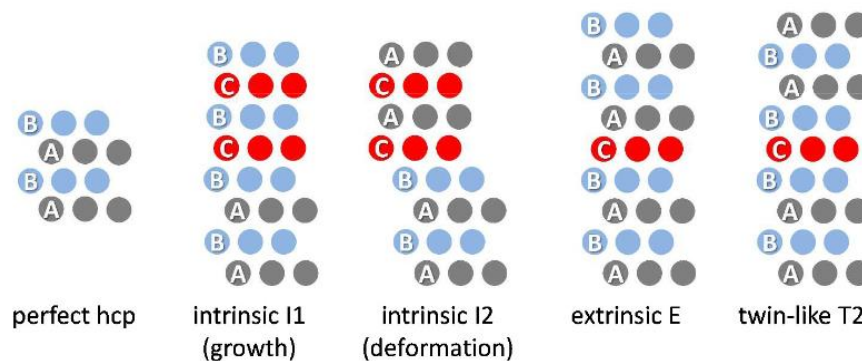


2019 - Annual School on Neutron Diffraction Data Treatment using the FullProf Suite

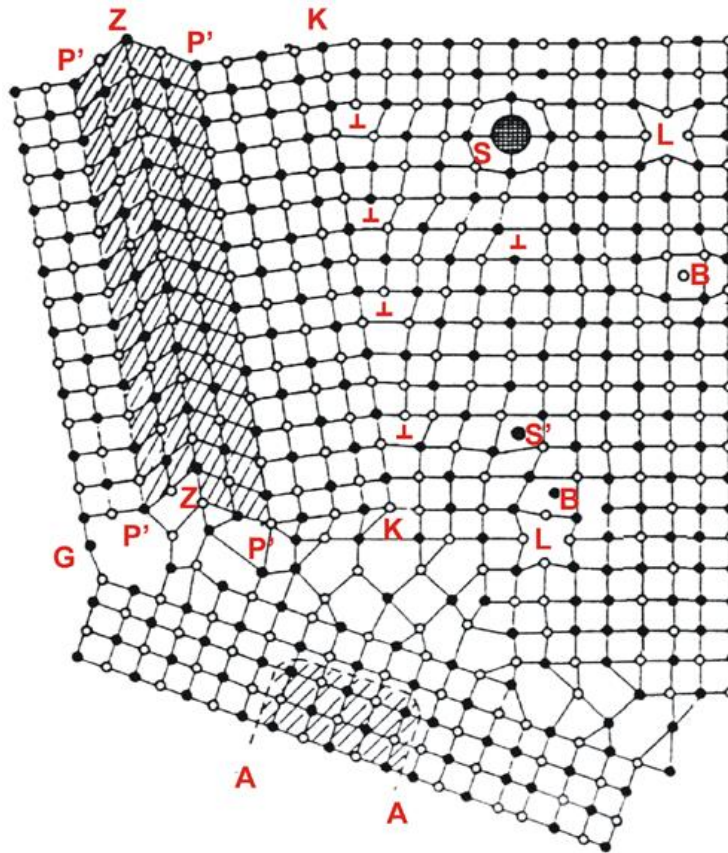
Introduction to the FAULTS program

Montse Casas Cabanas



Defects in crystalline materials

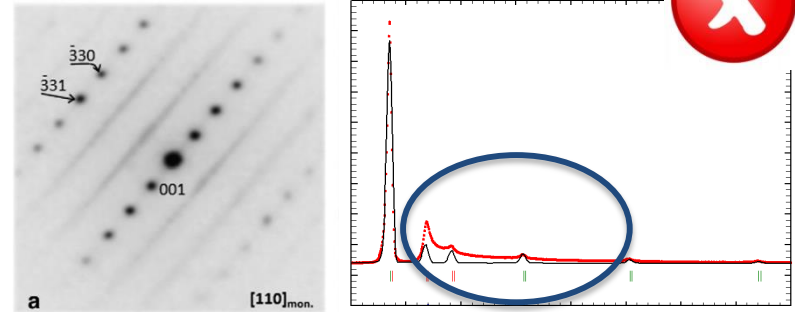
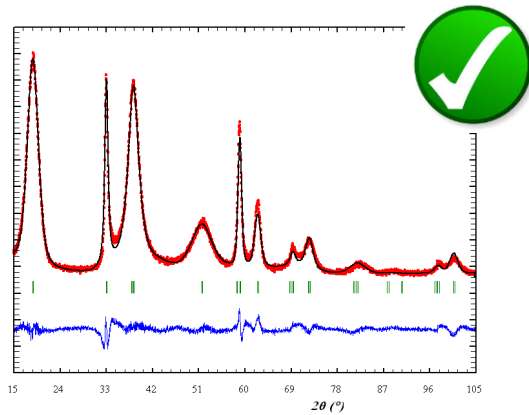
REAL materials can be complex...



- A antiphase domain
- B interstitial atom
- G, K grain boundary
- L vacancy
- S substitutional impurity
- S' interstitial impurity
- P, Z stacking faults
- ⊥ dislocations
- intergrowths

FAULTS program

Rietveld softwares (FullProf, GSAS, etc.) include advanced models for anisotropic size and strains and antiphase domains BUT cannot model non-averaged structures



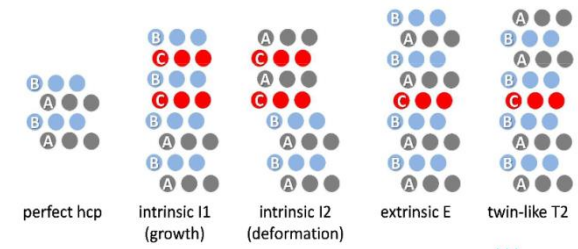
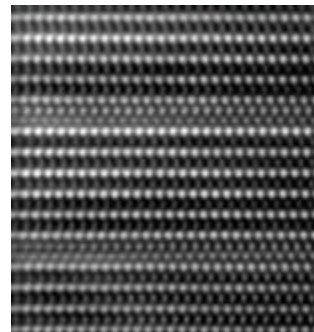
Boulineau *et al. Solid State Ionics* **2010**, 180, 1652.

Casas-Cabanas *et al. Journal of Power Sources* **2007**, 174, 414.

FAULTS

- ✓ Fast
- ✓ Robust
- ✓ User friendly
- ✓ DiFFaX2FAULTS convertor
- ✓ Secondary phases
- ✓ Background refinement

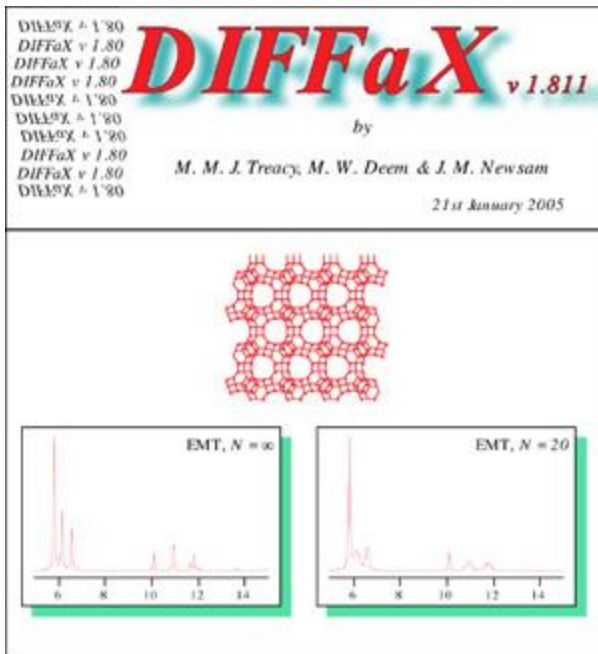
...



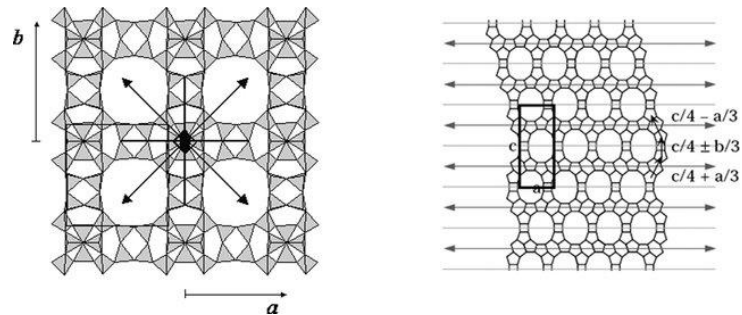
FAULTS program

History

1991 **DIFFaX**: recursion algorithm for computing diffraction from faulted crystals with coherent planar defects. [Simulation](#) code in Fortran 77.



Developed by M.M. Treacy and J.M. Newsam to study zeolite-type materials



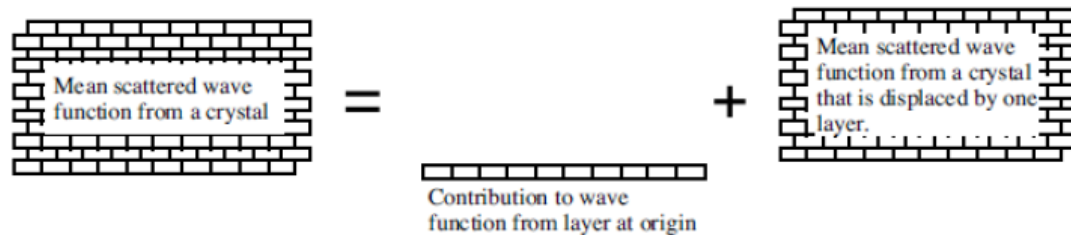
Treacy M.M.J., Newsam J.M. and Deem M.W. A general recursion method for calculating diffracted intensities from crystals containing planar faults. Proc. R. Soc. Lond. A, 433:499-520, 1991.

http://www.public.asu.edu/~mtreacy/DIFFaX_manual.pdf

FAULTS program

DIFFaX recursion algorithm

DIFFaX exploits the recurring patterns found in randomized stacking sequences to compute the average interference wavefunction scattered from each layer type occurring in a faulted crystal.



$$\Psi(\mathbf{u}) = F(\mathbf{u}) + \exp(-2\pi i \mathbf{u} \cdot \mathbf{R}) \Psi(\mathbf{u}) \quad \Longleftrightarrow \quad \Psi(\mathbf{u}) = \frac{F(\mathbf{u})}{1 - \exp(-2\pi i \mathbf{u} \cdot \mathbf{R})}$$

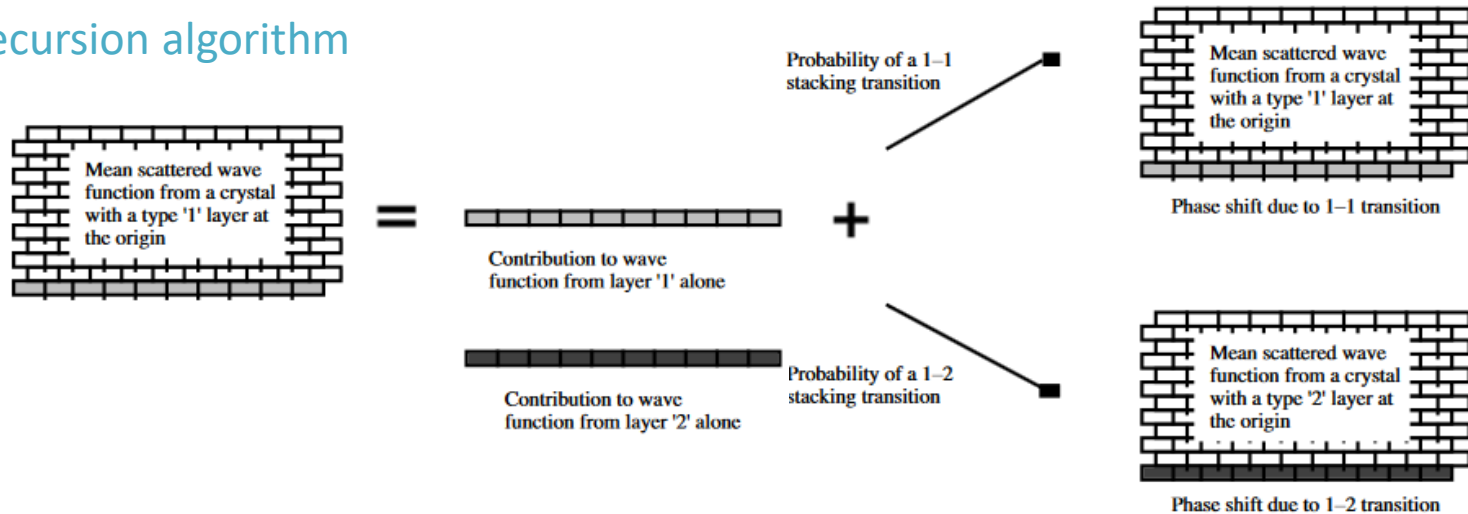
The scattered wave function from a crystal centered on any layer, is equivalent to the scattering contribution from that layer plus the scattered wavefunction from the displaced crystal centered at the next layer.

Treacy M.M.J., Newsam J.M. and Deem M.W. A general recursion method for calculating directed intensities from crystals containing planar faults. Proc. R. Soc. Lond. A, 433:499-520, 1991.

http://www.public.asu.edu/~mtreacy/DIFFaX_manual.pdf

FAULTS program

DIFFaX recursion algorithm



$$\Psi_i(\mathbf{u}) = F_i(\mathbf{u}) + \sum_{j=1,2} \alpha_{ij} \exp(-2\pi i \mathbf{u} \cdot \mathbf{R}_{ij}) \Psi_j(\mathbf{u})$$

The intensity of a statistical ensemble of crystallites is given by the incoherent sum :

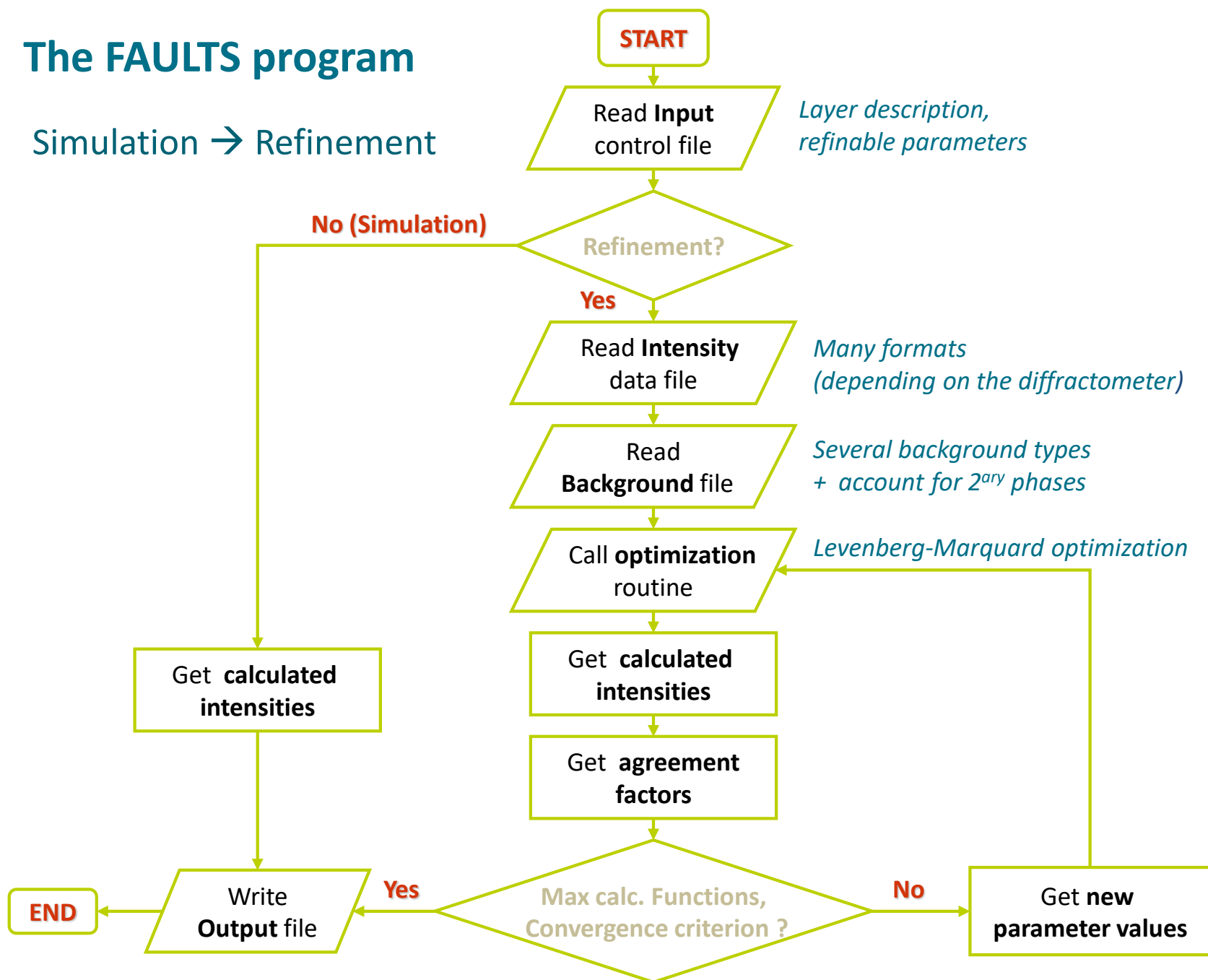
$$\frac{I(\mathbf{u})}{N} = \sum_{i=1,2} g_i \left(F^*(\mathbf{u}) \Psi(\mathbf{u}) + F(\mathbf{u}) \Psi^*(\mathbf{u}) - |F_i(\mathbf{u})|^2 \right)$$

where the layer existence probability factors g_i are given by:

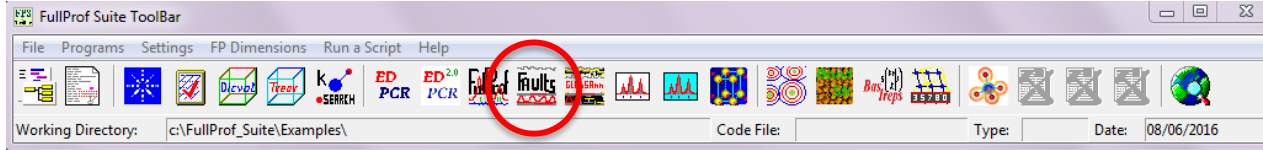
$$g_i = \sum_{j=1}^N g_j \alpha_{ji} \quad \sum_{i=1}^N g_i = 1$$

The FAULTS program

Simulation → Refinement



The FAULTS program



FullProf Suite ToolBar

File Programs Settings FP Dimensions Run a Script Help

Working Directory: c:\FullProf_Suite\Examples\ Code File: Type: Date: 08/06/2016

```
Command Prompt
C:\FullProf_Suite\Examples\Faults_Examples>faults

_____ FAULTS 2015 _____

A computer program based on DIFFaX for
refining faulted layered structures

Authors of DIFFaX:
M. M. J. Treacy , M. W. Deen & J. M. Newsam

Authors of FAULTS:
Montse Casas-Cabanas (CIC Energigune)
Jokin Rikarte (CIC Energigune)
Marine Reynaud (CIC Energigune)
Juan Rodriguez-Carvajal (Institut Laue-Langevin)

[version: Oct. 2015]

=> Enter the complete name of the structure input file: LiNiO2_refine.flts
=> Structure input file read in
=> Reading scattering factor datafile:c:\FullProf_Suite\data.sfc'. . .
=> Scattering factor data read in
=> Reading Pattern file=LiNiO2_simul.dat
=> Diffraction point symmetry is -1
=> Layers are to be treated as having infinite lateral width.
=> Checking for conflicts in atomic positions . . .
=> No overlap of atoms has been detected
=> Start LWA refinement
=> WARNINGS: Layer 4 does not occur in any significant quantity.
=> WARNINGS: Layer 5 does not occur in any significant quantity.
=> WARNINGS: Layer 6 does not occur in any significant quantity.
=> Iteration 0 R-Factor = 45.61575 Chi2 = 186.38556
=> WARNINGS: Layer 4 does not occur in any significant quantity.
=> WARNINGS: Layer 5 does not occur in any significant quantity.
=> WARNINGS: Layer 6 does not occur in any significant quantity.
=> Iteration 1 R-Factor = 37.86483 Chi2 = 57.88659
=> WARNINGS: Layer 4 does not occur in any significant quantity.
=> WARNINGS: Layer 5 does not occur in any significant quantity.
=> WARNINGS: Layer 6 does not occur in any significant quantity.
=> Iteration 2 R-Factor = 34.17787 Chi2 = 51.39943
=> WARNINGS: Layer 4 does not occur in any significant quantity.
=> WARNINGS: Layer 5 does not occur in any significant quantity.
=> WARNINGS: Layer 6 does not occur in any significant quantity.
=> Iteration 3 R-Factor = 30.33366 Chi2 = 42.09781
=> Iteration 4 R-Factor = 25.80530 Chi2 = 31.54553
=> Iteration 5 R-Factor = 17.37586 Chi2 = 14.19661
=> Iteration 6 R-Factor = 11.64187 Chi2 = 5.95918
=> Iteration 7 R-Factor = 6.76640 Chi2 = 1.70764
=> Iteration 8 R-Factor = 5.72253 Chi2 = 1.27427
=> Iteration 9 R-Factor = 4.93433 Chi2 = 1.04050
=> Iteration 10 R-Factor = 4.86496 Chi2 = 1.03878

=> Correlation Matrix:
Correlation: 51 > 30% for parameters: pos_#0302 & Scale_Factor
=> There are 1 values of Correlation > 30%

FINAL LIST OF REFINED PARAMETERS AND STANDARD DEVIATIONS
-----
# Parameter name No.(Model) Final-Value Standard Deviation
1 cell_b 1 2.81512 0.00009
2 pos_#0302 2 0.07157 0.00015
3 Scale_Factor 3 1.01035 0.00233
4 alpha0306 4 0.14305 0.00001
5 alpha0606 5 0.15793 0.00582
6 cell_c 6 13.36379 0.00068

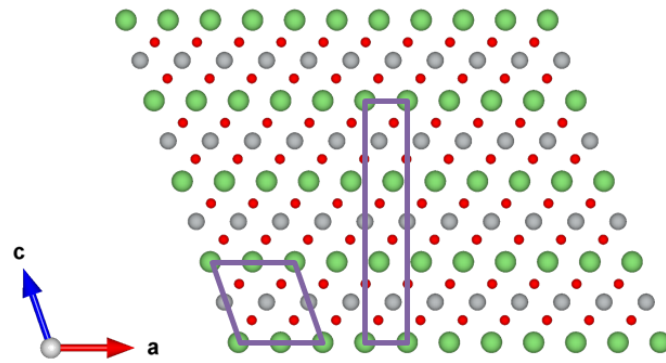
=> Final value of Chi2: 1.0388
=> Initial Chi2: 186.39 Convergence reached: The relative error between x and the solution is at most 0.10000E-04
=> Writing Bragg positions ...
=> Number of layers and atoms for FP_Studio: 7 29
=> FAULTS ended normally....
=> Total CPU-time: 2 minutes and 13.1781 seconds
=> Press <Enter> to finish ...
```

Included in FullProf Suite

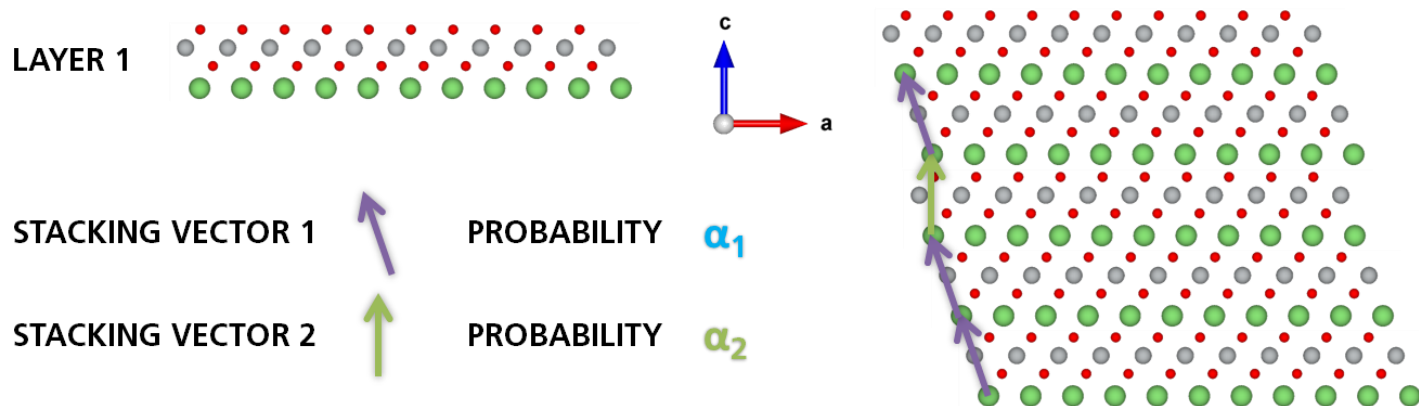
The FAULTS program

Building your structural model

no crystallographic unit cell
no space group



but **layers** interconnected via **stacking vectors** that occur with certain **probabilities**



The FAULTS program

Building
your
structural
model

4 layers are required to describe fault clustering in diamond

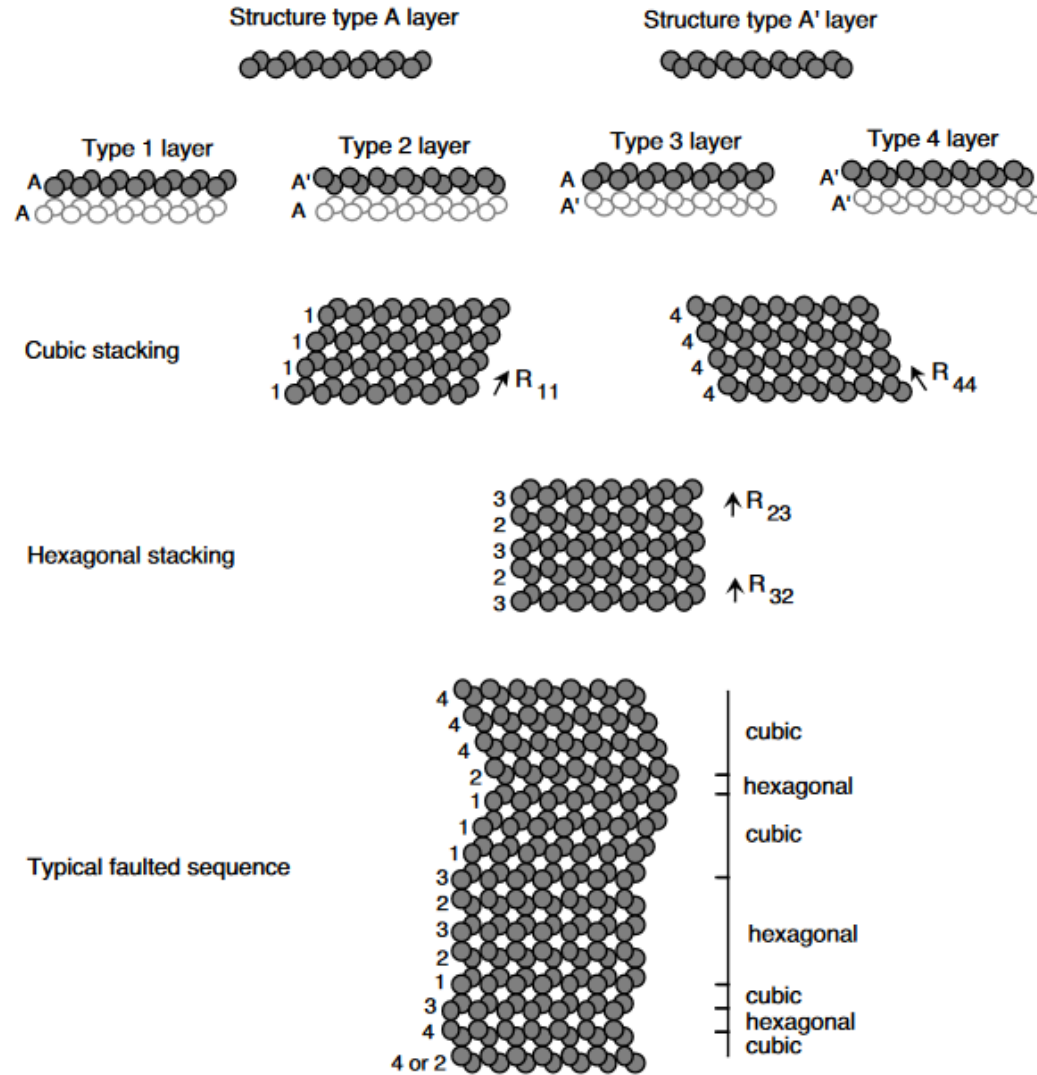


Figure 7: $[1\bar{1}0]$ view showing fault clustering in diamond/lonsdaleite.

The FAULTS program

The *.flts input file

Imq - Notepad

```
File Edit Format View Help

TITLE
NI(OH)2 WITH DEFORMATION AND GROWTH FAULTS

Instrumental And Size Broadening
!Type of Radiation
Radiation X-Ray
!wavelength 1.5406 lambda1 lambda2 ratio
!instrumental aberrations zero sycos sysin
Aberrations 0.0000 0.0000 0.0000 0.0000

!instr. broadening u v w x Dg
Pseudo-voigt 0.032948 -0.003558 0.227400 0.000000 479.26
1.00 0.00 0.00 0.00 1.00

Structural
!Cell a b c gamma
Cell 3.128608 3.128608 4.608609 120.00
21.00 21.00 1.00 0.00

!Laue symmetry
Symm -3m
!number of layer types
Nlayers 4
!layer width
Lwidth Infinite

Layer 1
!Layer symmetry
LSYM Centrosymmetric
!Atom name number x y z Biso Occ
Atom N12+ 1 0.67000 0.33000 0.00000 1.06197 0.50000
0.00 0.00 0.00 0.00 0.00
!Atom name number x y z Biso Occ
Atom O2- 2 0.33000 0.67000 0.22265 0.75961 1.00000
0.00 0.00 71.00 0.00 0.00

Layer 2 = 1
Stacking
!stacking type
Recursive
!number of layers
40.0
61.0

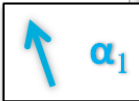
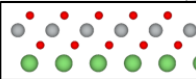
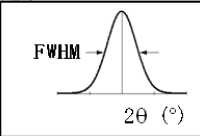
Transitions
!layer 1 to layer 1
LT 0.808196 0.000000 0.000000 1.000000
-92.000000 0.000000 0.000000 0.000000
FW 0.00 0.00 0.00 0.00 0.00 0.00
0.00 0.00 0.00 0.00 0.00 0.00
!layer 1 to layer 2
LT 0.095902 0.333000 0.666700 1.000000
91.000000 0.000000 0.000000 0.000000
FW 0.00 0.00 0.00 0.00 0.00 0.00
0.00 0.00 0.00 0.00 0.00 0.00
!layer 2 to layer 1
LT 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000
FW 0.00 0.00 0.00 0.00 0.00 0.00
0.00 0.00 0.00 0.00 0.00 0.00
!layer 2 to layer 2
LT 0.919278 0.000000 0.000000 1.000000
-101.000000 0.000000 0.000000 0.000000
FW 0.00 0.00 0.00 0.00 0.00 0.00
0.00 0.00 0.00 0.00 0.00 0.00
```

Instrumental parameters and size broadening

Structural description of the layers







Refinable parameter + refinement code

Stacking vectors and probabilities



The FAULTS program

Output files

Final report	Contains refined values for refinable parameters. Same structure as input file, can be used as input file for further iterations.	 LiNiO2_refine_new.flts
Crystallographic structure files	Contains structural model to be read with visualization programs.	 LiNiO2_refine1.fst  LiNiO2_refine1_fts.cif  LiNiO2_refine1_fts.vesta
Progress report	contains information about the different steps of the calculation.	 LiNiO2_refine1.out
Observed and calculated profile	Contains experimental pattern, calculated one with the best fit, their difference plot and Bragg reflections.	 LiNiO2_refine1.prf

The FAULTS program

Some important information:

- Profile parameters

$$H_G^2 = U \tan^2 \theta + V \tan \theta + W + \frac{4 \ln 2 \lambda^2}{\pi D_G^2 \cos^2 \theta} \left(\frac{180}{\pi} \right)^2$$

$$H_L = X \tan \theta + \frac{2 \lambda}{\pi D_L \cos \theta} \left(\frac{180}{\pi} \right)$$

The combination of profile parameters should not lead to a profile function with negative values!

- Tabs are not allowed in the input files of FAULTS (use Notepad++ or similar)
- A missing refinement code will not be considered as zero but will produce an error
- All the non-optional sections and keywords have to be present in the *.flts input file

The FAULTS program

Some important information:

- Filename extension is limited
- DIFFaX2FAULTS permits to convert DIFFaX input files into FAULTS input files
- Check output files and message errors from the commander window
- Read the manual! It contains valuable information

FAULTS manual

Montse Casas Cabanas (CIC energiGUNE), Marine Reynaud (CIC energiGUNE)
Jokin Rikarte Ormazabal (CIC energiGUNE), Pavel Horbach (ILL)
and Juan Rodriguez Carvajal (ILL)

September 2018

The FAULTS program

Building your structural model



- the creation of error-free files is surprisingly difficult
- Frequently, the plane of the layers will not coincide conveniently with any of the unit cell faces of the parent crystal
- There can be different equivalent structure descriptions
- Check your model with vesta or FPStudio!

Example 1

Graphite

Building structural model

Layer description different from unit cell (3R)

Simulation

Example 2

LiNiO_2

Building structural model of a layered material (ideal vs defects)

Simulation and refinement

Use of secondary phases

Generation of the Bragg positions of the average cell

Example 3

Li_2MnO_3

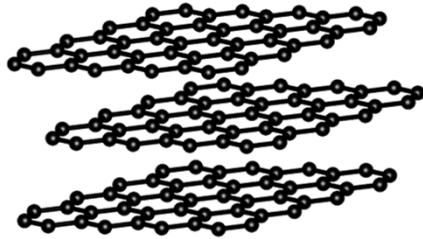
Building structural model of a monoclinic cell

Simulations of XRD and ED patterns

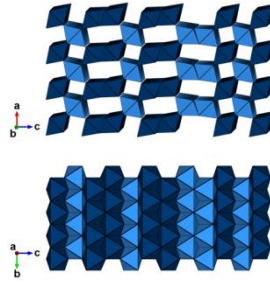
FAULTS program

Energy storage

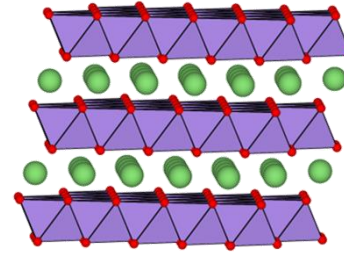
Graphite



γ -MnO₂



Layered transition metal oxides

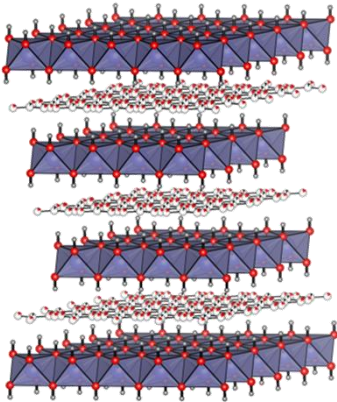


PHYSICAL-CHEMICAL PROPERTIES



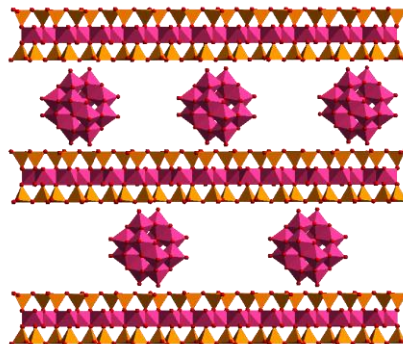
STRUCTURAL FEATURES

Catalysis



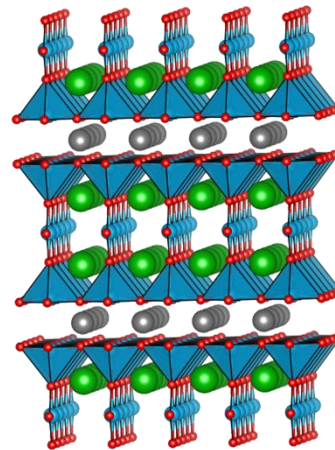
Layered double hydroxides (LDHs)

Drug delivery



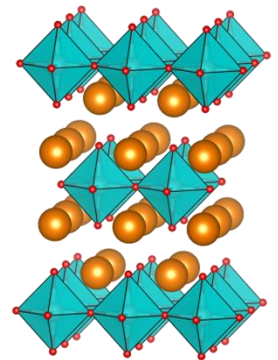
Pillared Clays (PILCS)

Superconductors



Cuprates

Magnetism



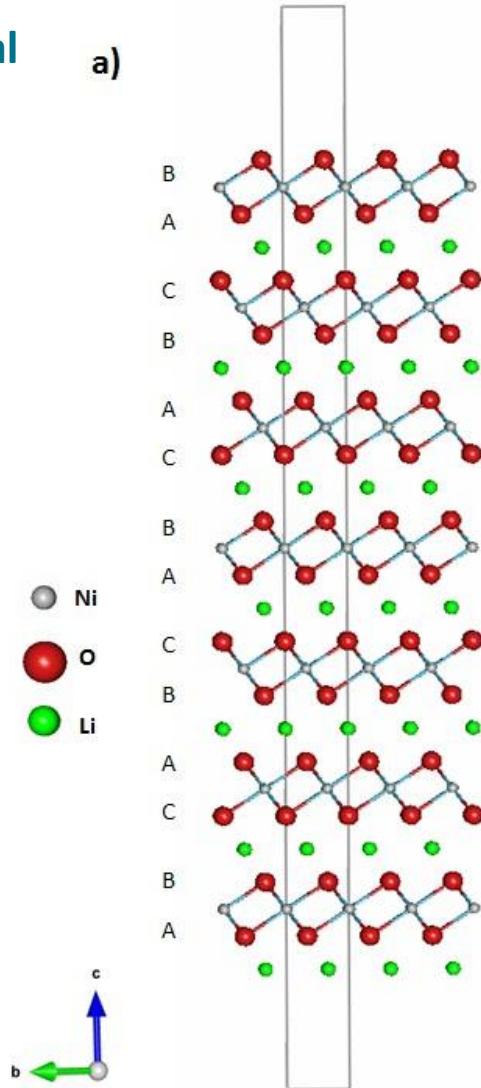
Layered perovskites

The FAULTS program

Example 2 LiNiO_2

Ideal
O3

a)



Faulted

b)

