An Introduction to the Program

FullProf

Comments on the **Examples Kit**:

/pub/divers/fullp/examples/prc_dat.zip

of the anonymous ftp-area in the server

bali.saclay.cea.fr

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Preface:

These notes have been written to help the people starting to use the program **FullProf**. They will constitute part of the future manual of the program. The notes are not yet finished and the author apologize for the errors they content. The description of the main control file MYFILE.pcr has been suppressed for simplicity. The user can always look at the horrible text-file FULLPROF.INS for details concerning all comments and references to MYFILE.pcr given in these notes.
As stated in the disclaimer of FULLPROF.INS,

> Powder diffraction is becoming more and more powerful but **FullProf** is not an *automatic* (black-box) program, as is usually found in single crystal structure determination. No attempt has been made to predict the behaviour of the program against bad input data. The user must check his(her) data before claiming a misfunction of the program.

So, a beginner cannot start to use the program without any background in crystallography, magnetism, diffraction physics and data analysis. Even an expert in these fields can expericence difficulties the first time (or even the n-th time!) he(her) use the program. An effort is presently being developed to facilitate the use of **FullProf**. The author expects to have a GUI (Graphical User Interface) prepared by the end of the next summer. This GUI will be independent of the platform (it is being developed in Java) and should helps considerably new users.
The notes begin with a short description of the way to obtain **FullProf** from the anonymous ftp-area. They follow with a chapter where it is given a brief description of the purpose of the program and the list of input and output files. The second chapter is dedicated to the description of strategies for using the program and the description of examples. The best way to start is using examples that work properly if the good parameters are provided to the program. To that end a kit of examples has been istalled in an accessible area of the server *bali.saclay.cea.fr*. This kit is in a single file called *pcr_dat.zip*. This file must be *unzipped* with the well known PKWARE software. The format of the files is for a PC, but they can be converted easily to UNIX with an editor or with a simple application like *dos2unix*.
In the third chapter the mathematical expresions used inside **FullProf** are written and discussed briefly. At present the notes finish with the description of the magnetic structure factor, Fourier coefficients of the magnetic moments, etc... In future releases everything concerned with data treatment in **FullProf** will be included. For the moment the user can consult FULLPROF.INS for futher details.

Juan Rodríguez-Carvajal
Saclay, 7 April 1997

Availability of FullProf

The most recent version of **FullProf** is always in *pub/divers/fullp* of the anonymous ftp-area of the LLB unix-cluster. Users interested in creating their own subroutines to link with FULLP-library are asked to read the file **fpreadme** in the above mentioned ftp-area. To access this area from the Internet, one has to type in the local host the following commands:

- `LocalPrompt> ftp 132.166.17.100 <cr>` , or
- `LocalPrompt> ftp bali.saclay.cea.fr <cr>`

Answer with the word: `anonymous` , to the Login request and password. To get, for instance, the file **fpreadme** the user should, after the ftp prompt, do:

```
From a UNIX host:

ftp>cd pub/divers/fullp <cr>  -> Go to FullProf area
ftp>get fpreadme        <cr>  -> Obtain the document
ftp>bye                 <cr>  -> Return to host
```

This should also work in modern Open-VMS systems but, from some VMS-VAX hosts:

```
ftp>set def "pub/divers/fullp" <cr>    -> Go to FullProf area
ftp>get "fpreadme"             <cr>    -> Obtain the document
ftp>ex                         <cr>    -> Return to host
```

Experienced users of ftp can go directly to the subdirectories and get the files they want. The structure of subdirectories match the different platforms in which **FullProf** can be run. Details are given in the file **fpreadme**. Recently the anonymous ftp-area can be accessed via the WEB through the URL of the LLB:

http://www-llb.cea.fr

It is of capital importance to have a plot program in order to visualize the observed versus calculated powder pattern and their difference. Such a program is not included at present in the **FullProf** executable code. Different free-ware, share-ware, or commercial programs can be user for this task. On the PC (under DOS) a very useful program is PLOTR (written by Thierry Roisnel at the LLB). PLOTR can be obtained in the same ftp-area as **FullProf** in the directory `pub/divers/plotr`.

Chapter 1

GENERAL INFORMATION ON FullProf

1.1 Purpose, references and documentation

The program is mainly developed for Rietveld analysis [1, 2] (structure profile refinement) of neutron (nuclear and magnetic scattering) or X-ray powder diffraction data collected at constant step in scattering angle 2θ [4, 5]. The program can be also used as a Profile Matching tool, without the knowlegde of the structure. Single Crystal refinements can also be performed alone or in combination with powder data. Time-of-flight (TOF) neutron data analysis will be available in future versions.

The program **FullProf** is based on the code of the DBW program, which, in turn, is also a major modification of the original Rietveld-Hewat program. An early version is discussed in the Young and Wiles article published in [6] and described in the user's guide distributed by R.A. Young. The program **FullProf** was developed starting with the code DBW3.2S (Versions 8711 and 8804), but it has been so much modified that only the name and some basic subroutines keep their original form. However, the main control input file created for use with DBW (and DBWS) program can be used by **FullProf** with minor modifications. This file is accepted by **FullProf** which read it in *interpreted free format*. The file generated, at the end of a run, by **FullProf** cannot be read by DBWS. The file can content comments starting with the symbol ! in the first position of a line. These comments are useful for remembering the name of variables and flags and greatly simplify the use of the program.

The source is written in standard FORTRAN 77 language, and is organized as to be easily adapted to different computers. The present version can be run under VMS, Open-VMS, Unix, MacOS and DOS-Windows (Lahey Computer Systems Inc. FORTRAN-compiler, minimum 386/4Mb with co-processor required). The transformation of the source code to Fortran 90 is projected for the future. The future version 4.0 will work with allocatable arrays, so that the dimensions of arrays can be directly controlled by the user at run time.

1.2 Features of FullProf

Some of the most important features of **FullProf** are summarized below:

- Choice of peak shape (Gaussian, Lorentzian, modified Lorentzians, pseudo-Voigt, Pearson-VII, Thompson-Cox-Hastings, numerical) for each phase
- Neutron and X-ray (laboratory and synchrotron sources)
- One or two wavelengths (eventually with different profile parameters)
- Background: fixed, refinable, adaptable, or with Fourier filtering
- Multi-phase (up to 8 phases)
- Preferred orientation : two functions available
- Absorption correction for cylinder and flat plate sample shape.
- Choice between three weighting schemes: standard least squares, maximum likelihood and unit weights.
- Choice between automatic generation of *hkl* and/or symmetry operators and file given by user.
- Magnetic structure refinement (crystallographic and spherical representation of the magnetic moments). Two methods: describing the magnetic structure in the magnetic unit cell of making use of the propagation vectors using the crystallographic cell. This second method is necessary for incommesurate magnetic structures.
- Automatic generation of reflections for an incommensurate structure with up to 24 propagation vectors. Refinement of propagation vectors in reciprocal lattice units
- *hkl*-dependence FWHM for strain and size effects
- *hkl*-dependence of shift and asymmetry for special kind of defects
- Profile Matching. The full profile can be fitted without prior knowledge of the structure (needs only good starting cell and profile parameters)
- Quantitative analysis without need of structure factor calculations.
- Chemical(distances) and magnetic(magnetic moments) slack constraints
- Resolution function (Voigt function) may be supplied in a file
- Structural or magnetic model could be supplied by an external subroutine for special purposes (rigid body, TLS, polymers, form factor refinements, small angle scattering of amphifilic crystals, description of incommensurate structures in real direct space, etc.)

- Single crystal data or integrated intensities can be used as observations (alone or in combination with a powder profile)
- Neutron (or X-rays) powder patterns can be mixed with integrated intensities of X-rays (or neutron) from single crystal or powder data
- Montecarlo search of starting parameters in a user-defined box for integrated intensity data

1.3 Running the program, input and output files

To run the program the user has to invoke the name of the executable file or an appropriate *alias*, for instance:

```
FULLPROF <cr>, or FullProf <cr>, or Fp <cr>...etc
```

Of course, the executable file must be placed in an accessible path. **FullProf** can also be run from a command file. After invoking the execution of the program the following dialog appears in the current window:

```
  *******************************************************
  *** PROGRAM FULLPROF (Version 3.2 - Jan97-LLB JRC)  ***
  *******************************************************
     Rietveld, Profile Matching & Integrated Intensity
          Refinement of X-ray and/or Neutron Data
                       (PC-version)

==> Give the code of the files (xx for xx.pcr):
```

After entering a value for xx, hereafter assumed to be CODFIL, the program prompts the following question [1]:

```
==> Give the name of data file (yy for yy.dat)
                           ( or yy.uxd, yy.acq)
                    (<cr> = CODFIL          ):
```

If the user answer with `<cr>` the name of the data file is CODFIL.dat (or CODFIL.uxd). We assume, in the following, the user has attributed the value FILE to the item `yy`. The file CODFIL.pcr must be created (from the scratch

[1] If xx=*starting*, the program enter in a new dialog to create an example of CODFIL.pcr file (called *starting.pcr*) for making a pattern calculation. The user can modify this generated file to adapt it to his(her) own problem

or by modifying an existing one) with the help of an ASCII editor. This file contents the diffraction conditions and crystallographic information needed by the program. The optional file FILE.dat (or FILE.uxd, FILE.acq) contents the profile intensity of the powder diffraction pattern.

For doing sequential refinements the user can run the program using a command file, or answer CYC to the prompt asking for the code of the files. In the last case another dialog opens:

```
==> Code of the starting *.pcr file (xx for xx.pcr):
```

Here the user should answer with the xx explicit name (let us assume that the code is CODFIL).

```
==> Give the code of data files (yy for yynnn.dat,uxd,acq)
                                       (<cr> = CODFIL    ):
```

As suggested by the question the name of the data files should have a part that constitutes the code followed by a ordinal number. The user should give here the code. Let us assume that the code is FILEDAT.

```
==> Number of the starting *.dat file: 46
==> Number of the     last *.dat file: 133
```

The user should give the ordinal numbers of the first and last files to be processed. The numbers 46 and 133 are examples. The program works by using the file CODFIL.pcr to process the file FILEDAT46.dat. The updated CODFIL.pcr are, then, used to process the file FILEDAT47.dat, etc... At the end, when the file FILEDAT133.dat has been processed, the control file contents the parameters adequate to the last treated file. The results of the whole set of treatments are stored in file CODFIL.RPA.

1.3.1 Input files

There are some references to names of control variables in this and the following sections. The precise meaning of these variables is described in FULLPROF.INS.

CODFIL.pcr (unit i_Pcr)

> Input control file. It must be in the current directory to run the program. This file contains the title and crystallographic data of the problem to be treated and must be prepared by user with a file editor. There are two different formats for this file: the first one is free format and closely related to that of the DBWS program. The second is based on keywords and commands [2].

[2]This last format is not available at present

Warning! this file is normally up-dated every time you run the program (see parameter NXT on LINE 3). In the first stages of a refinement, it is wise to save a copy of this file with a different name.

The complete description of the file CODFIL.pcr is given in the manual of the program. This is, at present, in the text-file FULLPROF.INS of the anonymous ftp-area: $/pub/divers/fullp/doc/$ of the server $bali.saclay.cea.fr$.

The following files are optional:

FILE.dat (unit i_Dat)

Intensity data file, its format depends on instrument. If you do not specify the name FILE, the program takes FILE=CODFIL. Not necessary for pattern calculation modes.

FILE.bac (unit i_Bac)

Background file. This file can also be generated by the program. The format of this file is the same as that of FILE.DAT for INSTRM=0:

- first line : 2θ(initial) step 2θ(final), any comment
- following lines: list of intensities in free format.

CODFILn.hkl or **hkln.hkl**

Set of files with the reflections corresponding to phase n (n is the ordinal number of a phase). These files are optional and depend on the value of the parameter IRF(n). This file can also be generated by the program.

MYRESOL.inst

File describing the instrumental resolution function. Any legal filename can be used and its content depend on the value of the parameter IRESO.

global.shp or **CODFIL.shp**

File providing a numerical table for calculating the peak shape and its derivative. The peak shape should be given in a normalized form $P(x)$ where the variable $x \in [x_1, x_2]$ is chosen to give a FWHM=1 and the area is 1, so $\int_{x_1}^{x_2} P(x)dx = 1$. That allows the use of the conventional U,V,W parameters for defining the FWHM as a function of angle.

The format of this file is the following:

- Line1: Any comment
- Line2: $Np8, nupr, 2\theta_1, 2\theta_2, ...2\theta_{nupr}$

- $Np8$: Number of points
- $nupr$: Number of different profiles
- $2\theta_j$: Angle to which profile j is best adapted

The rest of the lines are columns with $x, P_1(x), P_1'(x), P_2(x), P_2'(x)$, ...$P_{nupr}(x), P'_{nupr}(x)$ in free format. $P_j'(x)$ is the derivative of $P_j(x)$ with respect to x. The profile of a reflection situated between $2\theta_j$ and $2\theta_{j+1}$ is linearly interpolated between the profiles $P_j(x)$ and $P_{j+1}(x)$.

CODFIL.cor

User-defined intensity corrections. The corrections are applied to the integrated intensities as a multiplicative constant. The file CODFIL.cor starts with a comment and a list of pairs: Scattering Variable - Correction

1.3.2 Output files

Except for CODFIL.out and CODFIL.sum, their creation depends on the value of a flag which is quoted in parenthesis. The short name of the flag (controlling the output) used in the *commented* pcr-file is given in brackets.

CODFIL.out (unit i_Out) [3]

This is the main output file which contains all control variables and refined parameters.

CODFIL.prf (unit i_Prf)

Observed and calculated profile : to be fed into PLOTPOW, PLOTR, ...(if IPL2 [Prf] different from zero)

CODFIL.rpa (unit i_Rpa)

Summary of refined parameters. Short version of CODFIL.SUM (if JCIL=1)

CODFIL.sym (unit i_Sym)

List of symmetry operators (if IPL1=JSY=1)

The last two files are necessary to run DISTAN or BONDSTR

CODFIL.sum (unit i_Sum)

Parameter list after last cycle: summary of the last parameters, their standard deviations and reliability factors. An analysis of the goodness of the refinement is included at the end if IANALY=1.

CODFIL.fou (unit i_Fou)

(If JFOU=1)

[3] The actual numbers of the logical units for input-output files are given in file FUL0.inc

h, k, l, Structure Factors in Cambridge format to be fed into FOURTK (FOURPL) to produce Fourier maps. It corresponds to the file usually called HKLFF.DAT but you must prepare the second file CRYST.cry.

(If JFOU=2)

List of 'observed' structure factors in SHELXS format $h, k, l, F_{obs}, \sigma(F_{obs})$ (3I4,2F8.2)

CODFILn.shx

If JFOU=2, template of SHELXS *.IN file.

CODFILn.hkl

Files that can be input or output files. Depending on the value of IRF(n)

CODFIL.hkl (unit i_hkl)

Complete list of reflections of each phase.

- JLKH=1
  - ⇒ If JOBTYP<2
    Code, $h, k, l, mul, d_{hkl}, 2\theta$, FWHM, $I_{obs}, I_{calc}, I_{obs} - I_{calc}$.
  - ⇒ If JOBTYP >1
    $h, k, l, mult, I_{calc}, 2\theta, d_{hkl}$
- JLKH=2
- ⇒ Output for SIRPOW92
  $h, k, l, mul, sin\theta/\lambda, 2\theta, Fwhm, F^2, \sigma(F^2)$
- JLKH=3
  - ⇒ Output of real and imaginary part of structure factors (only for crystal structures)
    $h, k, l, mult, F_{real}, F_{imag}, 2\theta, Intensity$

(the obtained file can be used as a CODFILn.HKL file for new runs)

CODFIL.sav (if JCIL=2)

List of reflections between two selected angles
$h, k, l, mult, I_{obs}, 2\theta, d_{hkl}$

Chapter 2

THE RIETVELD METHOD IN PRACTICE

In this chapter some simple rules for starting a Rietveld refinement are stated. After discussing some of these rules and comment about the problems the user can experience in running the program, a short description of the examples given in the file *pcr_dat.zip* is given. The examples treated in this chapter are quite simple. Experienced users can apply other techniques and more sophisticated sets of parameters of peak shapes that are not discussed here.

2.1 Rietveld refinement

Although the principles behind the Rietveld profile refinement method are rather simple, the use of the technique requires some expertize. This results merely from the fact that Rietveld refinement uses a least-squares minimization technique which as any local search technique gets easily stuck in false minima. Besides, correlation between model parameters may easily cause divergence in early stages of the refinement. All these difficulties can actually be readily overcome by following a few simple prescriptions:

- Use the best possible starting model: this can be easily done for background parameters and lattice constants. In some cases, in particular when the structural model is very crude, it is advisable to analyse first the pattern with the total pattern fitting (profile matching) algorithm in order to determine accurately the profile shape function, background and cell parameters before running the Rietveld method.

- Do not start by refining all structural parameters at the same time. Some of them affect strongly the residuals (they must be refined first) while others produce only little improvement and should be held fixed till the latest stages of the analysis.

- Before you start, collect all the information available both on your sample (approximate cell parameters and atomic positions) and on the diffractometer and experimental conditions of the data measurement: zeroshift and resolution function of the instrument, for instance. Then a sensible sequence of refinement of a crystal structure, using X-ray diffraction, is the following:

1. scale factor
2. scale factor, zero point of detector , 1rst background parameter and lattice constants (in case of very sloppy background, it may be wise to actually refine at least two background parameters)
3. same + atomic positions + overall Debye-Waller factor (especially for low or high temperature data)
4. same + peak shape function (PSF) and asymmetry parameters
5. same + atom occupancies (if required)
6. same + individual isotropic thermal parameters (Debye-Waller)
7. same + individual anisotropic thermal parameters (if justified)
   To finish up, you may wish to refine also:
8. additional background parameters
9. the parameters SYCOS and SYSIN (line 10-1) to correct for instrumental or physical 2θ aberrations with a COS or SIN angular dependence.

In all cases, it is essential to plot frequently the observed and experimental patterns: examination of the difference pattern is a quick and efficient method to detect blunders in the model or in the input file which controls the refinement process and may also provide useful hints on the best sequence, to follow to refine the whole set of model parameters.
When large and unrealistic fluctuations of certain parameters occur from one cycle to the next, examine the correlation matrix: if large values (say larger than 50%) are observed, refine separately the corresponding parameters, at least in the early stages of the refinement.
Finally it must be remembered that there is a limit to the amount of information that can be retrieved from a powder diffraction pattern. Indeed structures with up to a hundred or more structural parameters can be refined from neutron powder data but such refinements must be performed with great care; for refinements involving a large number of variables the physical significance of certain parameters must be carefully examined. For instance thermal and PSF parameters can become poorly defined and act as a *dumping ground* for systematic errors. In such cases it is preferable to fix their values to a physically reasonable number and exclude them from the refinement.
When the uncertainty concerns the atomic parameters, it may help to provide some external information to the program. This can be achieved for instance by using strict constraints: for instance the displacement (thermal) parameters of chemically similar but crystallographically distinct atoms may be constrained to be identical, or the occupancy of two distinct and partly occupied sites of a structure may be compelled by the chemical analysis of the material.

2.2 Total-pattern fitting (Profile Matching)

This procedure does not require any structural information except approximate cell parameters. This makes the data input much simpler and enlarges considerably the field of application of powder pattern profile refinement. However the constraints applied to the refinement are far less severe than for Rietveld refinement and total-pattern fitting is thereby more prone to instabilities. This refinement mode can be used in two ways:

1. Profile Matching with constant scale factor (JBT=2). In this mode the scale factor is not allowed to vary and intensities are refined individually using, iteratively, the Rietveld formula for getting the *observed* integrated intensities. The recommended procedure is as follows:

   - For the first refinement, set IRF(n) of the phase n undergoing profile matching to 0 and the number of refined parameters (maxs on line 9) to zero. Run **FullProf** for a few (say 10) cycles. This will set up the *hkl*'s and intensity file CODFILn.hkl.
   - If the result of the above step is satisfactory (see plot!), rename the file CODFIL.new to CODFIL.pcr, or use directly CODFIL.pcr if it was automatically updated. Edit the new CODFIL.pcr file to select the parameters to refine. The progression of the refinement is very similar to that used for Rietveld refinement: zero point of detector, 1rst background parameter and lattice constants.

   In this mode of refinenent **FullProf** cannot calculate *theoretical* line intensities and all *hkl* values permitted by the space group are considered and included in the refinement... which sometimes means a lot of reflections!. Using this type of refinement one has to bear in mind that the starting cell parameters and resolution function determines to a large extend the obtained intensity parameters. One cannot expect to refine properly the cell parameters of a compound with a severe overlap of reflections if the starting parameters are of poor reliability. It is wise to start with low angle reflections (without refining the FWHM parameters) and progressively increase the angular domain.

2. Profile Matching with constant relative intensities (JBT=3). In this mode the intensities are held fixed and only the scale factor is varied. Since WPF does not require the calculation of the structure factors it runs faster than Rietveld refinement.

2.3 Hints'n tricks

Even if you follow carefully the recommendations mentioned above, you may experience difficulties to refine your data; most of them can be avoided by following a few simple rules:

- If the number of measured reflections is limited, select carefully the refined parameters and keep the others fixed to physically reasonable values (for instance refine the overall displacement (temperature) parameters, not the individual ones).

- Exclude regions where the background is strongly distorted if any (e.g. background from sample environment may show odd variations) for the background function used in the code may not be able to cope with it.

- Look carefully for the values of the *standard* profile parameters of the instrument used for getting the data. If, for any reason, you do not know the shape of the diffraction profiles, start with pure gaussian, i.e. use first NPROF=0 on line 2. In the final stages of refinement examine the difference profile to look for departure from a gaussian shape and change to pseudo-Voigt (first with a small η value) if required. If the value of η is much larger than zero, remember to increase the range of the calculated profile (WDT on line 4); failure to increase properly this parameter will lead to discontinuities in the edges of the calculated profile.

- The profile parameters are sometimes difficult to refine especially for data spanning only a limited angular range or samples giving broad diffraction lines. In such case, it is normally advisable to fix one or more FWHM parameter or to constraint their variation with a proper use of the code-words. As profile parameters may vary from sample to sample (strain and/or size broadening) and depend from instrumental set-ups, you must, at some stage, refine U, V and W from your own data.
  The best method is of course to refine first a standard pattern with no sample broadening in order to determine the U, V, W parameters of your instrument.

2.4 Trouble shooting

- If you experience difficulties from the very beginning (for instance a singular matrix at the first refinement), start refining the scale factor only and examine the difference pattern with a plotting program. This will most of the time reveal a glaring blunder in the input data (zero-shift, step size, angular limits etc).

- Owing to the complexity of the control file, error messages given in the terminal are not always easy to decipher in that they do not necessarily point to the initial error but merely to one of its consequences. Most of the time, run time errors result from an error in the sequence of lines in the control file, e.g., an inadequacy between the number of atoms stated on line 11.2 and the number of atomic positions given on lines 11.4. Look at the output file CODFIL.OUT to verify if the different items have been properly read by the program.

- Errors in the generation of *hkl* have been observed for a few space groups: check carefully your list of reflections at the end of file CODFIL.out.

2.5 Examples. Content of *pcr_dat.zip*

To test the installation of the program, or for training purposes, a list of complete examples are provided together with **FullProf**. The file *pcr_dat.zip* can be obtained by anonymous ftp to the server *bali.saclay.cea.fr* in the area */pub/divers/fullp/examples*. Set the mode to *binary* in order to get properly the file. This file must be *unzipped* with PKUNZIP under Windows or DOS. The format of the files is for DOS, so they have to be converted to other platforms using the appropriate utility. Among the files obtained after a successful *unzip* that called PCR_READ.ME gives an explanation of the whole set of files inside *pcr_dat.zip* from the point of view of an installation test. This file is displayed below:

```
CONTENT of PCR_DAT.ZIP (February 1997)

1:The files contained in pcr_dat.zip can be used for testing FullProf.
  They have been selected in order to illustrate the use of FullProf in
  a variety of situations. In no way the proposed models pretend to be
  the most adequate to the data. In some cases there is a clear
  disagreement between the data and the model.

2:For a quit test under DOS or under UNIX the user can type at the
  command line:
                    fullprof_alias < tempo.inp

  FullProf will be executed for all files existing in file: tempo.inp
  where the answers expected by FullProf are collected.

3:The files are in PC format. They have to be converted to UNIX, Mac,
  or VMS using one of the appropriate utility (dos2unix, editor,...).

4:The number and nature of files can change with different releases.

  At present the files are:

PCR code           Purpose                                      Data File
---------------------------------------------------------------------
c60   : compares C60 x-tal data to form-factor sin(Qr)/Qr: c60.int
ce1   : refinement of a CeO2 standard                      : ceo2.dat
ce2   :          "                                         :    "
dy    : Four different ways of refining the crystal        : dy.dat
dya   : and magnetic structure of DyMn6Ge6                 :    "
dyb   :                                                    :    "
dyc   :                                                    :    "
hobb  : Refinement with integrated intensities (Nuc+mag) : hobb.int
hob   : Montecarlo search for mag. moments in Ho2BaNiO5  :     "
hobk1 : Three different ways of refining the crystal     : hobk.dat
```

```
hobk2 : and magnetic structure of Ho2BaNiO5              :    "
hobk3 :                                                  :    "
la    : Two ways for strain refinement in La2NiO4        : la.dat
lab   : with low resolution neutron powder data.         :    "
monte : Montecarlo test with single crystal data         : monte.int
pb    : Profile matching test of PbSO4 neutron data      : pbso4.dat
pbso4 : Crystal structure refinement of PbSO4            :    "
pbso4a:             "                (anisotropic b's)   :    "
hmt   : Rigid body refinement of simulated data          : hmt.dat
urea  : Test Rigid body  with satellites (simulated data): urea.dat
ycbacu: YBaCuO with Ca. Data from D1A                    : ycbacu.dat
```

In general, the user must first run the program to verify that the provided `pcr`-files behave correctly. After that, the user should make a copy of the control files for saving them before running his(her) own options. The best way is to modify the given values for different sets of parameters and run the program. The beginner must make extensive use of editor-plot cycles. The plot of the file CODFIL.prf is of absolutely necessity for knowing the behaviour of the program under bad (or inaccurate) input parameters.

To use the above files for training, the unexperienced user must start with the most simple cases, that is `ce1.pcr` and `ce2.pcr` used to process the file `ceo2.dat`. This file corresponds to a data collection on cerium oxide with a good laboratory X-ray powder diffractometer, using CuK_α doublets.

The next files to be processed are those of $PbSO_4$. The data file correspond to neutron powder diffraction on D1A (ILL) that was used in a Round Robin on Rieveld refinement (*R.J. Hill (1992), J.Appl.Cryst* **25**, *589*). For people working mainly with crystal structures the next files to be studied are: `ycbacu, hmt, urea` for powder diffraction.
Some files for single crystal data are also given: `c60, monte`. The first one use a too simplistic model (just a spherical shell) for describing the C_{60} molecule that give poor results. The user can try this file as an example of special form factor refinement. The free parameters are the radius of the C_{60} molecule and its isotropic temperature factor. The file `monte` correspond to an artificial use of the Montecarlo technique for searching a starting set of initial parameters. Data are from neutron diffraction on a single crystal of oxidized $Pr_2NiO_{4+\delta}$.

People interested in magnetic structures can use the rest of the files in the following order.

- `la, lab`: refinement of the low temperature phase crystal and magnetic structure of La_2NiO_4. The data are from a medium-low resolution neutron powder diffractometer (D1B at ILL). This phase present a microstrain that is refined using two equivalent methods in the two files. The magnetic structure is very simple. A peak from an impurity phase is near the first magnetic peak.

- The files `hobb, hob, hobk1, hobk2, hobk3` concern the refinement of the crystal and magnetic structures of Ho_2BaNiO_5 at 1.5K, using different methods and conditions. The user can verify that `hob.pcr` can *solve* the magnetic structure of Ho_2BaNiO_5 just testing random configurations. This is a very favourable case and this method cannot be applied for general magnetic structure determination. The data are from D1B.

- The files `dy, dya, dyb, dyc` use different methods to refine the incommensurate magnetic structure of $DyMn_6Ge_6$. This is a conical structure that can be refined using a *real space approach* as in `dy` and `dya` or using Fourier components of the magnetic moments, which is the general formalism of **FullProf** for handling magnetic structures. This is the case of files `dyb` and `dyc`

The only right way to learn about crystal and magnetic structure refinements is practicing with real data as these are. However, it is better when the user try with its own data on a problem of interest to him(her).

Chapter 3

MATHEMATICAL INFORMATION

In this chapter the basic equations concerned with the calculations performed in **FullProf** are discussed. It is supposed that the reader has a good knowledge of powder diffraction, so the explanations given below concern mainly the *description* of the terms involved in the formulae. The references to numbered lines (eg. LINE 3, Line 11-4-1) correspond to lines of the main input control file CODFIL.pcr described in FULLPROF.INS.

3.1 Calculated profile

A powder diffraction pattern can be recorded in numerical form for a discrete set of scattering angles, times of flight or energies. We will refer to this scattering variable as T. Then, the experimental powder diffraction pattern is usually given as two arrays $\{T_i, y_i\}_{i=1,..n}$. In **FullProf** the array $\{T_i\}$ is not actually stored because it is supposed that the values of the scattering variable are equally spaced [1]:

$$T_i = T_{init} + (i-1)\mathrm{STEP}$$

The profile can be modeled using the calculated counts y_{ci} at the ith step by summing the contribution from neighbouring Bragg reflections plus the background:

$$y_{ci} = \sum_{\phi} S_\phi \sum_{\mathbf{h}} I_{\phi,\mathbf{h}}\ \Omega(T_i - T_{\phi,\mathbf{h}}) + y_{bi} \tag{3.1}$$

The vector $\mathbf{h}$($=\mathbf{H}$, or $=\mathbf{H}+\mathbf{k}$) labels the Bragg reflections, the subscript ϕ labels the *phase* and vary from 1 up to the number of *phases* existing in the model. In **FullProf** the term *phase* is sinonymous of a *same procedure for calculating the integrated intensities* $I_{\phi,\mathbf{h}}$.

$$I_{\phi,\mathbf{h}} = \{LF^2ATPC\}_{\phi,\mathbf{h}} \tag{3.2}$$

[1] In some cases the program can trasform internally the data to constant step by making the appropriate interpolation

For simplicity we will drop the ϕ-index. Sometimes we will refer to the whole arrays $\{y_i\}$ and $\{y_{ci}\}$ as y_{obs} and y_{cal} respectively. The meaning of the different terms appearing in 3.1 and 3.2 is the following:

- S_ϕ is the scale factor of the phase ϕ
- $L_{\mathbf{h}}$ contains the Lorentz, polarization and multiplicity factors.
- $F_{\mathbf{h}}$ is the structure factor.[2]
- $A_{\mathbf{h}}$ is the asymmetry function
- $T_{\mathbf{h}}$ is the transmission factor
- $P_{\mathbf{h}}$ is the preferred orientation function
- Ω is the reflection profile function that models both instrumental and sample effects.
- C is a user-defined correction
- y_{bi} is the background intensity

In the following sections we discussed the different terms in more detail.

3.2 Background

The background intensity y_{bi} at the ith step is obtained (see LINE 2 and LINE 6* or Line 10-2*) either from an user-supplied table of background intensities, or from a refinable background function:

$$y_{bi} = \sum_{m=0}^{5} B_m \left(\frac{T_i}{\mathrm{BKPOS}} - 1\right)^m + \sum_{j=1}^{6} B_{Cj} \frac{\sin(Q_i d_j)}{Q_i d_j} \tag{3.3}$$

The origin of the background polynomial is given by a selectable input parameter BKPOS (LINE 4) and should be supplied by the user. The second sum is used only if NBCKGR=-1. The parameters to be refined are: $B_0, B_1, ...B_5, B_{C1}, ...B_{C6}, d_1, ...d_6$. Q_i is the modulus of the scattering vector ($\mathbf{Q}$=$2\pi\mathbf{h}$) at the ith step, and is given by:

$$Q_i = 4\pi \frac{\sin\theta_i}{\lambda} \tag{3.4}$$

where $\lambda = \lambda_1$ (first wavelength) in **FullProf.** The parameters d_j are distances in Å.

The background can be also read from a supplied file FILE.bac. The actual background is calculated from the read background applying the following formula:

$$Background(2\theta) = b_1 BackgRead[(1 + b_3)2\theta + b_4] + b_2 \tag{3.5}$$

[2]The ratio of the intensities for the two wavelengths handled by the program is absorbed in the calculation of $F^2_{\mathbf{h}}$, so that only a single scale factor is required.

The background parameters and codes, given in Line 10-2*, correspond to the coefficients of the above formula in the order: b_1, b_2, b_3, b_4. If b_1 is given as zero, the program puts b_1=1. Limits against divergence are fixed by program. The parameter b_3 is allowed to vary up to a maximum value ABS(b_3)=0.1 and ABS(b_4) is kept below 3 degrees (2θ). The user can chek the excursion of those parameters out of the allowed range when they are strictly zero and their standard deviation is (fixed arbitrarily to) 0.99999. This option is useful when complicated background shapes are present due to sample environment.

Another procedure for treating the background has been introduced. The background is ajusted iteratively at each cycle by using a Fourier filtering technique. The starting background is read from the file FILE.bac. At cycle n the new background is calculated from the old one, cycle $n-1$, with the formula:

$$Background(n) = Background(n-1) + Filtered[y_{obs} - y_{cal}](n-1) \quad (3.6)$$

where $Filtered[y_{obs} - y_{cal}]$ is a strongly smoothed version of $y_{obs} - y_{cal}$. The parameter controlling the smoothing is FWINDOW which is equivalent to PST described in subroutine SMOOFT described in Numerical Recipes (see [23]). The implementation of SMOOFT in **FullProf** is not the same as in [23]. When using this method it is wise to draw the final background to see if it is really a smooth curve. This option is only justifiable in cases of a very wavy background. The starting background should be close to the real one.

3.3 Peak-shape functions

The profile function Ω is selected by the control variable NPROF (LINE 2). All the profile functions used in **FullProf** are normalized to 1 (i.e. $\int_{-\infty}^{+\infty} \Omega(x)dx = 1$). The variable is $x = T - T_{\mathbf{h}}$, the FWHM will be called H. The definition of $\Omega_i(x)$, where the subscript i stands for the value of the variable NPROF, is the following:

$$\text{GAUSSIAN: } \Omega_0(x) = G(x) = a_G \exp(-b_G x^2) \quad (3.7)$$

where:

$$a_G = \frac{2}{H}\sqrt{\frac{\ln 2}{\pi}} \qquad b_G = \frac{4\ln 2}{H^2}$$

$$\text{LORENTZIAN: } \Omega_1(x) = L(x) = \frac{a_L}{1 + b_L x^2} \quad (3.8)$$

where:

$$a_L = \frac{2}{\pi H} \qquad b_L = \frac{4}{H^2}$$

$$\text{MODIFIED LORENTZIAN: } \Omega_2(x) = ML(x) = \frac{a_{ML}}{(1 + b_{ML}x^2)^2} \quad (3.9)$$

where:

$$a_{ML} = \frac{4\sqrt{\sqrt{2}-1}}{\pi H} \qquad b_{ML} = \frac{4(\sqrt{2}-1)}{H^2}$$

$$\text{INTERMEDIATE LORENTZIAN: } \Omega_3(x) = IL(x) = \frac{a_{IL}}{(1+b_{IL}x^2)^{3/2}} \tag{3.10}$$

where:

$$a_{IL} = \frac{\sqrt{2^{2/3}-1}}{H} \qquad b_{IL} = \frac{4(2^{2/3}-1)}{H^2}$$

$$\text{PEARSON VII: } \Omega_6(x) = PVII(x) = \frac{a_{VII}}{(1+b_{VII}x^2)^m} \tag{3.11}$$

where:

$$a_{VII} = \frac{\Gamma(m)}{\Gamma(m)-1/2}\frac{2\sqrt{2^{1/m}-1}}{\sqrt{\pi}H} \qquad b_{VII} = \frac{4(2^{1/m}-1)}{H^2}$$

$$\text{PSEUDO-VOIGT: } \Omega_5(x) = \Omega_7(x) = pV(x) = \eta L'(x) + (1-\eta)G'(x) \qquad 0 \le \eta \le 1 \tag{3.12}$$

The $pV(x)$ function is a linear combination of a lorentzian (L') and a gaussian (G') of the same FWHM (H) [3]. The profile function NPROF=4, $\Omega_4(x)$, is a superposition of three $pV(x)$ functions (see below 3.21). The difference between NPROF=5 and NPROF=7 is that in the later the parameter η is not directly refinable but calculated from H_L and H_G Let us precise this point. The pseudo-Voigt function is an approximation to the Voigt function defined as the convolution of a lorentzian and a gaussian:

$$\text{VOIGT: } V(x) = L(x) \otimes G(x) = \int_{-\infty}^{+\infty} L(x-u)G(u)du \tag{3.13}$$

where $L(x)$ and $G(x)$ have different FWHM (H_L and H_G, respectively). The $pV(x)$ function is an approximation that substitutes the two shape parameters H_L and H_G by the pair (η, H). The Voigt function can be written in a closed form in terms of the complex error function and the integral breaths of the Lorentzian (β_L) and Gaussian components (β_G):

$$V(x) = \beta_G^{-1} Re\left[erf\left(\frac{\sqrt{\pi}}{\beta_G} \mid x \mid + i\frac{\beta_L}{\beta_G\sqrt{\pi}}\right)\right] \tag{3.14}$$

where:

$$erf(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}dt$$

Numerically is more easy to calculate the pseudo-Voigt approximation 3.12 using a numerical approximation relating the pairs (H_L, H_G) and (η, H) (see []):

$$H^5 = (H_G^5 + 2.69269 H_G^4 H_L + 2.42843 H_G^3 H_L^2 + 4.47163 H_G^2 H_L^3 + 0.07842 H_G H_L^4 + H_L^5) \tag{3.15}$$

$$\eta = 1.36603\frac{H_L}{H} - 0.47719\left(\frac{H_L}{H}\right)^2 + 0.11116\left(\frac{H_L}{H}\right)^3 \tag{3.16}$$

[3] The reader can verify that the FWHM of $pV(x)$ is also H

The inversion of the above two expressions leads to the relations:

$$\frac{H_L}{H} = 0.72928\eta + 0.19289\eta^2 + 0.07783\eta^3 \tag{3.17}$$

$$\frac{H_G}{H} = (1 - 0.74417\eta - 0.24781\eta^2 - 0.00810\eta^3)^{1/2} \tag{3.18}$$

The difference between the pV-functions calculated with NPROF=5 or NPROF=7 concerns only the parametrization of η and H which can be simply related to significant physical parameters unsing NPROF=7.

The dependence of the peak-shape parameters (including FWHM) on the scattering variable (2θ for constant wavelength diffractometers) is parametrized mainly through the variables defined in Line 11-6-1: U, V, W, X, Y, I_G, S_Z.

For profiles NPROF=0 to NPROF=6 :

$$H^2 = (U + D_{ST}^2)\tan^2\theta + V\tan\theta + W + \frac{I_G}{\cos^2\theta} \tag{3.19}$$

For NPROF=5 (pseudo-Voigt) the η parameter can be dependent on X through the formula:

$$\eta = \eta_0 + X2\theta \tag{3.20}$$

For NPROF=4 (tripled pseudo-Voigt), the three components are assumed to have the same η_0 and FWHM, so the effective total width depends on the additional shape parameter S_{h1} (see Line 11-8-3). The profile function is given by the formula:

$$\Omega_4(x) = p_4(x) = XpV(x - D) + (1 - X - Y)pV(x) + YpV(x + D) \tag{3.21}$$

where:

$$D = \frac{S_{h1}}{d\cos\theta}$$

So, apart from the FWHM that is calculated from U, V, W, D_{ST} and I_G parameters for a single component, the profile function has FOUR shape parameters η_0, X, Y and S_{h1}. This function is adapted for medium resolution neutron powder diffractomers having defects on the monochromator and/or the guide spacial spectral distribution giving rise to a non-gaussian distribution of wavelengths.

For NPROF = 6 (Pearson-VII) the m parameter can be dependent on X and Y through the formula:

$$m = m_0 + 100\frac{X}{2\theta} + 10000\frac{Y}{(2\theta)^2} \tag{3.22}$$

For NPROF=7, the FWHM of the Gaussian (H_G) and Lorentzian (H_L) components is calculated as:

$$H_G^2 = (U + D_{ST}^2)\tan^2\theta + V\tan\theta + W + \frac{I_G}{\cos^2\theta} \tag{3.23}$$

$$H_L = X\tan\theta + \frac{(Y + F(S_Z))}{\cos\theta} \tag{3.24}$$

The units of parameters U, V, W, I_G are (degrees2θ)^2. The physical meaning of I_G, D_{ST}^2 and $F(S_Z)$ is briefly discussed in FULLPROF.INS.

3.4 Monochromator, Lorentz and geometrical corrections

Bragg-Brentano or Debye-Scherrer geometry

Monochromator polarization correction (CTHM and K in LINE 4); the Lorentz polarization factor Lp is calculated as :

$$Lp = \frac{1 - K + K\cos^2 2\theta_{Monok}\cos^2 2\theta}{2\sin^2\theta\cos\theta} \tag{3.25}$$

with CTHM $=\cos^2 2\theta_{Monok}$. For instance with a Graphite monochromator, CTHM = 0.8351 and 0.7998 for CuK_β and CuK_α respectively.

Note that K is used only for synchrotron data (INSTRM=4) and does not have to be input for other kind of data taken with the specified geometry.

- For neutrons, K=0.0.
- For characteristic X-Ray radiation (unpolarized beam), K=0.5.
- For synchrotron radiation, K must be given ($K \approx 0.1$)

Transmission flat-plate geometry

In the transmission geometry, flat plate with the scattering vector within the plate (Stoe geometry for X-rays, ILOR=2) the Lorentz factor is:

$$L = \frac{1}{\sin 2\theta} \tag{3.26}$$

and the polarization correction is given by:

$$p = K\frac{1 + c_1\cos^2 2\theta}{1 + c_1} + (1 - K)\frac{1 + c_2\cos^2 2\theta}{1 + c_2} \tag{3.27}$$

where

$$c_1 = \mid \cos 2\theta_{Monok} \mid = \sqrt{\mathrm{CTHM}}$$

$$c_2 = \cos^2 2\theta_{Monok} = \mathrm{CTHM}$$

$$K = \text{fraction of perfect crystal contribution}$$

This geometry (ILOR=2) requires the use of a non-zero absorption coefficient.

3.5 Asymmetry

The default asymmetry correction (see RLIM in LINE 4) follows the expression given in [12]. The asymmetry correction adopts the form:

$$A_{\mathbf{h}} = 1 + \frac{P_1F_a(z) + P_2F_b(z)}{\tan\theta_{\mathbf{h}}} + \frac{P_3F_a(z) + P_4F_b(z)}{\tan 2\theta_{\mathbf{h}}} \tag{3.28}$$

Where

$$z = \frac{2\theta_i - 2\theta_{\mathbf{h}} - S_{shf}}{\mathrm{FWHM}}$$

S_{shf} includes the zero-point and other shifting terms,

$$F_a(z) = 2z\exp(-z^2), \qquad F_b(z) = 2(2z^2-3)F_a(z)$$

The asymmetry correction 3.28 has four independent parameters, (P_1, P_2, P_3, P_4) which are read in Line 11-8-1.

If NPHASE<0 the method proposed by C.J.Howard (see [11]), is used. The approximation of the convolution integral is performed using the Bode's rule (Simpson's formula for five points). The profile is calculated as a superposition of five profile functions $g(x)$ (only pseudo-Voigt NPROF=5 and NPROF=7 are implemented for this correction) calculated at displaced points:

$$\Omega(x) = \frac{1}{90}\{7g(x) + 32g(x+c_2P) + 12g(x+c_3P) + 32g(x+c_4P) + 7g(x+c_5P)\} \tag{3.29}$$

Where $x = 2\theta_i - 2\theta_{\mathbf{h}} - S_{shf}$, P is the asymmetry parameter and

$$\cot 2\theta = 16c_2 = 4c_3 = \frac{16}{9}c_4 = c_5$$

The parameters P_1, P_2 normally suffice for neutron diffraction. The starting value of these parameters should be significantly lower than unity (e.g. 0.01) to get good results. If the value of the asymmetry parameter used in the Rietveld's formula (see [2]) is kept fixed in **FullProf** the refinement could be very bad and couldn't converge.

3.6 Preferred orientation

Only two preferred orientation functions are currently implemented in the program:

- NORI=0 → the exponential function:

  $$P_{\mathbf{h}} = G_2 + (1-G_2)\exp(G_1\alpha_{\mathbf{h}}^2) \tag{3.30}$$

  Where G_1 and G_2 are refinable parameters and $\alpha_{\mathbf{h}}$ is the acute angle between the scattering vector and the normal to the crystallites (platey habit). Note that setting G_1 to any number >99.0 for a phase causes the program to generate, for that phase, only those reflections for which $[hkl]^*$ is parallel to the preferred orientation vector PREF specified in Line 11-2.

- NORI=1 → Modified March's function:

  $$P_{\mathbf{h}} = G_2 + (1-G_2)\left((G_1\cos\alpha_{\mathbf{h}})^2 + \frac{\sin^2\alpha_{\mathbf{h}}}{G_1}\right)^{-3/2} \tag{3.31}$$

  Where G_1 and G_2 are refinable parameters. This expression is adapted to both fiber and platey habits:

- $G_1 < 1$: Platey habit (α is the acute angle between the scattering vector and the normal to the crystallites)
- $G_1 = 1$: No preferred orientation
- $G_1 > 1$: Needle-like habit (α is the acute angle between the scattering vector and the fiber axis direction)

Note that these values of G_1 correspond to the Bragg-Brentano geometry of usual X-ray powder diffractometers; for the Debye-Scherrer geometry of most neutron powder diffractometers the opposite holds.

The parameter G_2 represents the fraction of the sample that is not textured. The program put its value between 0 and 1 in case of divergence.

3.7 Absorption and micro-absorption

For Debye-Scherrer data, intensities may be corrected for the effects of sample absorption by applying the following transmission factor:

$$T_{\mathbf{h}} = \exp\{-(1.7133 - 0.0368\sin^2\theta_{\mathbf{h}})\mu R + (0.0927 + 0.375\sin^2\theta_{\mathbf{h}})(\mu R)^2\} \tag{3.32}$$

Where μ is the linear absorption coefficient and R the radius of the cylindrical sample.

For a flat plate in transmission geometry for X-rays (ILOR=2) the absorption correction is implemented as:

$$T_{\mathbf{h}} = \frac{\exp(-mt/\cos\theta_{\mathbf{h}})}{\cos\theta_{\mathbf{h}}} \tag{3.33}$$

Where t is the *effective* thickness of the sample. The product mt is given in the same place as μR.

For Bragg-Brentano geometry in X-rays an angular-dependent microabsorption correction has been introduced following [24] and [25]. The factor $T_{\mathbf{h}}$ becomes:

$$T_{\mathbf{h}} \Rightarrow T_{\mathbf{h}} S_r(\mathbf{h}) = T_{\mathbf{h}} (1 - P(\mathbf{h})) \tag{3.34}$$

Where $S_r(\mathbf{h})$ is given by the formula 6 of [24] (or $P(\mathbf{h})$ is given by formula 17 of [25]).

$$P(\mathbf{h}) = P_0 C_p \frac{\tau}{\sin\theta_{\mathbf{h}}}\left(1 - \frac{\tau}{\sin\theta_{\mathbf{h}}}\right) \tag{3.35}$$

The limitations and degree of applicability of the above formula are explained in the cited references.

3.8 Systematic line-shifts

Powder diffraction data are sometimes affected by systematic aberrations arising either from the sample itself or from an improper setting of the sample or diffractometer. **FullProf** gives the possibility to correct for two of the most commonly occurring errors by refining the parameters called SYCOS and SYSIN

(Line 10-1). These parameters relate to errors having a $\cos\theta$ and $\sin 2\theta$ dependency, respectively. The corresponding errors originate from a different physical or/and geometrical problem depending on the diffraction geometry. They are summarized below:

3.8.1 Bragg-Brentano parafocusing arrangement

The two largest systematic aberrations of $\theta - 2\theta$ powder diffractometers operating in this geometry arise from specimen displacement and transparency; the sample displacement error is one of the largest systematic error affecting line positions in this geometry. It is given by:

$$\Delta 2\theta = \frac{-2s}{R}\cos\theta \qquad \text{[in radians]} \tag{3.36}$$

where s is the displacement of the sample surface with respect to the axis of the goniometer and R the radius of the goniometer circle. The negative sign means that a displacement away from the center of the focusing circle moves the diffraction lines to lower 2θ angle. The refinable parameter is SYCOS $= -2s/R$. This is by far the largest systematic aberration in this geometry. As the angles are expressed in degrees in **FullProf**, the sample offset can be calculated as:

$$s = \frac{\pi}{180} R\,\mathrm{SYCOS}$$

The transparency correction is given by the relation:

$$\Delta 2\theta = \frac{1}{2\mu R}\sin 2\theta \qquad \text{[in radians]} \tag{3.37}$$

where μ is the linear absorption coefficient of the sample. This relation holds in the case of thick absorbing samples and the refinable parameter is SYSIN $= 1/(2\mu R)$. For thin transparent samples, the correction would write:

$$\Delta 2\theta = \frac{t}{R}\cos\theta \qquad \text{[in radians]} \tag{3.38}$$

where t is the sample thickness; this (less usual) correction is not explicitly included in the code but can be accounted for by the displacement correction which turns out to show the same 2θ dependency. Note however that samples requiring that kind of correction would also give biased integrated intensities; correction for this effect is not implemented in **FullProf**. For further details on systematic aberrations in Bragg-Brentano geometry, see [16].

3.8.2 Debye-Scherrer

The largest shifts of Debye-Scherrer rings result from sample off-centering and absorption. Eccentricity perpendicular to the incident beam direction is normally a second order effect if both sides of the Debye-Scherrer ring are measured.

If only one side of the cone is measured, the line shift takes the form:

$$\Delta 2\theta = \frac{e}{R}\cos\theta \qquad \text{[in radians]} \tag{3.39}$$

where e denotes the eccentricity, that is the refined parameter is SYCOS = e/R.

Eccentricity in the incident beam direction is observed in both cases and takes the form:

$$\Delta 2\theta = \frac{e}{R}\sin 2\theta \qquad \text{[in radians]} \tag{3.40}$$

i.e., the refined parameter is SYSIN = e/R. The correction is negative for a shift along the beam direction towards the detector. For highly absorbing specimen with radius r, diffraction is limited to a cylindrical surface layer resulting in a maximum peak shift:

$$\Delta 2\theta = \frac{r}{R}\cos\theta \qquad \text{[in radians]} \tag{3.41}$$

i.e., in this case, SYCOS = r/R. The latter effect also leads to disymmetrical line profiles.

3.8.3 Curved position sensitive detector with flat plate sample

For the asymmetric geometry of diffractometers using a curved position sensitive detector (CPSD) with a flat-plate sample, the displacement correction takes the form:

$$\Delta 2\theta = \frac{-e}{R\sin\alpha}\sin 2\theta \qquad \text{[in radians]} \tag{3.42}$$

where R is the radius of the CPS and α the incident beam angle (in degrees) at sample surface. Thus, the parameter refined by **FullProf** is SYSIN $=-s/(R\sin\alpha)$. The negative sign means, as in the case of Bragg-Brentano geometry, that a displacement away from the center of the focusing circle moves the diffraction lines to lower 2θ angle; the value of the sample offset is given by:

$$s = \frac{\pi}{180}R\sin\alpha\,\text{SYSIN}$$

3.9 Crystal structure factors

The crystallographic structure factor $F_{\mathbf{h}}$ is calculated in **FullProf** by using the formula:

$$F_{\mathbf{h}} = \sum_{j=1}^{n} O_j f_j(\mathbf{h})\exp(-B_j \mid \mathbf{h} \mid /4)\sum_{s=1}^{m} T_{js}(\mathbf{h})\exp\{2\pi i(\mathbf{h}^T S_s \mathbf{r}_j + \mathbf{h}^T \mathbf{t}_s)\} \tag{3.43}$$

where n is the number of atoms in the asymmetric unit, m is a the number of the reduced set of symmetry operators (centering lattice translations and inversion center operators removed). O_j is the occupation factor, $f_j(\mathbf{h})$ is the scattering length (in electron units for X-rays, in 10^{-12} cm for neutrons), B_j is the isotropic temperature parameter given in Å^2, and $\mathbf{r}_j$ is the position vector of atom j. The symmetry operator $\{S_s \mid \mathbf{t}_s\} = \{S \mid \mathbf{t}\}_s$ is applied to the scattering vector $\mathbf{h}$ (treated here as a column matrix) instead of the position vector. $\mathbf{h}^T$ is a row matrix with elements (hkl). The temperature factor $T_{js}(\mathbf{h})$ is given by:

$$T_{js}(\mathbf{h}) = \exp\{-\mathbf{h}^T S_s \boldsymbol{\beta}_j S_s^T \mathbf{h}\} \tag{3.44}$$

where $\boldsymbol{\beta}_j$ is the symmetrical matrix representing the anisotropic temperature parameters of the atom j. For the first atom position ($S_{s=1} = I$) the expression of the anisotropic temperature factor is the well-known expression:

$$T(hkl) = \exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\} \tag{3.45}$$

where the subscript j has been droped for simplicity. Of course, if the isotropic temperature factor $T_j(iso) = \exp(-B_j \sin^2\theta/\lambda^2)$ is used the parameters $\beta_{\alpha\beta j}$ should be set to zero. The β's have no direct physical meaning. They have to be converted to a cartesian **U**-matrix that provides, after diagonalization, the r.m.s (root mean squares) atom displacements (see [17]). **FullProf** does this work at the end of the refinement, the results are given in the file CODFIL.out.

Apart from the standard scattering factor for indivual atoms existing in an internal library of **FullProf**. The version 3.2 and higher can handle complex form-factors as a standard option. In the general expression of the nuclear structure factor (see 3.43) the form factor $f_j(\mathbf{h})$ is normally dependent on the module of $\mathbf{h}$. For molecular plastic crystals the treatment of rotating molecules cannot be done using an atomic description. The approach of a molecular form-factor that takes into account the particular dynamics of the object is more reliable. $f_j(\mathbf{h})$ depends on a series of parameters for different types of objects. Coefficients of Symmetry Adapted Spherical Harmonics, geometrical parameters (radius of a sphere, length and radius of a cylinder or disk, etc), scattering density, for instance, could serve for describing the scattering factor of a complex object. In the **FullProf** version 3.2 or higher the available (or projected) objects are the following: spherical shell (SPHS), dense sphere (SPHE), elipsoid (ELLI), cylinder/disk of eliptical section (DISK), etc.

For the calculation of the integrated intensities (3.2) two types of factors are applied to $F_{\mathbf{h}}^2$. One is an overall temperature factor ($\exp\{-B_{ov} \mid \mathbf{h} \mid /2\}$) and the other is the constant: $NLAT = (LAT \cdot ICEN)^2$, where LAT is the number of centering translations (1 for P, 2 for A,B,C and I, 3 for R and 4 for F) and $ICEN$=2 for centrosymmetric and $ICEN$=1 for non-centrosymmetric space groups.

3.10 Magnetic scattering calculations

For a magnetic phase $F_{\mathbf{h}}^2$ is calculated using the general formula of Halpern and Johnson:

$$F_{\mathbf{h}}^2 = \mid \mathbf{F}_{\perp}(\mathbf{h}) \mid^2 = \mid \mathbf{F}_m(\mathbf{h}) \mid^2 - (\mathbf{e} \cdot \mathbf{F}_m(\mathbf{h}))^2 \tag{3.46}$$

where $\mathbf{F}_m(\mathbf{h})$ is the magnetic structure factor, and $\mathbf{e}$ is the unit vector along the scattering vector $\mathbf{h}$. Here the scattering vector is written as $\mathbf{h}$=$\mathbf{H}$+$\mathbf{k}$ where

$\mathbf{H}$ is a reciprocal lattice vector of the crystal structure and $\mathbf{k}$ the propagation vector corresponding to the current magnetic reflection. The magnetic structures that can be refined with **FullProf** must have a distribution of magnetic moments that can be expanded as a Fourier series:

$$\boldsymbol{\mu}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}\,j} \exp\{-2\pi i \mathbf{k}\,\mathbf{R}_{\,l}\} \tag{3.47}$$

In such a case the magnetic structure factor is given by:

$$\mathbf{F}_{\,m}(\mathbf{H}+\mathbf{k}) = p \sum_{j=1}^{n_c} f_j(\mathbf{H}+\mathbf{k})\mathbf{S}_{\mathbf{k}\,j} \exp\{2\pi i(\mathbf{H}+\mathbf{k})\mathbf{r}_{\,j}\} \tag{3.48}$$

The sum is over *all the atoms* in the crystallographic cell. The constant $p(= r_e\gamma/2)$ is 0.2695 and allows the conversion of the Fourier components of magnetic moments, given in Bohr magnetons (μ_B) to scattering lengths units of 10^{-12}cm. $f_j(\mathbf{H}+\mathbf{k})$ is the magnetic form factor and $\mathbf{r}_{\,j}$ is the vector position of atom j. In the above expression the atoms have been considered at rest. If thermal motion is considered and if symmetry relations are established for coupling the different Fourier components $\mathbf{S}_{\mathbf{k}\,j}$, we obtain the general expression of the magnetic structure factor used in **FullProf** for the reflection with scattering vector $\mathbf{h}= \mathbf{H}+\mathbf{k}$:

$$\mathbf{F}_{\,m}(\mathbf{h}) = p \sum_{j=1}^{n} O_j f_j(\mathbf{h}) T_j(iso) \sum_s M_{js} \mathbf{S}_{\mathbf{k}\,j} T_{js} \exp\{2\pi i[\mathbf{h}\{S \mid \mathbf{t}\}_s \mathbf{r}_{\,j} - \psi_{\mathbf{k}\,js}]\} \tag{3.49}$$

The sum over j concerns the atoms of the magnetic asymmetric unit for the wavevector $\mathbf{k}$ (the Fourier component with index $\mathbf{k}$ contributes only to the $\mathbf{k}$-satellite). The sum over s concerns the different symmetry operators of the crystal space group that belong to the wave vector group. The matrix M_{js} transform the components of the Fourier term $\mathbf{S}_{\mathbf{k}\,j}$ of the starting atom $j1$ to that numbered as js in the orbit of j. The anisotropic temperature factor, T_{js}, is simplified in the calculation to only diagonal terms ($\beta_{\alpha\alpha}$), but it is not generally necessary to use these terms in magnetic refinements. The phase factor $\psi_{\mathbf{k}\,js}$ has two components:

$$\psi_{\mathbf{k}\,js} = \Phi_{\mathbf{k}\,j} + \phi_{\mathbf{k}\,js} \tag{3.50}$$

$\Phi_{\mathbf{k}\,j}$ is a phase factor which is not determined by symmetry. It is a refinable parameter and it is significant only for an independent set of magnetic atoms which respect to another one. $\phi_{\mathbf{k}\,js}$ is a phase factor determined by symmetry. The Fourier component $\mathbf{k}$ of the magnetic moment of atom $j1$, $\mathbf{S}_{\mathbf{k}\,j}$, is transformed to

$$\mathbf{S}_{\mathbf{k}\,js} = M_{js}\mathbf{S}_{\mathbf{k}\,j} \exp\{-2\pi i \phi_{\mathbf{k}\,js}\} \tag{3.51}$$

The sign of $\phi_{\mathbf{k}\,js}$ changes for -$\mathbf{k}$. The reflection $\mathbf{H}+\mathbf{k}$ has the *negative* sign indicated in the above formulae and the reflection $\mathbf{H}-\mathbf{k}$ has the positive sign.

In the general case $\mathbf{S}_{\mathbf{k}\,j}$ is a complex vector (in general there are six components. In old versions of **FullProf** one could simulate this complex vector by splitting the atom contributing to propagation vector **k** in two parts by putting a magnetic phase $\Phi_{\mathbf{k}\,j}$ of $\pi/2$ with respect to the real part of $\mathbf{S}_{\mathbf{k}\,j}$. The magnetic phases are given in fractions of 2π, then for the above purpose one can use a fixed Phase=0.25. In the new version this splitting is not needed. The imaginary components are read in the place which was reserved for anisotropic temperature factors (see Lines 11-4-3). For the scattering vector $\mathbf{H}-\mathbf{k}$ the Fourier component is the complex conjugate of the Fourier component used for calculating the structure factor for $\mathbf{H}+\mathbf{k}$. The program takes into account automatically this fact. If **k** is at the interior of the Brillouin Zone a factor 1/2 is applied to the Fourier coefficient.

Let us consider a single index j for all the magnetic atoms in the unit cell as in 3.49. The Fourier coefficient for the sublattice j is explicitely given by:

$$\mathbf{S}_{\mathbf{k}\,j} = \frac{1}{2}\{R_{xj}\mathbf{e}_1 + R_{yj}\mathbf{e}_2 + R_{zj}\mathbf{e}_3 + i[I_{xj}\mathbf{e}_1 + I_{yj}\mathbf{e}_2 + I_{zj}\mathbf{e}_3]\}\exp\{-2\pi i\phi_{\mathbf{k}\,j}\} \tag{3.52}$$

The vector -**k** must also be given either explicitly or implicitly by giving NVK<0 (see NVK on Line 11-2). If NVK<0 the program applies the factor 1/2 because it is supposed that **k** is non equivalent to -**k** even if **k** belong to the surface of the Brillouin zone. If the option JHELIX=1 is used, the number of free parameters per magnetic atom is reduced. The Fourier coefficients are considered of the form:

$$\mathbf{S}_{\mathbf{k}\,j} = \frac{1}{2}[m_{1j}\mathbf{u}_j + i m_{2j}\mathbf{v}_j]\exp\{-2\pi i\phi_{\mathbf{k}\,j}\} \tag{3.53}$$

where $\mathbf{u}_j$ and $\mathbf{v}_j$ are orthogonal unit vectors. If $m_{1j} = m_{2j}$ the magnetic structure for the sublattice j corresponds to a classical helix (or spiral) of cylindrical envelope. All j atoms have a magnetic moment equal to m_0. If $m_{1j} \neq m_{2j}$ the helix has an elliptical envelope and the moments have values between $min(m_{1j}, m_{2j})$ and $max(m_{1j}, m_{2j})$. If $m_{2j} = 0$ the magnetic structure corresponds to a modulated sinusoid of amplitude $A = m_{1j}$.

In general, the user has to calculate the real magnetic moments from the refined values of the Fourier components: the phrase "Magnetic Moment" in the output file means the modulus of the corresponding Fourier component. The program MOMENT has been written in order to help the user with these calculations. In any case the calculation of the magnetic moment of the atom j in the unit cell of index l should be done by using the formula:

$$\boldsymbol{\mu}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}\,j}\exp\{-2\pi i\mathbf{k}\,\mathbf{R}_l\}$$

$$\boldsymbol{\mu}_{lj} = \sum_{[\mathbf{k}]}\{\mathbf{R}_{\mathbf{k}\,j}\cos 2\pi[\mathbf{k}\,\mathbf{R}_l + \psi_{\mathbf{k}\,j}] + \mathbf{I}_{\mathbf{k}\,j}\sin 2\pi[\mathbf{k}\,\mathbf{R}_l + \psi_{\mathbf{k}\,j}]\}$$

where the last sum is extended for half the number of propagation vectors, i.e. over the number of pairs (**k**,-**k**).

If the propagation vector $\mathbf{k}$ is commensurate (rational components) one can use the magnetic unit cell and $\mathbf{S}_{\mathbf{k}\,j}$ can be identified with the magnetic moment at site j. In this case one can describe the magnetic structure with $\Psi_{\mathbf{k}\,j} = 0$ and $\mathbf{Q}$=$\mathbf{H}$, being $\mathbf{H}$ an integer vector of the reciprocal lattice of the magnetic cell. If $\mathbf{k}=\frac{1}{2}\mathbf{H}$, one can use the chemical unit cell and real magnetic moments. In such a case only one propagation vector is needed: if NVK is given as negative the generation of magnetic reflections could be in error. For centered crystallographic unit cells one can use only the content of a primitive cell and generate the satellites from the symbol of the centering followed by -1 (e.g. I -1 for a I-centered cell). In order to take the advantage of the crystallographic conventions (propagation vector given with respect to the reciprocal basis of the conventional cell) one can use the dimensions and the metrics of the convencional cell provided that, putting the content of a primitive cell in the conventional cell frame, the ocupation factors are multiplied by the number of centering vectors. See the files hob*.pcr in the example directory of the anonymous FTP-area.

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