USER'S GUIDE

to

PROGRAM DBWS-9807a

for

RIETVELD ANALYSIS OF X-RAY AND NEUTRON POWDER DIFFRACTION PATTERNS

with a `PC' and various other computers

R. A. Young, Allen C. Larson[1] and C.O. Paiva-Santos[2]

School of Physics
Georgia Institute of Technology
Atlanta, GA 30332

(17.5.99)
20.8.00

Copyright notice:
© 1998, 1999,2000 R. A. Young
All rights reserved

Current Addresses:

1) Dr. Allen C. Larson, 14 Cerrado Loop, Santa Fe, NM 87505-8248

2) Prof. C. O. Paiva Santos, Instituto de Quimica - UNESP, C.P. 355, 14800-900 Araraquara, SP, BRAZIL

CONTENTS OF THIS GUIDE

Item	Page
Part 1. Preliminaries	
I. Foreword -	
A. History of DBWS	4
B. What is new in the 9807 version	5
II. Platforms and Environments	8
A. Portability	
B. Windows environment	
III. Contents of the Distribution Package	9
Part 2. The refinement programs	
I. General information	
A. General plan and data types accommodated	11
B. Calculated intensities	12
C. Selectable models	
1. Profile shape models (functions)	13
2. Preferred orientation models	17
3. Profile asymmetry models	17
4. Background representation - four types	18
5. Models for surface roughness effects	18
D. Quantitative phase analysis	
1. Procedure	
a) With no internal standard	19
b) With an internal standard	20
2. Microabsorption	20
E. Codewords and constraints	21
F. Array size selection and executable program size	22
II. Description of input files	
A. The Input Control File (ICF)	
1. What it is and how to create and update it	24
2. Line by line instructions	25-35
3. Example	36

B. The observed data files
Category 1: Constant incident flux and a single detector
(7 data formats accepted) 37
Category 2: Varying incident x-ray flux (e.g., synchrotron) and
a single detector 39
Category 3. Fixed wavelength and multiple detectors
(e.g., CW neutron sources) 40
C. Background data files
1. 'Tape 3' 40
2. 'Tape 11' 40

III. Description of output files
A. Plot files
1. PLOTINFO file for general use 42
2. PLOT FILES when NBCKGD = -1 42
B. Updated Input Control File 43
C. Output to terminal during run 43
D. The main output file
1. Standard parts of the main output file 44
2. Optional outputs to this and other files 44
E. Definitions and interpretations of the numerical criteria of fit,
1. e.s.d.'s, R's, GofF, DW-d 45
2. Comment about interpretation of R's 46

Part 3. Further comments on using DBWS-9411 and 9807 with a PC
A. Compiling 48
B. Plots
1. Production and chacteristics 48
2. Use - An adroit example 49
C. Execution procedure
1. In DOS 50
2. Using DBWS in Windows 51

REFERENCES 54

APPENDICES
A. Other programs
1. Other Rietveld refinement programs 56
2. Programs ancillary to DBWS
a) ICF preparation programs 57

b) DB2dI assembly program 57
B. Copyright and Fair Use 59

FIGURES 60 - 74

PART 1. Preliminaries

I. FOREWORD - History of DBWS and what is new in this version

A. **History**

The program is designed to carry out Rietveld refinements with X-ray or neutron powder diffraction data in digitized form collected under any of several of the most commonly used instrumental conditions. Fixed wavelength(s) and equal increments in the scattering angle, 2?, are required conditions.

The current program is the latest in a long chain of versions, each updated and upgraded from its predecessor and each distributed in a `distribution package' containing the source code, a User's Guide, plus data and Input Control Files for test cases. For the 1990 (the date of the first PC version) and later distributions, executable versions of PC-compatible (MSDOS) plot programs were included. These plot programs were offered by third parties as Shareware items.

The chain started with DBW2.9 (Young and Wiles, 1981) which was written in FORTRAN IV and incorporated some parts of Rietveld's (1969) original code, particularly the codeword system, A. W. Hewat's code for anisotropic thermal parameters, and A. C. Larson's code for dealing with space group symmetries and reflection multiplicities. However, it was otherwise written `from scratch' and incorporated many new features, some quite major. It was written to be used with x-ray as well as neutron data, to be modular, single pass, and portable. Some of the other new features were choice of a variety of profile functions, a refinable background model, a multiple phase capability, and a number of other features listed in Wiles and Young (1981). DBW2.9 (which, incidentally, had several `bugs') was soon followed by DBW 3.2 (1982) written in FORTRAN V. DBW3.2 was superseded in 1987 by DBW3.2S, a rather major revision made by A. Sakthivel and more nearly conforming to ANSI 77 standards. Next followed versions DBWS-8711 (November, 1987) and, in turn, DBWS-8804 (April 1988). Version DBWS-8804 had a small bug which allowed only 2 phases, rather than the intended 8, to be refined correctly. That error was corrected in version DBWS-8804a. In the next major modification, the program was adapted to run on PC-type computers and was named DBWS-9006PC. This version, with the CalComp instruction routine omitted, was fully ANSI77. Subsequently, various of the several hundred users of record have successfully compiled and run DBWS-9006 on a variety of computers, both small and large. The principal differences between successive versions, up to this point, were listed in the appendices to the relevant versions of the User's Guide and, for the DBWS-8804 to DBWS-9006 differences, in the Foreword of the User's Guide for DBWS-9006.

The principal differences between the next version, DBWS-9411, and DBWS-9006 were (1)

rearrangement of the input control file (ICF) to make it more user-friendly, (2) correction of the long-standing error (noted in the earlier User's Guides) of a factor of two in the multiplicities calculated for some Laue groups, (3) addition of four surface-roughness models with refinable parameters, (4) addition of a split Pearson VII profile function to provide another means of modeling (still imperfectly) profile asymmetry, (5) addition of a quantitative phase analysis routine (see comments below), (6) an improved method for inputting the selectable sizes of certain arrays at compilation time (via a `param.inc' file) plus readout of those sizes to screen during and to output file after each refinement, (7) addition of a dynamic screen display of the progress of the current refinement cycle, (8) additions to the output to the plotting file PLOTINFO and addition of PLOTINFO.BIN so that the plotting program DMPLOT can display the Miller indices at each reflection location and can display (simultaneously) the separate calculated patterns for each of the various phases being refined in a multiphase specimen, (9) change of the Durbin-Watson statistic, d, to the mathematically preferred unweighted version, and (10) some additional diagnostics. We are indebted to Dr. H. Marciniak (author of DMPLOT) for providing features 6, 7 and 8, above.

The split Pearson VII code is based on the mathematics actually used by Toraya for this function in his program PRO-FIT introduced in Toraya (1986).

The quantitative phase analysis calculation, provided by Paiva-Santos, uses the formulation of Hill and Howard (1987) to produce the phase fraction, by weight, that each modelled phase constitutes of the total weight of the modelled phases. The calculation is based on the refined values of the scale factors, lattice parameters, and atom-site occupancies as updated in each least-squares cycle plus the incorporated table of atomic weights. The atomic-weights table covers all atoms for which scattering factors are included in their incorporated table. If other atoms are used, their atomic weights must be supplied by the user in line 8.1 of the ICF (Input Control File; see §IIA). If the mol fraction is also wanted, the number of formula units per cell must be provided by the user. It is important to note that in the version 9411 form the phase-fraction calculation is made <u>WITHOUT any correction for microabsorption.</u> In x-ray work, especially, that can be a serious problem requiring separate analysis. But see (9), below and §II1D2.

B. **What is new in the 9807 and 9807a versions**

The changes from version 9411 made to produce the current version, 9807, include the following. (Listed in arbitrary order.)

1) The **format of the ICF** (Input Control File) has been changed, particularly with respect to atom-site multiplicity and site occupation number. In the ICF for the 9411 version, the parameter N for the 'site occupancy multiplier' for an atom was in the last position in the first of the four lines for the atom. In the 9807 (the current) version, N has been replaced by the actual, refinable site occupancy, 'So', in the last position and the actual site multiplicity, M, (not refinable) is called for in the newly created third position. The user must supply M. It is always an integer value which depends on the particular space group and Wyckoff site. The values of M for all space groups and Wyckoff sites are given in the

International Tables for Crystallography. They can also be found in the Inorganic Crystal Structure Database for many of those materials for which the crystal structures are included. They can also be deduced from the atom's coordinates and the full set of symmetry operations for the space group. Setting flag 9 in line 3 of the ICF will cause the full set of symmetry operators to be printed out. Categories 2 and 3 remain unchanged.

2) A subroutine for **converting the format of an ICF** for the 9411 version to the format for the 9807 version is provided. It is called up by setting NPROF, the profile function identifier in the second position of line 2 of the ICF, to any single integer value <0. Runnning the program as though one were doing a cycle of least squares then produces the converted ICF under the name specified as the output file in the command line. The user has then to fill in correct values for M, So and other parameters, if any, not present in the 9411 version. As a further aid to the user, the multiplicity of the general site (for the space group involved) is printed in the first part of the main output file, on the line between the first mention of the space group and the listing of the initial parameters.

3) The **variety of data formats accepted** by DBWS in Category 1 (See § **2**.II.B) has been increased to include, in addition to the ‘standard DBWS format, a free format, the GSAS 'standard' format, Philips UDF format, a Scintag text format, a Siemens UXD format, and a Rigaku ASCII format. All of the additions are based on equal steps in 2?, a single detector, and constant incident beam intensity.

4) The **output of structure-factor magnitudes**, called for by flag 3 in line 3 of the ICF, can now be called to report the **structures factor phases,** as well.

Setting the flag at '2' calls for the **phase angles** to be reported, as such, for use in

$$F_K = |F_K| \exp (i f_K)$$

where f_K is the phase angle and i is the square root of (-1).

Setting the flag at '3' calls for this output to include **phase angle information** by reporting F in the A + iB form.

In the process of making these changes to the structure factor outputs, an earlier error was corrected so that the |F|'s are now reported to 3 decimal places and do not differ for the a1 and a2 wavelengths.

5) The **number of phases** that can be handled at once has been increased from 8 to 15. The main rational for this increase is to accommodate quantitative phase analyses which can benefit from inclusion of many phases for which the structure is known and only the scale factor and one or two other parameters need to be refined. Dr. Marciniak's DMPLOT also handles 15 phases now.

6)* The quantitative phase analysis routines have now been extended to include an option for operation

directly with an **internal standard.**

7)* A calculation of the wt% of the **'amorphous' component** is now offered when an internal standard is used.

8) **X-ray anomalous dispersion coefficients** for the atoms have been added for 5 more wavelengths, bringing the total to 10 sampling the wavelength range from 2.75 to 0.18 A. We are grateful to Ian Madsen and Dr. R. J. Hill of CSIRO Minerals (Australia) for providing the values and associated coding for these coefficients.

9) The **preferred orientation correction** now works correctly for high-symmetry, non-unique axis cases as well as the others. The existence of the now-fixed problem and conditions under which it might have had significant effects were pointed out in the User's Guide to the 9411 version.

10) **FWHM**. As recommended by the ICDD (Lowe-Ma, et al, 1997) and by Cheary and Cline (1994), a term in $\cot^2$? has been added to the 'Caglioti' (Caglioti, et al. 1958) expression for the FWHM (Full Width at Half Maximum) in profile functions 0,1,2,3,5 and 6, i.e., for the Gaussian, Lorentzian, simple pseudo-Voigt and symmetric Pearson VII functions.

11) A tentative model for **microabsorption effects** (relevant to quantitative phase analysis) has been provided for testing and user suggestions for improvements.

12) Much of the source code, primarily that relating to space groups and symmetry operations and multiplicities, has been **'cleaned'** in the sense of improved readability, consistency in formatting and in use of variable names (e.g., floating point and integer arrays can not use the same name even though used in different places), and removal of unused code.

Additions 13 through 17, below, have been made at the suggestion of Fagherazzi's group in Italy, who made these and other additions to their copy of DBWS-9006 (Riello, Canton, and Fagherazzi, 1995; Riello, Fagherazzi, et al., 1995). We thank them for kindly supplying their code for us to work with.

13) An alternative model for profile asymmetry has been added.

14) Code has been added for calculation of the background contributions of Compton scattering and disorder-diffuse scattering. This is a part of their (Riello, et al.) 'physically based background'.

15) An intensity correction for transmissivity (low absorption) has been added which may be useful for a flat-plate sample mounted in forward transmission geometry.

16) A model data set for some component of the sample may now be imported (Tape 11) and have its scale factor refined along with the parameters related to the main data set and the instrument. Reillo, et al. developed this feature to model an amorphous component of the background with a pattern of an amorphous material stored on Tape 11. The possibility is being explored that this scheme may work for a crystalline component for which the diffraction pattern is known but not the structural data needed for regular Rietveld refinement. In version 9807, a modest step has been taken to deal with this problem.

17) Plots can be made of the separate contributions to the background (e.g,, Compton and disorder) as well as the entire modeled background.

---

*New in version 9807a.

II. Platforms and Environments

A. Portability

The source code provided can be used to carry out Rietveld refinements on various mainframes, workstations, and PC's as well as MacIntosh personal computers. The user must comment out the parts not applicable to the platform at hand. For example, it might be necessary to verify that the bitwise-mapped logic statements AND, OR and XOR are properly recast in all occurrences. The DBWS source code now provided is fully ANSI 77 as passed by Microsoft FORTRAN PowerStation 1.0a.

The executable code provided for DBWS is DOS-executable, but can be run rather advantageously in the Windows-95/98 environment. (See §IIB, below.)

Only executable code is provided for the Shareware plotting program included in the distribution package for making the plots of the Rietveld results (see Note 3, below). The DBWS program does output two files which can be used for plotting, PLOTINFO and PLOTINFO.BIN. PLOTINFO can probably be used by a number of plotting programs including the formerly distributed Shareware program SPLOT by Sakthivel and the presently distributed Shareware program DMPLOT (DMPLOT3.48 as of this writing) by Diduszko and Marciniak. PLOTINFO.BIN is a binary file tailored specifically for the program DMPLOT which, then, can display the Miller indices and the patterns of the separate phases, as noted above. The plots can be produced on-screen and dumped to a printer or produced directly on a plotter.

B. Windows environment

Although they are DOS programs, the executables provided for DBWS can run in the Windows 95

(also 98 and NT) environments in a DOS window automatically called up when the program execution starts. Advantage can thereby be taken of some of the 'drag and drop' and file handling conveniences of Windows 95/98/NT. In combination with a windows-based file editor that does not leave ‘tracks’ (i.e., control characters, etc.) incompatible with program, the convenience and ease of operation under Windows can be equal to that to be expected if DBWS were written as a Windows based program. Further, detailed information about how to achieve this convenience and ease is given in Part 3, §C3.

III. CONTENTS OF THE DISTRIBUTION PACKAGE

The files in the distribution package for DBWS-9807a are generally provided on two 3-1/2 inch 1.44 MB diskettes written under MSDOS. Distribution on other media can be arranged on special request.

The **distribution package** consists of this User's Guide plus the following files on magnetic media in six subdirectories, all written under MSDOS.

1. In subdirectory FOR:

DBWS-9807a.FOR (the DBWS source code)
PARAM.INC
DOSXMSF.EXE

The file, PARAM.INC, is needed at compilation time. It conveys the user's choice of the sizes for the five most-likely-to-be-redimensioned arrays.

DOSXMSF.EXE must be either in the path or in the same directory with the executable version of DBWS that is running.

2. In subdirectory FTEST: files for a test case with fluorapatite. This is a single phase case with a moderate quantity of “lines” (Bragg reflection profiles).

FDATA - the observed-data file
FIN - the ICF (set up for refining 31 parameters) as rewritten after the last cycle run.
PLFAP - the PLOTINFO file needed by SPLOT and DMPLOT, renamed for saving
PLFAP.BIN - the binary file needed by DMPLOT to display the Miller indices and the calculated patterns for the separate phases.
FOUT - the main output file from a run based on FIN
README - Comments about this example.

3. In subdirectory QTEST: files for a two phase case of quartz with alumina as a minor impurity:

QOUT - the main output file from a run based on QIN
PLQ - the PLOTINFO file, renamed for saving, needed by DMPLOT.
PLQ.BIN - the binary file needed by DMPLOT to display the indices and separate phase patterns
QDATA - the observed-data file
QIN - the Input Control File (ICF) as rewritten at the end of the last cycle.

4. In the subdirectory QPATEST you find the files for a somewhat more advanced case involving quantitative phase analysis: 3 phases, one of which is the internal standard, plus an amorphous component. To be determined are the wt% present of two phases plus the amorphous component.

QPADATA - the observed data (3 crystalline phases plus an amorphous component)
QPA .IN - the input control file (ICF)
QPA.OUT
'TAPE11" - whole-pattern observed data for an amorphous silica sample
PLQPA - thePLOTINFO file for this case (note how well the amorphous component is fit)
PLQPA.BIN

5. In subdirectory DMPLOT: files for using this proprietary program offered as a SHAREWARE item:

DMPLOT.CFG - Configuration for DMPLOT
DMPLOT.EXE (Version 3.48)
DMPLOT.TXT - Notes on DMPLOT

6. In the subdirectory XCUTABLE there are three DOS-executable versions of DBWS-9807. They differ only in the choices of dimensions of the five arrays listed in PARAM.INC. See the accompanying Read.me file for details.

7. The current distribution program includes another diskette with a PC-executable program named **DB2dI** provided by the International Center for Diffraction Data (ICDD). The ICDD hope you will use it to provide good patterns properly formatted for acceptance in their PDF (Powder Diffraction File.) See §2b of Appendix A (p. 54) for further information about this program.

NOTES

1) Some of the test-case data files are rather long (e.g., 20 - 140 °2? in 0.02° steps). You may wish to use only a portion of each, e.g., 20 - 60°, to save computer time when you are making your first trial runs. See the discussion (**Part 2**, §II B) of the data file to find how to do this.

2) At the beginning of refinement with a new data set, it is advantageous to refine just a few parameters at first, then those plus a few more, etc. It is, therefore, advantageous to assign the lowest-numbered codewords to those first-to-be-refined parameters. The choice of codeword sequence in the Input Control Files (**Part 2**, §IIA) for these test-cases has been influenced (but not fully controlled) by that

thought.

PART 2. The Rietveld refinement program

I. General Information

A. General plan and data types accommodated

This program is designed to perform Rietveld (1967, 1969) analysis on x-ray or neutron (nuclear scattering, only) powder diffraction data collected:

(i) with a fixed-slits ? - 2? diffractometer (`Bragg-Brentano' geometry) operated in a step-scan mode (equal steps in 2?) with a single detector and with either one or two (e.g., a-doublet) wavelengths in the constant intensity incident x-ray beam (Data in this category are now accepted in six specific formats and a free format.)

(ii) as for (i) but with a varying incident x-ray beam intensity as from a synchrotron source, or

(iii) with fixed incident neutron-beam intensity (or monitor count) and wavelength and with multiple counters which do not all contribute at every step, such as the HRNPD instrument at Brookhaven National Laboratory (USA) and the D1A and D2B instruments at ILL (France).

It can also be used with data collected in HDS geometry from non-absorbing specimens.

It can be used with other geometries if an external data-preparation step is taken, e.g. to compensate for the differences, e.g., the effects of a varying divergence slit or the angle-dependent absorption in absorbing specimens used in HDS or Guinier geometry.

The program can also be used in a **pattern calculation**, only, mode.

The program is currently set up to handle up to fifteen phases simultaneously. The previously used number, eight, was chosen on the presumption that most powder diffraction patterns are not likely to have enough information in them to support refinement of structural details in more than eight phases at once. However, there is now widespread and growing recognition that multiphase Rietveld refinement is the very best way to do quantitative phase analysis (QPA) if the structures are known or are known well enough to be refined. Therefore cases will occur commonly, in quantitative phase analysis, in which only a few parameters, often only the scale factor, need be refined for most of the phases. In such cases, sensible QA results can be expected for many more than 8 phases with good data. Even the 15 now accommodated may not always be enough.

The program uses the Newton-Raphson algorithm to minimize the quantity:

$$S_y = S\ w_i(y_i - y_{ci})^2$$

where

$w_i = 1/y_i$,

y_i = observed (gross) intensity at the ith step,

y_{ci} = calculated intensity at the ith step,

and the sum is over all data points.

The <u>normal matrix elements</u> formally given by

$$M_{jk} = -S_i\ 2w_i[(y_i-y_{ci})\ \frac{\partial^2 y_{ci}}{\partial ?_j\ \partial ?_k}\ (\frac{\partial y_{ci}}{\partial ?_j})\ (\frac{\partial y_{ci}}{\partial ?_k})]\ ,$$

(where the $?_k$ are the adjustable parameters) are approximated by deletion of the

$$(y_i - y_{ci})\frac{\partial^2 y_{ci}}{\partial ?_j \partial ?_k}\ \text{term.}$$

Parameters are stored internally in arrays XL(I,J), GLB(I), and PAR(I,J). XL contains the data for the atoms. The first index runs over the atoms; the second over the parameters for the atom. GLB contains `global' parameters, those which apply to all phases, such as surface roughness, 2?-zero, specimen displacement, background and others. PAR contains crystalline-phase dependent parameters such as lattice constants, scale factor, profile shape parameters ? and m, and preferred orientation parameters. The first index runs over the phases. There are corresponding arrays LP, LGLB, and LPAR which map the parameters to the normal matrix elements. This mapping is determined by the user through the use of `codewords'. See §ID, below.

B. Calculated intensities

The calculated counts y_{ci} are determined by summing the contributions from neighboring Bragg reflections, K, for all phases, p, plus the background, b_i:

$$y_{ci} = S_R[\Sigma_p\ s_p\ \underline{Ab}\ [S_K\ [\,|F_K|^2\ F(2?_i - 2?_K)\ \underline{As}\ L_K\ P_K]]_p + y_{bi}]$$

where

s_p is the scale factor for phase p (note that quantitative phase analysis depends on this),

S_R is a function to model the effects of surface roughness. A choice of 4 models is provided (§IC4).

Ab is an absorption factor, here left at 1.00. That is, it is not implemented. That is acceptable for (1) the x-ray case of an "infinitely" thick flat specimen in a diffractometer using fixed slits and Bragg-Brentano geometry (the most common case) and (2) the neutron case of any shape of specimen with negligible absorption and completely bathed in the neutron beam.

F_K is the structure factor,

F is a reflection profile function which approximates the effects of both instrumental and, possibly, specimen features. A choice of 8 analytical functions is provided. See §I.C.1.

As is a profile asymmetry function (two choices are available)

L_K contains the Lorentz, polarization and multiplicity factors,

P_K is a preferred orientation function. The user has a choice of two models. See §I.C.2.

b_i is the background contribution. The user has a choice of four ways to represent it. The fourth method has a number of subsets. (**2**§I.C.4).

The ratio of the intensities for the two a wavelengths (if used) is absorbed in the calculation of $|F_K|^2$, so that only a single scale factor is required for each phase.

C. Selectable models

C.1. Profile shape models (functions), F .

The profile function to be used in a given run is selected with the control variable NPROF in line 2 of the ICF (Input Control File, see §IIA). The currently available functions are listed below. The origins and performances of most of these functions are discussed in Young and Wiles (1982). The TCHZ function is discussed in Young and Desai (1989).

NPROF	FUNCTION	NAME
0)	$\frac{\sqrt{C_o}}{H_K\sqrt{p}} \exp(-C_o (2?_i - 2?_K)^2 / H_K^2)$	Gaussian (`G')
1)	$\frac{\sqrt{C_1}}{p\, H_K} \quad 1/[1+C_1(2?_i - 2?_K)^2/H_K^{2]}$	Lorentzian (`L')
2)	$\frac{2\sqrt{C_2}}{p\, H_K} \quad 1/[1+C_2(2?_i - 2?_K)^2/H_K^2]^2$	Mod 1 Lorentzian
3)	$\frac{\sqrt{C_3}}{2\, H_K} \quad 1/[1+C_3(2?_i - 2?_K)^2/H_K^2]^{3/2}\}$	Mod 2 Lorentzian
4)	Split Pearson VII	(`SPVII)

Low-angle side, Split Pearson VII (`SPVII-L')

$$C_4 [1+(\frac{1+A}{A})^2 (2^{1/m_L}-1)(2q_i - 2q_K)^2]^{-m_L}$$

High-angle side, Split Pearson VII (`SPVII-H')

$$C_4 [1+(1+A)^2 (2^{1/m_H}-1)(2q_i - 2q_K)^2]^{-m_H}$$

`A' in this function is a refinable asymmetry parameter. The shape parameters m_L and m_H can be refined individually as a function of 2? in the same way as can m in the single PVII, profile function 6. These formulations of the normalized SPVII functions are taken from Toraya (1986).

5) ?L + (1-?)G pseudo-Voigt (`pV')

The mixing parameter, ?, can be refined as a linear function of 2? wherein the refinable variables are NA and NB:

? = NA + NB*2?

Hastings, et al. (1984) have shown how the FWHM's of the individual L and G components can be recovered from the ? values in this profile function.

6) $(C_5/H_K)\,[1 + 4(2^{1/m} - 1)(2?_i - 2?_i)^2/H_K^2]$ Pearson VII (`PVII')

and m can be refined as a function of 2? as

$m = NA + NB/2? + NC/(2?)^2$,

where the refinable variables are NA, NB, and NC.

We note that PVII = L if m = 1 and G if m = ∞.

7) Modified* Thompson-Cox-Hastings pseudo-Voigt Mod-TCH pV (`TCHZ')
(Thompson, et al., 1987)

[Note: The G used in the description of this function is simply a symbol related to the profile breadth and is not to be confused with the gamma function represented by G(m) in the definition of the normalizing constants, C4 and C_5, in the PVII functions.]

TCHZ = ?L + (1-?)G
where

$? = 1.36603q - 0.47719q^2 + 0.1116q^3$

$q = G_L/G$

$G = (G_G^5 + AG_G^4G_L + BG_G^3G_L^2 + CG_G^2G_L^3 + DG_GG_L^4 + G_L^5)^{0.2} = H_K$

A = 2.69269 B = 2.42843
C = 4.47163 D = 0.07842

$G_G = (U \tan^2 ? + V \tan ? + W + Z/\cos^2 ?)^{1/2}$

$G_L = X \tan ? + Y/\cos ?$

[*The modification consists of addition the parameter Z to provide a component of the Gaussian FWHM which is constant in **d***, as is the Y component of the Lorentzian FWHM (Young and Desai, 1989)]

In the above profile functions, the refinable parameters are those in ?, m, H_K and (in the SPVII functions) A.

The normalizing constants are

$C_o = 4 \ln 2$

$C_1 = 4$

$C_2 = 4(\sqrt{2} - 1)$

$C_3 = 4(\sqrt{2^{2/3}} - 1)$

$C_4 = \frac{2}{\sqrt{p}} \frac{(1+A)}{H_K} [\frac{A\Gamma(m}{\sqrt{2^{1/m_L} - 1}}$

$C_5 = \frac{2\,\Gamma(m)(2^{1/m} - 1)^{1/2}}{\sqrt{p}\;\Gamma(m - 0.5)}$

H_K is the full-width-at-half-maximum (FWHM) of the Kth Bragg reflection. Except as otherwise specified (e.g., in Profile 7), the angular dependence of H_K is modeled in accord with the ICDD recommendation (Lowe-Ma et al., 1997) as

$$H_K^2 = U \tan^2 ? + V \tan ? + W + CT \cot^2 ?$$

where U, V, W and CT are refinable parameters.

C.2. **Preferred orientation (P_K) models**

In position 8 of line 2 in the ICF, a **0** selects the Rietveld-Toraya model and a **1** selects the March-Dollase model. The Rietveld-Toraya model, Toraya's modification of the function Rietveld put in his original code, is

$$P_K = [G_2 + (1-G_2) \exp(G_1 a_K^2)]$$

and the March-Dollase model is

$$P_K = (G_1^2 \cos^2 a + (1/G_1) \sin^2 a)^{-3/2}),$$

where G_1 and G_2 are refinable parameters and a_K is the angle between $\mathbf{d}^*_K$ and the presumed cylindrical-symmetry axis of the texture (e.g., fiber axis direction). We note that the value of G_1 corresponding to no preferred orientation is 0 in the Rietveld-Toraya function and 1.00 in the March-Dollase function.

It may be noted here that in the Rietveld-Toraya model, the G_1 parameter tends to be correlated with the scale factor, S_p, highly so if the preferred orientation is strong.

C. 3. **Profile asymmetry models**

Two choices are available:

Setting flag 9 in ICF line 2 to 0 selects the "usual Rietveld asymmetry model":

$$\underline{As} = 1-P*\mathrm{sign}(2?_i-2?_K)*(2?_i-2?_K)^2/\tan?_K$$

Setting that flag to 1 selects the Riello, Canton and Fagherazzi (1995) model

$$\underline{As}(2q - 2q_K) = 1 + \frac{C_M(2q - 2q_K)}{w_K(\tan q_K)} \exp\left(-\frac{|2q - 2q_K|}{2 w_K}\right)$$

where C_M is the refinable parameter, $2?_K$ is the position of the peak of the Kth reflection profile, (2? - $2?_K$) is the displacement of the observed peak from the calculated one` and w_K is the refined value of the FWHM of the Kth reflection.

C.4. **Background representation**

The background intensity y_{bi} at the ith step may be obtained by any of several methods. The user's choice is indicated by the value of NBCKGD entered in the fourth position in line 2 of the ICF. The choices are

(1) an operator-supplied table ('Tape 3') of background intensities (NBCKGD = 1), or
(2) linear interpolation between operator-selected points in the pattern
(NBCKGD = n, where n is the number of points), or
(3) a specified background function (NBCKGD = 0) or
(4) the alternative background representation of Reillo, et al (NBCKGD = -1)

If the background is to be refined in the NBCKGD = 0 option, y_{bi} must be obtained from a refinable background function. The one available in the current version of DBWS is

$$y_{bi} = \sum_{m=0}^{5} B_m \, [(2?_i/BKPOS)-1]^m.$$

where BKPOS is user-specified in line 4 of the Input Control File (ICF). See §IIA.

If the alternative background (NBCKGD = -1) is to be used, there are several choices to be made.

(1) Absorption correction for Bragg-Brentano geometry
(2) Compton and disorder diffuse scattering contribution for each phase using either individual isotropic or overall atom-displacement factors.
(3) Refinement of the scale factor for an 'amorphous' (or other?) component represented by whole-pattern intensity data on Tape 11.

C.5. **Models for Surface Roughness effects (S_R)**

As was dramatically demonstrated by Sparks, et al. (1992), surface roughness has a far more important effect on the relative intensities than had been generally appreciated. Here we offer the user a choice among four models in the spirit of experimentation: no guarantees that any of them are particularly

appropriate. Their refinable parameters are likely to be highly correlated with each other and, of course, with the overall scale factor. However, they do represent a gesture in the right direction. We would be grateful to learn of your experiences in using one or more of these options.

The user's choice among the 4 different models is indicated by the digit entered for IABSR in line 2 of the ICF.

The choices of model are:

IABSR	Model
1	Combination of the Sparks and Suortti models
2	Sparks, et al., (1992) model (straight line)
3	Suortti (1972) model (exponential)
4	Pitschke, et al., (1993) model

The models, as recast and normalized to 1.00 at ? = 90° by us, are:

1 - Combination model:
$S_R = r\{1.0 - p(\exp[-q]) + p(\exp[-q/\sin(?)])\} + (1-r)(1+t(?-p/2))$

2 - Sparks, et al., model:
$S_R = 1.0 - t(?-p/2)$ [? in radians]

3 - Suortti, et al., model:
$S_R = 1.0 - p(\exp[-q]) + p(\exp[-q/\sin(?)]$

4 - Pitschke, et al., model:
$S_R = 1.0 - [pq(1.0-q)] - [pq/\sin(?)][1.0-q/\sin(?)]$

The refinable parameters are p,q,r, and t. Note that ? is expressed in radians.

If no correction is being applied for surface roughness effects, then set (and fix) p = q = 0 and r = 1.0 if IABSR = 1 and p = q = r = t = 0 for all other choices of IABSR (2,3,4). In the Pitschke, et al. model, q must not be 0 (zero) if a codeword is declared for it, else a `divide by zero' error message will appear.

D. Quantitative phase analysis

1. Procedure.

a) No internal standard

If no internal standard is used and amorphous content is taken to be negligible, the program calculates the weight fraction for each phase refined, on the assumption that the phases being refined account for 100% of the specimen, via the following relation (Hill and Howard, 1987):

$$W_p = \frac{S_p(ZMV)_p}{\sum_{i=1}^{N} S_i(ZMV)_i}$$

where p is the value of i for a particular phase among the N phases present, S_i is the refined scale factor, ZM is the weight of the unit cell in atomic weight units (number of formula units, Z, per cell times the atomic weight, M, of the formula unit), and V is the volume of the unit cell. For this calculation, the program uses internally tabulated atomic weights and the refined lattice parameters, scale factors, and atom site-occupancies. Atomic weights not in the incorporated table may be inserted in line 8.1 of the ICF. Mole fractions, as well as weight fractions, will be reported at the end of each cycle if the user supplies the number of formula units per unit cell in ICF line 11.2.

b) With internal standard

DBWS can also make use of an internal standard in Quantitative Phase Analysis. The fact that an internal standard is to be used is signified with a number in the last position (the twelfth) in line 2.1 of the ICF. The crystallographic data for the internal standard phase are entered as a set of l1-* lines, just as is done for the other phases present. The sequence number of this internal standard phase among all of those entered in this section of the ICF is the ISPHASE number to be entered in line 2.1. The wt% which this phase contributes to the total sample weight is entered in line 11.2 at the last position in the line in F72 format. For example, if the standard constitutes 28.42% of the weight of the entire sample, the number 28.42 will be entered there.

CAUTION: As they stand, above, these QPA calculations **do <u>not</u> take into account any microabsorption effects** (see, for example, Taylor and Matulis, 1991). They will be important unless the linear absorption coefficients are the same, or nearly so, for all phases being analyzed. Therefore, the neglect of microabsorption effects will generally be a much more serious error in the x-ray powder diffraction case than in the neutron powder diffraction case.

2. Microabsorption

A beginning effort at providing a microabsorption correction has been made in DBWS-9807. It involves the use of a particle absorption factor for each phase. Necessarily such a correction also involves the sizes and shapes, and distributions thereof, of the particles. An approximation to the needed value for

this particle absorption factor, AFQPA in the ICF, can be obtained from table V, page 368, of the Brindley paper (1945, Philos. Mag. **36,** 347-369) or after evaluation of equation (3) in the Taylor & Matulis paper (1991, J. Appl. Cryst. **24**, 14-17), which is:

$$t_a = (1/V_a) \int \exp[-(\mu_a - (\mu\text{-bar}))] \times dV_a .$$

where t_a is a particle absorption factor for phase a, the integral is taken from 0 to V_a, V_a is the particle volume of phase "a", μ_a is its linear absorption coefficient, x is the path of the radiation in particle "a" when diffracted by the volume element dV_a, and μ-bar is the mean linear absorption coefficient of the solid matrix of the powder. The user needs to be cautious with the μ-bar. According to Brindley (1945. p. 349), this value must be the mean value for the solid material, excluding the spaces between particles.

Table V in the Brindley paper was computed for spherical particles for use as a 'better than none' approximation. He well recognized, of course, that a naturally occurring material consisting entirely of spherical particles of identical size would not be often found.

The value of t (herein coded as AFQPA) for each phase is then used to correct the scale factor for each phase in the specimen for microabsorption. The equation for phase abundance then becomes (Taylor and Matulis, 1991)

$$W_p = \frac{S_p(ZMV)/t_p}{\sum_{j=1}^{N} S_j(ZMV)_j / t_j}$$

E. Codewords and constraints

This effective codeword system has been carried over from Rietveld's original code. A `codeword' is entered for each parameter. Each codeword has two parts, (1) the designation of a matrix position for the parameter and (2) specification of the fraction of the calculated shift that is to be applied to this parameter. The codewords have the form

sdddc.cc

where the *ddd* digits specify the matrix position for the particular parameter. The *c.cc* digits specify what fraction (or multiple) of the calculated shift is to be applied to update the parameter and s is the sign (+ or -) desired for the applied shift. (A positive shift will be applied if no minus sign (-) is present.) Separately from the codewords, the user may also supply a group `relaxation' factor to be applied to the

calculated shifts for all parameters in each of four different groups of parameters. See line 5 of the Input Control File.

As an example, assume that one wishes to refine the x,y,z coordinates of an atom and that y = x/2 is required by the crystallographic symmetry. If we let the codewords be given as

x: 131.00, y: 130.50, and z: 141.00,

then x and y will be assigned to the 13th normal matrix parameter and z to the 14th. Also, 1.00 times the calculated shift in the 13th parameter will be applied to x and 0.50 times it to y. The full calculated shift in the 14th parameter will be applied to z. If, on the other hand, one were to set up the codewords as

x: 131.00 y: -131.00

then the sum of x and y would remain constant.

This **`constraint by codewords'** feature can be useful in connection with site occupancies also. One may let two different atoms occupy the same crystallographic site and then determine how much of each is present in that site by refining their site occupancies under the constraint that the total site occupancy (atomic per cent) is to remain constant, i.e., by assigning the same codeword to both atoms but beginning one with a negative sign, so that the applied shift in the occupancy for one atom is the negative of that for the other.

Zero values for the three *c*'s in a codeword result in the parameter not being refined. However, this is not always an advisable way to `turn off' a parameter: If some codewords are non-zero but their applied shifts are set to zero, the result can be the physically unrealistic one of correlation-matrix elements >100%.

If N parameters are to be refined, then no codeword with a *ddd* value in the range from 1 to N can be missing. If any are, the program will stop, a "hole in the matrix" error message will be sent to the screen (in the PC context) along with identification of the missing codeword. The missing codeword(s) will also be specified at the end of the aborted main output file.

The number of codewords declared (i.e., entered as non-zero in the Input Control File), whether or not called for to be refined (line 9 of the ICF), must not exceed the declared size for the array MSZ (see below).

F. Array size selection and executable program size

Although the issue is rapidly being made moot with the recent great increases in PC memory and speed, redimensioning of certain arrays was often wanted in order to make best use of limited memory

and time. This requires making changes in the array sizes at all occurrences in the source code and then recompiling. With today's powerful PC's, one may be able to do the bulk of one's Rietveld refinement work by just setting the array sizes to arbitrarily large values and leaving them there. However, if that is not feasible for some reason, the following are the array-size statements one would most often wish to modify:

IDSZ = number of data points
IRS = maximum number of allowed reflections (Ka1 + Ka2)
NATS = maximum number of atoms in the asymmetric unit allowed
MSZ = maximum number of elements in the normal matrix, i.e., codewords
NOTE: If the number of codewords declared exceeds the declared value of MSZ, the excess will be quietly ignored.
NOV = maximum number of reflections allowed to contribute to the intensity y_i at a single data point

The task of changing the numbers in these statements at every occurrence in the DBWS source code has been greatly simplified in 'modern' versions of DBWS: One need only specify the numbers a single time in the file PARAM.INC and then keep that file in the same subdirectory with the source code file, or in the path, when the compiling is done.

If the refinement stops and an error message to the effect that "IDSZ is less than MSZ*MAXS" appears, it will be necessary to increase IDSZ or reduce MSZ or MAXS until IDSZ is equal to or greater than MSZ*MAXS. The reason is that the space in memory set aside for IDSZ is also used, at different times, by MSZ*MAXS. MAXS is the number of parameters being varied (line 9 in the ICF).

Obviously, as the matrix size and number of parameters being refined increases, one could quickly run into the `640K barrier' characteristic of MSDOS and PCDOS. Compilers are commonly available that can overcome that problem and also make use of the full 32-bit architecture in today's PC's. One such is the compiler is a part of Microsoft's FORTRAN PowerStation. It makes use of a separate memory manager program, DOSXMSF.EXE, which then must be in the same directory or in the path with the *.exe program being used.

The executable versions of DBWS-9807a in the distribution package have been so prepared. Even under Windows 95/98 the DOSXMSF.EXE file is needed because the actual carrying out of the operations is still (subliminally!) a DOS activity.

II. Description of input files

A. The input control file (ICF), (`Tape/Unit 5')

1. What it is and how to create and update it

For compatibility with other programs (e.g. DB2dI which produces 'd and I' files in the format needed by the ICDD for the PDF), the name you give this file should include the extension .in or .inp. This also guards against the propensity Windows 95/98 has for opening a file with a program selected on the basis of that file's extension.

This file, the ICF, contains the control variables along with the structural and other refinable parameters. If output of a new ICF is selected (flag 5 for NXT in line 3), the current ICF will be updated at the end of the last cycle.

The following line-by-line description tells the user how to set up the ICF control file for any given case. Some users have developed menu-driven preparation programs with which to set up the input control files. A good program of that sort can certainly be a help to the beginner. However, once one becomes familiar with the format detail, then to set up a new ICF using an old one as a template, or to make adjustments to the ICF between runs it is probably quicker and easier to do so by editing the ICF directly on-screen using a full screen editor. Particularly for making adjustments to the ICF between runs (of successive batches of cycles), using the the full-screen approach is quicker and easier than plodding through a menu-driven approach which forces one through preset sequences.

Users who are not fully familiar with the format detail of the ICF, and either do not have or do not wish to use a menu-driven file-preparation program, will find useful the example ICF placed at the end of this line-by-line description. It is based on the quartz-plus-alumina case.

An ICF format conversion subroutine is provided for the convenience of users who have on hand the ICF's from problems for which they used DBWS-9411. This routine will convert an ICF in DBWS-9411 format into one in the format needed for DBWS-9807. It is called up by entering a negative integer for NPROF in line 2.1 of the ICF. One then goes through the steps of starting a refinement cycle. As is stated elsewhere in this Guide, the basic command line to run a Rietveld refinement with DBWS is

PGM DATA ICF OUT

where the actual names are to be entered for the four files indicated. PGM is to be the name for the executable version of DBWS being used. DATA is to be replaced by the name of either a real data file (as it is in an actual Rietveld refinement run) or a dummy name, ICF is to be replaced by the name of the ICF being converted, and OUT is to be replaced by the name wanted for the converted ICF. In special cases, another file may need to be specified in the command line, that relating a separately determined whole-pattern background if it is called for in the ICF being converted. See §C1 of Part 2 of this Guide

for further comment on these files.

2. Line by line instructions for setting up the Input Control File (ICF)

The line-by-line instructions follow. A star (*) before a line number indicates that the line's existence depends on the value of a control variable.

Line Format Description

1. (A70) TITLE - any 70 characters to be used to label the main output file and the plots

2 Selection of modules in the Refinement model
2.1 (**12**I4)

JOBTYP
0 X-ray case
1 Neutron case (nuclear scattering only)
2 pattern calculation only, X-ray
3 pattern calculation only, Neutron

NPROF Profile selection
0 Gaussian
1 Lorentzian (Cauchy)
2 Mod 1 Lorentzian
3 Mod 2 Lorentzian
4 Split Pearson VII (asymmetric)
5 pseudo-Voigt (pV)
6 Pearson VII (symmetric)
7 Modified Thompson-Cox-Hastings ('TCHZ') pV
<0 If you set NPROF < 0, an ICF from DBWS 9411 will be converted to DBWS-9807 format and given the name you specified for the output file. See §IIA1 (p. 24) for further "how to" information.

NPHASE = number of phases (up to **15** possible)
NBCKGD = background model control
0 - background to be refined (5th order polynomial in 2θ)
1 - background to be read from file tape 3
2,3,.,N - background to be determined by linear interpolation between the N given points (see instructions for ICF line 6.)
-1 - Alternative, physically based background (Riello, Fagherazzi, Clemente, & Canton,

1995)

NEXCRG = number of excluded regions
NSCAT = number of atomic scattering factor sets to be added manually
INSTRM = Laboratory _-2θ X-ray, synchrotron X-ray, or neutron diffractometers using a fixed wavelength radiation
0 - Laboratory ___2θ X-ray data or single detector neutron data
1 - varying incident intensity data (e.g., synchrotron X-ray) and a single detector or multiple counters and "fixed" (e.g., constant monitor counts per step) incident intensity (e.g., neutron CW data)

IPREF= preferred orientation function
0 - Rietveld-Toraya function
1 - March-Dollase function

IASYM = 0 for usual Rietveld asymmetry model
= 1 for Riello, Canton and Fagherazzi (1995) model
IABSR= Choice of surface roughness model
1 - Combination model
2 - Sparks, et al. model
3 - Suortti model
4 - Pitschke, et al. Model

IDATA = Additional identification of the format of the particular i nput diffraction-data file for the 7 cases in Category 1 (single detector, constant incident beam intensity and wavelength). See section II.B. Category 1 for further description of these formats and how DBWS utilizes them.
.
0 - the standard DBWS format
1 - free format (see §IIB category 1b)
2 - GSAS format
3 - Philips UDF format
4 - Scintag text format
5 - Siemens UXD format as converted from a RAW file by XCH program ver.1.4 (DOS)
6 - Rigaku ASCII format

Note: It will sometimes be possible to utilize data in some other formats by reducing the format to one of the above, particularly the free format case (1).

ISPHASE = Sequence number of the internal-standard phase as it appears in the ICF. If '0' is placed here (item 12 in line 2 of the ICF), no internal standard will be used or sought in the refinement process. If an internal standard is specified here, its weight % of the total sample will be entered for ISWT in the last position in line 11.2 of the ICF.

Line Format Description

*2.2 (2I4) This line applies only if NBCKGD = -1, i.e., for the 'alternate' background. All modules on this line are from Riello, et al. (1995)

IAS= Absorption correction

0 - no correction

1 - an 'absorption' (really transmissivity) model for B-B reflection geometry:

$A = 1 - \exp(-2mT/\sin\theta)$ where m (coded as TMR) is the linear absorption coefficient for the sample and T (coded as SW) is the effective sample thickness

FONDO: 'alternate'-background module choice

0 - Standard background

[with options 1& 2, below, the 'standard' polynomial background can also be used and the Compton and disorder scattering will be added to it.]

1 - Individual isotropic "temperature factors" (the IUCr recommends the term ‘atom displacement' rather than 'temperature' or 'thermal') will be used in calculation of the Compton and disorder-diffuse scattering contribution of each phase to the background.

2 – Overall “temperature” factor will be used in the above calculations.

3. 4(5I1,1X) Output control flags.

A flag is set "off" with 0 and "on" with 1, 2 or 3.

(For further information about what these flags control, see §III.D.2)

Flag No. Flag setting and output called for

(1) IOT =1, observed & calculated intensities at each step

(2) IPL =1, line printer plot file

(3) IPC =1, $|\text{structure factors}|^2$ & R-Bragg

= 2, as for 1 plus $|F|_{obs}$, $|F|_{calc}$ & R- F with the phases with the phases reported directly as phase angles,

=3, as for 1 plus $|F|_{obs}$, $|F|_{calc}$ & R- F with the F_{obs} and F_{calc} written in A + iB form to include the phase information

NOTE that this flag must be set `on' (i.e., non-zero)

(i) to cause the inclusion of the possible Bragg reflection positions in the PLOTINFO file and

(ii) for the DMPLOT display of the calc’d patterns of the separate crystalline phases to work.

(4) MAT =1, correlation matrix

(5) NXT=1, input file updated from last-cycle results

(6) LST1=1, initial reflection list with indices, multiplicities, breadths, positions,

LP factors, and mixing parameters.

(7) LST2=1, data list (as corrected, e.g., for background)
(8) LST3=1, merged reflection list
(9) IPL1=1, symmetry operators
(10) IPL2=1, Not used. Reserved for possible alternate plot-file creation
11) IPLST:
=1, Stacked summary of the cycle-by cycle value of each parameter, applied shift, and R-value
=2, output file as for IPLST=1 plus a separate summary of the last-cycle parameters and their e.s.d.=s.

The following options, 12 - 18, to output the specified plot files are intended primarily for use in the NBCKGD = -1 case:

(12) PLOSS=1, Observed data plot file corrected for absorption scattering
(13) PLCAL=1, Calculated 'data' plot file
(14) PLPOL=1, polynomial background plot file
(15) PLCOM=1, Compton scattering plot file
(16) PLDIS=1, uncorrelated disorder plot file
(17) PLAM=1, Plot file of data in 'amorphous' diffraction data file. (Could be for a polycrystalline rather than an amorphous material.)
(18) PLOTBIG=1, Observed corrected for absorption, amorphous, amorphous plus Compton, C

NOTE: if PLOTBIG is set to 1, PLOSS, PLCAL, PLPOL, PLCOM, PLDIS, and PLAM, will not be created. To have these plotfiles created, set PLOTBIG=0

(9F8.0)

Fixed parameter values to be supplied by the operator

WAVELENGTH 1 of the incident radiation
WAVELENGTH 2 of the incident radiation
RATIO = intensity ratio e.g., a_2/a_1
BKPOS= origin of polynomial for background (in °2θ)
WDT = width (range on either side of peak max) of calc. profile in units of H_K
CTHM = monochromator coeff. in polarization term of the LP factor:
(1+CTHM*cos^2 2?)/(sin^2? cos ?)
TMR = linear absorption coefficient (cm^{-1}) needed for the transparency correction.
RLIM = A 2? value that determines the 2? range(s) over which the asymmetry correction is applied.
If IASYM = 0 (Rietveld model) , only the profiles below RLIM are corrected.
If IASYM =1 (Riello *et al.* model), the asymmetry correction is applied

in the regions

$2?_{min} < 2? < 90\text{-}RLIM$

and

$90+RLIM<2? <2?_{max}$

(so RLIM must be 0<RLIM<90_)

SW = Measured sample Thickness (cm)

5. (I4,5F4,3F8.0)

Some operational choices:

MCYCLE = number of cycles [can not be 0 or no calc'n will be done]

EPS = run terminates when all calculated shifts (not the actually applied shifts shown in the output) are < (EPS*e.s.d.)

Relaxation factors for shifts by parameter groups:

RELAX 1 - co-ordinates & isotropic atom displacement ("temperature") factors and site occupancies

RELAX 2 - anisotropic atom displacement parameters

RELAX 3 - profile width, asymmetry, overall atom displacement ("temperature"), preferred orientation parameters, lattice parameters and overall scale factor.

RELAX 4 -2θ-zero, specimen displacement, specimen transparency, surface roughness, amorphous scale factor and monochromator band-pass parameters.

Needed for pattern calculation only:

THMIN - starting angle (_2θ) for the pattern to be calculated

STEP - step size (_2_)

THMAX - ending angle (_2θ)

*6. (2F8.2) if NBCKGD >2 in ICF line 2, enter NBCKGD lines here specifying the background intensities measured at those NBCKGD points:

POS = position in degrees 2?

BCK = background counts at this position

*7. (2F8.2) if NEXCRG in line 2 is > 0, enter NEXCRG lines with

ALOW = low angle bound (°2?)

AHIGH = high angle bound

*8. Here is the place to enter scattering factors and scattering lengths which are not in the incorporate

If NSCAT>0, enter here NSCAT sets of lines in the formats shown below for your case:

The x-ray scattering factors and neutron coherent scattering lengths that are incorporated here are those listed in the 1974 version of Vol. 4 or, in some cases, the 1995 Vol. C of the International Tables for X- ray Crystallography.

NOTE that the anomalous dispersion corrections, ?f ' and ?f ", to the atomic scattering factors are now given in this program for 10 Ka_1 wavelengths (2.748510:Ti, 2.289620:Cr, 1.935970:Fe, 1.788965:Co, 1.540520:Cu, 0.709260:Mo, 0.559360:Ag, 0.215947:Ta, 0.209010:W, and 0.180195:Au in A) instead of only those of Cr, Fe, Cu, Mo and Ag given in previous versions of DBWS. The coefficients provided before were taken from the International Tables for X-ray Crystallography Vol. 1 (1974) and the now-added ones come from Vol. C (1995). One reason for providing these additional data is so that scattering factors for working wavelengths chosen from a continuum (e.g., synchrotron X-radiation) might be better approximated.

a) Line 8 for the X-ray case:

*8-1 (A4,3F8.0) NAM =symbol identifying this set
DFP =f ' (real part of the anomalous dispersion)

DFPP =f " (imaginary part of the anomalous dispersion)
AW - atomic weight (must be included as part of the set)

*8-2 (9F8.0) Either one line of the form
A1 B1 A2 B2 A3 B3 A4 B4 C,
the coefficients for the approximation to f, as used in the Int'l Tables,
or a set of lines of the form
Posi Scat
where
Posi = (sin _)/λ__and Scat=f
The set is terminated by a line with -100 in the first position.
If the first form is desired, A2 can not = 0

b) Line 8 for the neutron case:

*8.1 (A4,2F8.0) NAM symbol identifying this set
DFP - b (scattering length in units of 10^{-12} cm)
AW - atomic weight (must be included as part of the set)

9. (I8) MAXS = number of parameters to be refined in this pass

10. Refinable global parameters

10-1. (7F8.0)

ZER	-	offset of the 2_-zero point (in _2___
DISP	-	sample displacement
TRANS	-	parameter for effect of sample transparency on apparent 2_
P	-	surface roughness parameter p

Q - surface roughness parameter q
R - surface roughness parameter r
T - surface roughness parameter t

10-11 (7F8.0) FLZER codeword for 2θ-zero point offset
(codeword makeup is described near end of §I of Part 2.)
FLDISP codeword for sample displacement
FLTRNS codeword for transparency coeff.
FLGP codeword for surface roughness parameter p
FLGQ codeword for surface roughness parameter q
FLGR codeword for surface roughness parameter r
FLGT codeword for surface roughness parameter t
[See **2**§I.C.5 (this part) of this Guide for explanation of usage and how to nullify the surface roughness correction.]

*10-2 (3F8.0)
AM= scale factor for amorphous, or other, pattern on Tape 11.
MON1 = monochromator band-pass parameter
(if there is a monochromator in the diffracted beam, put MON1=1 and put MON2=0 if a monochromator works on the incident beam)
_____MON2 = monochromator band-pass parameter (for a focusing graphite monochromator, MON1 could be equal to 4 and MON2 could be equal to 2.
NOTE: MONO1 and MONO2 are needed mostly when Compton scattering, or other scattering which is not confined to a narrow band of wavelengths, is important to the experiment. For a description of these parameters and of their values and use, see Riello, Canton & Fagherazzi (1997).

*10-21 (3F8.0) FLAM= codeword for 'amorphous' (i. e., Tape 11 data) scale factor
FLMON1=codeword for the first monochromator constant, MON1
FLMON2=codeword for MON2

10-3 (6F9.4) BACK - background coefficients in 'standard' (NBCKGD = 0) polynomial representation
10-31 (6F9.4) FBACK - codewords for background coefficients

11. First group of phase-specific parameters: NPHASE (as specified in Line 2) sets of these lines numbered 11-* are needed, i. e., one set for each phase.

11-1 (A70) PHSNM = phase name and number

11-2 (2I4,F8.0,3F4.0, F7.2)

N - number of atoms in the asymmetric unit

FU - number of formula units in the unit cell (used only for reporting molar phase fraction)

AFQPA - particle absorption factor, t_p, for each phase, used in the microabsorption correction. The value can be taken from table V, page 368, in the Brindley paper (1945, Philos. Mag. 36, 347-369) or after evaluation of equation (3) in the Taylor & Matulis paper (1991, J. Appl. Cryst. 24, 14-17). Also see §IID2.

PREF* - preferred orientation direction in reciprocal space, expressed as Miller indices

ISWT = wt% of the total sample contributed by the internal standard

*__Note__: In previous versions of DBWS there was a problem with the preferred orientation correction that could be significant in cases of very high preferred orientation <u>and</u> high symmetry. That problem has now been corrected.

11-3 (20A1) SYMB = space group symbol

e.g., $P6_3/m$ = P 63/M

$P2_12_12_1$ = P 21 21 21

Pb = PB (and sometimes P 1 1 B, etc.)

$P\bar{3}$ = P -3

Fm3m = F M 3 M

(Note the upper case in this symbol. It is needed for some other space groups, also. The program treats the lower case m in this example as specification of an hexagonal space group and tries to be accommodating)

For rhombohedral space groups, add H to the symbol to be sure that hexagonal axes will be used, e.g., R -3 C H, and add R to demand rhombohedral axes.

11-4 Atom specific parameters: 4 lines for each of the N atoms

11-41 (A4,1x,I4,1x,A4,2x,5F8)

LABEL - identification characters for atom

M - multiplicity of the particular site, as given in International Tables for X-ray Crystallography, Vol 1 or Vol A. It is <u>not refinable.</u>

NTYP - link to scattering data for atom (use all caps): either

(a0 the atom's name from line 8.1, which will access its manually added scattering factor set or

(b0 its chemical symbol and valence, which will access the incorporated list of f-coefficients taken from the Int=l Tables. NTYP must start in column 11. The nominal valence is to be indicated for the X-ray case (e.g. Ca+2) but not the neutron case.

x, y, z - fractional atomic coordinates
B - isotropic atom displacement ('temperature') parameter for the atom
So = site occupancy. It should be 1.000 if all equivalent positions are exactly fully occupied. It is refinable.

11-42 (16X,5F8) CX, CY, CZ =codewords for fractional atomic coordinates
CB = codeword for the atom's isotropic 'thermal' parameter
CSo = codeword for site occupancy

11-43 (6F8) Beta11, Beta 22, Beta 33, Beta 12, Beta 13, Beta 23
anisotropic 'thermal' parameters

11-44 (6F8) CB11, CB22, CB33, CB12, CB13, CB23,
codewords for the atom's anisotropic thermal parameters

11-5

11-51 (2F8) SF = scale factor
B_o = overall 'thermal' parameter

11-52 (2F8) CS = codeword for scale factor
CB_o = codeword for overall 'thermal' parameter for the phase

11-6

11-61 (6F8) U, V, W, CT, Z, X, Y = FWHM ("H") parameters for the expression
$H_K^2=U\tan^2\theta+V\tan\theta+W+CT\cot^2$_ for NPROF = 0-3, 5,6
$H_K^2=U\tan^2$_ $+V\tan\theta+W$ for NPROF = 4 (split Pearson VII)
Z, X & Y are used only when NPROF = 7. When not used, their values must be set to zero (0.00)

11-62 (6F8) CU, CV, CW, CCT, CZ, CX, CY - codewords for the FWHM parameters

11-7

11-71 (6F8) A, B, C - cell dimensions a, b, c in Ångstroms
ALPHA, BETA, GAMMA - cell angles a , ß , ? in degrees

11-72 (6F8) CA, CB, CC, CALPHA, CBETA, CGAMMA - codewords for the cell constants.
Note that within the operations of the program the angles are expressed in terms of cross products of the reciprocal-space cell-edge vectors in the program. Thus, for example, in a trigonal or an hexagonal system the codeword CGAMMA must be the same as CA (=CB).

11-8

11-81 (3F8) Enter G_1, G_2, P, where G_1 and G_2 are the preferred orientation parameters (see formulae below) and P is the asymmetry parameter (see RLIM in line 4 for the 2θ range over which P is effective)

11-82 (3F8) CG_1, CG_2 - codewords for preferred orientation parameters
CP - codeword for asymmetry parameter

If IASYM = 0 in line 2 , the asymmetry function is that given by Rietveld (1969)

If IASYM = 1, the asymmetry function is that given by Riello et al, (1995).

For both asymmetry models, P and its codeword should be set = 0 when the split Pearson VII profile function (number 4) is used.

G1, G2 are the preferred orientation parameters used in the formulae (see Part **2,**§IC2):

(a) if IPREF = 0 (see line 2.1), $I_{cor} = I_{obs}(G_2+(1-G_2)*\exp[-G_1 a_K^2])$
(Rietveld-Toraya case, $G_1 = 0$ for no preferred orientation)
NOTE: Expect strong correlation between the Rietveld G_1 and the phase scale factor if strong preferred orientation is present.

(b) if IPREF = 1, $I_{cor} = I_{obs}(G_1^2\cos^2?_K+(1/G_1)\sin^2?_K)^{-3/2}$
(March-Dollase case, $G_1 = 1.000$ for no preferred orientation)

where a_K is the acute angle between the scattering vector (e.g. $\mathbf{d}_K$) and the orientation direction (e.g. fiber axis direction) specified in line 11-2.

A special feature: With the IPREF = 0 model, setting G_1 to any number >99.0 for a phase causes the program to generate for it only those reflections for which **d*** is parallel to the preferred orientation vector PREF specified in line 11.2, as though that phase had a 100% complete fiber-axis texture.

Note, however, that since the LP factor has not been corrected for the texture, the relative intensities among orders of a reflection so generated are not correct but are the same as those for a randomly oriented powder. This is true for all preferred orientation corrections in this program.

Line	Format	Description

11-9 MIXING/SHAPE PARAMETERS

NOTE: for the usual pseudo-Voigt (NPROF=5) the mixing parameter, ? , can vary with 2? as

?__ NA + NB *(2?)

where NA and NB are refinable and NC must be set = 0.

For the Pearson-VII functions (NPROF=4 and NPROF=6) the shape parameter, m, is calculated as

$$m = NA + NB/(2\theta) + NC/(2\theta)^2 \quad (m=m \text{ or } m_L \text{ or } m_H)$$

where NA, NB and NC are refinable parameters. For NPROF=5, NC and its codeword must be set =0.

For all other profiles listed (1-3, 7), NA, NB & NC and their codewords must all be set to zero.

11-91	(3F8.4)	NA,NB,NC for pV and PVII or the low angle side of SP7
11-92	(3F8.2)	CNA,CNB,CNC (Codewords for NA, NB, NC)
11-93	(3F8.4)	NA,NB,NC for the high angle side of SP7 ('Split Pearson VII')
11-94	(3F8.2)	Codewords for NA, NB, NC on the high angle side of SP7
11-95	(F8.4)	A, the SP7 asymmetry factor
11-96	(F8.2)	CA, codeword for A

NOTE: When the Split PVII function is not being used, the parameters and codewords for both m and A on the high angle side should be set to zero.
When the Split PVII function is being used, one should start with small parameter values and proceed cautiously, as this function tends to 'run away' easily. One strategy that has been used successfully is that of using the results from refinement with PVII for the initial values in SPVII and then alternating refinement of the parameters for the High side and the Low side.

NEXT PAGE: Example of an Input Control File for a simple two-phase case as it appears on the screen. This is a copy of the QIN file in the QTEST subdirectory on the distribution diskette. Other examples are provided in the test cases. The ICF for the test case with an internal standard and an underlying amorphous component may be particularly interesting for advanced users.

```
QDATA 2 PHASE TEST CASE QUARTZ+ alumina  8FWHM  13.5.99  2/24
   0   5   2   0   0   0   0   1   0   1   0   0             LINE 2.1
00211 10000 10000 000                                      LINE 3
 1.54050 1.54430  .50000 90.0000  8.0000   .8009  1.0000 35.0000   .0000
   2 .10 .95 .95 .95 .95                                   CYCLS EPS RELAX P_CALC
      24                                                   PARAMS REFINED
   .0000  -.0183   .0000   .0000   .0000  1.0000   .0000 ZER DISP TRANS p q r t
   .0000 21.0000   .0000   .0000   .0000   .0000   .0000 CODEWORDS
    38.62   116.96   134.91      .00      .00      .00   BACKGROUND
  31.0000  41.0000 181.0000    .0000    .0000    .0000   CODEWORDS
Alpha quartz                                               PHASE NUMBER  1
   2   3  1.0000 .00 .001.00    .00                        #ATMS #FU AFQPA PREFDIR ISWT
P 32 2 1                                                   SPACE GROUP
SI1     3 SI+4    .47002  .47002  .00000  .54982 1.00000  LBL M NTYP x y z B So
                   91.00   91.00     .00  190.50     .00  CODEWORDS
  .00490  .00270  .00490  .00140 -.00010 -.00002          BETAS
     .00     .00     .00     .00     .00     .00          CODEWORDS
O1      6 O-1     .14855  .41914  .11983 1.14715 1.03409  LBL M NTYP x y z B So
                  101.00  111.00  121.00  200.50  210.40  CODEWORDS
  .01430  .00000  .01900  .00850 -.00320 -.00420          BETAS
     .00     .00     .00     .00     .00     .00          CODEWORDS
.658E-02   .0000                                           SCALE Bo(OVERALL)
   11.00     .00
  .01959 -.00327  .00594  .00000  .00000  .00000  .00000 U V W CT Z X Y
  160.25     .00   80.25     .00     .00     .00     .00
  4.9139  4.9139  5.4052 90.0000 90.0000120.0000         CELL PARAMETERS
   61.00   61.00   71.00     .00     .00   61.00
 1.00000  .00000  .16680                                  PREF1 PREF2 R/RCF_ASYM
     .00     .00  130.50
   .5100   .0000   .0000                                  NA NB NC (MIX_PARAMS)
  140.50     .00     .00
   .0000   .0000   .0000                                  NA NB NC (HIGH SIDE)
     .00     .00     .00
   .0000                                                   PEARSON ASYM.FACTOR
     .00
PHASE 2   ALPHA ALUMINA                                    PHASE NUMBER  2
   2   6  1.00001.001.00 .00    .00                       #ATMS #FU AFQPA PREFDIR ISWT
R -3 C H                                                   SPACE GROUP
AL1    12 AL+3    .00000  .00000  .34998  .80000 1.00000  LBL M NTYP x y z B So
                     .00     .00  220.50     .00     .00  CODEWORDS
  .00000  .00000  .00000  .00000  .00000  .00000          BETAS
     .00     .00     .00     .00     .00     .00          CODEWORDS
O1     18 O-1     .31309  .00000  .25000 1.00000 1.00000  LBL M NTYP x y z B So
                  230.10     .00     .00     .00     .00  CODEWORDS
  .00000  .00000  .00000  .00000  .00000  .00000          BETAS
     .00     .00     .00     .00     .00     .00          CODEWORDS
.469E-04  3.2945                                           SCALE Bo(OVERALL)
   51.00  240.50
 -.03121 -.00327  .02430  .00000  .00000  .00000  .00000 U V W CT Z X Y
  170.10     .00  150.30     .00     .00     .00     .00
  4.7609  4.7609 12.9962 90.0000 90.0000120.0000         CELL PARAMETERS
     .00     .00     .00     .00     .00     .00
 1.00000  .00000  .00000                                  PREF1 PREF2 R/RCF_ASYM
     .00     .00     .00
```

```
.5850   .0000   .0000                                   NA NB NC (MIX_PARAMS)
  .00     .00     .00
.0000   .0000   .0000                                   NA NB NC (HIGH SIDE)
  .00     .00     .00
.0000                                                   PEARSON ASYM.FACTOR
  .00
```

II.B The observed data file, Tape/Unit 4

Tape 4 contains the observed (experimental) data from the 'diffractometer'. The format can be in any of several formats, depending on the type of instrument and the software used on it. The acceptable formats are here divided into categories which differ according to whether the incident beam intensity is fixed or varying and whether a single or multiple detectors are used. All require 'steps' consisting of equal increments in 2?.

The data format type is specified in the ICF by a combination of flags in line 2. For case (a) of Category 1 and for categories 2 and 3, set the flag IDATA=0. (That is the flag in position 11 in line 2.) For other cases in Category 1, the IDATA flag will be set to other values, as is shown below. For case (a) of category 1 and for categories 2 and 3 (IDATA=0), the data format is further identified in ICF line 2 by the combination of the settings of flags 1 (JOBTYP) and 7 (INSTRUM).

Category 1:
Constant incident x-ray or neutron flux and a single detector collecting x-ray or neutron data at equal increments in 2θ (JOBTYP = 0 or 1, INSTRUM = 0)

Case (0): The '**standard**' **DBWS** observed data file (Tape/Unit 4) . IDATA= 0

The first line contains the variables START, STEP, STOP, and DATAID in (3F8.3, A48) format:

START- beginning angle in degrees 2θ
STEP- step size in degrees 2θ
STOP- last angle in degrees 2θ
DATAID- An alphanumeric string identifying the data.

The rest of the file consists of the intensity data themselves in (8(F7.0,1X)) format. There may be, but need not be, a ninth column listing the 2? angle for the last datum in each row.

NOTE: The START angle assigned here must correspond to that of the first datum not in an excluded region. The STOP angle can be any angle less than that of the last datum in the file. One can select **any desired angular range** for the refinement, without removing any data from the file, by
(i) declaring an excluded region (NEXCRG in line 2 of the ICF) and specifying its bounds (line 7 of the ICF) as beginning at the START angle declared in the first line of the data file and ending at the desired beginning angle for the calculations and
(ii) assigning the desired ending angle to STOP.

Case (1): **Free format**. IDATA= 1

The first line contains the variables START, STEP, STOP, and DATAID in (3F8.2, A48) format, just as in case (0). The rest of the file consists of the intensity data, only, in free format. Any number of columns of any width are allowed. The delimiters are commas or spaces. Angle data are not allowed.

Case (2): **GSAS 'standard'** format. IDATA= 2.

The DBWS program searches through the header material that starts with 'BANK' to find the start angle, step size, and stop angle. The rest of the file consists of the intensity data in format 10(I2,F6.0). No commas or angle data are allowed. Note that in the 'standard' GSAS format for the data all rows must be filled out to 80 characters. Use spaces if necessary to fill out the row(s).

Case (3): **Philips UDF** format. IDATA= 3.

The program searches through the (voluminous!) header material for the lines "DataAngleRange" and "ScanStepSize", from which it gets the start angle, stop angle, and step size information. It then looks for the start of the data file immediately following the "RawScan" line. The intensity data are expected to be in format (8F8,1X) where X in this case is actually a comma

Case (4) **Scintag "text"** format. IDATA= 4.

The program searches through the multi-line header for the start angle, step size, and stop angle. It then ignores the 'axis' blocks and goes to the four column main output: angle, count, time, and e.s.d..

The DBWS program then reads the intensity data from column 2 and ignores the other three columns

Case (5) **Siemens UXD** format. IDATA = 5.

As in cases 2-4, above, the program searches through the header material to find the start angle, step size and stop angle (or step), ignores the rest of the heading material and proceeds to read just the intensity data (in counts) from the rest of the file.

Case (6) **Rigaku ASCII** format. IDATA = 6.
.
The program proceeds as in (5).
Category 2.
Varying incident x-ray flux (e.g., synchrotron x-radiation) and a **single detector** collecting data in equal increments of 2?.
(JOBTYP = 0, INSTRM = 1, IDATA= 0).

DBWS programs use the normalized intensity data both directly as the observed data and, with the other data provided in the file, to reconstruct the originally observed total count at each step and, from that, to assign the statistically correct weight to each observed step intensity y_{io} .

The first line contains the variables DATE (for date or place) and DATAID in (A5,A56) format:

Line Format Content

1 (A5,A56) DATE - Identifies the format of the data. Currently supported values are (a) OCT85, FEB respectively.

DATAID - an alphanumeric string identifying the data.

2 (I8,F8,G10) NRANGE - No.of blocks in which the data are written.
CHMBRI - Value of incident-beam counts-per-step to which all data are to be normalized. (DBWS assigns the weights on the basis of the actually observed, not normalized, number of counts at a step.)
TAUK - Coefficient for deadtime correction for the diffracted-beam detector (in seconds)

3. For each of the NRANGE no. of blocks:

3.1 (6F8) ANGMIN - beginning angle for this block in °2?.
STEP - step size in °2? (identical for all blocks)
ANGMAX - last angle for this block in °2?.
STPTIM - counting time at each step in seconds
OFSTI0 - "dark current" counts-per-step in the incident-beam monitor
OFSTI1 - "dark current" counts-per-step in the diffracted-beam detector

3.2 IPTS lines of data in one of the following formats, where IPTS is the no. of data points (i.e.

(24X,F7,1X,F7) for DATE = (OCT85 OR FEB86)

(51X,F10,1X,F10) for DATE = AUG86
(37X,F9.0,1X,F9.0) for DATE = SRS83
(29X,F9.0,10X,F9.0) for DATE = SRS91

where I_o and I_1 are the data entered in F format and
I_0 - actual total counts from the incident beam monitor at this step
I_1 - actual total counts from diffracted beam detector at a given step

Also, I_1 comes before I_o in the OCT85 and FEB86 formats and vice versa in the other three.

Category 3. Fixed wavelength, constant intensity (or monitor count) neutron beam (for example) incident and **multiple** diffracted-beam **detectors**, but not all detectors contribute to the count at every step (e.g., instruments D1A and D2B at ILL and the HRNPD at BNL).
(JOBTYP = 1, INSTRM = 1, IDATA= 0)

The first line contains the variables START, STEP, STOP and DATAID in (3F8,A56) format.
START - beginning angle in °2?.
STEP - step size in °2?.
STOP - last angle in °2?.
DATAID- An alphanumeric string identifying the data.

The rest of the file consists of the data and the no. of counters in (10(F2,F6)) format:

NCOUNT - no. of counters
Y(I) - Average intensity

DBWS programs use these data to reconstruct the originally observed total count at each step and, from that, to assign the statistically correct weight to each observed step intensity y_{io} .

II.C. Background data file -

1) **`Tape/Unit 3'**

If NBCKGD = 1 (ICF line 2), this file contains background data to be subtracted from the diffraction pattern data (Tape 4). The start angle, step size, stop angle, and data format must be the same as they are in Tape 4. In the present version of the program, this requirement probably means that this option for Tape 3 can only be used when the experimental pattern data are in the 'standard' DBWS format, (8(F7.0,1X)).

If NBCKGD <1, Tape 3 is used only as a scratch file.

If NBCKGD ≥2, (a) Tape 3 is used only as a scratch file and (b) the background will be interpolated from the NBCKGD number of intensity/angle points listed in the ICF by the operator according to the instructions in ICF line 6.

2) **Tape/Unit 11**

If NBCKGD = -1, this file contains "background" data for which the scale factor can be refined in the Rietveld refinement process. These data may be partly calculated (e.g., Compton and disorder-diffuse scattering) or real data from an amorphous or other sample, or both. (See Reillo, Fagherazzi, et al., 1995)

For the Tape 11 data (i.e., for the amorphous or other material for which only the scale factor is to be refined):

The first line contains the variables START1, STEP1, STOP1, TMV, SW1, DATAID1 (6F8.2, A16):

START1- beginning angle in degrees 2_, it must be equal to START in the main data file (tape 4)
STEP1- step size in degrees in 2θ, it must be equal to STEP in the main data file
STOP1- last angle in degrees 2θ, it must be equal to STOP in the main data file
TMV-linear absorption coefficient for the amorphous phase (cm^{-1})
SW1- sample thickness (cm)
DATAID1- an alphanumeric string identifying the data

The rest of the file consists of the intensity data in free format.

These background data from Tape 11 are called for by inclusion of the file name in the fifth position on the command line used to start a refinement. For example:

PGM DATA ICF OUT TAPE11

III. Description of Output files

A. Plot files.

1) PLOTINFO

A file called PLOTINFO (identified internally as Unit 9) is generated by DBWS. It is an alpha-numeric file containing the title information from line 1 of the Input Control File, a separately labeled listing of the geometrically possible Bragg reflection positions and their Miller indices h,k,l for each phase involved in the refinement (flag 3 in line 3 of the input control file must be `on' for these positions to be included), and a listing of the calculated and observed intensities at each step, i.e., y_{ic} and y_{io}. With PLOTINFO, the DMPLOT program (offered as a Shareware item with the PC version of the DBWS program) can produce a plot of the calculated and observed patterns, the difference plot, and position markers for the possible Bragg reflections from each of the phases involved either (a) on-screen, which can then be dumped to a printer to provide a hard copy, or (b) directly via a plotter. With PLOTINFO and the additionally generated binary file, PLOTINFO.BIN, DMPLOT can display on screen (1) the Miller indices for the various reflections and (2) the component patterns (one for each phase) which make up the total calculated pattern in a multiphase refinement. DMPLOT also offers Mouse control, dynamic `zoom', on screen display of 2? and d values at the cursor position, and several other advanced features. Apart from Rietveld refinement plots, DMPLOT can also display up to 4 `raw data' patterns simultaneously on screen and move them around relative to each other. To use DMPLOT in this mode, the raw data file names must have the extensions *.rit for x-ray data *.neu for neutron data.

It should be a relatively simple matter to make a useful Rietveld refinement plot from PLOTINFO with any of several other generally available software packages.

2) PLOT FILES that can be generated when NBCKGD = -1 (Riello, et al. case) and one or more of flags 12-18 in ICF line 3 is/are set to 1.

File name	Flag no.	Description
PLOTOSS	12	Total observed plot file corrected for ‘absorption’ scattering expressed in counts
PLOTCAL	13	Total calculated plot file, obtained by summing the background
PLOTPOL	14	Background representation obtained from refining it with a polynomial
PLOTCOM	15	Plot file for total Compton scattering contribution to the background, corrected for the monochromator band-pass function if a monochromator is present on the diffracted beam
PLOTDIS	16	Total uncorrelated, calculated disorder contribution to the

background

PLOTAM 17 Plot of Tape 11 data (e.g., "amorphous") corrected for 'transmissivity'

PLOTBIG 18 Multiple columns file, to do plots using commercial programs like Origin™_ Excel™ etc.. It contains, in each column respectively, PLOTOSS, PLOTCAL, PLOTAM, PLOTAM + PLOTPOL, PLOTAM +PLOTPOL +PLOTCOM, PLOTAM + PLOTPOL + PLOTCOM + PLOTDIS, and weighted residuals defined as $\Sigma(Ycal - Yobs)^2/\Sigma(Yobs)$]

NOTE: if the PLOTBIG flag in ICF line 3 is set to 1, the other 6 PLOT* files will not be created. To have those plotfiles created, set PLOTBIG=0

B. **An updated Input Control File** (`Tape 5'), which is updated with the final-cycle parameters, is output if flag 5 in line 3 of the ICF is set at 1. Routinely, one does want this file to be generated so that the next step of the refinement process can proceed from the last ending point without extra keyboarding.

NOTE:. The updated ICF is written over the old one, which is then lost.

C. Output to terminal during run

This file is assigned to the terminal when the program is run interactively, e.g., when the program is run on a PC or workstation. It displays the program name (DBWS) and version, the sizes declared for the five most frequently redimensioned arrays, the title information for the run, the number of cycles called for, the number of parameters being refined, the START and STOP angles plus the step size, and a dynamic series of dots marking the progress of the program through the current cycle. At the end of each cycle, it reports R-p, R-wp, R-exp, and S (GofF). We thank Dr. H. Marciniak for his very useful additions of much of the information content and the dynamic display to this output-to-terminal. A compilation of R-p and R-wp cycle-by-cycle values are saved to the working directory as "Unit 7".

D. The main output file - (`Tape 6').

1. <u>Standard parts of the main output file.</u>

All control variables and structure parameters are printed out so that a given run can be reconstructed unambiguously. At the end of each cycle, the parameters with their shifts (applied, not the full calculated ones), the quantitative phase analysis result (wt. % and molar %), plus various numerical

criteria of fit (e.g., R's and e.s.d.'s) and related values are printed out. See §III.E for definitions of the various criteria and comments about their interpretation.

2. Optional outputs.

The following optional outputs, mostly in the main output file, are selected (1, 2 or 3) or suppressed (0) by the settings of the flags in line 3 of the ICF (input control file). They are numbered below in the order of their appearance in ICF line 3.

Flag # Items output if flag setting is 1 or, for flags 3 and 11, 1 or 2.

1. Observed and calculated intensities. After the last cycle, a table of the observed and calculated counts at each step can be printed.

2. Line-printer plot. (For use when there is nothing else available!)

3. It is this same flag which must be set `on' to cause the inclusion of the possible Bragg reflection positions in the PLOTINFO file. Different choices of the flag ("IPC") value produce these results in the main output file:
IPC =1, $|\text{structure factors}|^2$ & R-Bragg
=3, as for 1 plus $|F|_{obs}$, $|F|_{calc}$ & R- F with the F_{obs} and F_{calc} written in A + iB form to include the phase information
= 2, as for 3 except that the phases are reported in terms of the phase angles

4. Correlation matrix.

5. This flag controls creation of the updated input control file, discussed in §III.B, above, which is out

6. Reflection list - A list of the reflections generated from each phase with the initial input para profile-component mixing parameters.

7. Corrected data list - A list of the point-by-point intensity data as corrected for background, the assigned weight, and the identifying number of the highest angle and the lowest angle reflections which contribute to the data point. The reflection list is sorted so that contributing reflections may be indicated by giving a pair of integers. K1 is the number of the reflection in the merged list at the smallest 2? angle contributing to the point. K2 is the highest angle (2?) reflection for contribution.

8. Merged reflection list (includes hkl, FWHM, 2?, I_c, I_o, & R-Bragg.)

9. Listing of the symmetry operators used

10. Plot files which are stored and printed out separately. See part A of this section, §III.

11. A stacked summary of the cycle-by-cycle values of each parameter, another of the R valu generation.

E. Definitions and interpretations of the numerical criteria of fit.

1. Numerical criteria

a) The standard deviation, a mathematical statistic that should not be confused with

$$\text{e.s.d.} = s_{jj} = \{ M^{-1}_{jj} S (y_{oi}-y_{ic})^2/(N-P+C) \}^{1/2}$$

where

M^{-1}_{jj} is the corresponding diagonal element in the inverted normal matrix,

N is the number of observations,

P is the no. of parameters that are refined, and

C is the total number of constraints.

b) The numbers after "R-factors" are:

R-p = $100\ S|y_{oi}-y_{ci}|/S|y_{oi}|$, the pattern R-factor.

R-wp = $100 \{ S\ w_i(y_{oi}-y_{ci})^2/S\ w_i\ (y_{oi})^2 \}^{1/2}$, the weighted pattern R-factor.
R-expected = $100 \{ (N-P+C)/S\ w_i\ (y_{oi})^2\}^{1/2}$,
where N is the total number of data points ("observations"), P is the number of parameters adjusted, and C is the number of constraints applied.

S is the "goodness of fit", the ratio R-wp/R-expected.

Calling for the reflection list (flag 3 in line 3 of the Input Control File) causes R-Bragg and R-F to be printed out at the end of the final cycle, where

R-Bragg = 100 S|"I_o "- I_c|/S"I_o",

which is the R-value for Bragg intensities, and

R-F = 100 S| |$F_{"obs"}$| - |F_{calc}||/ S |$F_{"obs"}$|,

which is the R-value based on the deduced "observed" and calculated structure amplitudes. Some workers find this useful in ab initio structure determination.

c) D-W D is the Durbin-Watson statistic, *d*, (Hill and Flack, 1987). It is included in the output from

$$d = \sum_{i=2}^{N} (\Delta y_i - \Delta y_{i-1})^2 / \sum_{i=1}^{NDELTA} y_i^2$$

each cycle as a possibly useful additional indicator of the progress of the refinement. It is given by

where ?$y_i = w_i(y_{io} - y_{ic})$. In DBWS-9411 and 9807 the w_i's are all taken to be 1.00 in order to yield the unweighted form. That is preferred by some statisticians over the weighted form discussed by Hill and Flack (1987) and given in Schwarzenbach, et al. (1989). (The weighted form is used in DBWS-9006.) This *d* is sensitive to misfit of the calculated and observed reflection profiles, both because their areas may differ as well as their positions and, importantly, because their shapes may be inherently different. Consider, for example, how *d* would be small for a symmetric calculated Lorentzian profile used to fit a symmetric Gaussian experimental profile even if the two profiles had the same peak positions, peak heights and areas.

2. A Comment about interpretation of R's:

R-p and R-wp are not directly comparable to the R-values obtained in single crystal refinements. R-Bragg and R-F come closer to that mark but suffer from the fact that "I_o" is not directly observable where reflection profiles overlap (the usual case). The actual observed intensity in a clutch of reflections is parceled out among the component reflections in proportion to the calculated reflection intensities to produce the "I_o's".

As is well known to experienced users, R-p and R-wp are also very sensitive to the background level if the background is included in the y_{oi}'s above. It is so included by DBWS-9807 when the refinable background model is used. It is obvious that R-wp (for example) will be decreased as the background level is increased (signal-to-noise level decreased) because it is easier to get a good fit to a function that varies slowly and near to monotonically with angle, as the background does, than to one that has many sharp maxima along the way, as the pattern of the Bragg reflections does. Experienced users therefore do not expect to judge the relative quality of Rietveld refinement's made with different data sets and even different materials by the relative R-wp or R-p values. Those R-values are, however, good

indicators of the progress of a particular refinement. Obviously, it would be helpful in some cases if the DBWS programs output the various R-values as calculated both with and without the background included. Coding for that would probably not be very difficult, but it has not yet been done. Users, particularly those to whom this effect of background is a new thought, may find interesting the Jansen, Schäfer and Will (1994) paper in which are given specific examples of the effects of excluding vs including the background in R-value calculations.

Almost all users may find interesting the Cox and Papoular (1996) paper on R-factors, Errors and Significance tests. Although 'Synchrotron Data' is a part of the title, the content of the paper has much wider potential applicability.

PART 3. Further comments on using DBWS-9411 AND 9807 with a PC

A. Compiling

The executables provided in this distribution package and used for the test-case examples given here were produced with the Microsoft FORTRAN PowerStation compiler. It has the capability of producing executable versions which can make use of nearly all of the RAM available (i.e, not limited to 640K). We have run some of the executable versions under MSDOS 6.0. We suppose, but have not demonstrated, that they would also run under some older versions of MSDOS. They also ran very well in the Windows 95/98 environment. See §C2 of Part **3**.

B. Plots

1. Production and character

Although it has no plotting code embedded in it, DBWS-9807 does produce the output file PLOTINFO which can be used by other programs to make `Rietveld refinement' (RR) plots.

The separate plotting program, offered as SHAREWARE, for which the MSDOS executable code is here included, is DMPLOT.EXE. It will use PLOTINFO or specified other file with the same structure to make a plot with selectable X and Y magnifications, either on-screen or (for better resolution) with many HP and similar plotters, of the observed and calculated patterns, the difference, and the Bragg-reflection position markers for all phases. The on-screen plots can then be dumped to a laser or dot-matrix printer. The program works with various commonly available graphics adapters for both monochrome and color monitors of various resolution capabilities. DMPLOT has many very useful features, including separate plots for the phases, multiple zoom, d and I readouts, etc.. See the “Read.me” file in the DMPLOT subdirectory on the distribution diskettes.

DMPLOT is the property of its author, Dr. H. Marciniak. The executable version is offered here as a 'Shareware' item, which means that you, the user, should try out the program and, IF you find it really useful, you should send the requested fee to the author. Dr. Marciniak's address is included on one of the screens you will see when you use his program.

The usual **format** of the RR plots is that the observed pattern is plotted in the upper field as a series of unconnected symbols (dots, squares, or e.s.d. bars) the calculated pattern is plotted in the same field as a solid line formed by straight line connections of adjacent points, the difference pattern (observed minus calculated) is plotted in the lower field as a continuous curve, and the positions of the geometrically possible Bragg reflections are indicated as a series of short vertical lines in the intermediate field. To let them be distinguished, the `Bragg markers' for each phase are plotted at different levels in the intermediate field to let them be distinguished. However, the user may choose other positioning of the plots and other

symbols or connections.

The RR plots in the FIGURES section are screen dumps of plots produced with DMPLOT. The jagged appearance of the enlarged plot sections is due to the pixel size, not to any problem with DMPLOT. Had we used the output-to-plotter feature of DMPLOT, this jagged appearance would not be present.

2. Adroit use - an example

In the following figures one may see an **example of the use of RR plots to guide** fine tuning of a refinement from a `maybe we can quit here' stage to a very much better stage. The data used are in the QTEST subdirectory in the distribution package. The codeword numbers assigned to the various paraemters varied are shown following table.

Codeword numbers for parameters in sample used for Figures 1-5.

I = quartz phase II = alumina phase

Codeword	Parameter(s)	Phase
1	Scale factor	I
2	displacement of sample	all
3	background coeff. #1	all
4	background coeff. #2	all
5	Scale factor	II
6	a, b	I
7	c	I
8	W - (in FWHM)	I
9	x,y of Si	I
10	x of O	I
11	y of O	I
12	z of O	I
13	asymmetry (profile)	I
14	NA - mixing parameter	I
15	W	II
16	U	I
17	U	II
18	background coeff. #3	all
19	B for Si	I
20	B for O	I

21	So (occupancy) for O	I
22	z of Al	II
23	x of O	II
24	B(overall)	II

Figures 1 - 5 show the progressive improvement in the refinement, done with a part of the QDATA (20.12 - 60.10 °2?), as the `zoom' feature first revealed the character of the remaining misfit at each stage and then appropriate changes were made in the calculated profile tail lengths and in the number and selection of parameters varied. In the process, the Goodness-of-Fit parameter went from being >2.0 (usually not considered to be very good) to 1.40 (usually considered to be quite good) and R-wp went from 18.1% to 13.77%. From the data in the heading for each plot and the preceding table of the codewords numbers of the parameters varied in this refinement sequence, one can deduce just what was changed at each step. The length set for the calculated profile tails is the number of FWHM's given in the heading. The note resembling a fraction that appears there, i.e., 5/21, is the (number of cycles in this pass)/(number of parameters varied). From the following table, one can see which parameters have codeword numbers small enough so that they were included in the number of parameters varied, 21 in this case.

Figure 6 is the RR plot corresponding to data in the subdirectory FTEST on the distribution diskette. Fig. 6a shows the plot for the range of the fluorapatite data used (15 - 90 °2?). Figure 6b shows a closeup of the most troubled looking portion of Figure 6a. On such inspection, and noting that the R-exp is unusually small, one sees that the refinement appears to be better than would be expected from the GofF ('S', the "Goodness of Fit") alone.

Figure 7 is an enlarged portion of a RR plot from a recent PZT study of Dr. Paiva's. It is an example of how DMPLOT can display the separate calculated patterns in a multiphase refinement. In this case, there are four phases.

C. **Execution procedure with a `PC'**

1. In DOS

A possible Start-up routine:

Create a subdirectory on the hard disk

Copy all related files in to that subdirectory, including the executable versions of the programs yc

Make sure that you are using a version of your ICF that is compatible with this version of the DBWS program. You can use DBWS-9807 to convert an ICF used for DBWS-9411 to a format compatible with DBWS-9807. See the instructions given in Part 2, §IIA1.

Execution:

Modify the INPUT CONTROL FILE (ICF) and DATA files as needed, using the instructions in **Part 2** of this guide for the Input Control File (`Tape 5') and the observed data file (`Tape 4').

To run the program in the MSDOS environment, on the command line type:

DBWS DATA INPUT OUTPUT [Tape 11] [Tape 3]

using single spaces between the entries, the actual file names you have for the executable program, the observed data file, the Input Control File, and your choice of output file name, respectively. Tape 11 and Tape 3 relate to (a) data representing an 'amorphous' component and (b) a predetermined or assumed whole-pattern background, respectively. For most work, they are not used.

2.**Using DBWS in a Windows environment**

Although they are DOS programs, the executables provided for DBWS can run in the Windows 95 (also 98 and NT) environment in a DOS window automatically called up when the program execution starts. Advantage can thereby be taken of some of the 'drag and drop' and file handling conveniences of Windows 95/98.

In a Windows environment you may either (1) work in a DOS window into which you can drag-and-drop the command line files, in sequence, or (2) you can drag-and-drop them onto the command line that is brought up when you select "run" from the Windows Start Up menu. The second option here takes more advantage of Windows features and eliminates retyping of the same command line..

With a good text editor that will operate in Windows and not leave 'tracks' (e.g., control characters and anything else not compatible with ASCII text), one may enjoy essentially all of the benefits of the Windows operating system while using DBWS.

The text editor that we are presently using with considerable satisfaction is the Programmer's File Editor ('PFE32') from Alan Phillips at Lancaster University (UK). It is available free from his website:

http://www.lancs.ac.uk/people/cpaap/pfe/

We find it is very helpful to keep a 'Shortcut to Pfe32.exe' icon on our 'desktop', preferably in or near one corner of the screen where it can be accessed with little or no movement of the windows that are open.

<u>A procedure for using DBWS under Windows that has worked well for us</u>

The first step in the procedure is to prepare all of the files that will be needed for the next set of Rietveld refinement cycles (the next 'run') and to put them in one subdirectory not far from the root directory. The results worth keeping can be transferred later from this 'working directory' to another, more comprehensive file directory. The purpose of the 'not far' specification is to maximize the probability that files generated during the refinement run will find their way back to your working directory rather than going off someplace where you have to hunt for them, e.g. in the Windows directory. *

The files that are always wanted in the working directory are (1) the executable version of DBWS to be used (e.g., DB9807.exe), (2) the DOS extender file DOSxmfs.exe, (3) the data file for the particular case (e.g. case1.dat), (4) the input control file (the “ICF”, e.g., case1.in), (5) the output file named as wanted (e.g., case1.out. It can be an empty file at this point), and (6) the two DMPLOT files (i. e., dmplot.exe and dmplot.cfg) which you will use to examine the refinement results as you proceed. Other files that are needed in this working directory for some refinement options are the 'amorphous' data file (Tape/Unit 11) for which the scale factor will be refinable and a file containing predetermined whole-pattern background data (Tape/Unit 3) which are to be subtracted from the experimental diffraction pattern data.

The next step is to click on START (lower left corner of your screen) and select ‘run’. That opens a command line (labeled 'open') into which you will drag-and-drop the needed files from the working directory in the sequence: program file, data file, ICF, and 'out' file. For some refinement options you will have to put a fifth and sometimes a sixth file name on the command line. These are the file names for the data in Unit 11 and in Unit 3, described in the previous paragraph. If both are used, the file containing the whole-pattern 'amorphous' component data is entered in the fifth place. Be sure to put all of the files that will be needed into the working directory first so you can drag-and-drop them onto the command line. By doing so you will avoid the tedium and typographical errors of having to type in both the file names and the paths to them.

If all has gone well, when the specified number of cycles is completed you will find in the working directory the new 'out' file, the ICF (rewritten if you called for that with flag 5 in line 3 of the ICF), a PLOTINFO file, a POTINFO.BIN file and a file called 'unit 7' along with the files that have not been changed. You will probably want first to look at the 'Rietveld' plot resulting from the run just finished. You can do that by dragging PLOTINFO onto DMPLOT.EXE and following the screen instructions. The PLOTINFO.BIN file is the one that makes it possible for you

(1) to see all of the reflection indices for all phases by simply pressing the F3 key and

(2) to see the individual calculated patterns for all phases superimposed on the standard Rietveld plot.

You can now look at the content of, and edit, any text file by dragging it to the desktop and dropping it on the Pfe32.exe icon. If you have enough information from the plot to make wise choices now for improving the fit, you may wish to go directly to editing the ICF for the next run (i. e., batch of cycles).

You do that, of course, by dragging the ICF to the Pfe32.exe icon to open the file and then using the Pfe features to do the desired editing. You may want to look at the 'unit 7' file to see, again, the R values that appeared on the screen during the run. At some point, you will want to look at the 'out' file, perhaps print parts of it, (all easily done with Pfe32.exe) and perhaps check the magnitude and pattern of the parameter shifts, the calculated e.s.d.'s for them, and the correlation matrix in order to guide your choice of changes to make in the ICF for the next run.

When you have finished setting up the ICF for the next run, you can press the Start button and then 'run', again. The command line you used before now appears. If the file names have not changed you need do nothing but press the 'OK' button and the computer takes off on the next set of refinement cycles while you look on with delight at seeing all this work being done for you while you just sit there.

---

*If you do not keep all of the needed files, including program files, in the working subdirectory, the problem may then occur that a file created during the operation of the program will go to another directory. That will usually be the Windows directory, where at t he expense of some effort and exasperation it can be captured and brought back to the working directory. However, DBWS-9807 includes some special programming that is supposed to avoid that problem by sending a newly created file (e.g., PLOTINFO) to the same place that the main output file (e.g., *.out or whatever other name was specified in position 4 of the command line) goes. To assure that the place to which it goes will be the working directory, it is necessary either (1) to have the *.out file in the working directory before it is dragged over and dropped on the DOS window in which the DBWS program is about to run or (2) to type out, in the command line being constructed in the window, the full path for the *.out file --- which, of course, gives but little advantage over the plain DOS procedure. With option (1), above, the *.out file thereby brings its path information with it. This feature has worked well for the PLOTINFO and PLOTINFO.BIN files in our PC operating system (WIN95/98 with a PII chip).

REFERENCES

Caglioti G, Paoletti A, and Ricci FP, (1958) Nuclear Instruments and Methods, **35**, 223-228.

Cheary, R. W. and Cline, J. P., (1994) Adv. in X-ray Analysis **38**, 75-82.

Cox, D. E. and Papoular, R. J., (1996) Mat. Sci. Forum, v. **228-231**, pp. 233-238.

Hastings JB, Thomlinson W, and Cox DE (1984) J. Appl. Cryst. **17**, 85-95.

Hill RJ and Flack HD, (1987) J. Appl. Cryst. **20**, 356-361.

Hill RJ and Howard CJ, (1987) J. Appl. Cryst. **20**, 467-474.

Jansen E, Schäfer W, and Will G, (1994) J. Appl. Cryst. **27**, 492-496.

Lowe-Ma, C. K., Cline, J. P., Crowder, C. E., Kaduk, J. A., Robie, S. B., Smith, D. K., and Young, R. A

Pitschke W, Hermann H, and Mattern N, (1993) Powder Diffraction **8**, 74-83.

Pitschke W, Mattern N, and Hermann H, (1993) Powder Diffraction **8**, 223-228.

Riello, P., Canton, P., and Fagherazzi, G. (1995) Powder Diffraction, **10**, 204-206.

Riello, P., Fagherazzi, P., Clemente, D. and Canton, P. (1995) J. Appl. Cryst. **28,** 115-120.

Riello, P., Canton, P., and Fagherazzi, G. (1997) Powder Diffraction **12,** 160-166.

Rietveld HM, (1967) Acta Crystallogr. **22**, 151-2.

Rietveld HM, (1969) J. Appl. Cryst. **2**, 65-71.

Schwarzenbach D, Abrahams SC, Flack HD, Gonschorek W, Hahn Th, Huml K, Marsh RE, Prince E, R

Smith, DK and Young RA, (1998) "Extracting Peak-Height d-I data from Rietveld analyses for the Powder diffraction File", Presented at the 47th Annual Denver X-ray Conference 3-7 August 1998; To be published in Advances in X-ray Analyis **42**, 1999? 2000?

Sparks CJ, Kumar R, Specht ED, Zschack P and Ice GE, (1992) Adv. in X-RayAnalysis **35**, 57-62.

Suortti P, (1972) J. Appl. Cryst. **5**, 325-331.

Taylor JC and Matulis CE, (1991) J. Appl. Cryst. **24**, 14-17.

Thompson P, Cox DE, and Hastings JB (1987),J. Appl.Cryst. **20**, 79-83.

Toraya H, (1986) J. Appl. Cryst. **19**, 440-447.

Wiles DB and Young RA, (1981) J. Appl. Cryst. **14**, 149-151.

Young RA and Desai P, (1989) Archiwum Nauki o Materialach **10, 71-90.**

Young RA, Sakthivel A, Moss TS and Paiva-Santos CO (1995) "DBWS-9411, an Upgrade of the DBWS*

Young RA and Wiles DB, (1982) J. Appl. Cryst. **10**, 262-269.

APPENDIX A

OTHER PROGRAMS

1. Other Rietveld-refinement programs

There are now many other Rietveld analysis programs available. Most are distributed by the authors or their institutions for a nominal distribution-cost reimbursement fee or no fee. A few are commercial products, of which most seem to be based on the DBWS programs. The DBWS programs have always been (and still are) distributed without charge for the software. A report prepared for the IUCr Commission on Powder Diffraction (Smith, D. and Gorter, S., 1991, "Powder Diffraction Program Information 1990 Program List", J. Appl. Cryst. **24**, 369-402) lists 25 Rietveld analysis programs, of which 5 can be run on a PC. [That report also lists programs for many other kinds of powder diffraction analyses for a total of 280 programs.]

Of the Rietveld analysis programs listed in that report, the two most widely distributed, at least on the record, during the last decade have been DBWS*.* (Young et al.) and GSAS (General Structure Analysis System, Allen C. Larson and Robert B. Von Dreele). FULLPROF, by Rodriguez(France) and RIETAN by Izumi (JaPan) are being increasingly widely distributed and cited. GSAS runs under UNIX as well as VMS. Recently (8 years), it has been adapted to run on a PC. It is a very comprehensive (about 100,000+ lines of code, now), sophisticated, and up-to-date program which can handle most of the calculations one could wish to do in carrying out and assessing the quality of the results of structure refinement with powders or single crystals. It can utilize multiple data sets, even of different kinds, simultaneously. The executable codes and necessary files are available by anonymous FTP from machine MIST.LANSCE.LANL.GOV (or 128.165.83.145). For `user' type `anonymous' and for the password give your e-mail address or any other identifier. Then go to subdirectory `DOS' and transfer the main files as binary files. GSAS is upgraded frequently.

FULLPROF is a PC-based distant descendant of an earlier DBW*.* program that has been much upgraded and extended. FULLPROF is rapidly becoming more and more widely used. It is available from its author: Dr. Juan Rodriguez-Carjaval, Laboratoire Leon Brillouin (CEA-CNRS), Centre d'Etudes de Saclay. 91191 Gif sur Yvette Cedex, FRANCE. It has many extra features, including models for crystallographic anisotropy in the reflection profile breadths. Dr. Rodriguez makes no charge for the program if it is to be used strictly for scientific, non-commercial purposes. The beta version of FULLPROF.98 is discussed in CPD Newsletter, No. 20, Summer 1998, pp. 35-37. It is “freely available” at

ftp://charybde.saclay.cea.fr/pub/divers/fullprof.98/windows/winfp98.zip.

A `Bucky ball' (C_{60}) module is available in an earlier version of DBWS from Dr. Theo Seigrist, 1D-348, AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974, U.S.A

There are, no doubt, many other PC-based Rietveld refinement programs available from the authors, some but not all based on DBWS*.*. For example, D. Mucha and W. _asocha (Faculty of Chemistry, Jagellonian University, ul. Ingardena 3, 30-060 Kraków, POLAND) have implemented XRS-82 to run on 386/486 PC's. A Rietveld program is incorporated. See their note in J. Appl. Cryst. **27**, 201-202 (1994).

Among the PC versions, if one is willing to pay for a program, that by Schneider (WYRIET) might be especially interesting because of its improved speed, its use of extended memory, and all of the ancillary programs that come with it. e.g., "Fourier" (electron density) mapping, bond distance and angle calculations, menu-driven preparation of the input control file, and various kinds of plots. It is available from

Margarita Schneider E D V - Vetrieb,
Starnbergerweg 18,
D-8134 Pöcking
GERMANY

2. Programs ancillary to DBWS

a) Input-file Control File preparation programs

As distributed, the Input Control File is to be prepared with a full-screen editor. For the experienced user, that method is more convenient and faster than a menu-driven system such as might be preferred by the beginning user. Such a menu system is provided as WYIN.EXE and WYIN.HLP in J. Schneider's WYRIET package. Free distribution of WYIN.EXE has been permitted.

2) **DB2dI assembly program**

The ICDD (International Centre for Diffraction Data) is always interested in adding more high quality diffraction patterns of well characterized materials to its Powder Diffraction File (PDF-2), in the established, searchable format. The PDF-2 now has >100,000 patterns in the form of d's and I's plus much related information. The ICDD offers some incentives for submission of patterns. (See the ICDD home page at www.icdd.com). Every successful Rietveld analysis results in a powder diffraction pattern which is potentially a source of a high quality d & I type pattern of a well characterized material. A direct listing of the d's and I's as they are normally output from a Rietveld refinement program is not sufficient. See below.

On behalf of the ICDD, the **DB2dI** program has been developed (D. K. Smith and R. A. Young, DXC 1998) to extract d's and peak-height I's plus other wanted information from the output and input files of a Rietveld refinement (RR) made with the DBWS-9411 or DBWS-9807 program. DB2dI then to

arrange all of the data for a pattern in a form ready to go into the PDF-2 file. A menu driven program, DB2dI uses the calculated pattern to locate each resolvable peak and to determine its position and height. It then determines all the contributing reflections to each peak and retains for the final listing the *hkl's* of the two strongest contributors. The DB2dI routine obtains other necessary information from the RR files and from interrogation of the user. Once all the necessary information is gathered, DB2dI prepares an output file in AIDS format ready for direct submission to

Editor, Powder Diffraction File
International Centre for Diffraction Data
12 Campus Boulevard
Newtown Square, PA 19073-3273, USA.

APPENDIX B
COPYRIGHT AND FAIR USE

Program DBWS-9807 is copyrighted by us, as is this User's Guide. Permission is hereby granted to individual scientists to use the program for their own scientific work, but not for commercial exploitation. We have no objection to its being shared with other users meeting the same criteria.

It may not be incorporated into other products which are then sold nor otherwise used for commercial gain without specific arrangements being made with the copyright holder.

From those individual users sharing the program with colleagues in the aforementioned, non-commercial spirit, we ask the following:

1) Please pass on a copy of the entire distribution package, not just a bare-bones electronic copy of the program alone. This package includes all test case files and a hard copy of this User's Guide. The requests that we have received, and still receive, for missing parts of the package show clearly that many, perhaps most, people who get copies from their friends are really not getting fully functional copies of the distribution package and will surely have unnecessary trouble trying to use the program.

2) So that the recipients may receive our future notices of errors and upgrades, please communicate to Prof. Young (address on cover page)

a) Full name and address of recipient
b) Program number and version transferred
c) A listing of the package elements transferred
d) Date of transfer

3) Please inform the recipient that we can not accept any responsibility for missing parts of the primary distribution package, such as documentation and test-case files, nor for any modifications that might have been made in the program, nor for the currency of the version so distributed. Unfortunately, such problems do seem to be common in secondary distributions.

4) Please pass on to the recipient a copy of this notice, who should then pass on a copy with each copy of the program package he might distribute, etc..

5) From all users we request that proper credit (citation) be given in all written works for which this program played a role. The best citation to DBWS-9807a is as an upraded version of DBWS-9411, described by Young, Sakthivel, Moss and Paiva-Santos (1955). The full reference appears in the list of references in this Guide and in the print out of the main output file.