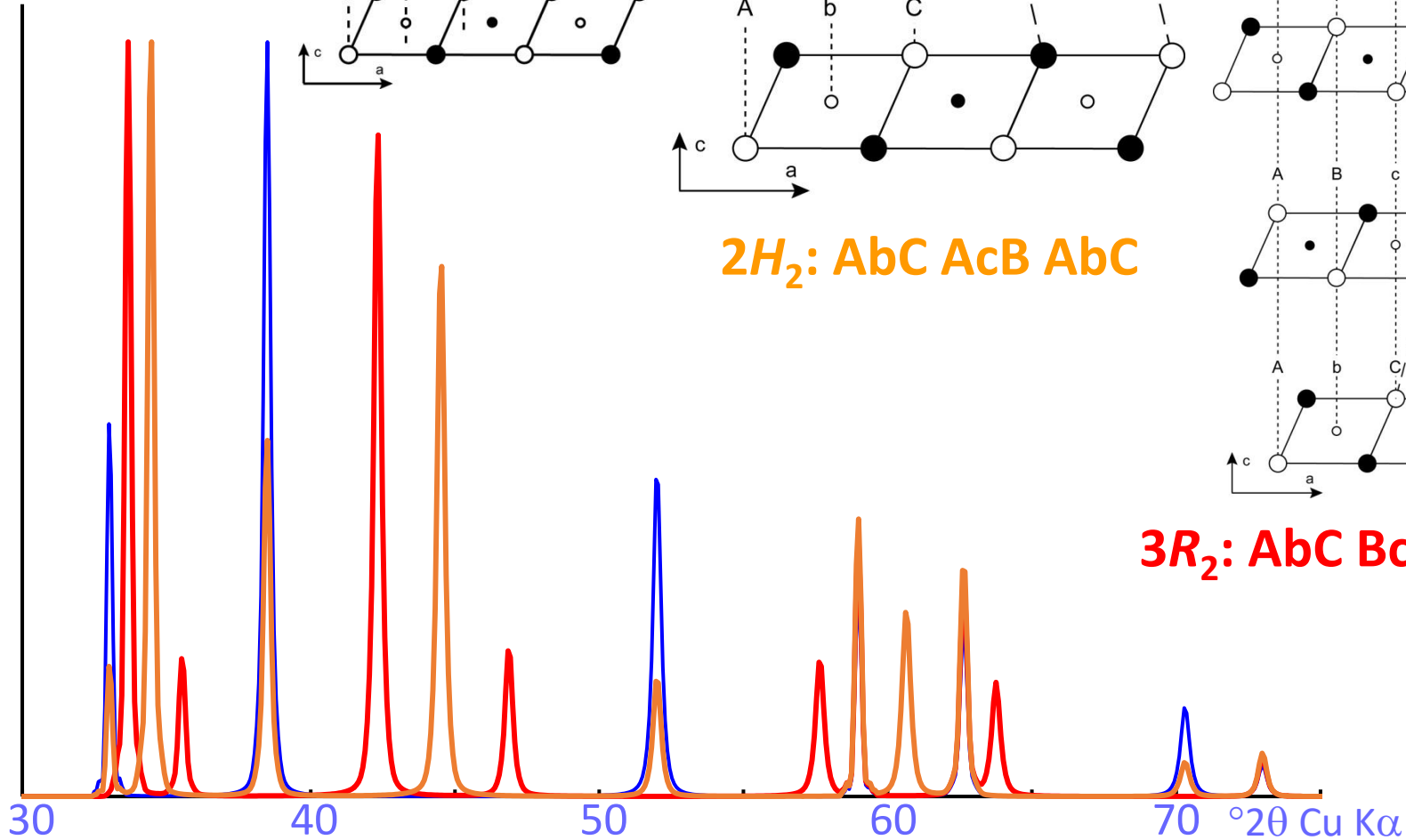
1H: AbC AbC



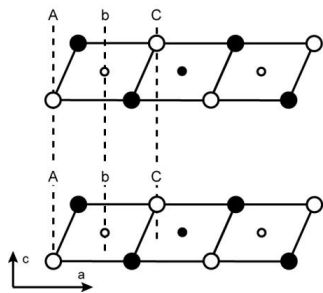
2H₂: AbC AcB AbC



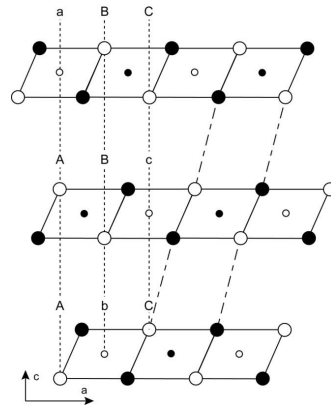
3R₂: AbC BcA CaB AbC



Interstratification of different polytypic fragments



1H: AbC AbC



3R₂: AbC BcA CaB AbC

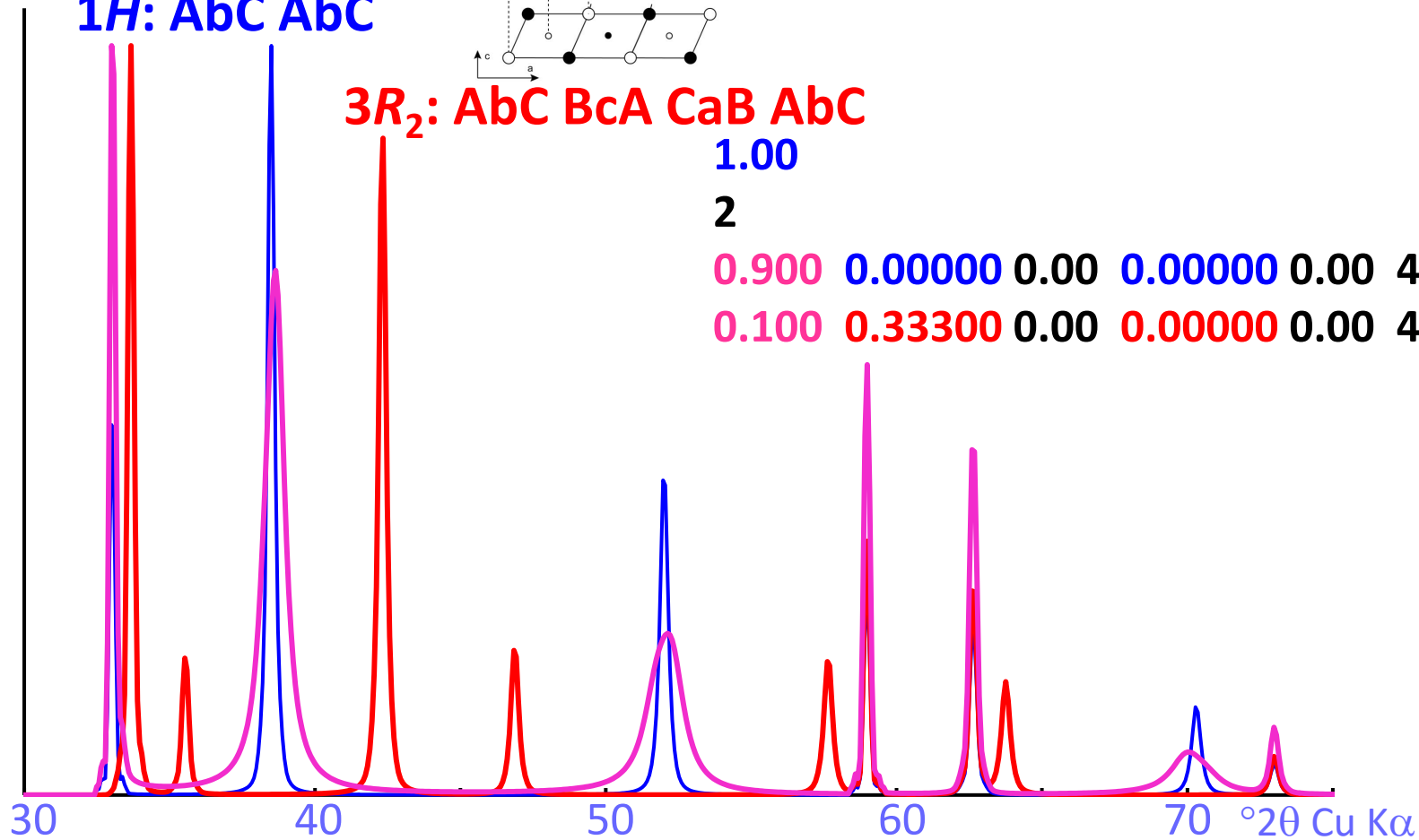
1.00

2

0.900 0.00000 0.00 0.00000 0.00 4.6147 0.000

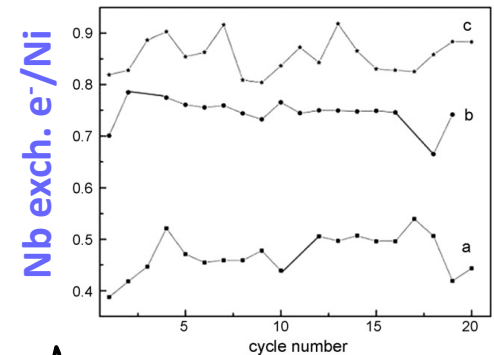
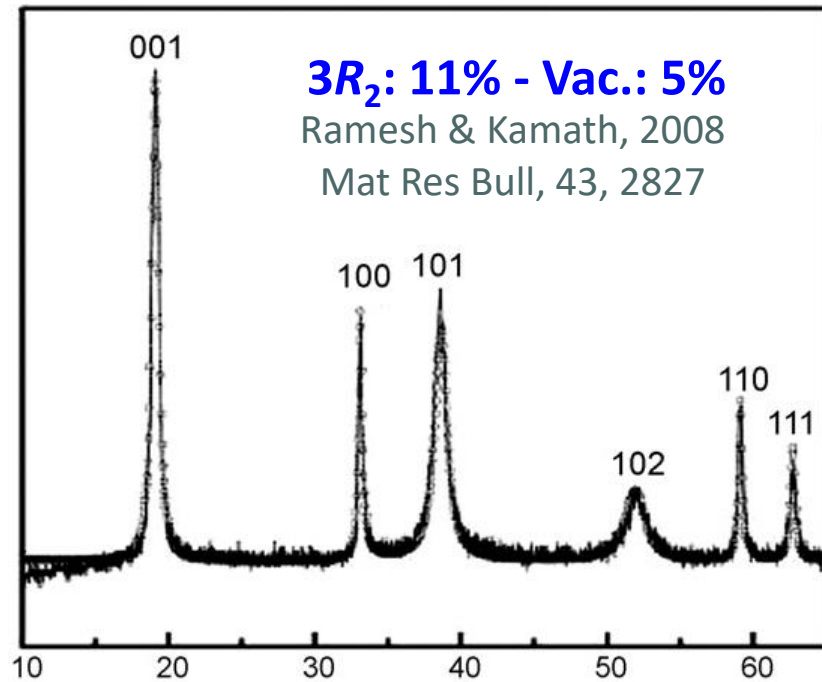
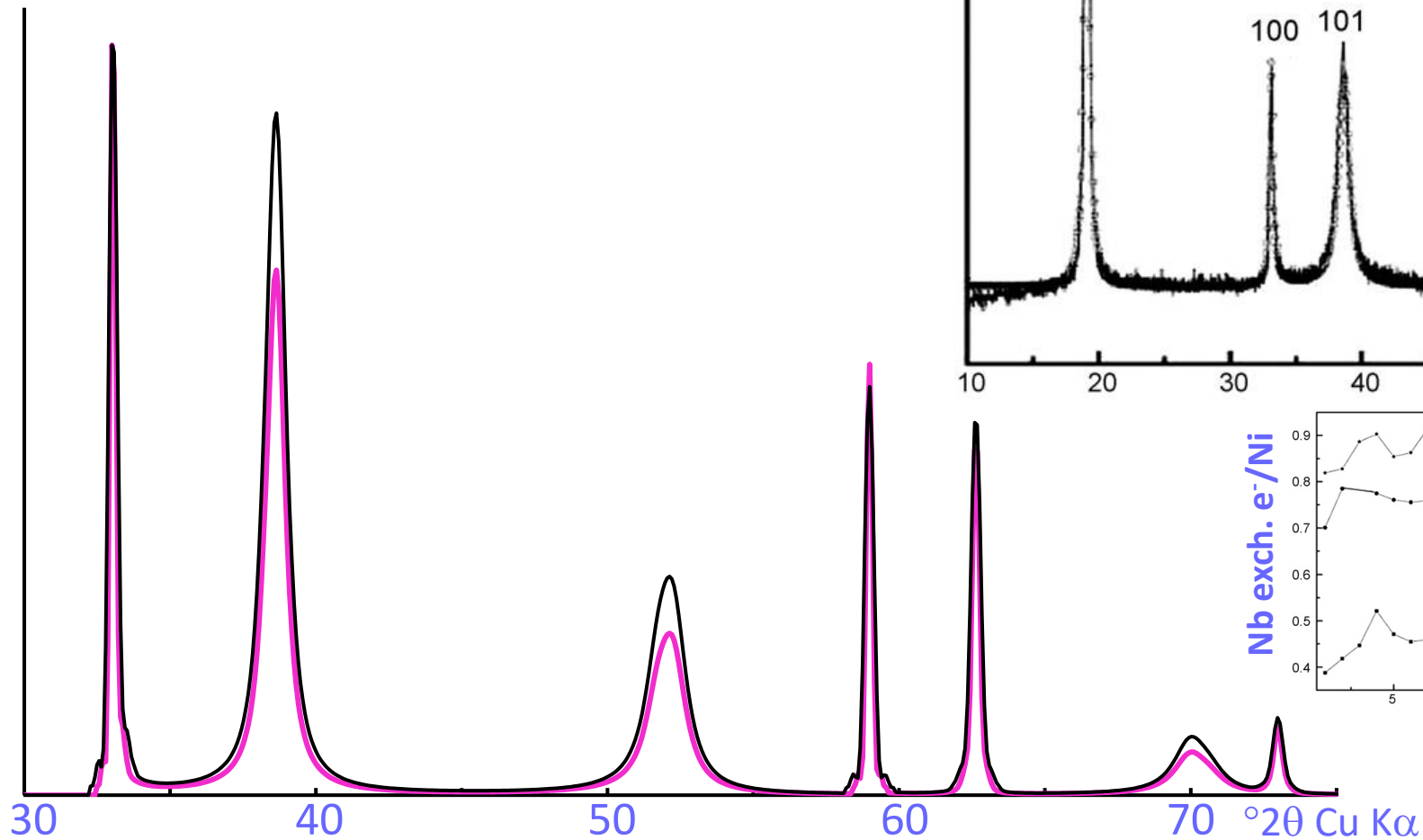
0.100 0.33300 0.00 0.00000 0.00 4.6147 0.000

Random interstratification of **1H** and **3R₂** fragments (90:10 ratio)



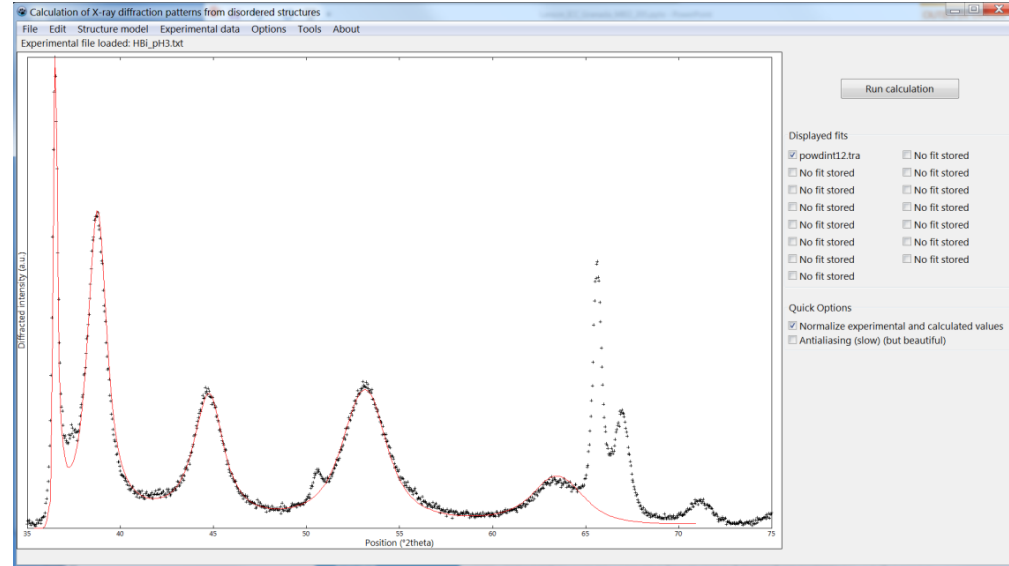
Stacking octahedral layers different ways

Relative intensity of the hkl lines
can be fitted further



Defects Matter

- No limitation as to the number of layers and/or stacking modes
- Random stacking faults can be easily added



- Extremely versatile calculation routine for disordered layered structure (hkl lines and hk diffraction bands):
Ni(OH)₂, Mn oxides, C-S-H, LDH, phyllosilicates,...

- User friendly (?), Freely available
- On-going development of different layer templates

No optimization routine (at the moment – but priority will be given to calculation of 00ℓ lines)

Tutorial - Instructions

- The easiest (in my opinion) way to go through the tutorials is the following: Start the Defects Matter.exe program (win32 version coming this week). You then load the “experimental” data file (NiOH2_Exp.txt or HBi_pH3.txt depending on the example).
- The next thing to do is to copy the content of the input file (0n_NiOH2_indications.dat or 9n_Hbi_pH3_Indications.dat depending on the example) in the window “Edit the raw file” opened through “Structure model”\“Edit raw configuration file” menu). Do not forget to “Save changes” and then “Run calculation” from the main window.
- To check input parameters, you may want to check the powdintnn.res file that is generated after each calculation and that contains all input parameters with explanations on what they are. This file also helps you to search for possible syntax errors in the input file in case nothing is calculated.
- If you get stuck do not hesitate to contact me @ bruno.lanson@univ-grenoble-alpes.fr

List of files – Example #1

- NiOH2_Exp.txt: “experimental” data file
- 01_NiOH2_1H.dat: 1H model no displacement between successive layers
- 02_NiOH2_3R2.dat: 3R₂ polytype defined with the same layer and a +0.333a displacement between successive layers
- 03_NiOH2_2H2_Double.dat: 2H₂ polytype defined as a double layer (the two successive layers are explicitly described) and no displacement between successive layers. Note i) the positions of Ni in the 2nd layer is 0.333a as the layer is rotated by 180° (+ no rotation) and ii) that the size of the domains along c* (no 25 layers in average) is divided by two as the unit cell contains two layers
- 04_NiOH2_2H2_2layers.dat: 2H₂ polytype defined as two individual layers (one in each orientation) and no displacement between successive layers. Stacking of the two layers has to be described: 50% (0.5) is the proportion of each layer 1st layer can only be followed by 2nd layer (0% probability of layer 1- layer 1 pairs, 100% chance for layer 1 - layer 2 pairs)

List of files – Example #1

- 05_NiOH2_0.1_3R2.dat: Interstratification between $1H$ and $3R_2$ polytypes (0.9:0.1 proportions). Both polytypes are described with the same layer (100% of layer 1) but different translations between successive layers. Interstratification is described from the probabilities of having no translation ($1H$: 90% chance) or a $+0.333a$ translation ($3R_2$: 10% chance) between successive layers
- 06_NiOH2_0.1_3R2_CSD.dat: Same as previous with smaller sizes of CSDs within the ab plane which is decreased from 20 to 14 nm – see almost at the end of the input file (sizes are given in Å)
- 07_NiOH2_Opti.dat: Same as previous with additional broadening related to the presence of stacking faults (15% line before the abundance of layer 1) and intensity distribution modified by the presence of vacant octahedral sites (10% as the occupancy of the Ni site is reduced to 90%)

List of files – Example #2

- Hbi_pH3_Exp.txt: “experimental” data file
- 90_Hbi_pH3_1H.dat: 1H model no displacement between successive layers. The layers contain 10% vacant sites capped on either side of the layer by interlayer Mn (5% on each side). Octahedral coordination of the interlayer Mn cations is ensured by the presence of OH/H₂O molecules in the interlayer.
- 91_Hbi_pH3_1H.dat_0.2_Wr: Same as previous with additional broadening related to the presence of stacking faults (20% line before the abundance of layer 1)
- 92_Hbi_pH3_1H.dat_3R1.dat: 3R₁ polytype defined with the same layer and a - 0.333a displacement between successive layers
- 93_Hbi_pH3_1H.dat_3R2.dat: 3R₂ polytype defined with the same layer and a +0.333a displacement between successive layers. From the last 3 plots, the presence of 3R₂ fragments (in a structure dominated by the 1H stacking mode) is more likely to account for the observed small positional shift than the presence of 3R₁ fragments

List of files – Example #2

- 94_Hbi_pH3_1H_0.1_3R2.dat: Interstratification between $1H$ and $3R_2$ polytypes (0.9:0.1 proportions). Both polytypes are described with the same layer (100% of layer 1) but different translations between successive layers. Interstratification is described from the probabilities of having no translation ($1H$: 90% chance) or a $+0.333a$ translation ($3R_2$: 10% chance) between successive layers
- 95_Hbi_pH3_1H_0.2_3R2.dat: Interstratification between $1H$ and $3R_2$ polytypes (0.9:0.1 proportions). Both polytypes are described with the same layer (100% of layer 1) but different translations between successive layers. Interstratification is described from the probabilities of having no translation ($1H$: 90% chance) or a $+0.333a$ translation ($3R_2$: 10% chance) between successive layers
- 96_Hbi_pH3_ok.dat: Same as previous with intensity distribution modified by the increased proportion of vacant octahedral sites (20% compared to 10%) and of interlayer Mn cations (10% compared to 5% on either side of the layer) and associated O atoms (OH/H₂O)