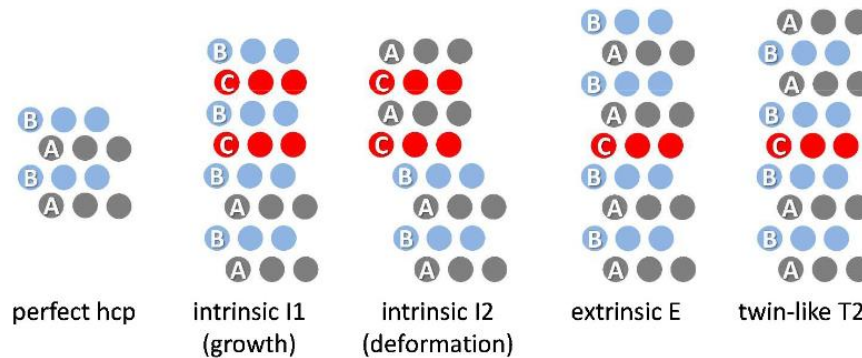


FullProf School

Introduction to the FAULTS program

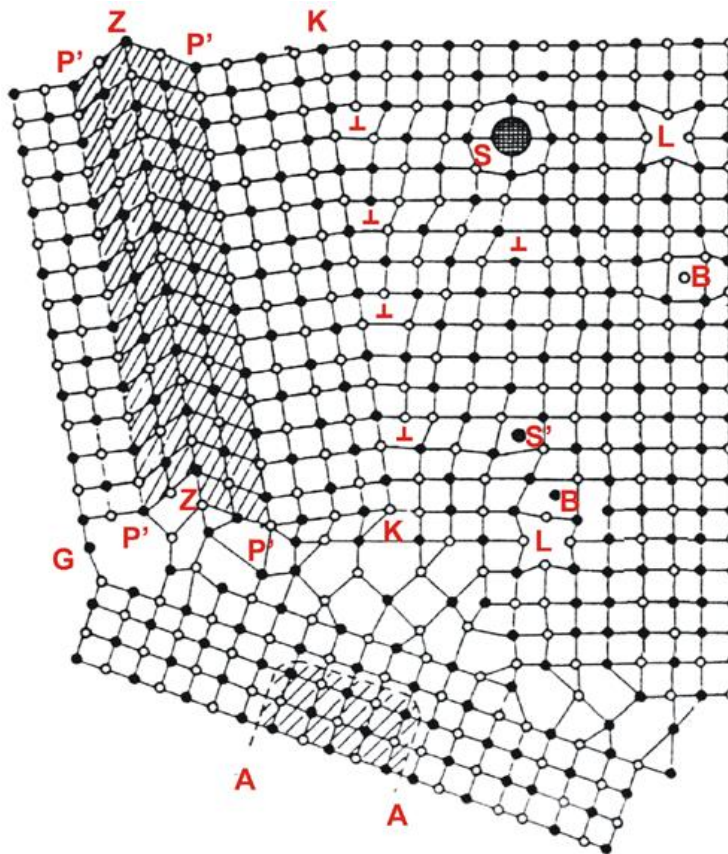
Montse Casas, Marine Reynaud and Jon Serrano



Support: faults@cicenergigune.com

Defects in crystalline materials

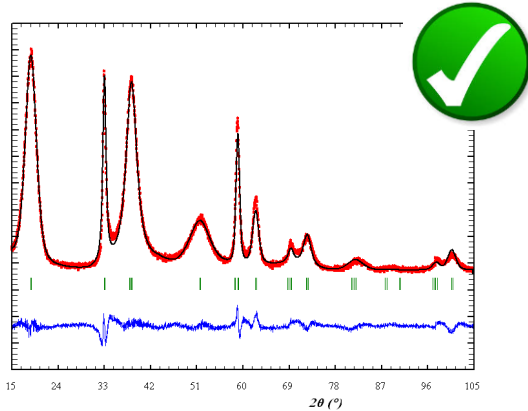
REAL materials can be complex...



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

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

FAULTS program



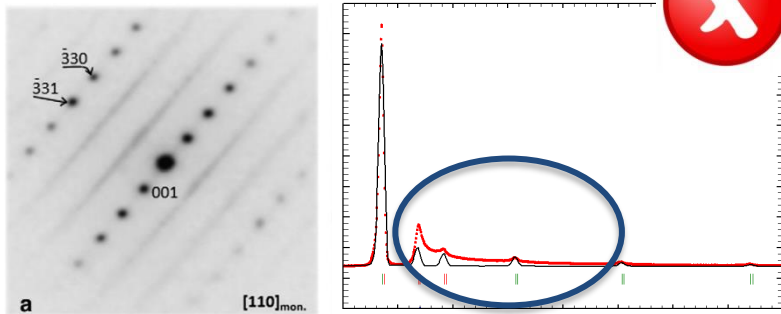
Casas-Cabanas *et al. Journal of Power Sources* **2007**, 174, 414.

Rietveld method:

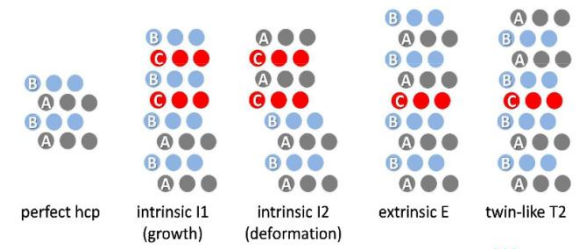
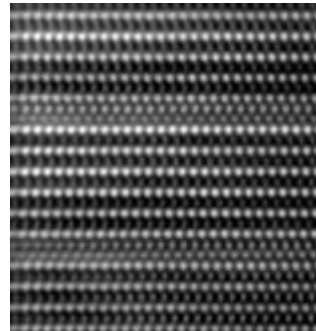
assumption of an **average 3D structure**

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).



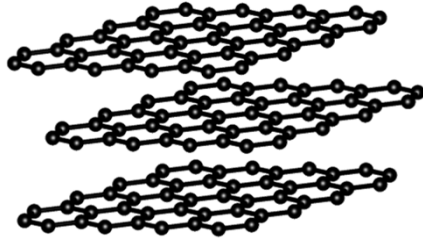
Boulineau *et al. Solid State Ionics* **2010**, 180, 1652.



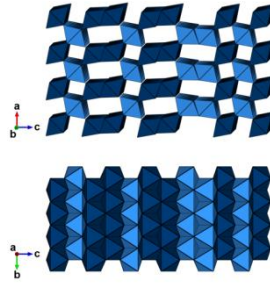
FAULTS program

Energy storage

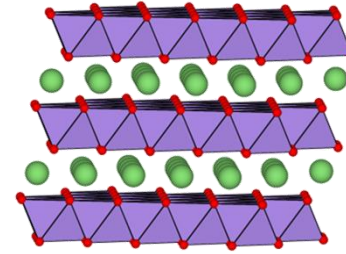
Graphite



γ -MnO₂



Layered transition metal oxides

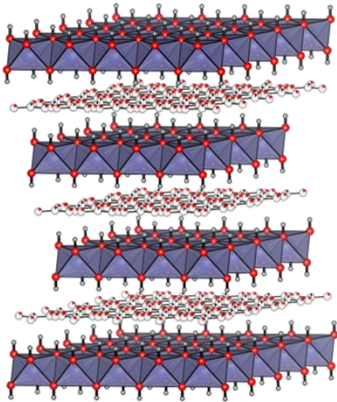


PHYSICAL-CHEMICAL PROPERTIES



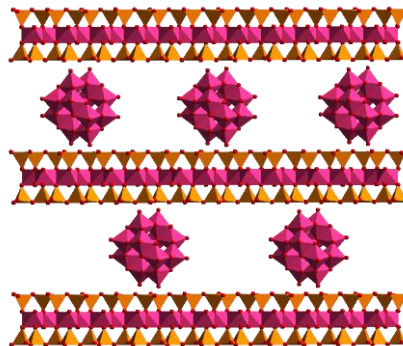
STRUCTURAL FEATURES

Catalysis



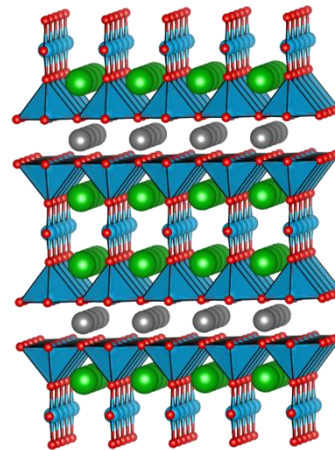
Layered double hydroxides (LDHs)

Drug delivery



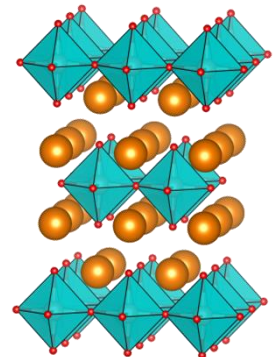
Pillared Clays (PILCS)

Superconductors



Cuprates

Magnetism



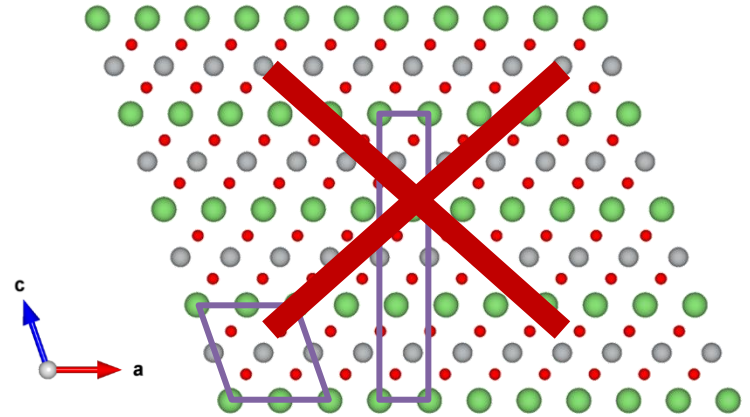
Layered perovskites

FAULTS program

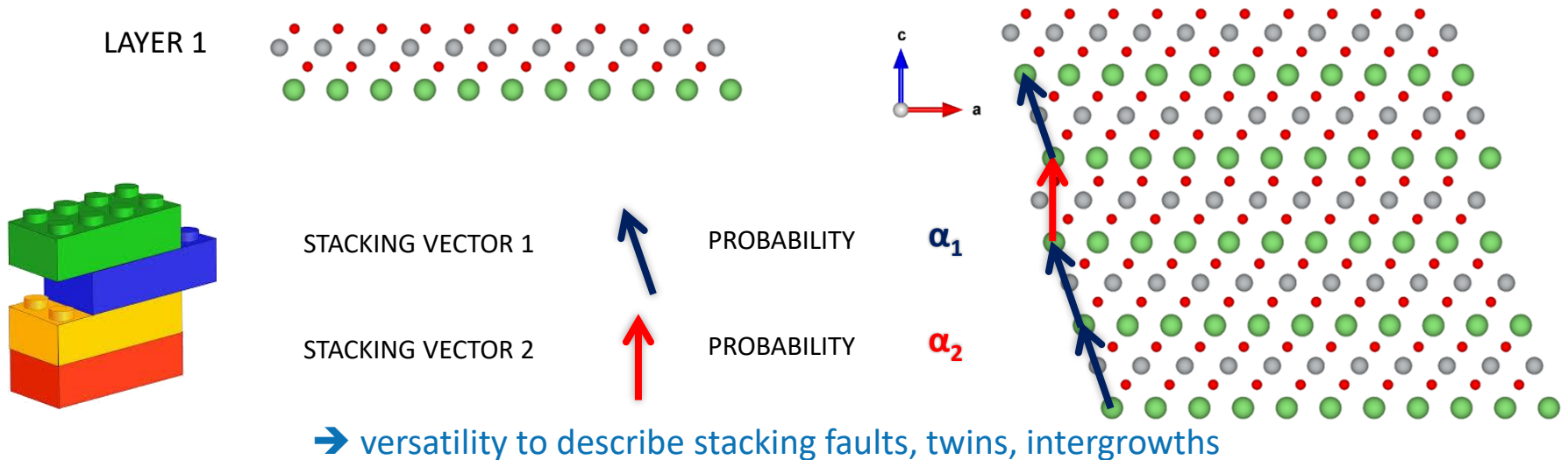
Building your structural model

Case of planar defects

no crystallographic unit cell
no space group



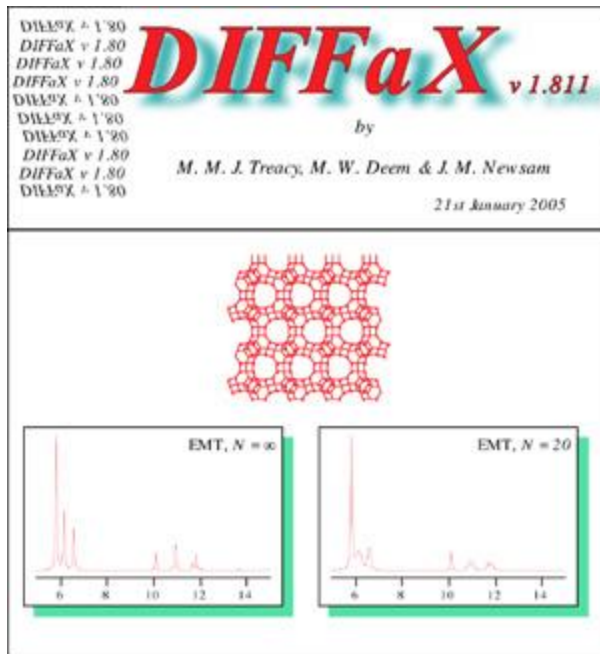
but **layers** interconnected via **stacking vectors** that occur with **probabilities**



FAULTS program

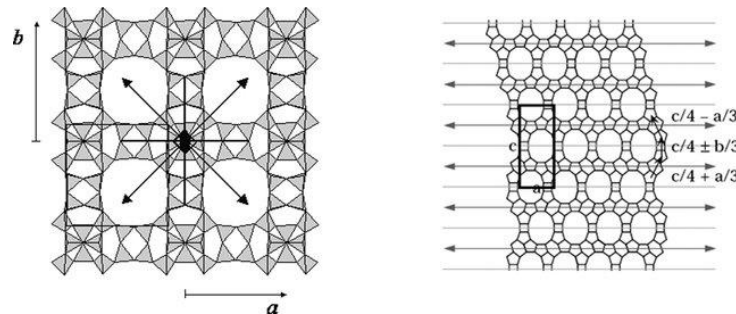
History

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



→ Simulate diffraction patterns of structures including planar defects

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



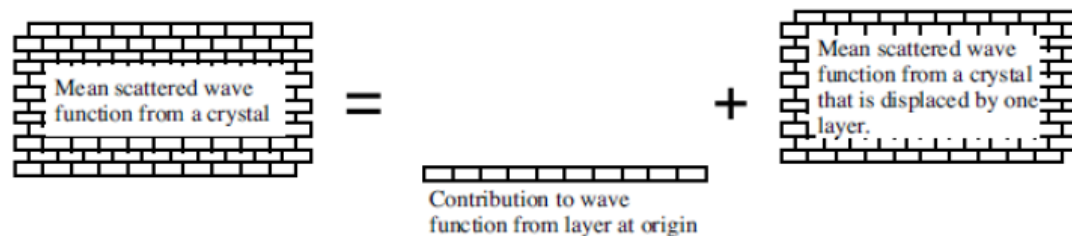
Treacy M.M.J., Newsam J.M. and Deem M.W. A general recursion method for calculating diffracted intensities from crystals containing planar faults. Proc. R. Soc. Lond. A, 433:499-520, 1991.

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.



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

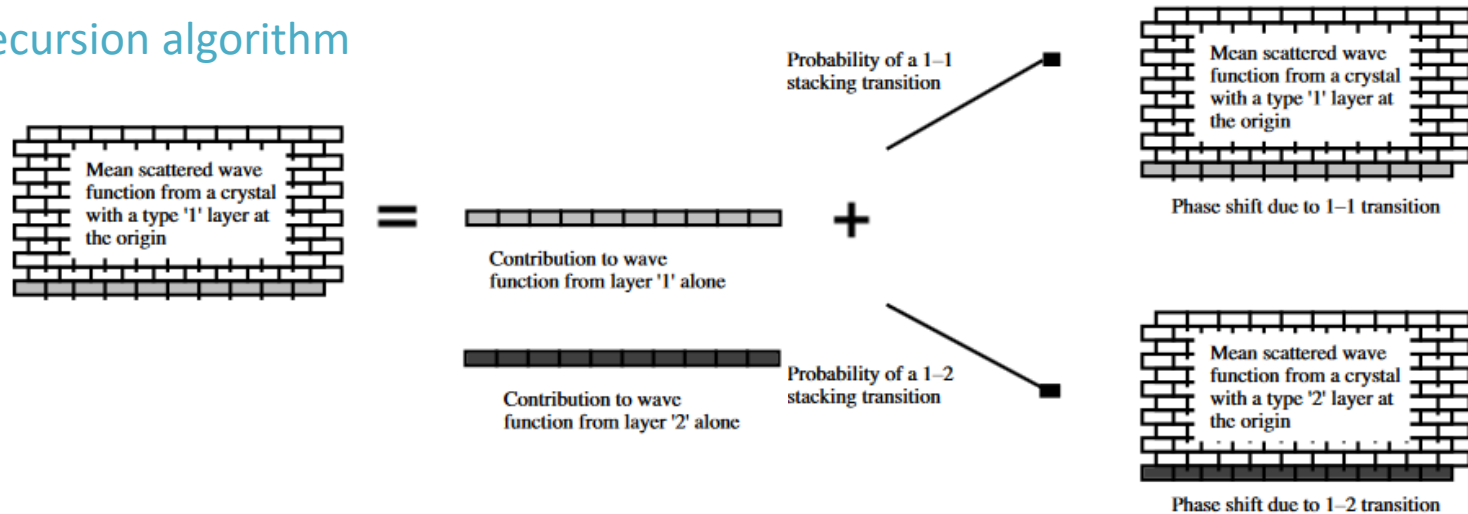
The scattered wavefunction from a crystal centered on any layer, is equivalent to the scattering contribution from that layer plus the scattered wavefunction from the displaced crystal centered at the next layer.

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

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

DIFFaX recursion algorithm



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



Simulate diffraction patterns of structures including planar defects



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}

†Institut de Chimie de la Matière Condensée de Bordeaux-CNRS and Ecole Nationale Supérieure de Chimie et Physique de Bordeaux. 33608 Pessac Cedex, France

^bSAFT-Direction de la Recherche, 91460 Marcoussis, France

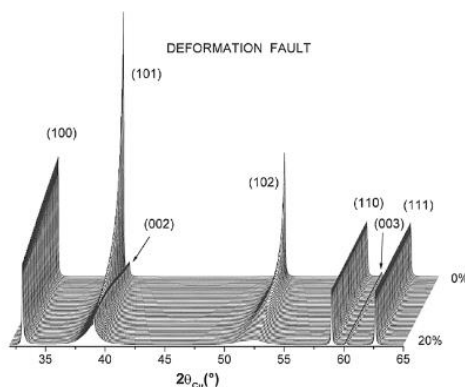


Figure 7. Simulation of the modifications of the X-ray diffraction pattern of nickel hydroxide in the presence of deformation faults in the range 0-20%.



Pergamon

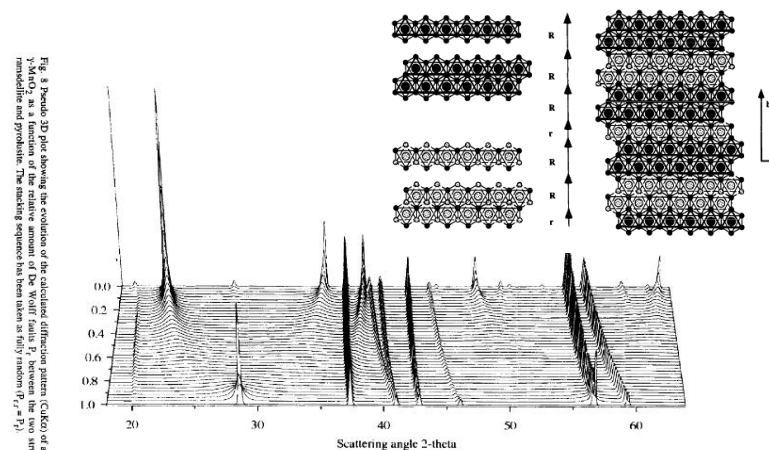
Prog. Solid St. Chem. Vol. 23, pp. 1-130, 1995
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Printed in Great Britain. All rights reserved.
0079-6786/95 \$29.00

0079-6786(94)00005-0

STRUCTURAL AND ELECTROCHEMICAL
PROPERTIES OF THE PROTON / γ -MnO₂
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



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

The FAULTS program: refine and quantify planar defects

Juan Rodríguez-Carvajal



Pavel Horbach

&

Montse Casas Cabanas



Marine Reynaud

Jokin Rikarte



Kernel of DIFFaX



Modules of the CrysFML library

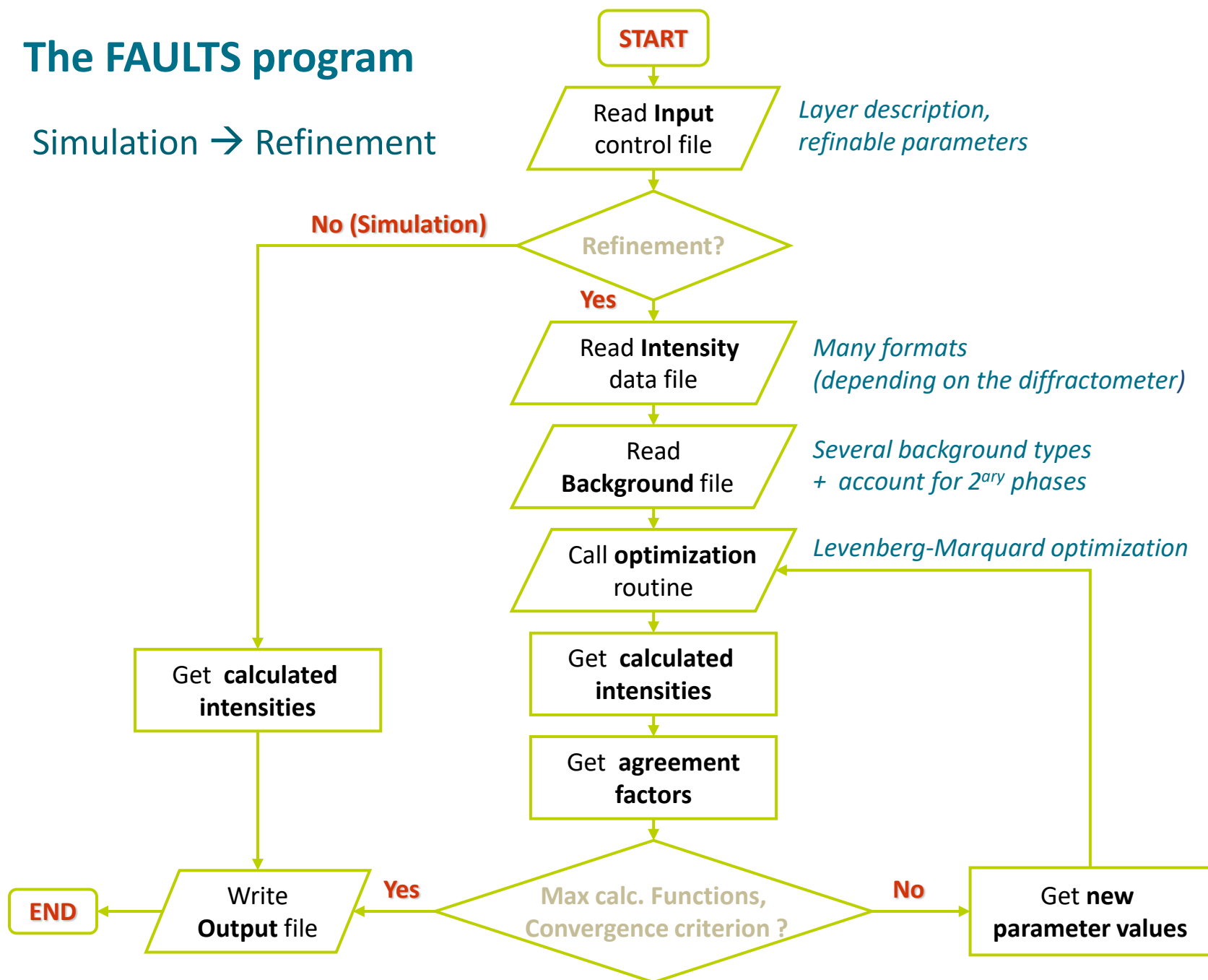
Recursion algorithm that calculates the incoherent sum of diffracted intensities of layered structures

- Anisotropic broadening due to planar defects

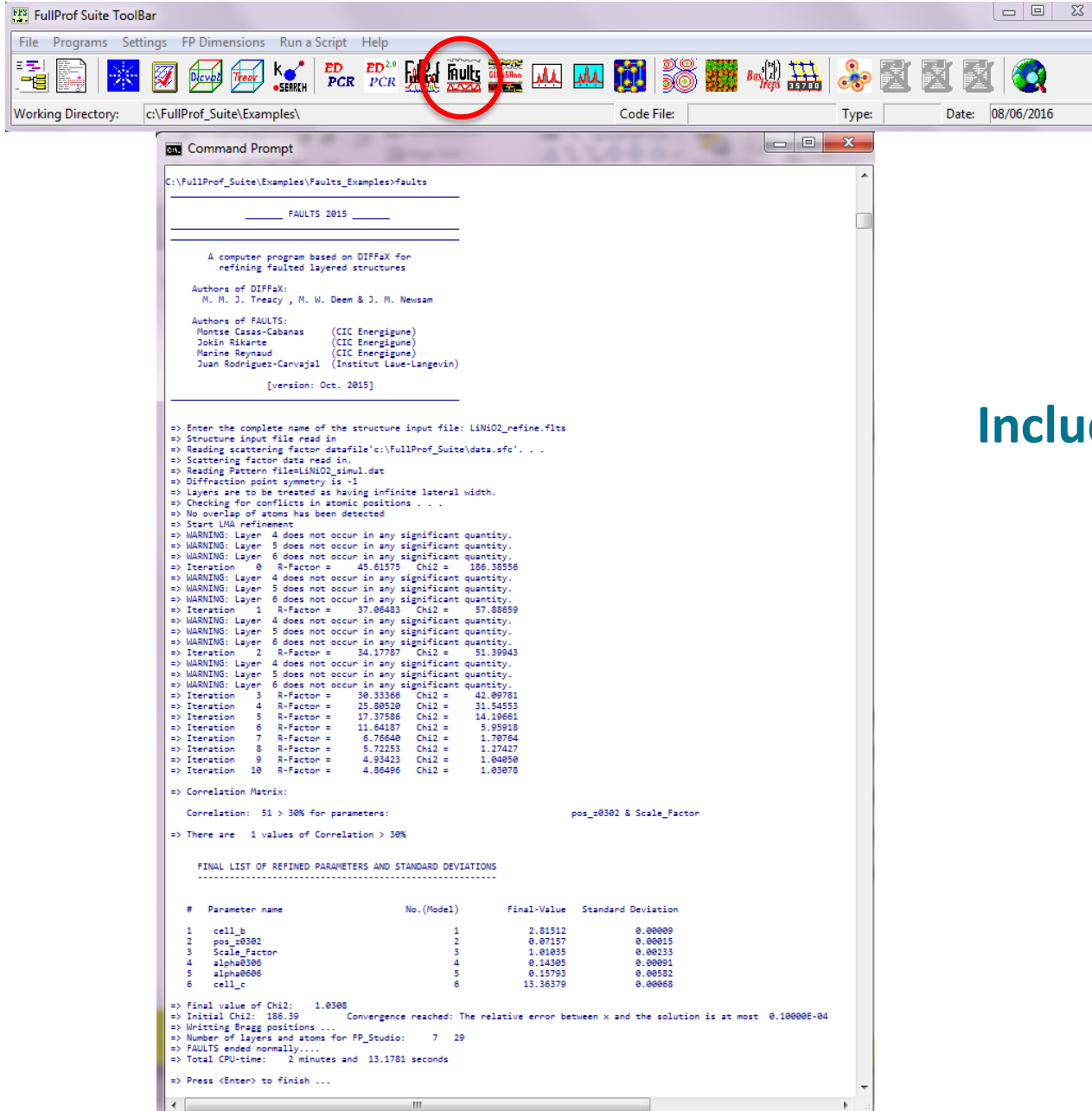
- Structural refinement
- Isotropic size and strain broadening treatment
- Background refinement and secondary phases
- Visualization of the structural model
- DiFFaX2FAULTS convertor

The FAULTS program

Simulation → Refinement



The FAULTS program



The screenshot shows the FullProf Suite ToolBar at the top, with the 'FAULTS' icon circled in red. Below it, a Command Prompt window displays the output of the FAULTS program. The output includes the program's purpose, authors, version, and a detailed log of the refinement process, including R-factor and Chi2 values for each iteration, a correlation matrix, and a final list of refined parameters.

```
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 LMA refinement.
=> WARNING: Layer 4 does not occur in any significant quantity.
=> WARNING: Layer 5 does not occur in any significant quantity.
=> WARNING: Layer 6 does not occur in any significant quantity.
=> Iteration 0 R-Factor = 45.61575 Chi2 = 186.38556
=> WARNING: Layer 4 does not occur in any significant quantity.
=> WARNING: Layer 5 does not occur in any significant quantity.
=> WARNING: Layer 6 does not occur in any significant quantity.
=> Iteration 1 R-Factor = 37.06483 Chi2 = 57.88659
=> WARNING: Layer 4 does not occur in any significant quantity.
=> WARNING: Layer 5 does not occur in any significant quantity.
=> WARNING: Layer 6 does not occur in any significant quantity.
=> Iteration 2 R-Factor = 34.17787 Chi2 = 51.39943
=> WARNING: Layer 4 does not occur in any significant quantity.
=> WARNING: Layer 5 does not occur in any significant quantity.
=> WARNING: Layer 6 does not occur in any significant quantity.
=> Iteration 3 R-Factor = 30.33366 Chi2 = 42.09781
=> Iteration 4 R-Factor = 25.80520 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 0.00091
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
=> Whittling 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

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
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 21.00 3.128608 21.00 4.608609 120.00
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


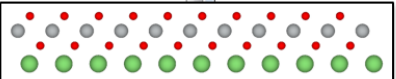
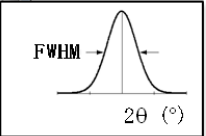
Transitions
!layer 1 to layer 1
LT 0.808196 0.000000 0.000000 1.000000
-92.000000 0.000000 0.000000 0.000000
FW 0.00 0.00 0.00 0.00 0.00 0.00
0.00 0.00 0.00 0.00 0.00 0.00
!layer 1 to layer 2
LT 0.095902 0.333000 0.666700 1.000000
91.000000 0.000000 0.000000 0.000000
FW 0.00 0.00 0.00 0.00 0.00 0.00
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_flts.cif  LiNiO2_refine1.fst  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

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.

Example 1

Graphite

Building structural model

Layer description different from unit cell (3R)

Simulation

Example 2

LiNiO₂

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

Li₂MnO₃

Building structural model of a monoclinic cell

Simulations of XRD and ED patterns

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

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

```
----- FAULTS 2018 -----  
  
A computer program based on DIFFaX for  
refining faulted layered structures  
  
Authors of DIFFaX:  
M. M. J. Treacy , M. W. Deem & J. M. Newsam  
  
Authors of FAULTS:  
Montse Casas-Cabanas      (CIC energigUNE)  
Marine Reynaud             (CIC energigUNE)  
Jokin Rikarte              (CIC energigUNE)  
Pavel Horbach              (Institut Laue-Langevin)  
Juan Rodriguez-Carvajal    (Institut Laue-Langevin)  
  
[version: October 2018]
```

- 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