

PROFIT Computer Program for Processing Powder Diffraction Data on an IBM PC with a Graphic User Interface

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Abstract—The PROFIT computer program for processing powder diffraction data on an IBM PC compatible computers is described. The program allows the resolution of multiplets consisting of up to 20 overlapping reflections, each of them possibly being a doublet. The diffraction pattern (or any part of it) containing up to 10000 experimental points can be analyzed. The line profiles are approximated by the asymmetric Pearson or pseudo-Voigt functions, as well as by an asymmetric pseudo-Voigt function with independent parameters of the Gauss and Lorentz components (the latter allows one to study samples with nonunimodal distributions of crystallite dimensions). The program provides possibilities for imposing various constraints on the parameters of individual reflections and separating the peaks into several groups, which is important for analyzing the diffraction patterns from multicomponent systems. The newly developed user interface is completely graphic and allows processing of all the data on one screen.

Powder diffractometry is widely used in experimental materials science for the determination of phase composition, micro- and macroscopic stresses, dimensions crystallites, materials texture, crystal systems and lattice parameters, and for the refinement (and, in some cases, for the *ab initio* determination) of crystal structures. In almost all of the above applications, the parameters of reflections comprising the powder pattern (the peak positions, their intensities, half-widths, asymmetry, etc.) are to be determined.

Even in the case of a powder pattern consisting of individual reflections, the determination of the peak parameters requires computer processing of the experimental data. The problem becomes considerably more complicated if the reflections overlap. Since the latter is a very common situation, the problem of resolving complex multiplets into separate components is very important. A large number of computer programs developed for solving such problems can be found in the literature [1–10]. The approach used most often is to approximate a multiplet by a sum of individual peaks with analytically expressed line profiles and to determine the unknown peak parameters by minimizing the difference between the calculated and experimental diffraction patterns. This approach is used in all existing programs, which differ in the type of the profile-shape functions employed for approximating the line shapes of individual reflections, in the methods of optimization, and in the user interface.

The variety of profile-shape functions includes the simplest Gauss and Lorentz functions [2–4], as well as the pseudo-Voigt [2–4, 6–8] and Pearson VII [6, 7] functions. The functions are usually adjusted for the asymmetry of the profiles. In some programs, this is accomplished by using the so-called split pseudo-Voigt

[1] and Pearson VII [1, 9, 10] functions, which allow for the use of different broadening parameters for the low- and high-angle sides of the line profile. In another approach proposed by Kogan [5], the line profile is modelled by taking into account the real geometry of the instrument, the spectral characteristics of the radiation source, the anisotropic crystallite-size and strain effects, and the porosity of the specimen.

The most frequently used optimization algorithms are the Gauss–Newton [3, 4, 7–10] and Marquardt [2, 6] techniques. The latter is intermediate between the Gauss–Newton and the gradient-search algorithms and provides a better convergence by minimizing the difference between the measured and calculated patterns. Worthy of mention are also the SIMPLEX optimization algorithm [1, 6] and the method of maximum likelihood [4].

The user interfaces employed in various programs are also quite different. In most cases, dialog [7] or interactive [2–4, 8] menus are used. In almost all programs, the data are represented in a graphic form, and there is the possibility to zoom in on a portion of the diffraction pattern to be processed (the latter possibility is important because, in most cases, the processing of the pattern as a whole is impossible). The most convenient for the user is a completely graphic interface. Its development has become possible due to the recent progress in personal computers and software. Such an interface was realized by Burattini *et al.* [6] for an Apple Macintosh computer and recently realized by Krumm [9] for an IBM PC compatible computer operating in the Windows environment (the latter program is currently under debugging).

The best quality of the above-mentioned software components is achieved in the commercial programs produced by the leading companies operating on the diffractometer market. These programs, however, are not readily available to Russian users.

The possible disadvantages of such programs are not only of a technical origin. In some cases, the programs provide a bad convergence of the optimization algorithm (its divergence or convergence to a false solution), which is usually caused by the impossibility of a correct setting of the initial approximation. The latter disadvantage depends to some extent on the quality of the interface.

Taking into account that most laboratories in Russia are equipped with DRON diffractometers and possess no suitable software packages, we developed the PROFIT program for IBM PC compatible computers. The program is intended for the resolution of multiplets containing up to 20 overlapping reflections, which can be either doublets or single lines. A distinctive feature that is unusual for crystallographic programs is a completely graphic user interface that allows the processing of diffraction patterns containing up to 10000 experimental points within one screen.

The algorithm employed in the program for determining the parameters of the reflections constituting a multiplet is as follows. The functional to be minimized is the sum of squared differences between the measured y_{io} and calculated y_{ic} diffraction patterns

$$R = \sum_{i=1}^N w_i (y_{io} - y_{ic})^2, \quad (1)$$

where w_i is the statistical weight of the i th measurement and the sum is taken over the angles $2\theta_i$ ($i = 1, \dots, N$).

The intensity y_{ic} is calculated as

$$y_{ic} = y_{ib} + \sum_{k=1}^n I_k G_{ik}, \quad (2)$$

where y_{ib} is the calculated background value, I_k is the integrated intensity of the k th reflection, and G_{ik} is the normalized line profile for the k th reflection.

The latter can be represented as the product of two functions

$$G = F A_S, \quad (3)$$

where F is the profile-shape function itself and A_S accounts for the asymmetry of the reflection.

Three different normalized functions are used in the program as profile-shape functions:

(1) the Pearson VII function

$$F_{ik} = \frac{\Gamma(m)}{\Gamma(m-1/2)} \frac{2\sqrt{C_1}}{\sqrt{\pi}H_k} \left[1 + 4C_1 \frac{(2\theta_i - 2\theta_k)^2}{H_k^2} \right]^{-m}, \quad (4)$$

where $C_1 = 2^{1/m} - 1$, Γ denotes the gamma function, and H_k is the full width at half-maximum;

(2) the pseudo-Voigt function that is a weighted sum of the Gauss and Lorentz components having the same half widths H_k :

$$F_{ik} = \eta \frac{2}{\pi H_k} \left[1 + \frac{4(2\theta_i - 2\theta_k)^2}{H_k^2} \right]^{-1} + (1 - \eta) \frac{2\sqrt{\ln 2}}{\sqrt{\pi}H_k} \exp \left[-\frac{4 \ln 2 (2\theta_i - 2\theta_k)^2}{H_k^2} \right]; \quad (5)$$

and

(3) the pseudo-Voigt function with various half-widths of the Gauss H_{kG} and Lorentz H_{kL} components:

$$F_{ik} = \eta \frac{2}{\pi H_{kL}} \left[1 + \frac{4(2\theta_i - 2\theta_k)^2}{H_{kL}^2} \right]^{-1} + (1 - \eta) \frac{2\sqrt{\ln 2}}{\sqrt{\pi}H_{kG}} \exp \left[-\frac{4 \ln 2 (2\theta_i - 2\theta_k)^2}{H_{kG}^2} \right]. \quad (6)$$

Here, $2\theta_k$ is the Bragg angle of the k th reflection and η is the mixing parameter ($0 \leq \eta \leq 1$) showing the contribution of the Lorentz component to the total line profile:

$$A_S = 1 + A_S \operatorname{sgn}(2\theta_i - 2\theta_k), \quad (7)$$

where A_S is the asymmetry parameter. The advantage of using the asymmetry correction in this form is that it approximates well the asymmetry of peaks that are not strongly distorted and does not violate the normalization of the profile-shape functions. In addition, the parameter A_S is stable to the optimization procedure.

The background is assumed to be either linear or quadratic, or it can be treated as a separate peak with a large half-width in the case of diffraction patterns containing a diffuse halo.

The minimization of functional (1) is reduced to finding a convergent sequence of corrections Δx to the vector of parameters x taken as the initial approximation. The set of linear equations for corrections Δx can be obtained by setting the derivatives of functional (1) equal to zero with respect to the refined parameters at the point of the minimum x_0 :

$$\frac{\partial R}{\partial x_k} = \sum_{i=1}^N w_i \left\{ y_{io} - y_{ic}(x_0) - \sum_{j=1}^n \frac{\partial y_{ic}(x_0)}{\partial x_j} \Delta x_j \right\} \frac{\partial y_{ic}(x_0)}{\partial x_k}, \quad (8)$$

where n is the total number of parameters. Note that expression (8) was obtained by expanding y_{ic} in a Tay-

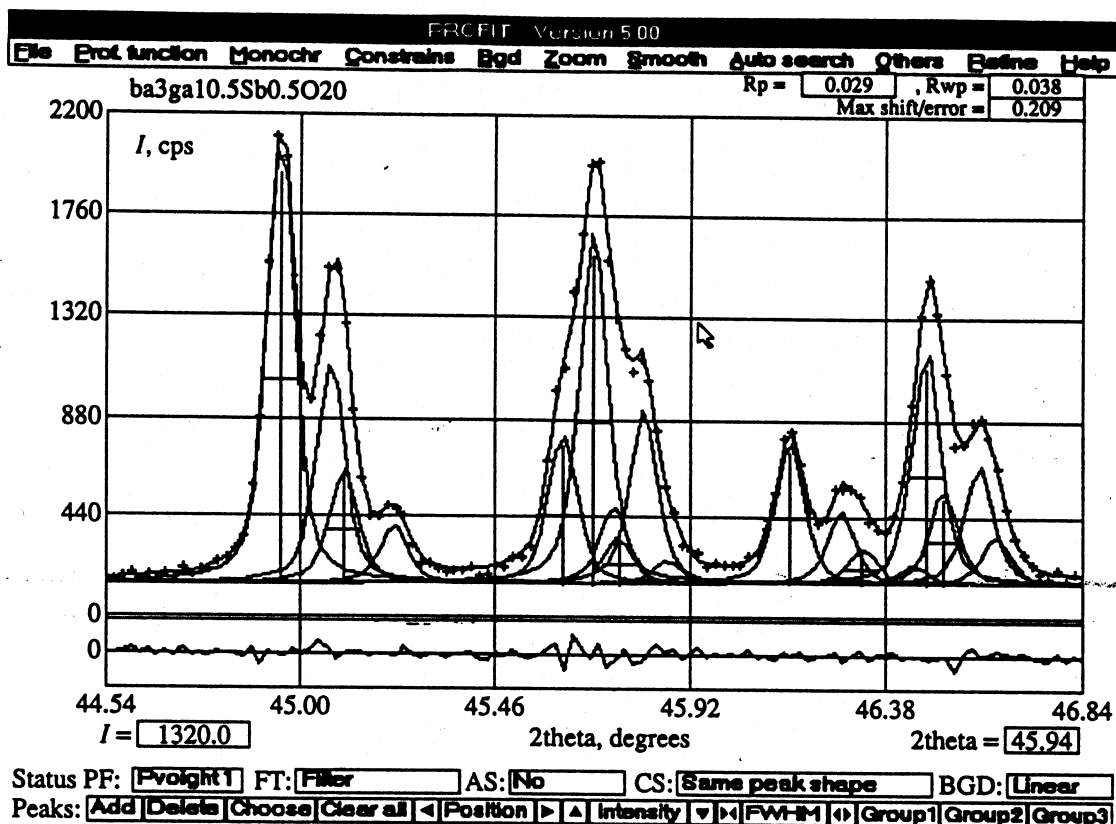


Fig. 1. Temporary display of the PROFIT program.

for series near the minimum and neglecting the higher order terms.

In the matrix representation, equations (8) can be rewritten as

$$M\Delta x = N, \quad (9)$$

where

$$M_{jk} = \sum_{i=1}^N w_i \frac{\partial y_{ic}(x_0)}{\partial x_j} \frac{\partial y_{ic}(x_0)}{\partial x_k}, \quad (10)$$

$$N_j = \sum_{i=1}^N w_i \{y_{io} - y_{ic}(x_0)\} \frac{\partial y_{ic}(x_0)}{\partial x_j}. \quad (11)$$

For a better convergence of functional (1) to the minimum, equation (9) is modified according to Marquardt [11] as

$$(M + \lambda \text{diag}(M))\Delta x = N. \quad (12)$$

This yields a solution to equation (9) at $\lambda \rightarrow 0$.

To speed up the solution of the set of linear equations (12), the Kholeskii expansion for a symmetric positively defined matrix M is used.

The quantitative criteria used to assess the fit of the approximation are the traditional profile R_p and the

weighted profile R_{wp} reliability factors [12]:

$$R_p = \sum_{i=1}^N |y_{io} - y_{ic}| / \sum_{i=1}^N y_{io}, \quad (13)$$

$$R_{wp} = \left[\sum_{i=1}^N w_i (y_{io} - y_{ic})^2 / \sum_{i=1}^N w_i y_{io}^2 \right]^{1/2}. \quad (14)$$

The above algorithm allows the resolution of rather complex multiplets with a significant overlapping of individual reflections (Fig. 1).

Let us consider the general requirements set on the program and on the final result of its work. In the ideal case, the user has only to load a data file and the program will yield the sought-for information on the parameters of all reflections constituting the diffraction pattern. However, in many cases, it is necessary to interrupt the optimization process to introduce some corrections and to see the results of such interventions. Thus, while running the program, the user should be able to control the analytical representation of the background and the diffraction peaks and to correct the initial approximation, i.e., to set the number of components in the multiplet and the initial values of the parameters for each component.

To increase the probability of obtaining a physically reasonable solution, it is often necessary to impose additional constraints on the parameter values. For example, if a weak reflection (with a low signal-to-noise ratio) is overlapped with a strong one and the line shape of the latter is well defined, it is quite natural to assume that the line profiles of both reflections are similar. This assumption will provide more reliable information on the position and intensity of the weak reflection. Therefore, the program should have wide possibilities for imposing various constraints on the parameters of individual peaks.

Based on the above considerations, we developed a completely graphic interface that allows rapid and flexible control over the execution of the program with the help of a standard mouse. The menu operations accessible to the user satisfy the above requirements and provide the possibility of imposing any needed constraints on the parameters of the reflections.

The possibilities furnished by the program are illustrated in Fig. 1 showing a temporary display. The screen is split into several fields:

(1) The upper line presents the main menu. This line is always present on the screen; its more detailed structure is shown in Fig. 2.

(2) The central part is the graphic window where the diffraction pattern or a part of it is displayed together with the values of the R factors, the maximum variations in the approximated parameters relative to their errors, the calculated overall pattern, the profiles of the constituent peaks, and the difference between the measured and calculated patterns. The current values of the intensity and angle corresponding to the cursor position are also displayed in this window.

(3) The status line shows the current settings of the program: the type of the profile-shape function used, the method of radiation monochromatization, the type of background correction, and the constraints imposed on the asymmetry and profile parameters of individual peaks.

(4) The bottom line is the peak menu used to manually set the parameter values or for varying the parameter values determined by the automatic search. The possibilities of this menu are as follows:

—to add (delete) a peak to (from) the refinement process;

—to select a peak for the manual setting of its parameters;

—to vary the position, intensity, and half-width of the selected peak continuously or step-by-step; and

—to set or to change the groupings of the peaks (the parameters of the peaks belonging to a group are refined under common constraints).

The program described was tested with an NIST standard reference material for Al_2O_3 (SRM) 676 and with 1976 standards. The results were presented at two international conferences [13, 14]. The program was

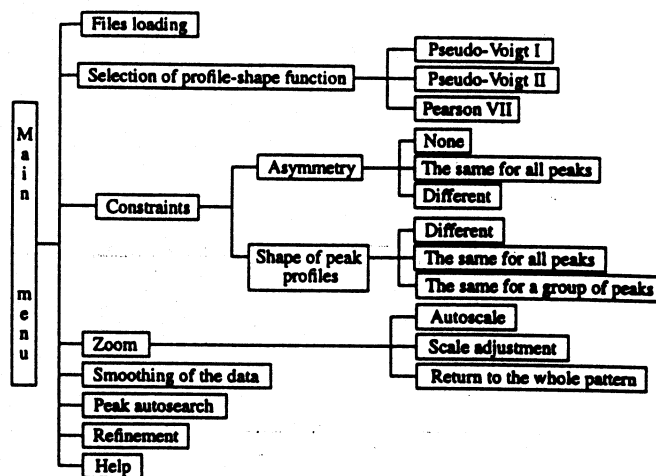


Fig. 2. Principal possibilities of the main menu.

used to study the structural changes upon phase transitions in monoclinic BaPbO_3 [15] (this compound has a slightly distorted perovskite-like structure, and as a consequence, its diffraction pattern consists of multiplets with strongly overlapped peaks) and the phase composition in $\text{IrO}_2\text{-Ta}_2\text{O}_5$ thin films [16] (several solid solutions with very close unit cell parameters exist in this system), as well as to process the diffraction patterns of more than 100 different compounds. The data obtained for 20 of these compounds were published in the PDF-2 database (vols. 44–45) of the International Center for Diffraction Data (ICDD).

We also carried out special reliability tests of the program for the integrated intensities obtained upon refining the diffraction patterns. An X-ray diffraction pattern of KTaO_3 cubic perovskite with the lattice parameter $a = 3.9889 \text{ \AA}$ was used for this purpose. The diffraction pattern was measured at $2\theta = 10^\circ\text{--}147^\circ$ (Cu-radiation) by accumulating 120 000 counts at each maximum position. The integrated intensities obtained with the program were compared to those obtained from the direct measurements. The latter were performed within the angular range of ± 12 half-widths for each peak. The linear background was calculated by using the average values for the first five and last five intensities within the interval. After the background was subtracted, the numerical integration of the measured profile was carried out. The difference between the intensities obtained by the two methods did not exceed the error associated with the counting statistics and the cutoff of the reflection tails.

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