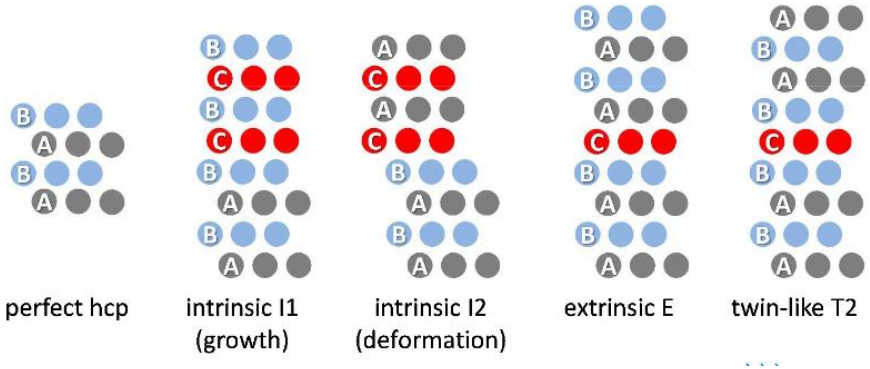
Second 2023 FullProf School

Introduction to the FAULTS program

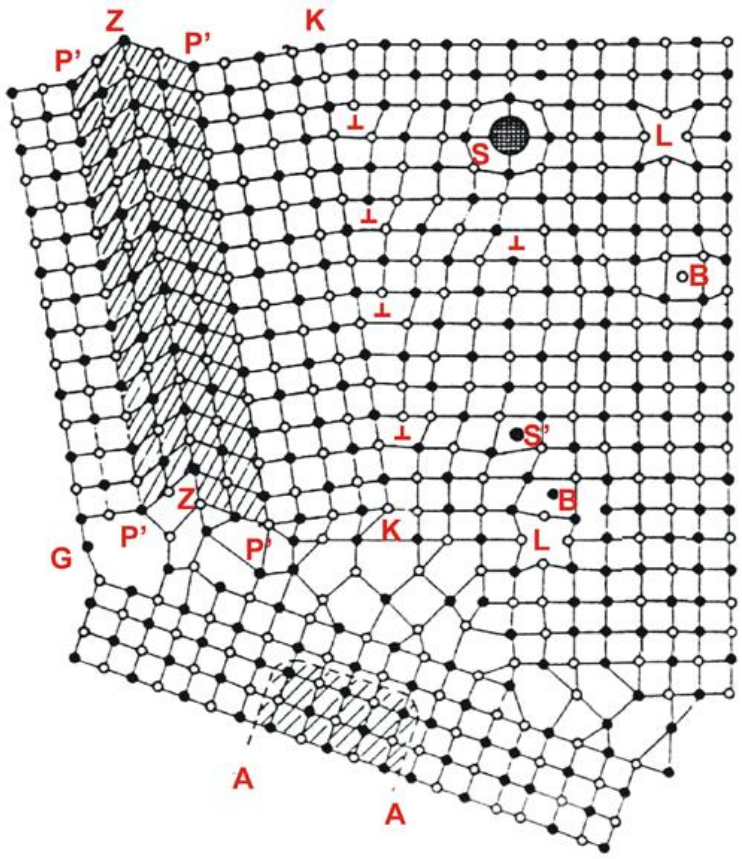
Marine Reynaud



Support: faults@cicenergigune.com

Defects in crystalline materials

REAL materials can be complex…



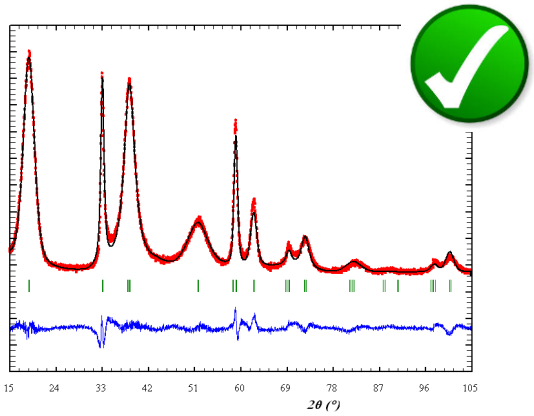
A	antiphase domain
B	interstitial atom
G, K	grain boundary
L	vacancy
S	substitutional impurity
S'	interstitial impurity
P, Z	stacking faults
⊥	dislocations
	intergrowths

Hornbogen E. and Petzow G. Z. Metallk., 61:81-94, 1970
Reynaud, Serrano-Sevillano, Casas-Cabanas, Chemistry of Materials 2023

Imperfection is a universal feature of crystalline materials, which has profound effects on macroscopic properties

FAULTS program

$Ni(OH)_2$



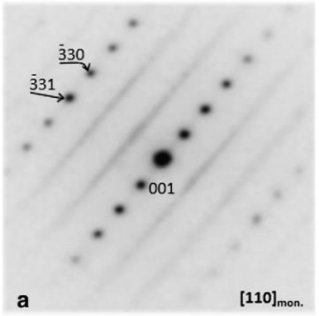
Casas-Cabanas *et al. Journal of Power Sources* **2007**, *174*, 414.

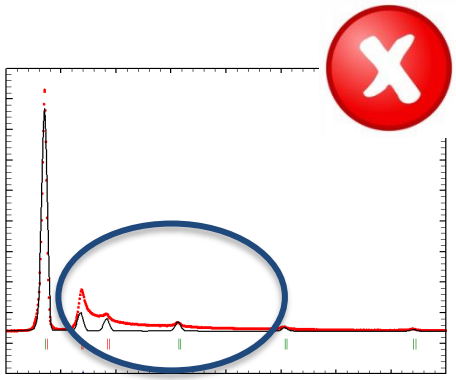
Rietveld method:
assumption of an **average 3D structure**

Most Rietveld-based softwares (FullProf, GSAS, etc) include advanced models for anisotropic size, strains, point defects, anti-phase boundaries, etc.

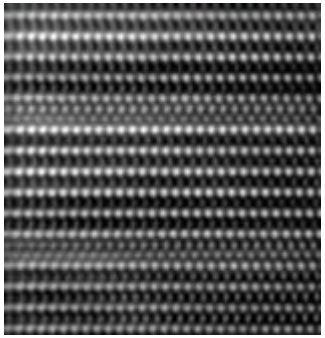
BUT unsuitable when there is **no strict periodicity on the three dimensions** (*i.e.* layered materials, planar defects, stacking faults, intergrowths).

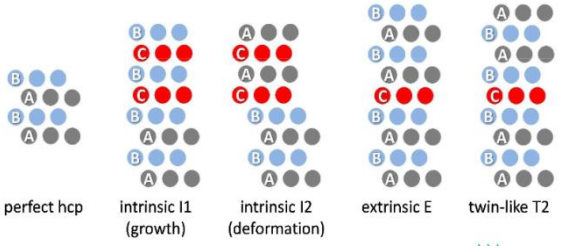
Li_2MnO_3





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

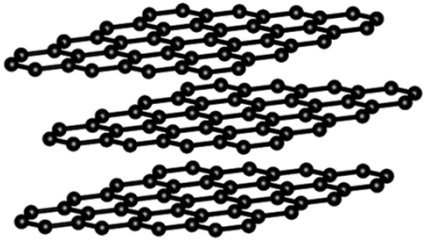




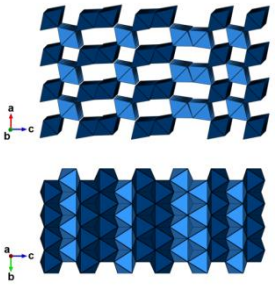
FAULTS program

Energy storage

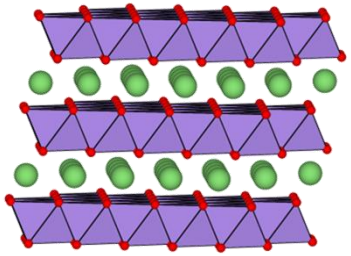
Graphite



γ-MnO_2



Layered transition metal oxides

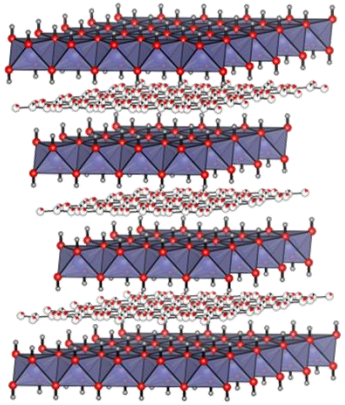


PHYSICAL-CHEMICAL PROPERTIES

↕

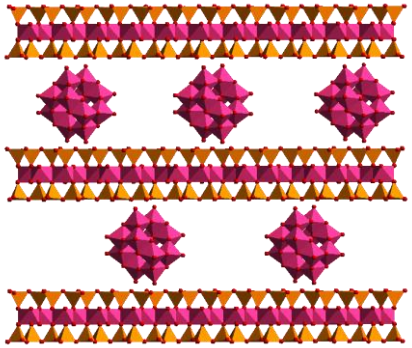
STRUCTURAL FEATURES

Catalysis



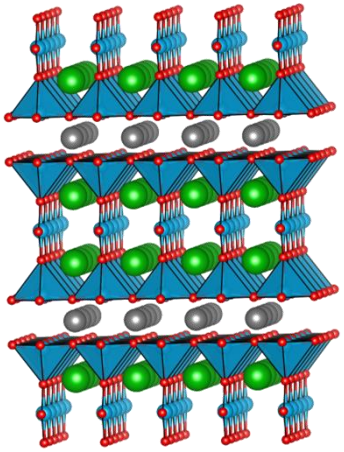
Layered double hydroxides (LDHs)

Drug delivery



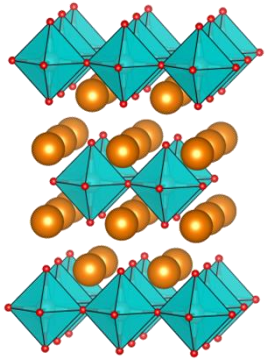
Pillared Clays (PILCS)

Superconductors



Cuprates

Magnetism



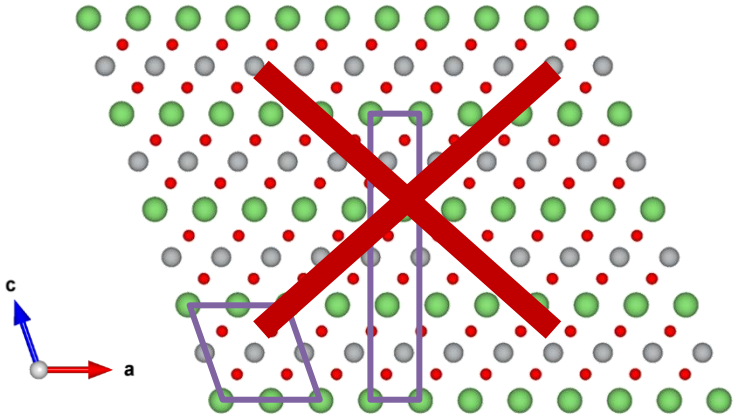
Layered perovskites

FAULTS program

Building your structural model

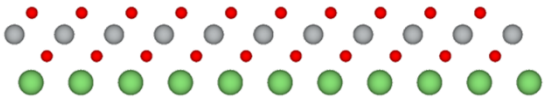
Case of planar defects

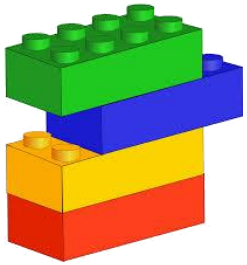
no crystallographic unit cell
no space group



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

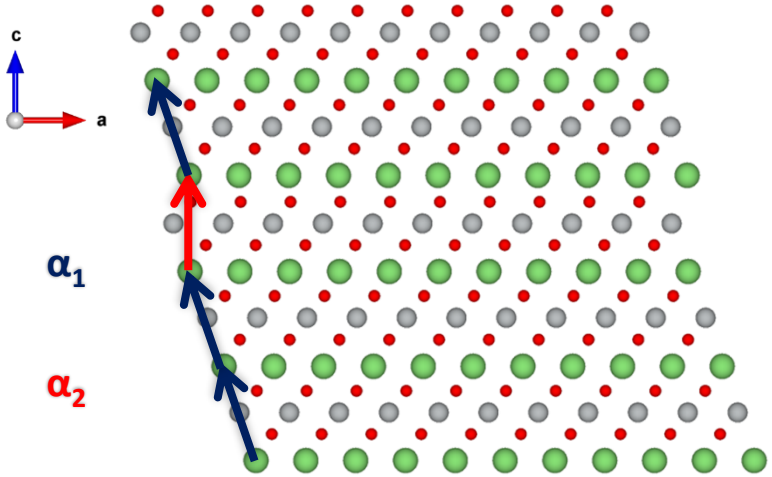
LAYER 1





STACKING VECTOR 1 PROBABILITY α_1

STACKING VECTOR 2 PROBABILITY α_2



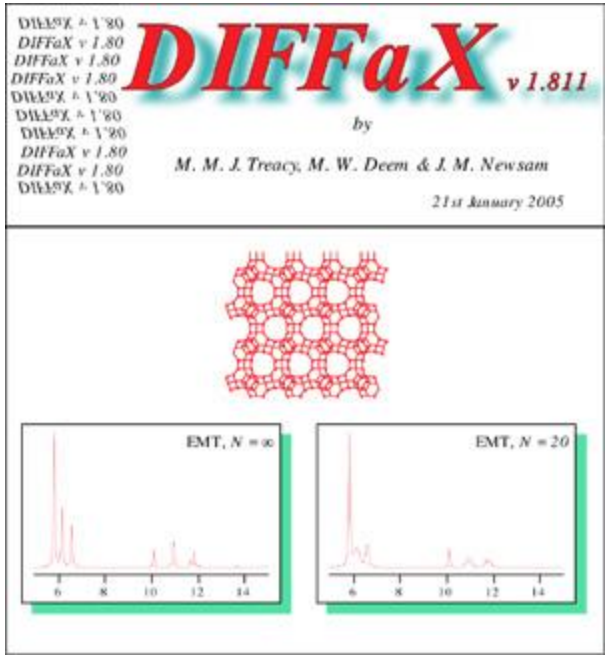
➔ versatility to describe stacking faults, twins, intergrowths

Treacy *et al. Proc. R. Soc. Lond. A* **1991**, *433*, 499 ; Casas-Cabanas et al. *Z. Kristllogr. Suppl.* **2006**, *23*, 243.
Rodriguez-Carvajal and Gonzalez-Platas, CrysFML repository, at https://forge.epn-campus.eu/projects/show/crysfml

FAULTS program

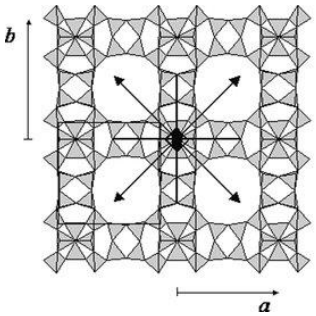
History

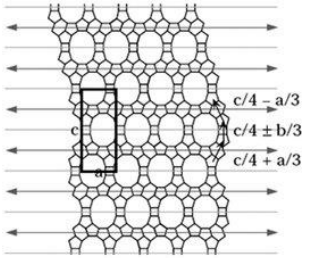
1991 **DIFFaX**: recursion algorithm for computing diffraction from faulted crystals with coherent planar defects. Simulation code in Fortan 77.



→ Simulate diffraction patterns of structures including planar defects

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



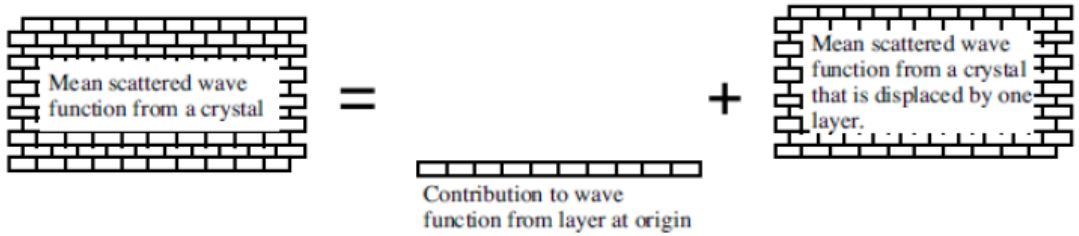


Treacy M.M.J., Newsam J.M. and Deem M.W. A general recursion method for calculating diracted intensities from crystals containing planar faults. Proc. R. Soc. Lond. A, 433:499-520, 1991.
http://www.public.asu.edu/~mtreacy/DIFFaX_manual.pdf

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.



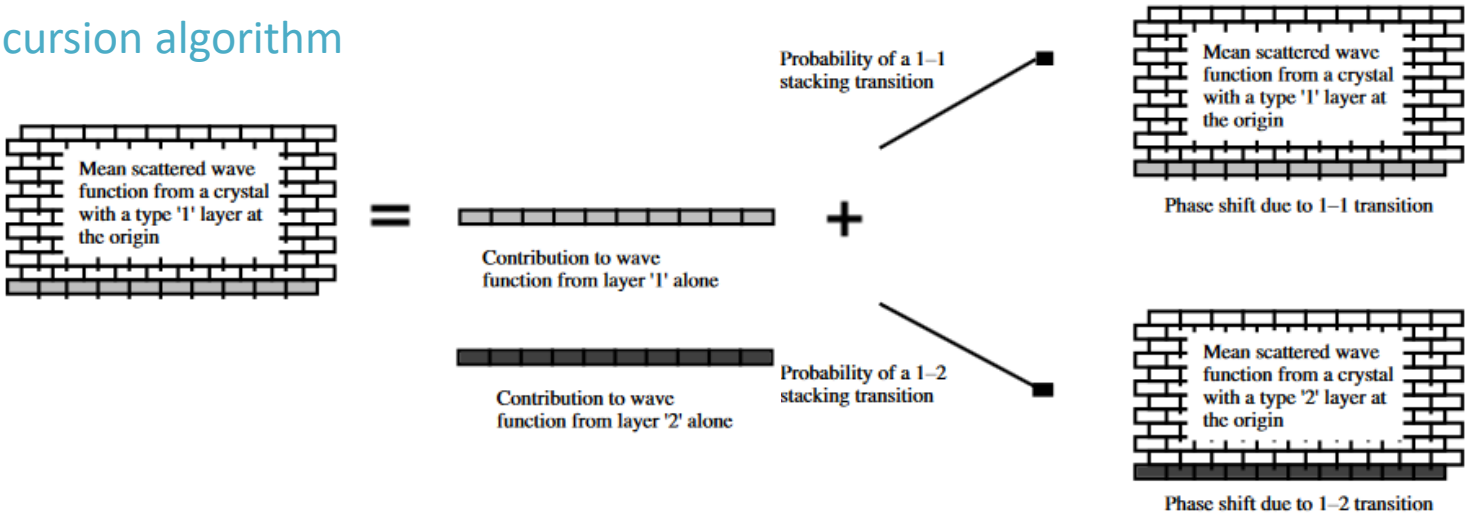
$$\Psi(\mathbf{u}) = F(\mathbf{u}) + \exp(-2\pi i \mathbf{u}\cdot\mathbf{R})\,\Psi(\mathbf{u}) \quad \Longleftrightarrow \quad \Psi(\mathbf{u}) = \frac{F(\mathbf{u})}{1-\exp(-2\pi i \mathbf{u}\cdot\mathbf{R})}$$

The scattered wavefunction 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 diracted 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 gi are given by: $g_i = \sum_{j=1}^{N} g_j \alpha_{ji}$ $\sum_{i=1}^{N} g_i = 1$

Treacy M.M.J., Newsam J.M. and Deem M.W. A general recursion method for calculating diracted 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 v 1.813
by
M. M. J. Treacy, M. W. Deem & J. M. Newsam
19th May 2010

➡ **Simulate diffraction patterns of structures including planar defects**

Treacy *et al. Proc. R. Soc. Lond.* A 1991, 433, 499

β-Ni(OH)$_2$

Journal of The Electrochemical Society, **146** (6) 2059-2067 (1999)
S0013-4651(98)08-048-3 CCC: $7.00 © The Electrochemical Society, Inc.

The Structure of Ni(OH)$_2$: From the Ideal Material to the Electrochemically Active One

C. Tessier,[a,b] P. H. Haumesser,[a] P. Bernard,[b] and C. Delmas[a,*,z]

[a]*Institut de Chimie de la Matière Condensée de Bordeaux-CNRS and Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, 33608 Pessac Cedex, France*
[b]*SAFT-Direction de la Recherche, 91460 Marcoussis, France*

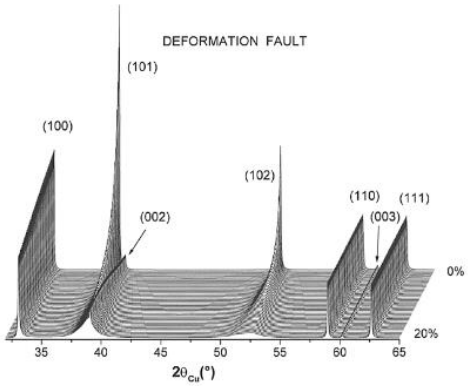
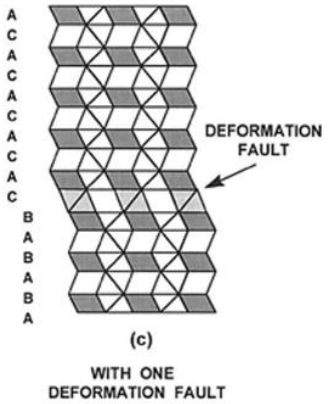


Figure 7. Simulation of the modifications of the X-ray diffraction pattern of nickel hydroxide in the presence of deformation faults in the range 0-20%.



MnO$_2$

Pergamon

Prog. Solid St. Chem. Vol. 23, pp. 1–130, 1995

0079-6786/95 $29.00
0079-6786(94)00005-0

STRUCTURAL AND ELECTROCHEMICAL PROPERTIES OF THE PROTON / γ-MnO$_2$ SYSTEM

Y. Chabre* and J. Pannetier†

* Laboratoire de Spectrométrie Physique, Université Joseph Fourier and CNRS BP 87, 38402 Saint Martin d'Hères, France
† Institut Laue-Langevin, BP 156, 38042 Grenoble, France

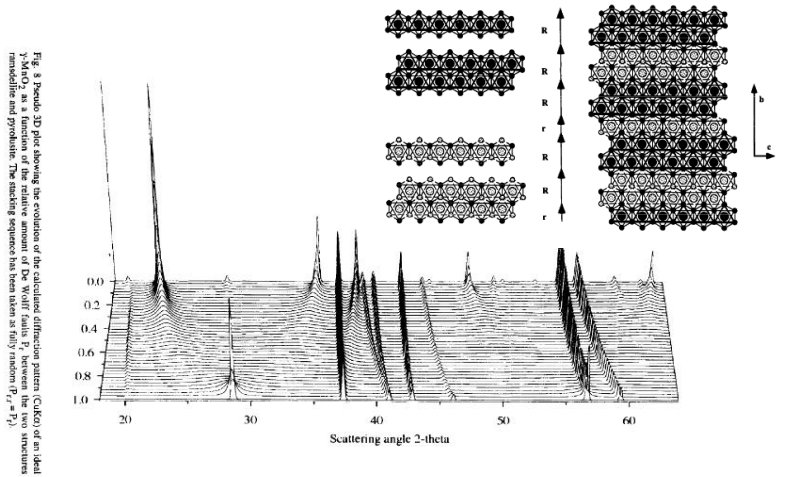


Fig. 8. Pseudo 3D plot showing the evolution of the calculated diffraction pattern (CuKα) of an ideal γ-MnO$_2$ as a function of the relative amount of the 'Wadsley' (ramsdellite) and pyrolusite. The stacking sequence has been taken as fairly random ($P_{1/1} = P_{2/1}$).

Treacy M.M.J., Newsam J.M. and Deem M.W. A general recursion method for calculating diracted 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

The FAULTS program: refine and quantify planar defects

Juan Rodríguez-Carvajal & *Montse Casas Cabanas*

Pavel Horbach *Marine Reynaud* *Jokin Rikarte*

Kernel of DIFFaX ✚ **Modules of the CrysFML library**

Recursion algorithm that calculates the incoherent sum of diffracted intensities of layered structures

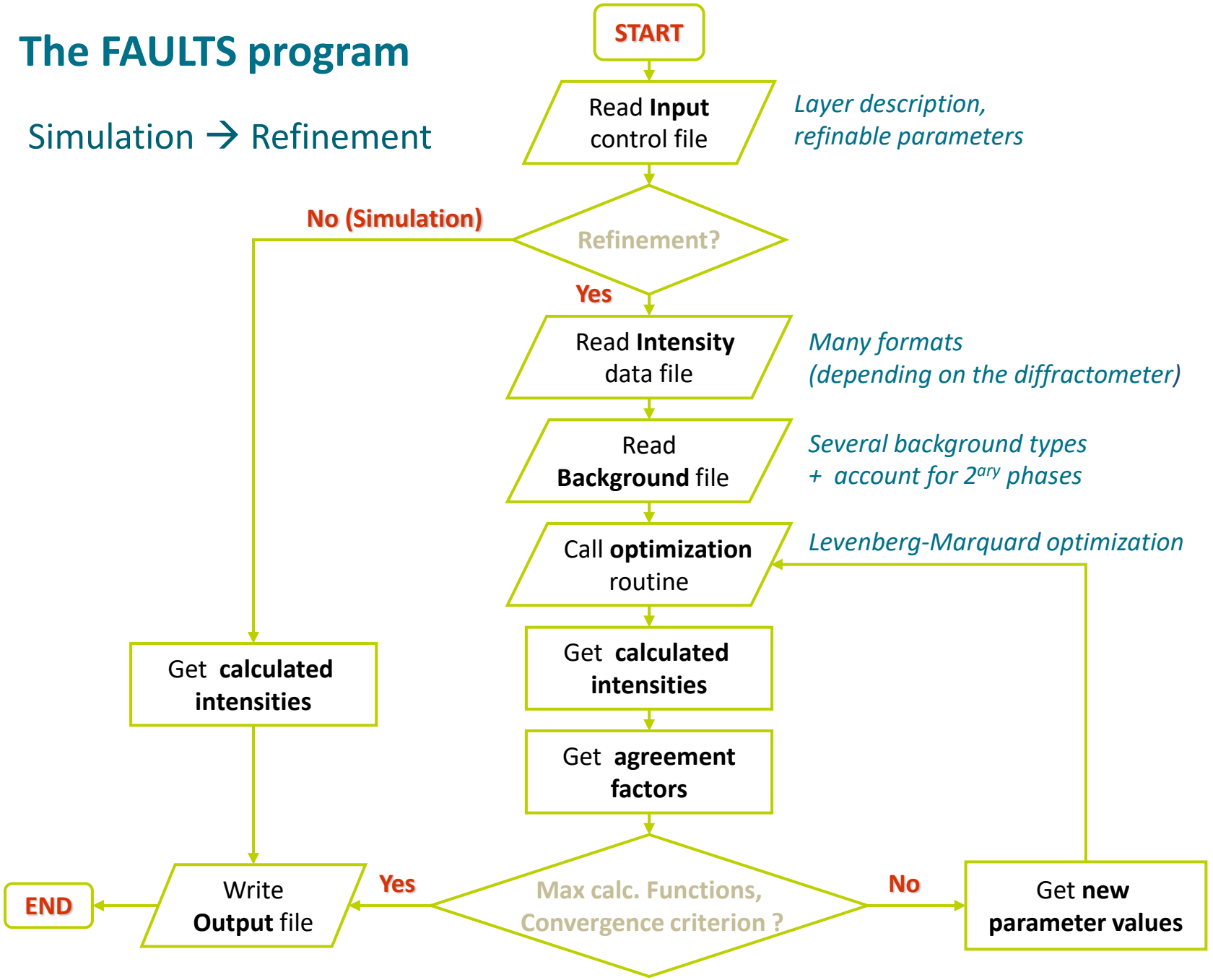
- Anisotropic broadening due to planar defects

- Structural refinement
- Isotropic size and strain broadening treatment
- Background refinement and secondary phases
- Visualization of the structural model
- DiFFaX2FAULTS convertor

FAULTS program: www.cicenergigune.com/faults and www.ill.fr/sites/fullprof
M. Casas-Cabanas et al. Z. Kristllogr. Suppl. 2006, 23, 243.
M. Casas-Cabanas, M. Reynaud, J. Rikarte, P. Horbach, J. Rodríguez-Carvajal J. Appl. Cryst. 2016, 49(6), 2259.

The FAULTS program

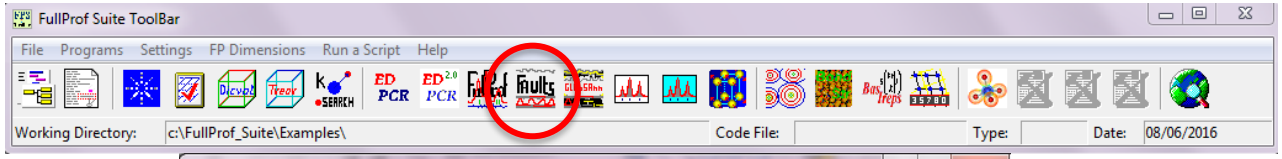
Simulation → Refinement

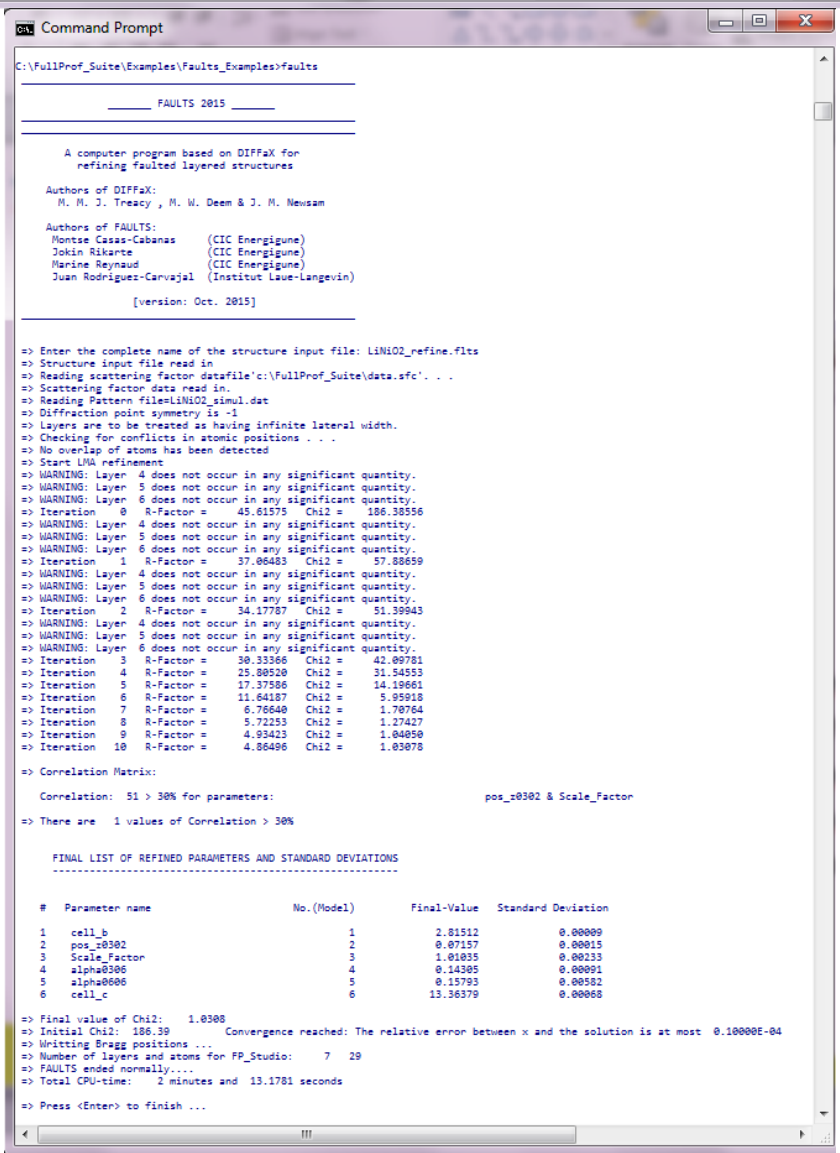


M Casas-Cabanas, J Rodríguez-Carvajal, MR Palacín *Zeitschrift für Kristallographie*, Suppl 23, 243-248, 2006

M. Casas-Cabanas, M. Reynaud, J. Rikarte, P. Horbach, J. Rodríguez-Carvajal *J. Appl. Cryst. 2016*

The FAULTS program





Included in FullProf Suite

The FAULTS program

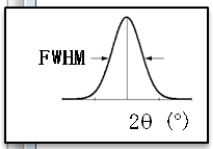
The *.flts input file

Imq - Notepad

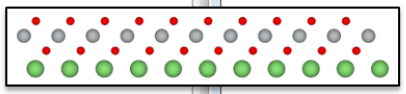
File Edit Format View Help

```
TITLE
NI(OH)2 WITH DEFORMATION AND GROWTH FAULTS

Instrumental  And  Size  Broadening
!Type of Radiation
 Radiation      X-Ray
!              lambda1    lambda2   ratio
 Wavelength     1.5406    0.0000    0.0000
!Instrumental aberrations      zero      sycos     sysin
 Aberrations                  0.0000    0.0000    0.0000
                              0.00      0.00      0.00
!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
 !       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 Ni2+        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

 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



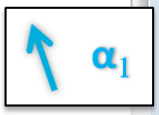
Structural description of the layers



z
0.22265
71.00

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_flts.cif  LiNiO2_refine1_flts.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

Building your structural model

Proposed methodology:

1) Choose or build an ideal structural model, and simulate the XRD pattern of the ideal structure using FullProf
2) Inspect the ideal structural model with VESTA, choose how to describe it with layers and stacking vectors
3) Built your FAULTS input file for the ideal structure, simulate the XRD pattern with FAULTS and compare it to the FullProf simulation (they should be identical). Check also visually your FAULTS structural model using VESTA.
4) When you have validated the FAULTS ideal structural model, introduce stacking faults. Use simulations to evaluate the effects of SF on the diffraction patterns.
5) When having a satisfactory initial model, switch to refinement mode.

- 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!

The FAULTS program

Building your structural model

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3) Built your FAULTS input file for the ideal structure, simulate the XRD pattern with FAULTS and compare it to the FullProf simulation (they should be identical). Check also visually your FAULTS structural model using VESTA.
4) When you have validated the FAULTS ideal structural model, introduce stacking faults. Use simulations to evaluate the effects of SF on the diffraction patterns.
5) When having a satisfactory initial model, switch to refinement mode.

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

The FAULTS program

Some important information:

- Profile parameters

$$H_G^2 = Utan^2\theta + Vtan\theta + W + \frac{4ln2\lambda^2}{\pi D_G^2 cos^2\theta}(\frac{180}{\pi})^2$$

$$H_L = Xtan\theta + \frac{2\lambda}{\pi D_L cos\theta}(\frac{180}{\pi})$$

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)

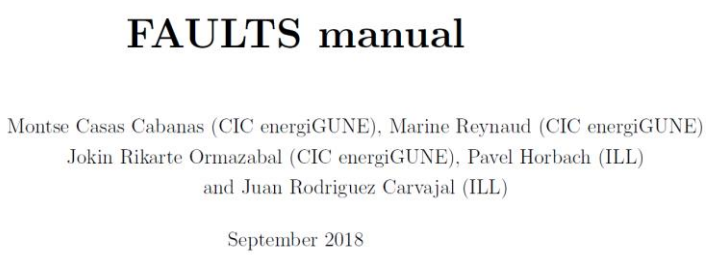
- A missing refinement code will not be considered as zero but will produce an error

- 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

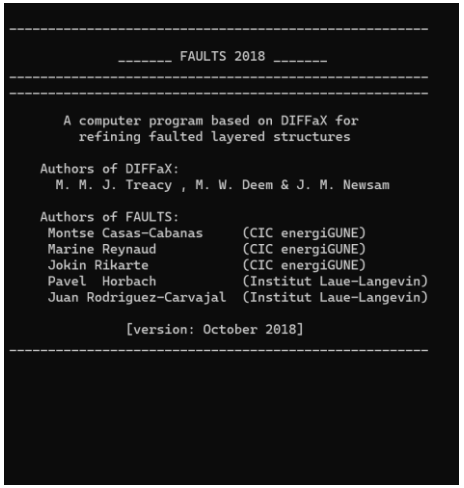


The FAULTS program

Common errors:

- If no calculation start in the prompt window:

This is due to the presence of tabulation in the input file. Remove them.
Avoid introducing tabs by setting the option "replace tabs by spaces" in your text editor



- If the prompt window closes automatically:

Run FAULTS in the as an independent program using a command prompt (cmd.exe; see FAULTS manual). Then read the error lines: this is usually due to the absence of a file in your working folder