

FAULTS, a new program for refinement of powder diffraction patterns from layered structures

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Abstract. A new program for refinement of layered structures is herein presented. FAULTS is based in the DIFFaX program, developed by Treacy et al. [1], which simulates selected area electron diffraction and powder (X-ray and neutrons) diffraction patterns by means of a recursion algorithm that calculates the incoherent sum of diffracted intensities of layered structures of any crystal system containing planar defects. In order to deal with the limitations of a simple simulation, refinement of all the parameters involved in the calculation of the diffracted intensities has been implemented in FAULTS.

Introduction

Layered systems include a large number of mineral families and synthetic compounds of great technological importance with applications as electroactive materials, superconductors, catalysts, lubricants, sensors and magnetic storage materials, among others. Their structural features, including those associated to certain defects, are directly related to their physical-chemical properties. Indeed the microstructural characterization of these materials is of essential importance and requires the determination of parameters specific to different types of defects, such as their amount and exact location.

So far, a widely used tool to interpret the diffraction data of one-dimensionally disordered systems is the DIFFaX program [1], which allows the simulation of powder X-ray and neutron diffraction patterns. As approximate, or merely qualitative, results may not be sufficient for a thorough microstructural characterization, a computerized comparison of the DIFFaX calculated intensities with experimental data would be of great help. A modification of the DIFFaX code including this possibility has been recently reported [2]. Independently, we have also developed an alternative code for the same purpose but following a quite different data treatment. The resulting code is the FAULTS program which can be used for the refinement of layered structures containing coherent planar faults.

Program specifications

As DIFFaX, FAULTS is a Fortran program but written in the new standard Fortran 95. The program FAULTS conserves the kernel of DIFFaX, which has been transformed into a Fortran 95 module, and adds other modules from the Crystallographic Fortran Modules Library (CrysFML) [3]. It can be used to refine XRD and NPD patterns of crystal systems with any type of coherent planar defect, such as twins and stacking faults.

The refinable parameters are read by FAULTS from a free format input data file, similar to that of DIFFaX, where the structure is described in terms of layers of atoms which interconnect via stacking operations that occur with a certain probability. Each value used to describe the structure is associated to a refinement code that allows the introduction of restrictions. The high and low limits of free parameters as well as the nature of the boundary conditions are provided by the user.

The experimental XRD or NPD patterns can be read from many different formats and background treatment can be achieved by linear interpolation or by polynomial fitting.

Another major feature of FAULTS is the implementation of a more adequate isotropic size broadening treatment which takes into account the Gaussian (HG) and Lorentzian (HL) contributions to the FWHM in addition to the consideration of a finite number of layers per crystallite already present in DIFFaX. The profile calculated by DIFFaX is convoluted with a Voigt function taking into account the size and instrumental effects. The FWHM of the Gaussian (H_G) and Lorentzian (H_L) components of the size/instrumental peak profile have an angular dependence given by equations (1) and (2):

$$H_G^2 = U \tan^2 \theta + V \tan \theta + W + \frac{4 \ln 2 \lambda^2}{\pi D_g^2 \cos^2 \theta} \quad (1)$$

$$H_L = X \tan \theta + \frac{2\lambda}{\pi D_l \cos \theta} \quad (2)$$

Where U , V , W , X , D_g and D_l are refinable parameters. Of course it is better to know a priori the parameters constituting the instrumental resolution function (IRF) and fix them. This treatment allows a successful description of the separate contributions to line broadening of instrumental features, finite crystallite size and planar defects.

The refinement can be carried out using local optimisation algorithms, like Nelder-Mead simplex [4], or global ones, as Simulated Annealing [5] or Multilevel Clustering [6, 7], all of them implemented in CrysFML [3].

The quality of the agreement between observed and calculated profiles is given by a set of indices such as the conventional R_p and R_{wp} values, or χ^2 , that are calculated at the end of each refinement cycle.

Example: Stacking faults in nickel hydroxide

Nickel hydroxide is used as the positive electrode material in Ni/Cd, Ni/H₂ or Ni/MH batteries. It presents a brucite type structure consisting in NiO₂ slabs made of edge-sharing octahedra. It is well known that the best electrochemical activities are obtained with small particle size materials [8]. It is also believed that the presence of structural defects enhances the elec-

trochemical performances of nickel hydroxide. DIFFaX simulations have been reported for this material with the hypothesis of the existence of stacking faults in the structure [9,10] in order to explain the abnormal broadening of the (10 l) and (20 l) diffraction lines ($l \neq 0$).

A stacking fault may be defined as a breaking in the normal stacking sequence of a structure. In the ideal structure of Ni(OH)₂, free of stacking faults, the oxygen atoms are placed alternatively in the A and B positions of a triangular lattice, whereas the nickel ions are in the centre of the oxygen octahedra, in C positions. Considering only the oxygen sheets, the perfect structure may thus be written as ABABAB. In the presence of a stacking fault, the oxygen atoms of the next sheet shift to position C instead of position A. If the following sheet of oxygen atoms is located just above those as two positions below, ABCBCB configuration, a growth type stacking fault is obtained. In contrast, if the following sheet of oxygen atoms is located just above those as three positions below, ABCACA configuration, the result is a deformation type stacking fault [11].

Considering both types of stacking faults, the oxygen sequence can be described with four different layer types, each one containing two sheets of oxygen atoms: AB, CA, CB and BC, as described in figure 1.

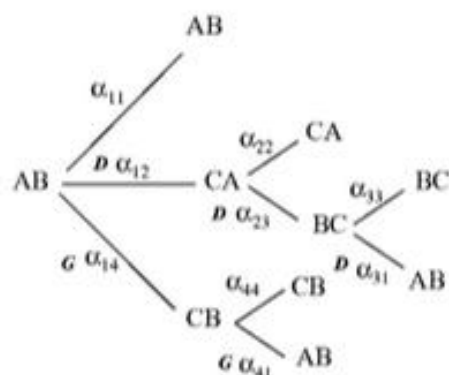


Figure 1. Possible layer transitions for a nickel hydroxide containing stacking faults, where α_{ij} is the probability transition from layer i to layer j and D and G indicate deformation and growth type faults respectively.

Analysis of simulated data

A simulated XRD pattern for Ni(OH)₂ has been used to analyse and test out the program. Most of the initial values of the refinement have been chosen far enough from the correct ones not to bias the result. All the refined parameters using the Nelder-Mead simplex optimisation algorithm are detailed in table 1 and a visual comparison between the calculated and the simulated powder patterns and their difference is shown in figure 2.

In the first stage of the refinement the R_p value was 133.26% and at the end of the refinement diminished down to 1.09%. 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 , V , and W lead to a Caglioti curve practically identical to the one obtained with the values of these parameters used in the simulation.

FAULTS refinement of the XRD pattern of a Ni(OH)₂ sample

The refinement of an experimental pattern corresponding to a Ni(OH)₂ sample has been carried out using the FAULTS program assuming the existence of stacking faults.

The $\text{Ni}(\text{OH})_2$ sample was synthesized by addition of 1M nickel sulphate solution to 2N NaOH solution at 70°C. The mean particle diameter is around 139Å as determined by TEM.

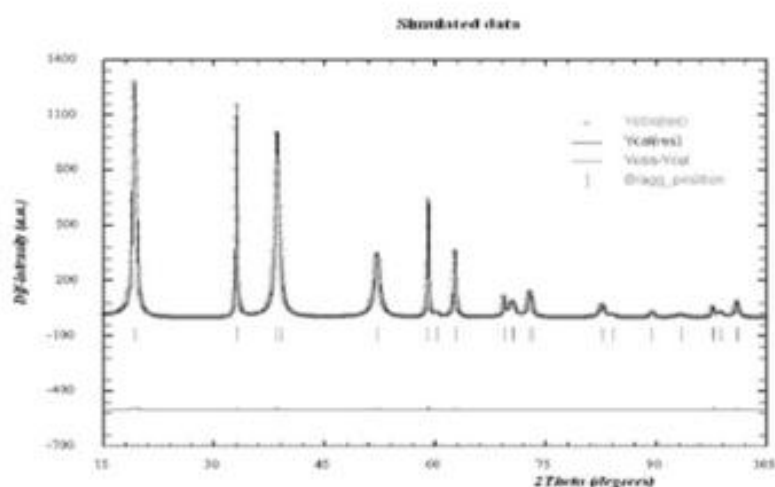


Figure 2. Simulated (“observed”) versus calculated patterns. The simulated pattern is the dotted curve and calculated pattern, using the FAULTS refinement, is the continuous curve; the diagram underneath shows the difference between them.

Table 1. Description, initial and refined value for all parameters used in the analysis of simulated data.

parameter	Description	Simulation	Initial	Refined
<i>U</i>	instrumental resolution function (IRF) parameter	0.0036	0.001	0.0013
<i>V</i>	IRF parameter	-0.0036	-0.001	-0.001
<i>W</i>	IRF parameter	0.0023	0.001	0.0012
<i>X</i>	Lorentzian contribution to FWHM parameter	0.0306	0.01	0.0122
<i>DI</i>	Lorentzian contribution to FWHM parameter	339.7	500	328.4
<i>a, b</i>	cell parameters	3.1293	3.3293	3.1286
<i>c</i>	cell parameter	4.6038	4.7038	4.6046
<i>Xo</i>	atomic position along c axis for atom2	0.2202	0.3202	0.2201
<i>Biso Ni</i>	Temperature factor atom1	1.0620	0.1	1.0696
<i>Biso O</i>	Temperature factor atom2	0.75961	0.1	0.7319
<i>Num_layers</i>	number of layers per crystallite	35.0	80.0	35.0
<i>a11</i>	stacking probability layer 1-1	0.80	0.75	0.80
<i>a12</i>	stacking probability layer 1-2	0.05	0.10	0.05
<i>a22</i>	stacking probability layer 2-2	0.95	0.90	0.95
<i>a23</i>	stacking probability layer 2-3	0.05	0.10	0.05
<i>a31</i>	stacking probability layer 3-1	0.05	0.10	0.05
<i>a33</i>	stacking probability layer 3-3	0.95	0.9	0.95

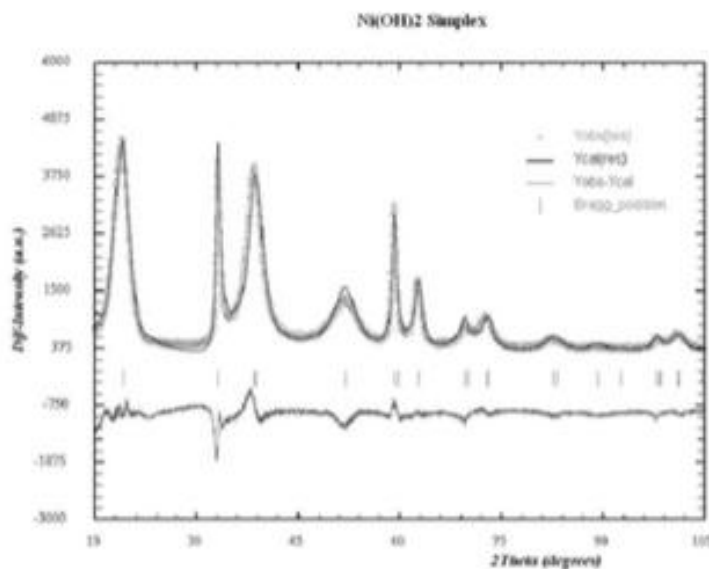


Figure 3. Comparison of observed and calculated patterns corresponding to nickel hydroxide. The observed pattern is the dotted curve and the calculated pattern, using the Nelder-Mead simplex optimisation algorithm, is the continuous curve; the diagram underneath shows the difference between them.

Table 2. Refined values for all parameters used in the analysis of an experimental XRD pattern corresponding to nickel hydroxide.

Parameter	Refined value (Simplex)	Refined value (Simulated Annealing)
x	0.0242	0.0131
Dg	1079.8	1091.7
Dl	91.8	85.1
a, b	3.1241	3.1251
c	4.6454	4.6525
$B_{iso} Ni$	0.6518	0.6398
$B_{iso} O$	0.1574	0.8995
$z O$	0.2266	0.2290
Num_layers	7.4	7.4
$a11$	0.60	0.61
$a12$	0.15	0.21
$a14$	0.25	0.18
$a22$	0.80	0.78
$a23$	0.20	0.22
$a31$	0.20	0.22
$a33$	0.80	0.78
$a41$	0.25	0.23
$a44$	0.75	0.77

The X-ray diffraction pattern was obtained with a Siemens D-500 diffractometer with Cu-K α radiation and a step size of 0.03° (2 θ). In order to avoid preferential orientation effects, the sample was side loaded in the sample holder.

The results of the refinement, performed with both Nelder-Mead simplex and Simulated Annealing optimisation algorithms, both leading to very similar results, are reported in table 2. The U , V , and W parameters from the instrumental resolution function were not refined as they were obtained from a LaB $_6$ standard. The obtained R_p values are 6.83% in the case of the Nelder-Mead simplex calculation and 7.12% for the Simulated Annealing. A comparison between the calculated, the observed and difference powder patterns is shown in figure 3.

The results indicate the presence of 20-25% growth faults. An important part of the anisotropic broadening comes from the size effect (refined number of layers ≈ 7.4). The accuracy of the results is further confirmed by the values obtained for the in-plane particle size, which are in agreement with the TEM observations.

Concluding remarks

An extension of the DIFFaX program, FAULTS, has been developed in order to refine XRD and NPD patterns of defective layered materials. The FAULTS program provides a useful tool in microstructural refinement and has already been tested in nickel hydroxide electro-active materials. A copy of the program is available from the authors upon request.

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