FAULTS, A NEW PROGRAM FOR REFINEMENT OF POWDER DIFFRACTION PATTERNS FROM LAYERED STRUCTURES

M. Casas-Cabanas^{1,2}, J. Rodríguez-Carvajal^{2,*}, M.R. Palacín¹

¹Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB E-08193 Bellaterra, Catalonia, Spain. ²Laboratoire Léon Brillouin (CEA-CNRS), CEA/Saclay, 91191 Gif-sur-Yvette Cedex, France.

Layered systems include a large number of mineral families and synthetic compounds of great technological importance. It is well known that 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 the proportions in which they occur and their 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 their powder X-ray and neutron diffraction patterns. 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, which can be used for the refinement of layered structures containing coherent planar faults.

Program specifications

As DIFFax, FAULTS is a Fortran program except that it is 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) [2]. 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 possibility of constraints. 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):

$$H_{G}^{2} = U \tan^{2} \theta + V \tan \theta + W + \frac{4 \ln 2\lambda^{2}}{\pi D_{g}^{2} \cos \theta}$$
(1)

$$H_{L} = X \tan \theta + \frac{2\lambda}{\pi D_{L} \cos \theta}$$
(2)

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

The refinement can be carried out using local optimisation algorithms, like Nelder-Mead simplex [3], or global ones, as Simulated Annealing [4] or Multilevel Clustering [5, 6], all of them implemented in CrysFML [2].

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.

FAULTS refinement of the XRD pattern of two different Ni(OH)₂ samples

Ni(OH)₂ is used as a battery positive electrode material. It presents better electrochemical activity when the particle size is small [7] and it is believed that defects also contribute positively to its behaviour.

The refinement of experimental patterns corresponding to two different Ni(OH)₂ samples has been carried out using the FAULTS program assuming the existence of stacking faults and using the Nelder-Mead simplex calculation. These samples were prepared by two different synthetic routes in order to achieve different microstructural characteristics, i.e. size and amount of defects. Both X-ray diffraction patterns were obtained with a Siemens D-500 diffractometer with Cu-Ka radiation and a step size of 0.03° (2 θ). In order to avoid preferential orientation effects, the samples were side loaded in the sample holder.

Sample A was synthesized by addition of 1M nickel nitrate solution to 28% NH₄OH solution at 60°C. The mean particle diameter is around 430Å as determined by TEM. Sample B was synthesized by addition of 1M nickel sulphate solution to 2N NaOH solution at 70°C. The mean particle diameter is around 139Å.



Figure 1. Comparison of observed and calculated patterns of sample A. The diagram underneath shows the difference between them. The insets show the crystallites as observed by MET and their "average apparent shape".

In the case of sample A, obtained R_p value is 7.61%. The results indicate the presence of 2% deformation faults. A comparison between the calculated, the observed and difference powder patterns is shown in figure 1, as well as a MET image and the "average apparent shape" of the crystallites obtained with the program FullProf [8]. For sample B the obtained R_p value is 6.83%. The results indicate the presence of 20% growth faults and 25% deformation faults. A comparison between the calculated, the observed and difference powder patterns is shown in figure 2, as well as a MET image and the "average apparent shape" of the crystallites obtained with the program FullProf [8]. An important part of the anisotropic broadening comes from the size effect (refined number of layers ≈ 7.4).

Figure 2. Comparison of observed and calculated



patterns of sample A. The diagram underneath shows the difference between them. The insets show the crystallites as observed by MET and their "average apparent shape".

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.

These results show that the synthetic method of sample B leads to a smaller and more defective $Ni(OH)_2$. Further electrochemical studies are to be performed in order to establish the relationship between amount and type of defects and electrochemical activity of these materials.

References

- 1. M.M. Treacy, J.M. Newsam, M.W. Deem, 1991, Proc. R. Soc. London Ser. A, 433, 499-520.
- 2. J. Rodríguez-Carvajal and J. González-Platas, 2003, IUCr CompCom Newsletter, 1, 50-58.
- 3. J.A. Nelder, R. Mead, 1965, *The computer journal*, 7, 308-313.
- 4. S. Kirkpatrick, C. D. Gelatt, Jr., M. P. Vecchi, 1983, Science, 220, 671-680.
- 5. Boender, C.G.E., A.H.G. Rinnooy Kan, G.T. Timmer, L. Stougie, 1982, Mathematical Programming, 22, 125-140.
- 6. Csendes, T., 1988, Acta Cybernetica, 8, 361-370.
- 7. McBreen J. 1990, Modern aspects of electrochemistry, 21. Plenum Press
- 8. Rodríguez-Carvajal J., 1993, Physica B, 192, 55-69.