

WinPLOTTR: a Windows tool for powder diffraction patterns analysis

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Abstract

WinPLOTTR is a graphic program for the analysis of powder diffraction patterns. It has been developed for a Windows 9x/2k/NT environment. It takes advantage of this graphical environment to offer a powerful and user-friendly powder diffraction tool. The program is able to display and analyse many different kinds of diffraction patterns as well as calculated and observed profiles coming from the Windows/DOS version of the program FullProf. It can also be used as a Graphic User Interface (GUI) for programs defined by the user.

Introduction

Recent advances in powder diffraction techniques such as synchrotron radiation, neutrons or X rays real time diffraction or thermodiffractometry experiments lead the diffractionist to handle many different kinds of diffraction pattern files. For example, high resolution synchrotron experiments produce currently huge data files with several thousands of points per diffraction patterns. On the other hand, X-rays or neutron data recorded with Position-Sensitive-Detectors as a function of a variable physical parameter (temperature, pressure, ...) are leading to analyse simultaneously many different patterns with a relatively small number of points per diagrams.

Graphical display on a computer screen of raw powder diffraction patterns is of great interest to have a rapid and realistic idea of the quality of the experiment: structural or magnetic phase transitions, sample crystallinity, parasitic peaks coming from the sample environment or detectors problems are then rapidly detected. Furthermore, the visualisation of the agreement between experimental data and those calculated from a physical model implemented in a particular software (for instance a Rietveld-type program) is of primary necessity to validate the interpretation of the experiment on the sample under study. The visual analysis of the graphic display provides more confidence on the fitness of a model than dubious reliability factors.

The program WinPLOTTR has recently been developed with these aims and allows the user to adapt the computer memory capacity to his(her) own needs. Furthermore, WinPLOTTR has been designed as a GUI for several crystallographic programs. In particular, it can be considered as a software partner of the refinement program FullProf [1], the automatic indexing programs Dicvol [2] or Treor [3], as well as for software provided by user.

Program specifications

Hardware requirement and software environment

WinPLOTTR has been written in Fortran 90, using the new syntax and features of this language (no COMMON statements, extensive use of modules, allocatable arrays ...). It has been developed for the Windows 9x/2k/NT operating system and it takes advantage of this graphical environment to provide a friendly tool to the user (windows, menus, dialog boxes, mouse handling ...). The program uses the RealWin Fortran library to access to the Windows API (Application Program Interface). WinPLOTTR has been adjusted for a colour screen display with a resolution of 1024 × 768 pixels.

WinPLOTTR package, availability and installation

The WinPLOTTR kit consists of a compacted ('winplotr.zip') file containing all the files needed to run and install automatically the program WinPLOTTR and the Windows versions of the Rietveld-type program FullProf (single and multiple patterns versions), Dicvol91 (WINDIC) [2] Treor90 (WTREOR90) [3]– automatic indexing of powder diffraction patterns– and others tools as for example a neutron periodic table (MENDEL) or SUPERCELL (search of a super cell or incommensurate components of a propagation wave vector) [4].

The WinPLOTTR kit is available free of charge for scientific non-profit institutions. It can be downloaded from the Web page: [http://www-llb.ccea.fr/fullweb/winplotr/winplotr.htm](http://www-llb cea.fr/fullweb/winplotr/winplotr.htm). The installation of the programs is performed by a automatic procedure that copy all the files in appropriate directories and creates environment variables for WinPLOTTR and FullProf.

WinPLOTTR setting file

WinPLOTTR uses a *settings* file (winplotr.set) in order to adapt the capabilities of the program to the different needs and wishes of the user. The dimensions of arrays (Max_Patterns: maximum number of diffraction patterns to be plot simultaneously, Max_Points: maximum number of points per file) can be defined. Different configurations can then be adopted, depending on the data files type to be displayed.

The programs that the user wish to be launched through the WinPLOTTR interface can be declared in the *settings* file. A part from the programs distributed inside the WinPLOTTR package (FullProf, Dicvol, Treor) the user may include his(her) favourite DOS or Windows editor or programs that are frequently used.

Many others parameters can be specified in this file: calculations parameters (thresholds for automatic peaks or background points search), diffractometer resolution (U, V, W Caglioti parameters [5]) as well as graphical options (default colours, markers, styles ..., use of grids, dimensions and position of the main WinPLOTTR window on the screen ...).

Data files format

The format of a powder diffraction data-file is strongly dependent on the diffractometer type that has been used for the experiment, and the institution providing the data. This leads the diffractionist to meet a great number of different types of data files. WinPLOTTR is compatible with a great number of different raw or normalised data-file formats (ASCII files), coming from different types of diffractometers (multiple counters, PSD or single moving detector) from neutron diffraction centres (LLB, ILL, ISIS...) and synchrotron radiation institutes (ESRF, LURE, ...) as well as commercial X-rays diffractometers. Neutron, conventional Xrays, synchrotron data recorded in constant wavelength, time of flight or energy-dispersive mode can also be loaded.

WinPLOTTR has also been developed to display and analyse Rietveld plots (Y_{obs} , Y_{calc} , $Y_{obs}-Y_{calc}$, reflections positions), created by the refinement program FullProf.

Some examples of WinPLOTTR capabilities:

1- Plot in a pseudo-3D mode

The first step to make a pseudo 3D plot is to create, with the help of a text editor (this can be done though the 'External applications / edit a *.* file' menu option), a buffer file containing all the data files of a single diffraction experiment (real time or temperature -or other external physical parameter-dependent experiment) with a common data file format, that will be loaded together in a further step. Shifting X and Y values leads to the simulation of a pseudo 3D plot versus the variable external parameter. Graphical options, such as the management of the hidden parts or a single colour and single marker type for all the data files may be set straightforwardly. This kind of plot helps to show clearly physical phenomena appearing during the diffraction experiment. As an illustration, the figure 1

represents neutron diffraction patterns recorded versus the temperature (in the 1.5 – 30 K temperature range) with a PSD diffractometer, showing the appearance of two magnetic phase transitions in the antiferromagnetic Tb₂Pd₂Sn compound [6].

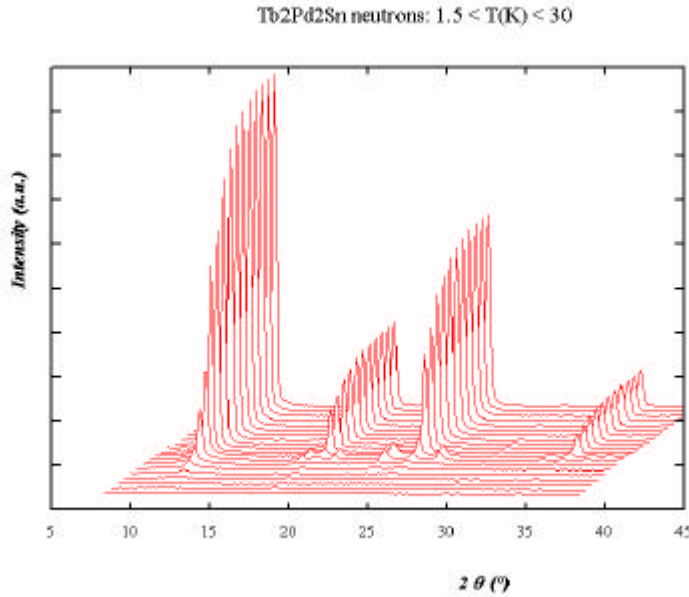


Fig. 1: Pseudo 3D plot of neutron diffraction patterns recorded versus temperature of the antiferromagnetic Tb₂Pd₂Sn compound

The current plot, with all the different graphic options, can be saved in a template file that may be loaded later.

2- Calculations facilities

Several calculations capabilities are available in the 'Calculations' menu: background subtraction, data files difference, centroid determination, integration... The result of these operations is automatically displayed as a superimposed file and data can be saved as an ASCII file.

An interactive profile fitting procedure using the no-linear least-squares Marquard algorithm has been implemented. This process uses independent pseudo-Voigt functions with a global FWHM (full width at half maximum) and a global η (Lorentzian component), and a linear background. Each peak is characterised by its position, intensity and the shifts of FWHM and η with respect to the global parents. The function that is minimised is the chi-square χ^2 :

$$\chi^2 = \frac{\sum_i w_i * |Y_{obs}^i - Y_{calc}^i|^2}{N - P}$$

where:

\sum_i : summation over the N points of the fitted region.

w_i : weighting factor ($w_i = \frac{1}{S(Y_{obs}^i)}$)

Y_{obs}^i : observed counts

Y_{calc}^i : calculated counts

P : number of refined parameters.

The profile fitting procedure can be performed in three different ways, depending of the status of the program:

- 1- Manual mode: reflection parameters are selected manually with the mouse, later on they may be modified and specified as refined or fixed parameter in a special dialog box before starting the profile fitting procedure.
- 2- Automatic mode: position, intensity parameters and background contributions are determined by an automatic search procedure implemented in the program. After entering instrumental resolution parameters, a first fitting run is performed, refining only the background points and the reflections integrated intensities.
- 3- Reading an input parameter file (created automatically by the previous two steps). The input file contains all the parameters and the conditions of the refinement: selected angular range, maximum number of cycles, data-file format, job type (single or doublets peaks $-\text{K}\alpha_1$, $\text{K}\alpha_2$) and all the free parameters as background points, resolution parameters, lorentzian fraction (constant and linearly 2θ -dependent terms), and reflections dependent parameters, as positions, integrated intensities, shift-FWHM and shift- η . Each parameter is accompanied by the corresponding flag (0 or 1 value), signifying that the parameter will be refined or not in the profile fitting procedure.

In all previous cases, graphical results (Y_{obs} , Y_{calc} , $Y_{\text{obs}} - Y_{\text{calc}}$, reflections positions) are automatically displayed in the main graphical window, since χ^2 evolution versus the cycle number and refined parameters values and sigma appear in text result windows (fig. 2).

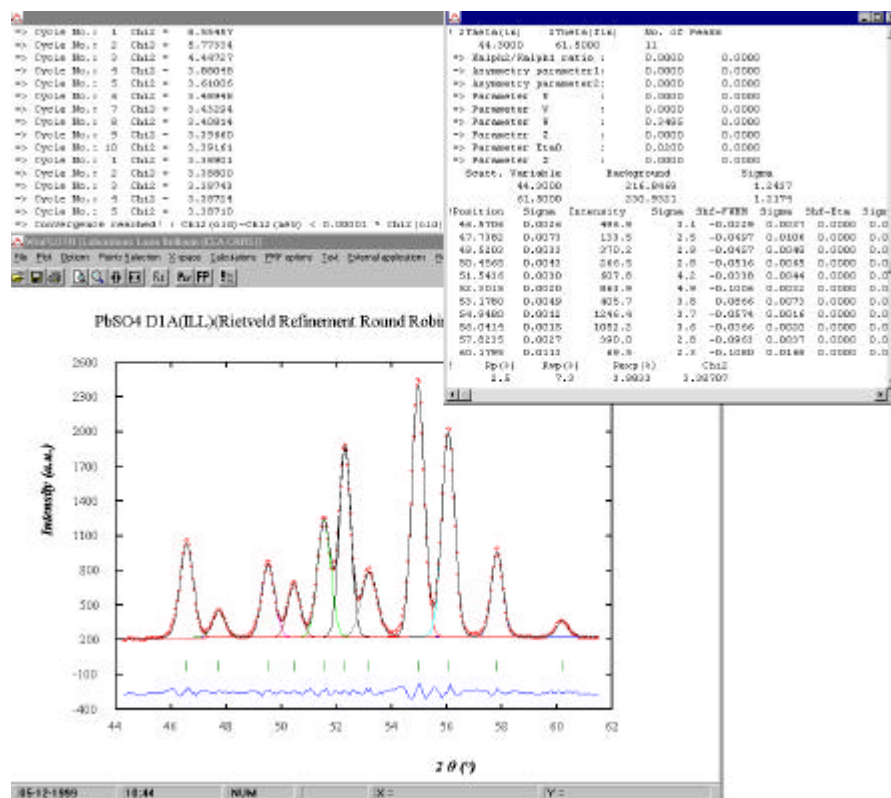


Fig. 2: Aspect on the screen after an interactive profile fitting session. The data correspond to a portion of the neutron diffraction pattern of a PbSO_4 powdered sample recorded on D1A (ILL).

3- WinPLOTR: a GUI for external programs

The following example, synchrotron powder diffraction pattern ($\lambda = 1.52904 \text{ \AA}$) of cimetidine ($\text{S}_1\text{C}_{10}\text{N}_6\text{H}_{16}$), illustrates the capabilities of WinPLOTR as a GUI, by using several crystallographic programs (all of them declared in the WinPLOTR *settings* file), in five different steps:

- 1- Peak position determination:

After zooming the diffraction pattern in the $0 - 20^\circ 2\theta$ range, peak positions can be obtained by manual mode (by clicking with the mouse), or by the automatic mode using a WinPLOTR

internal subroutine. The reflection positions are saved in input files for auto-indexing programs, such as WinDICVOL or WTREOR90.

2- Unit cell determination

Dialog box (fig. 4a) helps the user to enter parameters needed for the previous input files: tested symmetries, spacing data type, wavelength, maximum unit cell parameters ... One of the two programs, WinDICVOL or WTREOR90, is then launched through the WinPLOTTR interface. After successful indexing of the reflections positions (fig. 4b), an input file for FullProf is then created automatically in a full profile matching mode (i.e. without structural model), starting from unit cell parameters and symmetry coming from the auto-indexing program. The instrumental parameters are entered by the user through dialog boxes.

3- Integrated intensities extraction:

Several runs of FullProf (editing sessions of PCR files, launching the program and display of the resulting plots) performed in a suitable space group (obtained from an analysis of the systematic absences) using the whole profile fitting mode are needed to extract the integrated intensities from the diffraction pattern (fig. 4b).

4- Structure determination:

The previous integrated intensity set may be used directly by the program EXPO [7] to solve the crystal structure by direct methods (fig. 4c)

5- Structure refinement

Finally, a Rietveld refinement of the cimetidine pattern is performed with FullProf. The starting configuration is given by the atomic positions determined in the previous step. Fig. 4d presents the final Rietveld plot after the refinement of all the atomic positions (except those of the hydrogen atoms), i.e. superimposition of experimental and calculated data, difference curve and Bragg reflections positions represented as vertical ticks.

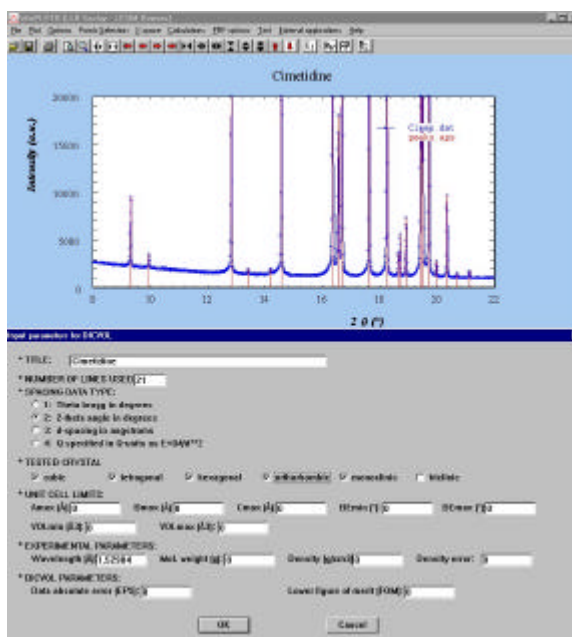


Fig. 4a: Save peaks positions as WinDICVOL input parameters file

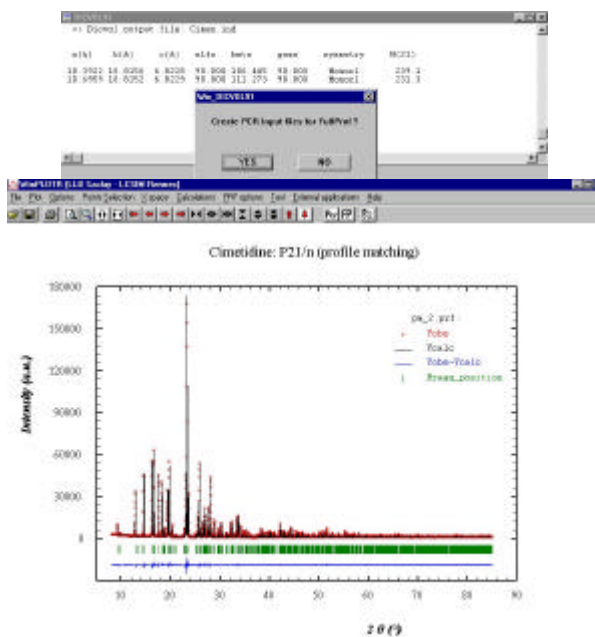


Fig. 4b: WinDICVOL results and extraction of integrated intensities with FullProf in a profile matching mode refinement

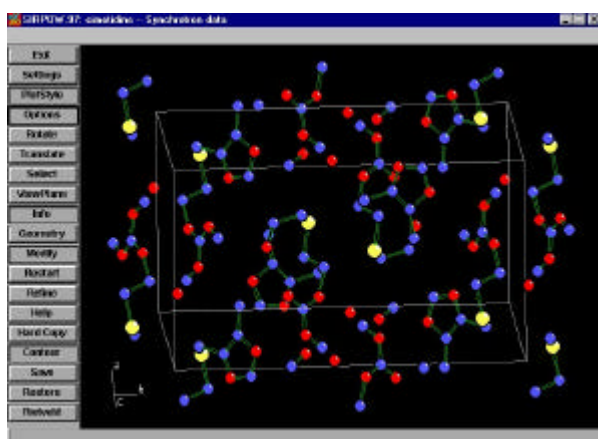


Fig. 4c: Structure determination with EXPO

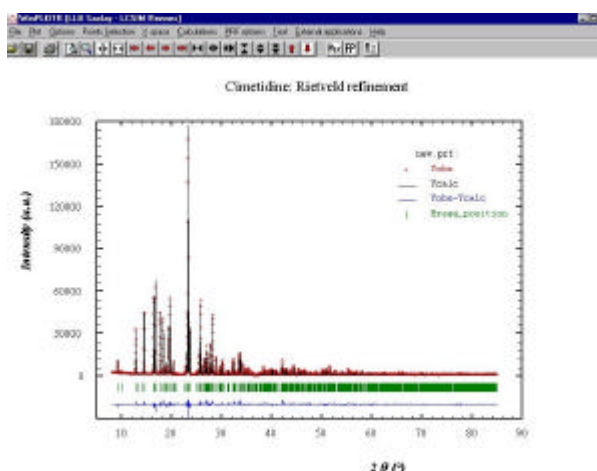


Fig. 4b: Rietveld plot after FullProf refinement

Aknowlegments

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