FAULTS manual

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Chapter 1

The FAULTS program

FAULTS is a Fortran90 program to refine XRD and NPD patterns of crystal systems with any type of coherent planar defect. This program is based on the DIFFaX program [1] and on the CrysFML Fortran 95 crystallographic library [2].

The DIFFaX program (Diffracted Intensities From Faulted Xtals) calculates diffraction intensities from defective crystals. This tool has been widely used to interpret the diffraction data of one-dimensionally disordered systems and it is based on an algorithm that 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. However, as approximate or merely qualitative results sometimes are not sufficient for a thorough microstructural characterization, a computerized comparison of the DIFFaX calculated intensities with experimental data has been developed. The resulting code is the FAULTS program. The program is distributed in the hope that it will be useful, but without any warranty of being free of internal errors. The authors acknowledge all suggestions and notification of possible bugs found in the program.

1.1 Program specifications

Conventionally, crystals are thought of in terms of unit cells of a determined symmetry. Nevertheless, to use FAULTS, as in the case of DIFFaX, we need to think of crystals in terms of sheets of atoms, or layers, which can interconnect via stacking operations that occur with a certain probability. By means of this description, planar defects can be described as different layer types and/or transition vectors. Frequently, the plane of the layers will not coincide conveniently with any of the unit cell faces of the parent crystal. Then, a transformation of atom coordinates to a new cell system is required.

The structural information as well as the refinement details are read by FAULTS from a free format input data file, with *.flts* extension. Each value used to describe the structure is associated to a refinement code that allows the possibillity of restrictions. The user must be aware of the way he(she) can control the refinement procedure: the number of parameters to be refined, fixing parameters, making constraints, etc. The experimental XRD or NPD patterns can be read from many different formats and background subtraction can be achieved by linear interpolation or polynomially after applying the scale factor. Impurities or other phases are treated as background as well, and their pattern information must be given by the user. Another major feature of FAULTS is the implementation of a more adequate isotropic size broadening treatment which takes into account the Gaussian and Lorentzian contributions to the FWHM in addition to the consideration of a finite number of layers per crystallite already present in

DIFFaX. The refinement is carried out using a Levenberg Marquardt fit. The quality of the agreement between observed and calculated profiles is given by the R-Factor and Chi^2 agreement factors that are calculated at the end of each refinement cycle and are defined as follows:

Profile factor:

$$Rp = 100 \frac{\sum_{i=1,n} | y_i - y_{ic} |}{\sum_{i=1,n} y_i}$$

where y_i is the profile intensity and y_{ic} is the number of calculated counts at the ith step.

Reduced Chi square:

$$Chi^2 = \left[\frac{R_{wp}}{R_{exp}} \right]^2$$

being $R_{\omega p}$ and R_{exp} the Weighted Profile Factor and the Expected Weighted Profile Factor respectively, which are defined as:

$$R_{wp} = 100 \left[\frac{\sum_{i=1,n} w_i \mid y_i - y_{ic} \mid^2}{\sum_{i=1,n} w_i y_i^2} \right]^{1/2}$$

and

$$R_{exp} = 100 \left[\frac{n - p}{\sum_i w_i y_i^2} \right]^{1/2}$$

where n-p is the number of degrees of freedom and $w_i = 1/\sigma_i^2$, with σ_i^2 referring to the variance of the "obserbation" y_i.

1.2 Input files

1.2.1 The input control file: CFILE.flts

The input control file is a free format file that contains all the structural data and the type of calculation to be done. This file must be written by the user. Free format means that it is not case sensitive and that the different sections do not have to follow a concrete sequence, however, a space is needed between each item and all the section headlines and parameter keywords must be present. When the program is run, mistakes will normally generate error messages. Empty lines as well as lines starting with the exclamation symbol (*!*) in the first column are considered as comments and are ignored by the program. Also, comments can be placed at the end of a line if they are in braces ({}).

An example of input control file can be found in figures 1.1 and 1.2. The different sections that constitute the input control file appear in orange color, comments appear in italics (and of course after a *!* symbol), parameters appear in blue and refinement codes appear in green. The latter are codewords that allow the control of the refined parameters. As in the FullProf program, these are the numbers C_x that are entered for each refined parameter. A zero codeword means that the parameter is not being refined. For each refined parameter, the codeword is formed as:

$$C_x = sign(a)(10p + |a|)$$

where p specifies the ordinal number of the parameter x and a is the factor by which the computed shift (the parameter variation in each refinement cycle) will be multiplied before use.

Below, each section, which has to begin with the corresponding keyword, is explained in more detail.

***Title* section**

The document must begin with this section. TITLE keyword must be followed in the next line by the title chosen by the user.

***Instrumental and size broadening* section**

The first line must contain the keyword INSTRUMENTAL AND SIZE BROADENING. The data that follow describe the type of radiation and the instrumental conditions as well as the parameters needed for size broadening, which are refinable parameters. To refine the parameters that constitute this section it is not necessary to recalculate the diffraction pattern in each cycle, so, for computational economy it is strongly recomended to refine them separately.

- **Radiation type:** The line must begin with the keyword *radiation*, followed by one of the different two options, which are X-RAY and NEUTRON.

- **Wavelength:** In addition to λ_1, FAULTS reads also the value of λ_2 and the intensity ratio I_2/I_1 (although in the case of monocromathic radiation it is only necessary to introduce λ_1). λ units are $\mathring{A}$ and this line must contain the keyword *wavelength* at the begining.

- **Aberrations:** Keyword *aberrations* followed by values for instrumental aberrations zero, sycos and sysin must be given. As they are re-

```
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         Dl
 Pseudo-Voigt       0.032948   -0.003558    0.227400    0.000000     479.26     459.87 Trim
                        1.00        0.00        0.00        0.00       1.00       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      0.00
 Layer 2 = 1

 Layer 3 = 1

 Layer 4
!Layer symmetry
 Lsym   Centrosymmetric
!Atom name   number   x         y         z         Biso      Occ
 Atom Ni2+        3   0.00000   0.00000   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-         4   0.33000   0.67000   0.22265   0.75961   1.00000
                         0.00      0.00     71.00      0.00      0.00
 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  1 to layer  3
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  1 to layer  4
LT   0.095902  0.000000  0.000000  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
```


Figure 1.1: **Example of input control file**

```
!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
!layer  2 to layer  3
LT   0.080722  0.333000  0.666700  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
!layer  2 to layer  4
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  3 to layer  1
LT   0.132589  0.333000  0.666700  1.000000
  -111.000000  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  3 to layer  2
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  3 to layer  3
LT   0.867411  0.000000  0.000000  1.000000
   111.000000  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  3 to layer  4
LT   0.000000  0.000000  0.000000  1.000000
     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  4 to layer  1
LT   0.108204  0.000000  0.000000  1.000000
   -41.000000  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  4 to layer  2
LT   0.000000  0.000000  0.000000  1.000000
     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  4 to layer  3
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  4 to layer  4
LT   0.891796  0.000000  0.000000  1.000000
    41.000000  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

 Calculation
 Lmq
 Corrmax      30
 Maxfun     2400
 Tol       0.100000E-04
 Nprint      0

 Experimental
!Filename                     Scale factor     code
 FILE  cer+simul.dat                 0.812         1.00
 Excluded_Regions   2
    0.0000    8.0000
  135.0000  180.0000
 FFORMAT  free
!Linear interpolation
 Bgrinter     Sim.Bgr
!Polynomial  Number of coefficients
 Bgrcheb          2
!Polynomial coefficients
     1.00000     0.20000
     1.0         1.0
!number of pattern backgrounds
 Bgrnum  1
!Pattern file           Filename      Scale factor     code
 Bgrpatt           cerusite1.sub        0.026000      1.00
```


Figure 1.2: **Cont. Example of input control file**

finable, refinement codes must be entered in the next line.

- **Profile parameters:** Instrumental and size broadening are treated differently than in DIFFaX. In both cases, the calculated pattern is convoluted with a profile function (indicated by the keywords *Gaussian*, *Lorentzian* or *Pseudo-Voigt*) that takes into account both instrumental and size effects. The FWHM of the Gaussian (H_G) and Lorentzian (H_L) components of the peak profile have an angular dependence given by:

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

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

U, V, W and X, which must be introduced by the user, are refinable parameters that constitute the instrumental resolution function (IRF). It is always advisable to know their values a priori and fix them during the refinement (although U and X can be refined to account for strains). They must be followed by D_g and D_l, which are the parameters that are used to model the isotropic size broadening due to a finite size of the crystallites (≤ 1 μm). They are also refinable. If the sample is not affected by size broadening, D_g and D_l can take any value ≥ 5000 Å.

- **Trim keyword:** As in DIFFaX, the optional keyword TRIM, which has to be put in the same line as the profile parameters, tells the program to ignore intensity information close to the origin when simulating the instrumental broadening for a powder diffraction pattern.

The peak at the origin is usually many orders of magnitude more intense than any other peak in the spectrum, and the background that is generated by the tail of this peak, when broadened, can easily swamp peaks close to the origin. When TRIM is specified, the unbroadened spectrum that is written to file retains the data at the origin, whereas the broadened data that is written to file suppresses the peak at the origin. It is generally desirable to specify TRIM whenever the powder pattern angular range includes the origin. TRIM has no effect if the powder pattern angular range requested by the user does not include the origin.

Structural **section**

This section must begin with a first line containing the keyword STRUCTURAL.

- **Cell parameters:** The keyword which this line has to begin with is *cell*. The value of **c**, perpendicular to the a-b plane (and therefore parallel to the stacking direction), is needed to provide a reference scale along the stacking direction with which to define the z-component of the stacking vectors. **c** does not have to correspond to any special periodic dimension along the stacking direction for any of the layers. However all the layers must share the same dimensions, **a**,**b** and γ. These are all refinable parameters and the units are Å for **a, b** and **c**, and degrees for γ.
  In case the cell parameters defined for the FAULTS refinement are different from the original cell (the cell from which the desordered model comes from ; for instance, in the case of monoclinic or triclinic average cells), the user can ask the program to generate the Bragg positions

corresponding to the average cell. To do so, the user should add the following four optional lines in the *Structural* section:

> !Average cell parameters (for Bragg positions in .prf file)
> Avercell 3.12 4.15 4.60 90.00 118.79 90.0
> !Average space group (for Bragg positions in .prf file)
> SpGR C 2/m

Note that the average cell parameters and the average space group are only used for the Bragg positions calculation for the .prf file and are not taken into account for the pattern calculation during the refinement or simulation.

- **Laue symmetry:** In this case the keyword is *symm*. There are 12 options : **-1, 2/M(1) , 2/M(2), MMM, -3, -3M, 4/M, 4/MMM, 6/M, 6/MMM, AXIAL** and **UNKOWN**. Axial constraints the program to integrate only along $00l$ (useful in turbostratic structures) and if UNKNOWN is specified the program will establish the symmetry by randomly sampling the reciprocal space. In this case, the user can specify a percentage of tolerance on intensity deviations for this search. Otherwise the program tests the user option and, if it is not consistent with the cell parameters, it is automatically changed.

- **Number of layer types:** The keyword is *nlayers*. It is the number of different layer types needed to describe the structure. If two layers are structurally identical but their stacking vectors are different, they are considered as two different layer types.

- **Layer caracteristic width:** Unlike in DiFFax, this line is compulsory, and it must begin with the keyword *lwidth*. Then the layer characteristic width is especified, in Å. There are two possible formats for this line: width along a and width along b or *infinite*. For example,

```
!layer width
Lwidth 120.00 300.00
         0.0     0.0
```

or

```
!layer width
Lwidth infinite
```

***Layers* section**

- **Layer number:** The layers have to be described with the header *LAYER* followed by the ordinal corresponding number. If two layers are structurally identical it will be enough to write *LAYER* $j = i$ where i and j are the ordinal numbers that correspond to each layer (a blank space is necessary between the number of layer and the = symbol). Then, for layer j the rest of the section can be avoided.

- **Layer symmetry:** The keyword *lsym* must be followed by one of the two options: **NONE** or **CENTROSYMMETRIC**. If the latter is specified, only the asymmetric half of the atom coordinates need to be entered, taking care to halve the occupancy of those atoms that are shared by the two asymmetric halves.

- **Atomic data:** For each atom the keyword *atom* must be written, followed by a specific 4 characters name. The first two characters correspond to the atomic symbol and the last two represent the valence. If the symbol has only a character, contrary to DIFFAX, there must not be a space between the symbol and the charge (Ex. F1-, Ni2+). Some atoms do not require any valence (ex. C). In case of doubt, the user can check the correct form in the file *data.sfc*. After the name, the atom will be identified by an ordinal number. Then the atomic coordinates *x, y, z* will be detailed as well as the atomic displacement factor and finally the occupation, which has to take a value between 0 and 1. If the layer is centrosymmetric, the atom located in the centre of symmetry will have 1/2 for full occupancy. All the parameters are refinable. They can be written as real numbers or as fractions, which ensures maximum machine precision (except for the atomic displacements, which cannot be given as a fraction).

Stacking section

The first line of this section must start with the keyword STACKING.

- **Stacking type:** There are two possibilities: EXPLICIT and RECURSIVE. For an explicit sequence of layers, the diffracted intensities will be calculated for a unique layer sequence that will be specified in the next line. For a recursive sequence of layers, the diffracted intensities are to be calculated for a statistical ensemble of crystallites, each with a distinct stacking sequence, but weighted by the probability that such a sequence will occur.

- **Explicit sequence:** If the stacking type is explicit, there are three possibilities. One of them is SPECIFIC, in which the user has to introduce a stacking sequence, up to 5000 layers. The list can occupy more than one line, and between each layer type there must be a space. Each line must not exceed 132 characters, taking into account the blank spaces. For example,

```
EXPLICIT
SPECIFIC
1 1 2 1 3 1 2
```

corresponds to a crystallite that consists of 7 layers of three different types. However, care has to be taken not to write a forbidden transition (with a zero stacking probability). If this happens, the program will stop and give an error message.

Another possibility is the RANDOM M option which tells the program to generate a sequence of M layers (with a maximum of 5000). The probability that a specific layer-to-layer transition will occur in the sequence will be weighted by the transition probabilities listed in the TRANSITIONS section, described next.

Finally, the program can also generate semi-random sequences of two different layer types, that is to say, the user can control certain parts of the sequence. To do so, the option SEMIRANDOM M must be used, where M is the number of layers (also with a maximum of 5000). Below this line, the user can specify parts of the sequence by the key word SEQ followed by the position of the first layer in the sequence, the position of the final layer and the two types of layers that will be alternated. For example,

```
EXPLICIT
SEMIRANDOM 60
SEQ 11 20 1 3
```

will generate a random sequence of layers but from layer 11 to layer 20 the sequence will be 1 3 1 3 1 3 1 3 1 3. If the sequence is incompatible with the last layer of the sequence that is generated automatically (due to the stacking probabilities), in this case layer number 10, this layer would be eliminated and the fixed sequence would move a position, starting in layer 10. If that was still not compatible with the stacking probabilities this process would be repeated until the program found a compatible sequence.

- **Recursive sequence:** In this case, the user can indicate the mean number of layers the crystallites contain. Any number larger than M $\geq$1022, will be treated as infinite. Alternatively, an infinite number can be specified by the keyword INFINITE. If the latter is chosen, the refinement code underneath must be eliminated. If the number of layers is lower than 1022, the program will apply a line broadening due to a finite size in the stacking direction. This value (which can be refined) will have no physical meaning, but it is the only way to introduce a certain anisotropy in size broadening. However, if the crystallites induce a purely isotropic size broadening (represented by D_g and D_l , that will be lower than 5000) this value should be INFINITE as size broadening has already been taken into account in the *Instrumental and size broadening* section.

Transitions **section**

First line must contain the keyword TRANSITIONS. This section contains as many subsections as different layers constitute the system; And each subsection will contain as many lines (without taking into account the refinement codes) as different layers constitute the system. Each subsection refers to the transitions of layer i to the rest of layers, including itself. Each line must contain, after the keyword LT: the stacking probability α_{ij}, that will be a value comprised between zero (forbidden transition) and 1 (unique possible transition) and the stacking vector R_x, R_y, R_z, relative to **a, b** and **c** respectively. A set of anisotropic Debye-Waller type factors (C_{11}, C_{22}, C_{33}, C_{12}, C_{23}, C_{31}) is specified after the stacking vector, in a separate line and beginning with the keyword FW. These factors are equivalent to specifying an ellipsoidal error spread for the stacking vectors and are useful for modeling systems where there is some coherence between nearest neighbor layers, but no long-range coherence, as in the case of liquid crystals or pillared clays. If the stacking probability α_{ij} is zero, everything on the line after it is ignored and set to zero. All the parameters constituting this section are refinable parameters and can be written as real numbers or as fractions.

Calculation **section**

First line must contain the keyword CALCULATION. This section contains the type of calculation the program is asked to perform. There are two options: SIMULATION and LMQ. The first one corresponds to the pattern calculation, and thus no parameter will be refined. The second option indicates that the refinement is to be done by means of the Levenberg Marquardt fit. Depending on the calculation type, the next lines must contain:

- **Simulation:** The user has to specify $2\theta_{min}$, $2\theta_{min}$ and the step (in degrees). For example,

CALCULATION
SIMULATION { type of optimization }
5.0 90.0 0.02 { $2\theta_{min}$, $2\theta_{max}$, step }

- **LMQ:** The user has to specify the maximum correlation parameter (which defines the minimum correlation used to build the correlation matrix that will be given in the output file; keyword *Corrmax*), the maximun number of function evaluations (keyword *Maxfun*), the tolerance (i.e. convergence criterion; keyword *Tol*) and the print control parameter (keyword *Nprint*). Each of these parameters must be placed in a new line. For example,

  CALCULATION
  LMQ
  Corrmax 30
  Maxfun 2400
  Tol 0.1E-04
  Nprint 0

  If the print control parameter *Nprint* is set to 0, the values of the agreement factors at the end of each evaluation are displayed in the FAULTS window (see subsection 1.4) during the refinement process. If *Nprint* is negative, the FAULTS windows displays the previous and new values of the refinable parameters at each evaluation step, in addition to the agreement factors, at the end of each evaluation.

Experimental section

This section is only necessary in case a refinement is to be done. The section must begin with a first line containing the keyword EXPERIMENTAL, followed by:

- **Filename:** In this line, which must begin with the keyword *file*, the user indicates the file name of the experimental intensity data file, which must not exceed 20 characters, extension included (.dat). After that, the scale factor and its refinement code must be given, in the same line.

- **Excluded regions:** Optionally the user can exclude some regions of the experimental data. To do so, *Excluded_Regions* must be written, followed by the number of excluded regions. In the next lines, 2θ min and 2θ max of each excluded region must be specified (in a separate line per excluded region). If these are not detailed, the program will use the whole 2θ range of the experimental data.

- **File format:** In this line the user writes a code to tell the program which is the format of the intensity data file, that depends on the instrument. The possibilities (which are detailed in the next subsection 1.2.2.) are: D1B, D20, NLS, G41, D1A, D2B, D1AOLD, D1BOLD, DMC, SOCABIM, XYSIGMA, GSAS, PANALYTICAL, TIMEVARIABLE and FREE. The line must begin with the keyword *Fformat*.

- **Background file:** To determine the background, three different possibilities are available, and at least one of them must be present. First, the background can be modeled by linear interpolation. To do so, the user must write the keyword *Bgrinter* followed by the name of the file (extension included) that contains background data. FAULTS only accepts **.bgr* files which are lines with pairs of values, scattering variable \ intensity, in free format (see subsection 1.2.3). Note that background points are not refinable parameters. For example,

!Linear interpolation

Bgrinter Sim.Bgr

If the background is to be treated as a polynomial, the keyword is *Bgrcheb* and the number of coefficients must be specified after it. In the following line the polynomial coefficients must be entered. These are refinable parameters, so the user must remember to write their refinement codes below them. For instance,

!Polynomial	Number of coefficients
Bgrcheb	2
!Polynomial	coefficients
1.00000	0.20000
1.0	1.0

Finally, a third background subsection is available in order to deal with possible impurities. In case the sample to be analysed has impurities, these will give extra peaks in the experimental pattern. In order to take them into account, FAULTS program can treat them as background. Thus, a file containing the diffraction pattern in free format (see next section 1.2.2) must be added for each impurity present in the experimental pattern. This information must be given as follows: first the number of pattern backgrounds is to be expecified, preceded by the keyword *Bgrnum*; then the user must write in a separate line the keyword *Bgrpatt* followed by the filename, scale factor and its refinement code. Optionally, the name of an *.hkl file can be given after the scale's factor refinement code so that the Bragg reflections of each additional phase appear in the calculated *.prf file. A separate line will be writen for every given pattern. For example,

!Number of pattern backgrounds				
Bgrnum 1				
!Pattern file	Filename	Scale factor	Code	hkl file
Bgrpatt	cerusite1.sub	0.026000	1.00	cerusite.hkl

1.2.2 Experimental pattern

The experimental intensity data file can have different formats that depend on the instrument. The files FAULTS is able to read are the following:

- **D1B o D20 (Ins=3 in FullProf):** These are the data file from D1B and D20 diffractometers (ILL) and have a **.dat* extension.

  Line 1-3: comments
  Line 4: 2θ min, step (deg.) + other parameters
  Line 5: number of points in the data file (npts)
  Lines1 : npts pairs D Y1 D Y2 ... D Y10 (where D is the detector number and Y the measured intensity)

- **NLS (Ins=4 in FP):** Data file from N.L.S.(Brookhaven) synchrotron radiation with **.dat* extension.

  Line 1:2θmin, step size, 2θ max (deg.)
  Lines1: pairs of lines with 10 items like
  Y1 Y2 ... Y10 (intensities)
  S1 S2 ... S10 (sigmas)

- **G41 (Ins=5 in FP):** Data file from G41 multidetector neutron diffractometer at LLB with **.dat* extension.

  Line 1-3: comments
  Line4: npts
  Line 5:2θmin, step size, 2θ max (deg.)
  Lines1: Y (one column)

- **D1A o D2B (Ins=6 in FP):** ”Multicounters diffractometers data with **.dat* extension.

  Line 1: Comments

  Line 2: step size (deg.)

  Line 3: 2θmin

  Line 4: Comments

  Lines1: D Y1 D Y2 ... D Y10

- **D1AOLD o D1BOLD (Ins=1 in FP):** These are the data file from D1B and D20 diffractometers (ILL) (old format).

  Line 1:2θmin, step size, 2θ max (deg.)

  Lines1: npts pairs D Y1 D Y2 ... D Y10

- **DMC (Ins=8 in FP):** These are files from DMC diffractometer from Paul Scherrer Institute with **.dat* extension.

  Line 1-3: comments

  Line 4: 2θmin, step size, 2θ max (deg.)

  Lines1: Lines1: pairs of lines with 10 items like

  Y1 Y2 ... Y10 (intensities)

  S1 S2 ... S10 (sigmas)

- **SOCABIM (Ins=9 in FP):** Thee are XRD files with **.uxd* extension generated by Socabim software.

  Line 1-29: comments

  Lines1: Y1, Y2, ..., Yn.

- **XYSIGMA (Ins=10 in FP):** Files with **.dat* extension

  Line 1: keyword XYSIGMA

  Line 2-6: comments

Lines1: X, Y, S

- **GSAS (Ins=12 in FP):** data file for the GSAS analysis data program.

  Line 1: text
  Line 2: npts
  Lines1: intensities (diverse formats)

- **TIMEVARIABLE (Ins=11 in FP):** data from variable time data collection.

  Line 1: 2θmin, step size, 2θ max (deg.)
  Lines1: T1 I1 T2 Y2 ... T10 I10 (T = time)

- **FREE (Ins=0 in FP):** free format files generally with **.dat* extension. Up to 7 lines of comments are accepted, the first real numbers are $2\theta_{min}$, step size and $2\theta_{max}$ (deg.), and the *npts* following lines are the intensity values.

1.2.3 Background: CFILE.bgr

This file that will be used to calculate the background at each value of the scattering variable, is created by the user from the experimental data. The extension must be **.bgr*. Comments can be written after a *!* symbol. Example:

```
! background: positions intensity:
!-----------------------------
          10.0        40.6745
          15.0        74.8976
             ...
```

1.3 Output files

Once the program has finished, FAULTS will create the following output files, depending on the users requirements. These files will be saved to the same directory as the input data files.

1.3.1 Calculated profile: CFILEn.dat

If a simulation is to be done, the program writes the calculated profile in a **.dat* file that is written in free format.

1.3.2 Observed and calculated profile: CFILE1.prf

If the user is performing a refinement, the program creates a file with the experimental pattern, the calculated one with the best fit, their difference plot and the Bragg reflections. This file is to be fed into a visualisation programs, such as WinPLOTR [3]. It is essential to plot frequently the observed and experimental patterns. The examination of the difference pattern is a quick and efficient method to detect blunders in the model or in the input file controlling the refinement process. It may also provide useful hints on the best sequence to refine the whole set of model parameters for each particular case. An example of this file can be found in figure 1.3.

1.3.3 Progress report: CFILE.out

An **.out* file is generated, which contains the information of the structural model given in the CFILE.flts file. If a refinement is done, it also contains the information of the refimenent process. The information this file contains is the values the refinable parameters have taken during refinement, the values of the agreement factors for each evaluation and the best values of each parameter obtained during refinement.

1.3.4 Final report: CFILE_new.flts

When the process is finished a **.flts* file is generated, containing the information of the refinement's final result. Its format is similar to the input file, with the same structure (section headings, keywords, parameters, refinement codes), but with the refined values for the refinable parameters. Thus, this file can be use as the input file in case the user wants to continue the refinement process. If the file is used as input file directly, at the end of the refinement it will be overwritten.

1.4 Running FAULTS

The program is invoked from a DOS window and it will appear as in figure 1.4.

Once the user enters the filename CFILE.flts , if a refinement is to be done, the layout of the program will appear as in figure 1.5. During the refinement process, depending on the option chosen by the user (see the comments on the keyword *Nprint* in the *Calculation* subsection page **??**), the DOS window will display the values of the agreement factors at the end of each evaluation, and optionally the list of the previous and new refinable parameters at each evaluation step.

Once the refinement has finished, the list of the best values obtained for the refinable parameters is displayed (see figure 1.6). The user can then open the CFILEn.prf to see the goodness of the refinement.

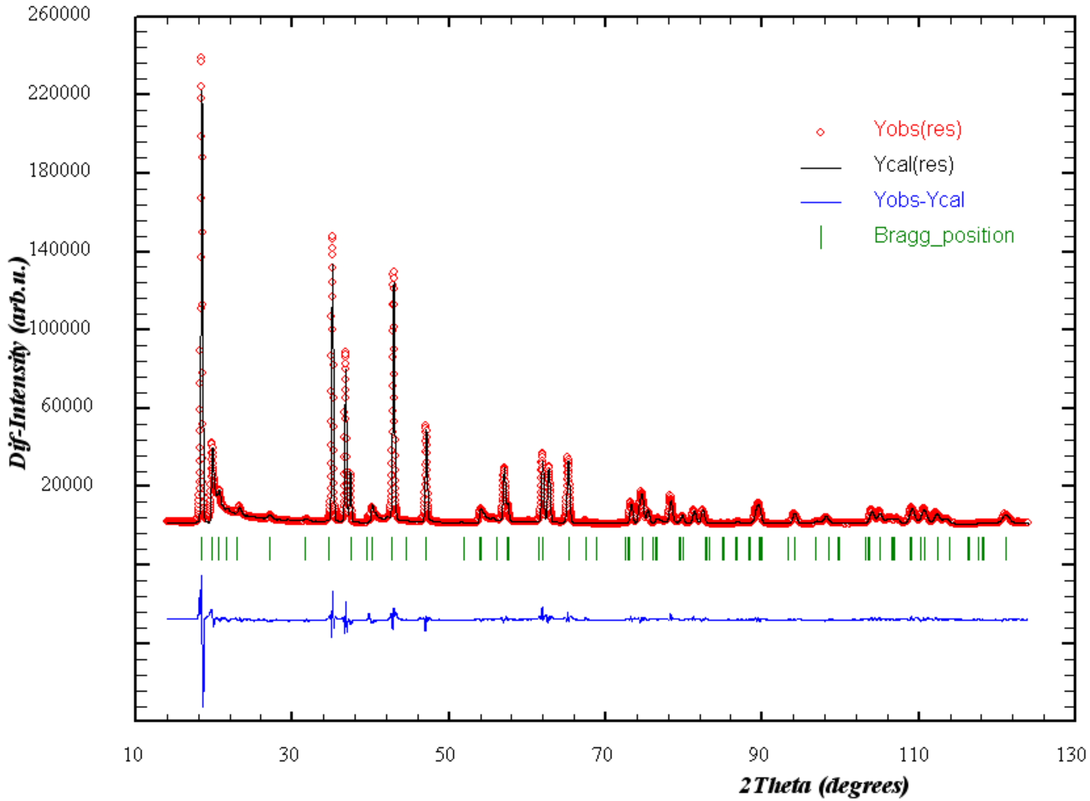


Figure 1.3: **Example of obsrved and calculated profile plot**

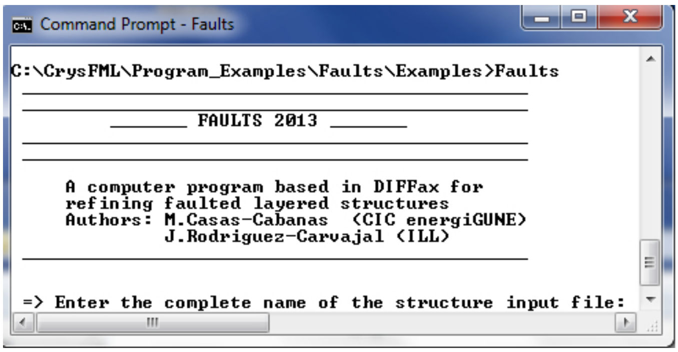
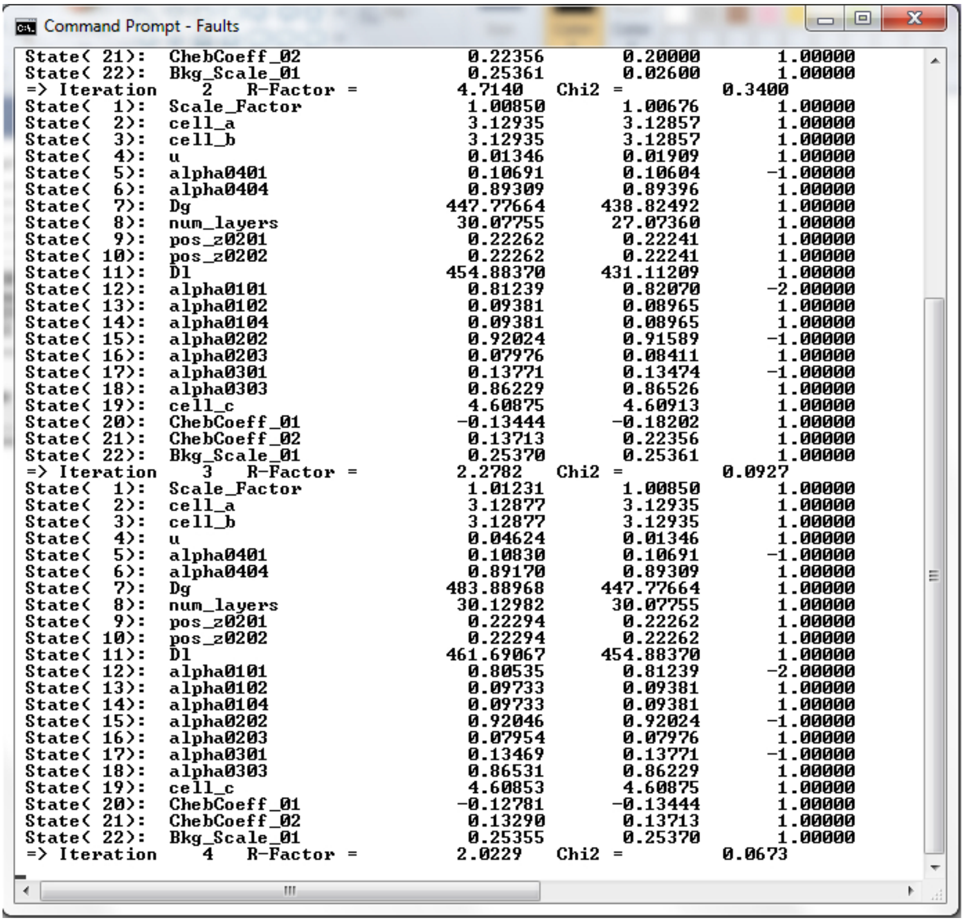
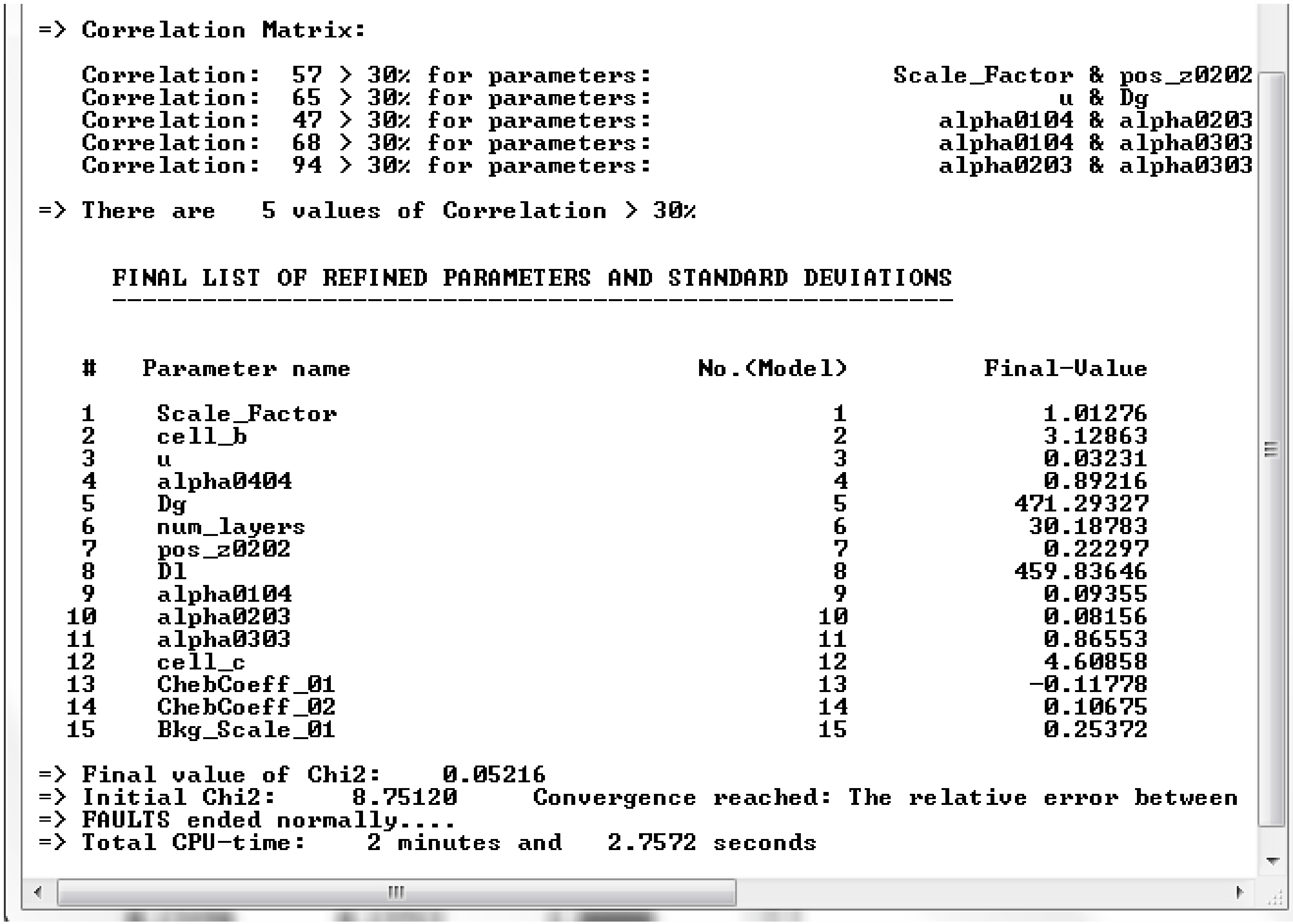


Figure 1.4: **FAULTS layout when invoked**



```
Command Prompt - Faults
State( 21): ChebCoeff_02        0.22356      0.20000      1.00000
State( 22): Bkg_Scale_01        0.25361      0.02600      1.00000
=> Iteration   2   R-Factor =   4.7140   Chi2 =      0.3400
State(  1): Scale_Factor        1.00850      1.00676      1.00000
State(  2): cell_a              3.12935      3.12857      1.00000
State(  3): cell_b              3.12935      3.12857      1.00000
State(  4): u                   0.01346      0.01909      1.00000
State(  5): alpha0401           0.10691      0.10604     -1.00000
State(  6): alpha0404           0.89309      0.89396      1.00000
State(  7): Dg                447.77664    438.82492      1.00000
State(  8): num_layers         30.07755     27.07360      1.00000
State(  9): pos_z0201           0.22262      0.22241      1.00000
State( 10): pos_z0202           0.22262      0.22241      1.00000
State( 11): Dl                454.88370    431.11209      1.00000
State( 12): alpha0101           0.81239      0.82070     -2.00000
State( 13): alpha0102           0.09381      0.08965      1.00000
State( 14): alpha0104           0.09381      0.08965      1.00000
State( 15): alpha0202           0.92024      0.91589     -1.00000
State( 16): alpha0203           0.07976      0.08411      1.00000
State( 17): alpha0301           0.13771      0.13474     -1.00000
State( 18): alpha0303           0.86229      0.86526      1.00000
State( 19): cell_c              4.60875      4.60913      1.00000
State( 20): ChebCoeff_01       -0.13444     -0.18202      1.00000
State( 21): ChebCoeff_02        0.13713      0.22356      1.00000
State( 22): Bkg_Scale_01        0.25370      0.25361      1.00000
=> Iteration   3   R-Factor =   2.2782   Chi2 =      0.0927
State(  1): Scale_Factor        1.01231      1.00850      1.00000
State(  2): cell_a              3.12877      3.12935      1.00000
State(  3): cell_b              3.12877      3.12935      1.00000
State(  4): u                   0.04624      0.01346      1.00000
State(  5): alpha0401           0.10830      0.10691     -1.00000
State(  6): alpha0404           0.89170      0.89309      1.00000
State(  7): Dg                483.88968    447.77664      1.00000
State(  8): num_layers         30.12982     30.07755      1.00000
State(  9): pos_z0201           0.22294      0.22262      1.00000
State( 10): pos_z0202           0.22294      0.22262      1.00000
State( 11): Dl                461.69067    454.88370      1.00000
State( 12): alpha0101           0.80535      0.81239     -2.00000
State( 13): alpha0102           0.09733      0.09381      1.00000
State( 14): alpha0104           0.09733      0.09381      1.00000
State( 15): alpha0202           0.92046      0.92024     -1.00000
State( 16): alpha0203           0.07954      0.07976      1.00000
State( 17): alpha0301           0.13469      0.13771     -1.00000
State( 18): alpha0303           0.86531      0.86229      1.00000
State( 19): cell_c              4.60853      4.60875      1.00000
State( 20): ChebCoeff_01       -0.12781     -0.13444      1.00000
State( 21): ChebCoeff_02        0.13290      0.13713      1.00000
State( 22): Bkg_Scale_01        0.25355      0.25370      1.00000
=> Iteration   4   R-Factor =   2.0229   Chi2 =      0.0673
```

Figure 1.5: **FAULTS layout during refinement**



```
=> Correlation Matrix:

   Correlation:  57 > 30% for parameters:               Scale_Factor & pos_z0202
   Correlation:  65 > 30% for parameters:                          u & Dg
   Correlation:  47 > 30% for parameters:                  alpha0104 & alpha0203
   Correlation:  68 > 30% for parameters:                  alpha0104 & alpha0303
   Correlation:  94 > 30% for parameters:                  alpha0203 & alpha0303

=> There are   5 values of Correlation > 30%


     FINAL LIST OF REFINED PARAMETERS AND STANDARD DEVIATIONS
     --------------------------------------------------------


   #   Parameter name                         No.(Model)        Final-Value

   1    Scale_Factor                                   1            1.01276
   2    cell_b                                         2            3.12863
   3    u                                              3            0.03231
   4    alpha0404                                      4            0.89216
   5    Dg                                             5          471.29327
   6    num_layers                                     6           30.18783
   7    pos_z0202                                      7            0.22297
   8    Dl                                             8          459.83646
   9    alpha0104                                      9            0.09355
  10    alpha0203                                     10            0.08156
  11    alpha0303                                     11            0.86553
  12    cell_c                                        12            4.60858
  13    ChebCoeff_01                                  13           -0.11778
  14    ChebCoeff_02                                  14            0.10675
  15    Bkg_Scale_01                                  15            0.25372

=> Final value of Chi2:    0.05216
=> Initial Chi2:     8.75120     Convergence reached: The relative error between
=> FAULTS ended normally....
=> Total CPU-time:    2 minutes and   2.7572 seconds
```

Figure 1.6: **FAULTS layout at the end of the refinement**

Chapter 2

Example

A simulated XRD pattern for $LiNiO_2$ has been used to analyse and test out the program. The initial values of the refinement have been chosen far enough from the correct ones not to bias the result. The refinement has been carried out using the Levenberg-Marquardt fit.

2.1 Stacking faults in $LiNiO_2$

Lithium nickel oxide has been intensively studied as a positive electrode material in Li-ion batteries [4]. As other lithium transition metal oxides it presents an O3-type layered structure, consisting in three NiO_2 slabs per unit cell with an ABCABC oxygen stacking sequence and lithium ions located in the octahedral sites of the interlayer spaces (see figure 2.1). In order to explain the significant broadening of the (10l) and (01l) diffraction lines, DIFFaX simulations have been used for this material with the hypothesis of the existence of O1 stacking faults in the structure [5]. These stacking faults represent a break in the normal stacking sequence of the structure, with a local ABAB oxygen stacking sequence.

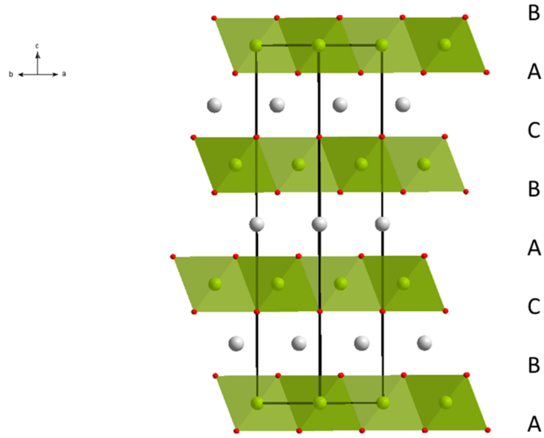


Figure 2.1: **Structure of lithium nickel oxide ($LiNiO_2$).**

The ideal structure can be described with three layers, each one containing a NiO_2 slab and a lithium sheet. The three layers are structurally identical, but shifted with respect to each other, resulting in transition vectors $\vec{t}12$=$\vec{t}23$=$\vec{t}31$=(2/3 1/3 1/3) and a stacking probability of 1 for each transition (figure 2.3). In the faulted structure the transitions $\vec{t}11$, $\vec{t}12$ and $\vec{t}33$ are allowed (see figure 2.2) and therefore the corresponding probabilities are no longer zero. In this case, the stacking vector is (0 0 1/3).

2.2 Analysis of simulated data

By means of the stacking description described above, FAULTS has been used to simulate a diffraction pattern with the parameter's values described in table 2.1. All the refined parameters using the Levenberg Marquardt optimisation algorithm are also detailed in table 2.1. The evolution of Chi^2,

R_p and the evolution of the cell parameter's throughout a run is shown in figure 2.4. Finally, a visual comparison between the calculated and the simulated powder patterns and their difference is shown in figure 2.5. Starting Rp and Chi^2 values were 76.38 % and 174.66 respectively and reached a final value of 0.96% and 0.06 respectively. All the refined parameters are very close to those used in the simulation except those involved in the IRF, but the obtained values of U, and X lead to a Caglioti curve practically identical to the one obtained with the values of these parameters used in the simulation.

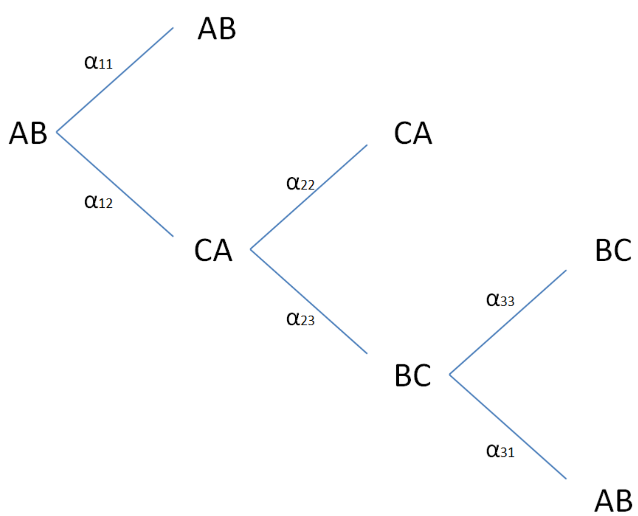


Figure 2.2: **Possible layer transitions for $LiNiO_2$ containing O1-type stacking faults, where α_{ij} is the probability transition from layer i to layer j.**

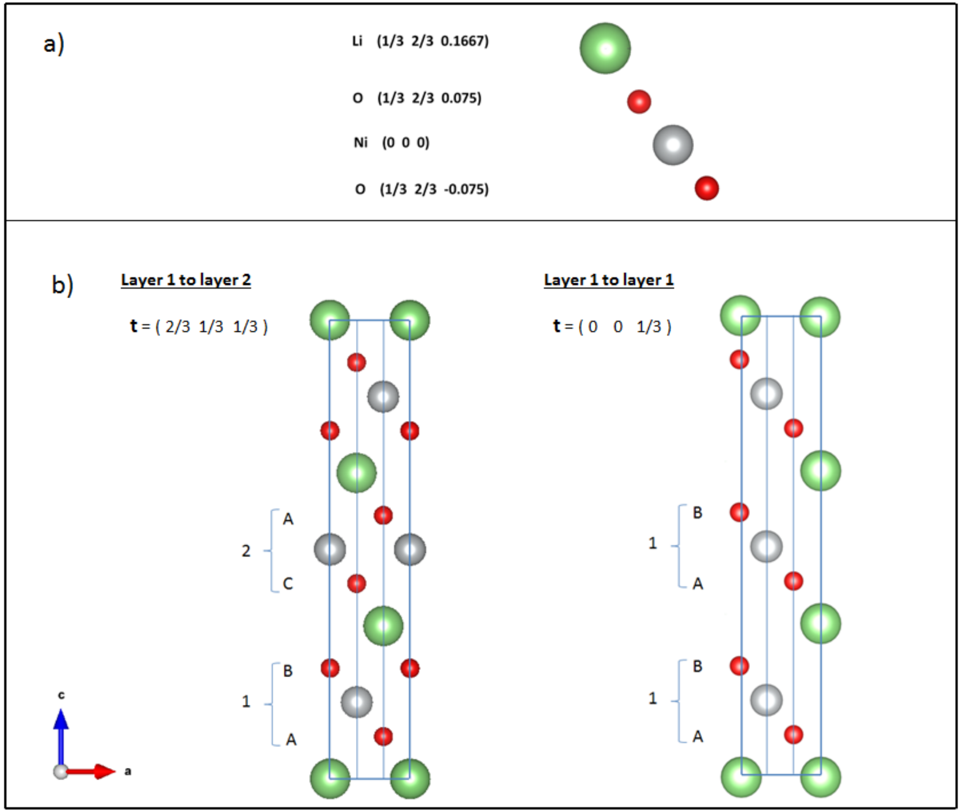


Figure 2.3: **a) Schematic representation and atomic coordinates of the layer required for describing stacking faults for $LiNiO_2$ in the FAULTS program. b) Graphic representation of the different transition possibilities from layer 1 and transition vectors.**

Refined parameter	Simulation	Initial value	Final value
x	0.600	0.700	0.604
a,b	2.8659	2.7868	2.8662
c	14.253	14.453	14.253
x_{Ni}	0.000	0.200	0.004
x_O	1/3	0.500	0.327
z_{Li}	0.167	0.267	0.162
α_{11}	0.112	0.142	0.111
α_{12}	0.888	0.858	0.889
α_{22}	0.112	0.142	0.111
α_{23}	0.888	0.858	0.889
α_{31}	0.888	0.858	0.888
α_{33}	0.112	0.142	0.112

Table 2.1: **Starting and final values of the parameters refined in the analysis of simulated data.**

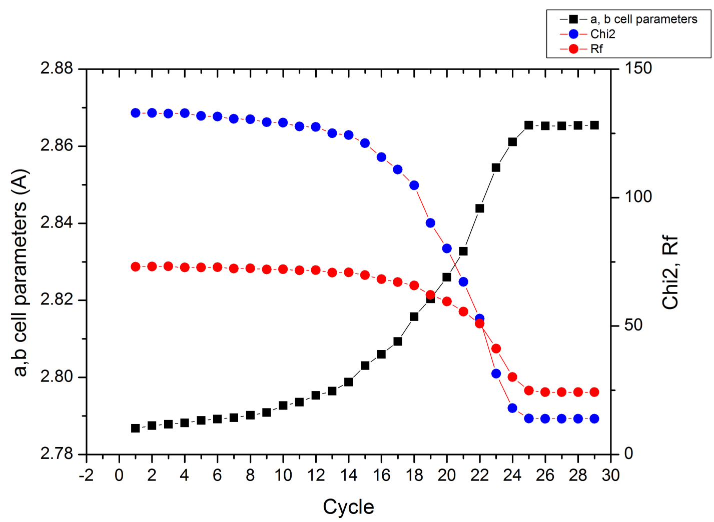


Figure 2.4: **Evolution of the functions Rp and Chi^2 and of the cell parameters a and b, versus the cycle number.**

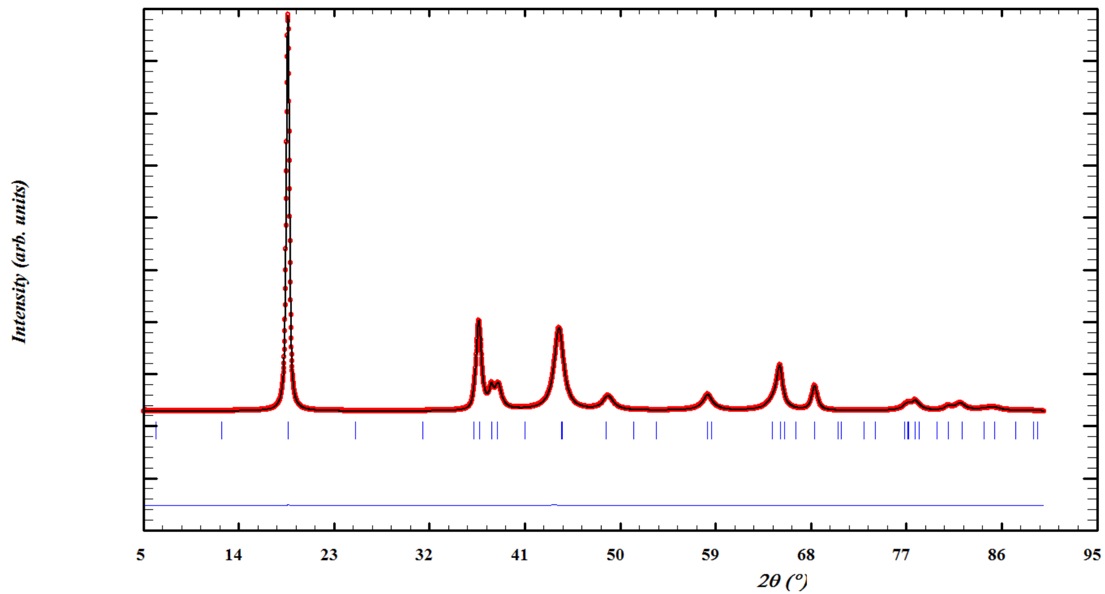


Figure 2.5: **Comparison of the X-ray diffraction patterns corresponding to the FAULTS analysis of the simulated data: simulated pattern (dotted curve) and calculated pattern using the FAULTS refinement (continuous curve). The diagram underneath shows the difference between them.**

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