

SHORT REFERENCE GUIDE

Powder Diffraction Structure Analysis Program

DDM

Version 1.6

Includes Rietveld and Derivative Difference Minimization (DDM) methods
[L.A. Solovyov, J. Appl. Cryst. 37 (2004) 743-749]

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General information

The program is designed for crystal structure analysis from powder diffraction data by making use of either Rietveld [H. Rietveld *J.Appl.Cryst.* (1969) 65], or Derivative Difference Minimization [L.A. Solovyov *J.Appl.Cryst.* (2004) 743] (DDM) method. In the DDM method the refinement is aimed not at minimizing the absolute difference between the experimental and calculated profiles but at minimizing the oscillations (or curvature) of the difference curve. The squared values of the difference curve derivatives are used in DDM as a measure of the difference curvature. The main advantage of this method is that it does not require the background line modeling or approximations. Eliminating the systematic errors caused by inadequate background definitions, DDM allows structure refinement with increased stability and precision.

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=====
COMMAND LINE: ddm.exe [Parameters file]
EXAMPLE: ddm.exe params.ddm
=====
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I. Parameters

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 those parameters which apply to all phases such as zero-point and background. PAR contains crystalline-phase dependent parameters such as lattice constants, scale factor, profile shape parameters n and m, preferred orientation parameters, etc. 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.

Codewords are entered for each parameter. A zero codeword means that the parameter is not being refined. Assume one wishes to vary the x,y,z coordinates of an atom and that $y = x/2$. If we let the codewords be given as:

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x: 31.00
y: 30.50
z: 41.00
```

then x and y will be assigned to the third normal matrix parameter and z to the fourth. Also, 1.00 times the calculated shift in the third parameter will be applied to x and 0.50 times to y. The full calculated shift in the fourth parameter will be applied to z. In general, the codeword is formed as:

$$\text{sign}(A) * (10P + |A|)$$

where P is the parameter position in the matrix and A is the factor by which the computed shift will be multiplied before use. P is optional; a parameter will be refined if A is nonzero. The shifts are also multiplied by a relaxation factor before being applied to the parameters. The user may supply four different relaxation factors which apply to four different classes of parameters.

If P is zero, then the parameter position in the matrix is assigned by the program AUTOMATICALLY. Only those parameters which need to be restrained to have the same position in the matrix (as x and y in the above example) should be numbered by P in the codewords. Holes in the sequence of numbered codewords are removed automatically by the program. Making a line with codewords blank (in the Parameters file) is equivalent to assigning them zero values.

Starting from version 1.4 the manual numbering of symmetry related parameters is optional as **the program imposes symmetry restrictions automatically.**

II. Description of input files

A. The Parameters file

This file contains the control variables and the structural parameters. If output of a new input file is selected, the current input file will be updated at the end of the last cycle (see flag NXT in Line 4). A star (*) before a line number indicates that the line's existence depends on the value of a control variable. The parameters are entered in **free format** and should be separated by at least one space.

In the mathematical expressions Q denotes the diffraction angle Theta.

Line	Par.N	Description
1.		Title - any 70 characters to be used to label the printout.
2.		Data file name
3.	1	JOBTYPE - 0 - x-ray case 1 - neutron case(nuclear scattering only) 2 - pattern calculation only, x-ray (does not work) 3 - pattern calculation only, neutron (does not work)
	2	NPROF - profile selection 0 - Gaussian 4 - [Not used] 1 - Lorentzian (Cauchy) 5 - pseudo-Voigt(pV) 2 - Mod 1 Lorentzian 6 - Pearson VII 3 - Mod 2 Lorentzian 7 - Thompson-Cox-Hastings pV
	3	NPHASE - number of phases (up to 8 phases can be refined simultaneously)
	4	NBCKGD - background correction control 0 - background to be refined 1 - background to be read from file named 'backgr' containing an array of the background intensities for each profile point in free format 2,3,..N - background to be determined by linear interpolation between N datapoints read from Line 9.
	5	NEXCRG - number of excluded regions read from Line 10.
	6	NSCAT - number of extra scattering sets read from Line 11.
	7	INSTRM - data type 0 - Laboratory Q-2Q X-ray data, or single detector neutron data (the Data file contains only profile intensities, see B. Tape 4) 1 - Other types of data (the Data file contains profile intensities and squared variances)
	8	IPREF - Preferred orientation function 0 - Rietveld-Toraya function 1 - March-Dollase function 2 - Ellipsoidal function
	9	ISZSTR - size-strain instrumental standard used (for NPROF=7) If ISZSTR=1, instrumental broadening parameters US ZS XS YS are read from Line 12.
4.		Output control flags (0 for off, >0 for on)
	1	IWP =1: prf-file for WinPLOTR =2: weighted prf-file for WinPLOTR
	2	IPL =1: text-files with calculated and observed intensities =2: text-files with weighted profile intensities
	3	IPC =1: list of reflections =2: list of F obs, F calc & R-F
	4	MAT =1: correlation matrix
	5	NXT =1: Parameters file is updated after the last cycle
	6	LST1 =1: number of last refinement cycles to output
	7	LST2 =1: not used
	8	LST3 =1: not used
	9	LSYM =1: symmetry operators output to CIF file

Line	Par.N	Description
5.	1	Lamda(1) - Wavelength1
	2	Lamda(2) - Wavelength2
	3	RATIO - Alpha2/Alpha1 intensity ratio
	4	BKPOS - Origin of polynomial for background (in °2Q)
	5	WDT - range of calculated profile in units of FWHM (beyond this the calc. profile is set to zero)
	6	CTHM - monochromator coefficient in polarization correction $[1 + CTHM * (\cos 2Q)^2] / [\sin 2Q \sin Q]$
	7	TMR - convolution interval for R-Bragg calculation and profile decomposition in units of FWHM
	8	RLIM - peaks below this angle (2Q) are corrected for asymmetry by the split-FWHM approach; the left side of a peak is given an additional broadening: $FWHM_{left} = FWHM_{right} + 2P1 * \exp(-2Q * 0.084) + P2 \tan Q$ where P1, P2 are the asymmetry parameters (Line 13.81)
	9	SAMPLE - angle (2Q) below which the intensities are corrected for the effect of the primary beam falling beyond the sample edges (Bragg-Brentano geometry only) An empirical correction is applied: $I_{cor} = I / (1 + (.0128 + .0106 * (SAMPLE - 2Q)) * (SAMPLE - 2Q))$
	10	BKCURV - number of average FWHM values used for estimating the output background curve (affects output only)
6.	1	MCYCLE - number of refinement cycles (starting from 0)
	2	EPS - run terminates when all shifts are < EPS*standard deviation
		RELAX - group relaxation factors for shifts
	3	(1) - coordinates & isotropic temperature factors
	4	(2) - anisotropic temperature parameters
	5	(3) - profile width, asymmetry, overall temperature, and preferred orientation parameters
	6	(4) - lattice parameters, 2Q-zero, overall scale factor, and site occupancies
7.	1	NDEC - number of cycles for profile decomposition run (either DDM or Le Bail methods depending on CDDM) If NDEC > 0, then the structure model is ignored and the squared structure factors F ² are read from the file named 'ffobs' which is overwritten with the refined F ² s after the final run cycle. If 'ffobs' file is absent, a set of equal F ² is applied at the first decomposition cycle. If both MCYCLE and NDEC > 0, then the refinement of the profile parameters is run first (with F ² s from 'ffobs' file) followed by NDEC decomposition cycles
	2	MAXS - refined parameters control flag MAXS = 0 denotes refinement of all parameters with nonzero codewords MAXS = -1 removes all refinement codewords
	3	WDDM - DDM convolution interval selection threshold If WDDM > 0, the counting statistics is used If WDDM < 0, the Durbin-Watson statistics is used If WDDM = 0, all convolution intervals are equal to CDDM
	4	CDDM - maximal DDM convolution interval in degrees 2Q If CDDM=0, Rietveld refinement is performed instead of DDM
	5	IWGHT - weighting scheme flag for DDM IWGHT = 0, 1, 2 for Rietveld IWGHT = 0, 1

Line	Par.N	Description
8.		Global parameters
8.1	1	ZER - zeropoint for 2Q (in degrees)
	2	DISP - sample displacement 2Q correction parameter
	3	SHASM - asymmetry-related peak shift correction parameter
	4	ABSORP1,
	5	ABSORP2 - absorption correction coeffs. for flat sample: $I_{cor} = I * [1 + ABSORP1 * \exp(-ABSORP2 / \sin Q)]$ ABSORP1 = -1 holds for the finite sample thickness effect ABSORP1 > 0 holds for the surface roughness effect
	6	ABSORP3 - absorption correction coeff. for cylindrical sample: $I_{cor} = I * \exp[-(1.7133 - 0.0368 * \sin^2 Q) * ABSORP3 + (0.0927 + 0.375 * \sin^2 Q) * ABSORP3^2]$
8.2		Codewords for ZER, DISP, SHASM, ABSORP
8.3		BACK - background coefficients (six values)
8.4		FBACK - codewords for background coefficients
*9.		If NBCKGD >= 2, then there are NBCKGD lines POS - position in degrees 2Q BCK - background counts at this position
*10.		If NEXCRG > 0, then there are NEXCRG lines ALLOW - low angle bound of excluded region AHIGH - high angle bound of excluded region NOTE: A reflection will be excluded if any part of its calculated tail falls in this range.
*11.		If NSCAT > 0, then there are NSCAT sets of lines for extra scatterers not included in the incorporated table of scattering factor coefficients
*11.1		NAM - symbol identifying this set DFP - f' DFPP - f'' XMAS - Molecular mass
*11.2		Either one line of the form A1 B1 A2 B2 A3 B3 A4 B4 C, the coefficients for the analytic approximation to f, or a set of lines of the form Posi - Scat, where $Posi = \sin Q / \lambda \text{ and } Scat = f$ The set is terminated by a line with -100 in the first position. If the first form is desired, A2 can not = 0
*12.		If ISZSTR = 1, then there are instrumental broadening parameters US, ZS, XS, YS for size-strain calculations (only for NPROF=7). They are subtracted from the FWHM terms defined in Line 13.6
13.		Phase parameters: NPHASE sets of lines (see Line 3)
13.1		PHSNM - name of phase (maximum 70 characters)
13.2	1	NATOM - number of atoms
	2	IFUR - Fourier output flag If IFUR=1, F-factors are written to ddm_cif.cif If IFUR=2, F-squared are written to ddm_cif.cif
	3	NDPAR - codeword number of the parameter responsible for structural defects (pseudoposition occupancy parameter, for instance) in the selective anisotropic broadening model [Solovyov (2000) J.Appl.Cryst. 338]
	4	PREF(3) - preferred orientation direction h k l
	5	SAQF - Brindley particle absorption contrast factor for QPA
13.3		SYMB - space group symbol, e.g. P-1, P63/m, P21/n, P 1 1 2/b, I41/acd, Pmmn, Pmmn S, R-3c, R-3c R, HALL -P 3* 2N, ... ending R means RHOMBOHEDRAL setting, S means ORIGIN CHOICE 1 By default (if S is omitted) the ORIGIN CHOICE 2 with the inversion centre at (0,0,0) is selected

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Line      Description
***** NATOM line sets *****
13.4      4 lines for each of the N atoms
13.41     LABEL - identification characters for atom (4 characters)
          NTYPE - link to scattering data for atom: either name from 11.1
                  or chemical symbol and valence to access the
                  incorporated list of f-coefficients taken from the
                  International Tables.
          x,y,z - fractional atomic coordinates
          B      - isotropic temperature parameter
          N      - occupation number (number of atoms in the unit cell)
          NOTE: if N = -1, the occupation number will be calculated by the program
          IANIS - isotropic (0) or anisotropic (1) temp. factor flag
          ADIST - maximal interatomic distance for this atom to output
13.42     CX,CY,CZ - codewords for the fractional atomic coordinates
          CB      - codeword for the isotropic temperature parameter
          CN      - codeword for the occupation number
          Lines 13.43 and 13.44 are entered only if IANIS = 1
*13.43     Beta11, Beta22, Beta33, Beta12, Beta13, Beta23
                  anisotropic temperature parameters
*13.44     CB11, CB22, CB33, CB12, CB13, CB23
                  codewords for anisotropic temperature parameters
*****
13.5
13.51     SF      - scale factor
                  If SF = 0 it will be estimated by the program
          BQ      - overall isotropic temperature factor
13.52     CSF     - codeword for scalefactor
          CBQ     - codeword for overall isotropic temperature factor
13.6
13.61     U,V,W,Z,X,Y - FWHM ("H") parameters
                  For NPROF = 0...6
                   $H^2 = U \cdot \tan^2 2Q + V \cdot \tan Q + W + Z / \cos^2 Q$ 
                  X & Y are used only when NPROF = 7, where
                   $H_{Gauss} = [U \cdot \tan^2 2Q + V \cdot \tan Q + W + Z / \cos^2 Q]^{0.5}$ 
                   $H_{Lorentz} = X \cdot \tan Q + Y / \cos Q$ 
13.62     CU,CV,CW,CZ,UX,UY - codewords for the FWHM parameters
13.7
13.71     A,B,C, - cell dimensions in Angstroms
          Alpha, Beta, Gamma - cell angles in degrees
          LAUE - reflection generation flag
                  When LAUE = 1, the set of reflections is generated as for
                  Laue class -1 disregarding the actual lattice symmetry. This
                  option is required when the preferred orientation or
                  anisotropic broadening directions are inconsistent with the
                  crystal symmetry.
13.72     CA,CB,CC,CALPHA,CBETA,CGAMMA - codewords for the
                  cell constants
13.8
13.81     G1, G2, P1, P2 where P1, P2 are the asymmetry parameters
                  and G1, G2 are the preferred orientation
                  parameters used in the formulae:

                  if IPREF=0,  $I_{corr} = I_{obs}[G2 + (1-G2)\exp(-G1 \cdot A^2)]$ 
                  if IPREF=1,  $I_{corr} = I_{obs}[(G1 \cos A)^2 + (\sin A)^2 / G1]^{-1.5}$ 

                  where A is the acute angle between the scattering vector
                  and the preferred orientation direction in reciprocal
                  space (see PREF in Line 13.2).
                  With IPREF=0, setting G1 to any number > 99.0 for a
                  phase causes the program to generate for that phase only
                  those reflections for which d* is parallel to the
                  preferred orientation vector PREF specified in Line 13.2
13.82     CG1, CG2, CP1, CP2 - codewords for G1, G2, P1, P2

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Line	Description
13.9	Profile Shape parameters
13.91	NA, NB, NC For the usual pseudo-Voigt (NPROF=5) the Shape parameter $n = NA + NB*2Q$ For the Pearson VII (NPROF=6) the Shape parameter $m = NA + NB/2Q + NC/(2Q)^2$ For all other profiles listed (1 - 3, 7), NA, NB, NC, and their codewords must all be set to zero.
13.92	codewords for NA, NB, NC
13.10	FWHMmin, FWHMmax - lower and higher FWHM limits for the FWHM estimation procedure (undocumented) IAN3 - anisotropic strain model flag = 1 or -1 indicates 2nd rank anisotropy tensor: $\text{Aniso2} = (\text{STR1}*h^2 + \text{STR2}*k^2 + \text{STR3}*l^2 + \text{STR4}*2hk + \text{STR5}*2hl + \text{STR6}*2kl)*0.001*d^2$ = 2 or -2 indicates 4th rank anisotropy tensor: $\text{Aniso2} = [\text{STR1}*h^4 + \text{STR2}*k^4 + \text{STR3}*l^4 + 3(\text{STR4}*h^2k^2 + \text{STR5}*h^2l^2 + \text{STR6}*k^2l^2) + 2(\text{STR7}*kh^3 + \text{STR8}*hl^3 + \text{STR9}*lk^3 + \text{STR10}*hk^3 + \text{STR11}*lh^3 + \text{STR12}*kl^3) + 4(\text{STR13}*klh^2 + \text{STR14}*hkl^2 + \text{STR15}*khl^2)]*0.00001*d^4$ For NPROF < 7, $H(a)^2 = H^2 + \text{Aniso2}*tan^2Q$ For NPROF = 7 only: if IAN3 > 0, $H\text{Lorentz}(a) = H\text{Lorentz} + \text{Aniso2}^{(1/2)}*tanQ$ if IAN3 < 0, $H\text{Gauss}(a) = H\text{Gauss} + \text{Aniso2}*tanQ^2$
13.11	
13.111	EPR(6) - six preferred orientation coefficients for the Ellipsoidal IPREF = 2) function: $\text{Icorr} = \text{Iobs}[1 + (\text{EPR1}*h^2 + \text{EPR2}*k^2 + \text{EPR3}*l^2 + \text{EPR4}*2hk + \text{EPR5}*2hl + \text{EPR6}*2kl)*0.001d^2]^{-1.5}$ NOTE: When EPR coefficients are refined without restrains, the scale-factor SF should be fixed.
13.112	CEPR(6) - codewords for EPR
13.113	SIZ(6) - six anisotropic size broadening coefficients The anisotropic broadening term is calculated as: $\text{Aniso1} = (\text{SIZ1}*h^2 + \text{SIZ2}*k^2 + \text{SIZ3}*l^2 + \text{SIZ4}*2hk + \text{SIZ5}*2hl + \text{SIZ6}*2kl)*0.001*d^2$ For NPROF < 7, $H(a)^2 = H^2 + \text{Aniso1}/cos^2Q$ For NPROF = 7, $H\text{Lorentz}(a) = H\text{Lorentz} + \text{Aniso1}^{(1/2)}/cosQ$
13.114	CSIZ(6) - codewords for SIZ
13.115	STR(1-6) - anisotropic strain broadening coefficients
13.116	CSTR(1-6) - codewords for STR
Lines 13.117 - 13.120	are entered if IAN3 = 2
*13.117	STR(7-12) - anisotropic strain broadening coefficients
*13.118	CSTR(7-12) - codewords for STR
*13.119	STR(13-15) - anisotropic strain broadening coefficients
*13.120	CSTR(13-15) - codewords for STR

B. The Data file

This file contains the data from the diffractometer. The first line contains the variables START, STEP, STOP and DATAID in free format:

START - beginning angle in degrees 2 θ
STEP - step size in degrees 2 θ
STOP - last angle in degrees 2 θ
DATAID - alphanumeric string identifier

The rest of the file consists of the data themselves in free format. Depending on the INSTRM parameter (Line 3) for each data-point either the profile intensity alone or both the intensity and its squared variance should be given.

NOTE: The START angle assigned here must correspond to that of the first datum. The STOP angle can be any angle less than that of the last datum in the file. Any desired angular range can be selected for the refinement by (i) declaring an excluded region (NEXCRG in Line 3 and bounds in Line 10) from the START angle to the desired beginning and (ii) assigning the desired ending angle to STOP.

C. Optional files 'ddm_bckgr', 'ddm_ffobs', and 'ddm_fwobs'

These files, if used, should be placed to the same folder from which the program was run.

From the file named 'ddm_bckgr' the background profile intensities are read in free format when NBCKGD=1 option is used.

The file 'ddm_ffobs' contains estimated observed squared structure factors after the last refinement (or decomposition) run. It is rewritten automatically by the program. It can be created and/or edited manually if the structure factors need to be entered at the initial step of the profile decomposition procedure (see NDEC description in Line 7).

The file 'ddm_fwobs' is optional. It may contain fixed FWHM values for selected reflections. Five parameters should be specified for each selected reflection: h, k, l, FWHM, Nphase where hkl are the indexes and Nphase is the number of phase to which the reflection belongs. The file format is free.

EXAMPLE:

```
1  0  0  0.149  1
1  3 -1  0.209  1
1  0  1  0.242  2
```

.....
If 'ddm_fwobs' file exists in the folder from which the program was run the FWHM values for the selected reflections are read from it and fixed (not refined). This option may be useful in difficult cases of anisotropic peak broadening when it can not be satisfactorily modeled.

III. Description of output files

File 'ddm_out.txt' contains detailed output listing

File 'ddm_prf.prf' contains the observed and calculated patterns, which can be viewed by the popular program WinPLOTR. WinPLOTR is freely downloadable from:
<http://www-llb.cea.fr/fullweb/winplotr/winplotr.htm>

File 'ddm_prf.txt' is a text file with the observed, calculated, difference, and background profile intensities and the DDM convolution interval widths (in degrees 2 θ).

File 'ddm_ref.txt' contains positions and integral intensities of reflections.

File 'ddm_cif.cif' is the Crystallographic Information File, which can be read by many programs for crystal structure visualization and analysis.

IV. MATHEMATICAL INFORMATION

1. Refinement method

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

$$MF = \sum_{i=1}^N w_i (Y_i - Y_{C_i})^2, \quad w_i = \sigma_i^{-p}$$

in the case of Rietveld refinement [Rietveld H. *J. Appl. Cryst.* (1969) 65], or

$$MF = \sum_{i=m+1}^{N-m} \left\{ w_i^1 \left[\sum_{j=-m}^m s_j^1 (Y_{i+j} - Y_{C_{i+j}}) \right]^2 + w_i^2 \left[\sum_{j=-m}^m s_j^2 (Y_{i+j} - Y_{C_{i+j}}) \right]^2 \right\}, \quad w_i^k = \left[\sum_{j=-m}^m (s_j^k \sigma_{i+j})^2 m^p \right]^{-1}$$

in the case of Derivative Difference Minimization [Solovyov L.A. *J. Appl. Cryst.* (2004) 743],

where Y_i and Y_{C_i} are the observed and calculated profile intensities at the i^{th} step, σ_i is the variance in the observed profile intensity Y_i and s_j^k are the Savitzky-Golay (SG) coefficients for the derivative of order k with the convolution interval $[-m, m]$. The weights w depend on the exponent factor p that is chosen by the flag IWGHT in Line 7 of the Parameters file. In the Rietveld scheme $p = 2(\text{IWGHT}+1)$; for DDM $p = \text{IWGHT}$.

The choice of the convolution interval $[-m, m]$ for each data-point is controlled by the variables WDDM and CDDM specified in Line 7 of the Parameters file. The interval selection consists in finding the widest interval for which the deviations of the profile intensities from the fitted SG polynomial P^{SG} satisfies certain criterion defined by the value of WDDM. This procedure generates narrower convolution intervals for profile regions with sharp features. CDDM limits the maximal interval width allowed (in degrees 2θ).

If $\text{WDDM} > 0$, the selection criterion is based on the counting statistics:

$$\sqrt{\sum_{i=-m}^m \sigma_i^{-2} (Y_i - P_i^{SG})^2 / (2m+1)} < \text{WDDM}$$

If $\text{WDDM} < 0$, the selection is done according to the Durbin-Watson correlational statistics:

$$\sum_{i=-m}^{m-1} (Y_i - P_i^{SG} - Y_{i+1} + P_{i+1}^{SG})^2 / \sum_{i=-m}^m (Y_i - P_i^{SG})^2 > 4 + 2\text{WDDM} + 2/(m-1) - 1/(2m+1)$$

The optimal ranges are: $1 < \text{WDDM} < 3$ and $-1.7 < \text{WDDM} < -1.3$.

The variable structural and profile parameters v_r are refined by solving the normal equations

$$\sum_{i=1}^N w_i (Y_i - Y_{C_i}) \frac{\partial Y_{C_i}}{\partial v_r} = 0 \quad \text{for Rietveld refinement, or}$$

$$\sum_{k=1}^2 \sum_{i=m+1}^{N-m} w_i^k \left[\sum_{j=-m}^m s_j^k (Y_{i+j} - Y_{C_{i+j}}) \right] \cdot \left[\sum_{j=-m}^m s_j^k \frac{\partial Y_{C_{i+j}}}{\partial v_r} \right] = 0 \quad \text{for DDM.}$$

The standard deviations of the refined parameters are estimated from the equation

$$Sd_r = [A_{rr} MF / (N - P + C)]^{1/2},$$

where A_{rr} is the diagonal element in the inverted normal matrix, N is the number of observations, P is the number of refined parameters and C is the total number of constraints.

The refinement reliability factors are calculated as:

$$\begin{aligned} R_p &= 100 \Sigma |Y_i - Y_{C_i}| / \Sigma (Y_i - Y_{b_i}), & \text{the profile R-factor;} \\ R_{wp} &= 100 [\Sigma w_i (Y_i - Y_{C_i})^2 / \Sigma w_i (Y_i - Y_{b_i})^2]^{1/2}, & \text{the weighted profile R-factor;} \\ R_{exp} &= 100 [(N - P + C) / \Sigma w_i (Y_i - Y_{b_i})^2]^{1/2}, & \text{the expected weighted R-factor;} \\ R_B &= 100 \Sigma |I - I_c| / \Sigma I_o, & \text{the Bragg R-factor;} \end{aligned}$$

where Y_{b_i} is the background intensity at the i^{th} step, I and I_c are the "observed" (estimated from the observed profile) and the calculated integral reflection intensities;

$$R_{DDM} = 50 \sqrt{\frac{\sum_{k=1}^2 \sum_{i=m+1}^{N-m} w_i^k \left[\sum_{j=-m}^m s_j^k (Y_{i+j} - Y_{C_{i+j}}) \right]^2}{\sum_{k=1}^2 \sum_{i=m+1}^{N-m} w_i^k \left[\sum_{j=-m}^m s_j^k Y_{i+j} \right]^2} + \frac{\sum_{i=m+1}^{N-m} w_i \left[Y_i - \sum_{j=-m}^m s_j^0 Y_{i+j} \right]^2}{\sum_{i=m+1}^{N-m} w_i Y_i^2}} \equiv 50 \sqrt{\frac{S2}{D2} + \frac{S0}{D0}}, \quad \text{DDM R-factor;}$$

$$\text{DDM-R}_w = 100 \sqrt{\frac{S2}{D2}}, \quad \text{simplified weighted DDM R-factor.}$$

2. Calculated profile

The profile intensities Y_{C_i} are calculated by summing the contributions from neighboring Bragg reflections, k , for all phases, p , plus the background, Y_{b_i} :

$$Y_{C_i} = \sum_p s_p \{ \sum_k [|F_k|^2 f(2\theta_i - 2\theta_k) As L_k P_k Sa] \}_p + Y_{b_i},$$

where s_p is the scale factor for phase p , F_k is the structure factor, f is a reflection profile function which approximates the effects of both instrumental and, possibly, specimen features, As is a profile asymmetry function, L_k contains the Lorentz, polarization and multiplicity factors, P_k is a preferred orientation function, and Sa includes the surface roughness, finite sample thickness and absorption corrections. The ratio of the intensities for the two wavelengths (if used) is absorbed in the calculation of $|F_k|^2$, so that only a single scale factor is required for each phase.

The currently available profile functions are:

NPROF	FUNCTION	NAME
(0)	$\exp[-C_0(2\theta_i - 2\theta_k)^2/H_k^2] \sqrt{C_0/H_k} \sqrt{\pi}$	Gaussian ('G')
(1)	$[1+C_1(2\theta_i - 2\theta_k)^2/H_k^2]^{-1} \sqrt{C_1/\pi H_k}$	Lorentzian ('L')
(2)	$[1+C_2(2\theta_i - 2\theta_k)^2/H_k^2]^{-2} 2\sqrt{C_2/\pi H_k}$	Lorentzian Mod 1
(3)	$[1+C_3(2\theta_i - 2\theta_k)^2/H_k^2]^{-1.5} \sqrt{C_3/2H_k}$	Lorentzian Mod 2
(5)	$n\mathbf{L} + (1-n)\mathbf{G},$ $n = NA + NB*2\theta$	pseudo-Voigt ('pV')
(6)	$(C_4/H_k) [1 + 4(2^{1/m} - 1)(2\theta_i - 2\theta_k)^2/H_k^2]^{-m},$ $m = NA + NB/2\theta + NC/(2\theta)^2$	Pearson VII ('PVII')

for NPROF < 7: $H_k = [(U + Aniso_2)\tan^2\theta + V\tan\theta + W + (Z + Aniso_1 Fder)/\cos^2\theta]^{1/2}$

(7)	$n\mathbf{L} + (1-n)\mathbf{G},$ $n = 1.36603q - 0.47719q^2 + 0.1116q^3$ $q = H_L / H_k,$ $H_k = (H_G^5 + 2.69269H_G^4 H_L + 2.42843H_G^3 H_L^2 + 4.47163H_G^2 H_L^3 + 0.07842H_G H_L^4 + H_L^5)^{0.2},$ for IAN3 > 0: $H_L = (X + Aniso_2^{1/2})\tan\theta + (Y + Aniso_1^{1/2} Fder)/\cos\theta,$ $H_G = [U\tan^2\theta + V\tan\theta + W + Z/\cos^2\theta]^{1/2},$ for IAN3 < 0: $H_L = X\tan\theta + (Y + Aniso_1^{1/2} Fder)/\cos\theta,$ $H_G = [(U + Aniso_2)\tan^2\theta + V\tan\theta + W + Z/\cos^2\theta]^{1/2},$	Thompson-Cox-Hastings (TCH) pseudo-Voigt [Thompson P., Cox D.E., Hastings J.B. <i>J. Appl. Cryst.</i> (1987) 79]
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where H_k is the full-width-at-half-maximum (FWHM) of the k^{th} Bragg reflection, NA , NB , NC , U , V , W , Z , X , and Y are refinable parameters, and

$$C_0 = 4\ln 2, \quad C_1 = 4, \quad C_2 = 4(\sqrt{2} - 1), \quad C_3 = 4(2^{2/3} - 1), \quad \text{and} \quad C_4 = 2\Gamma(m)(2^{1/m} - 1)^{1/2} / \Gamma(m - 0.5) \sqrt{\pi}.$$

The anisotropic peak broadening terms are calculated as follows:

the size term, $Aniso_1 = d^2(SIZ_1 h^2 + SIZ_2 k^2 + SIZ_3 l^2 + SIZ_4 2hk + SIZ_5 2hl + SIZ_6 2kl)/100$

the strain term depends on IAN3 flag,

$$\text{if IAN3}=1, \quad \text{Aniso}_2 = d^2(\text{STR}_1h^2 + \text{STR}_2k^2 + \text{STR}_3l^2 + \text{STR}_42hk + \text{STR}_52hl + \text{STR}_62kl)/100$$

$$\text{if IAN3}=2, \quad \text{Aniso}_2 = d^4[\text{STR}_1h^4 + \text{STR}_2k^4 + \text{STR}_3l^4 + 3(\text{STR}_4h^2k^2 + \text{STR}_5h^2l^2 + \text{STR}_6k^2l^2) +$$

$$+ 2(\text{STR}_7kh^3 + \text{STR}_8hl^3 + \text{STR}_9lk^3 + \text{STR}_{10}hk^3 + \text{STR}_{11}lh^3 + \text{STR}_{12}kl^3) +$$

$$+ 4(\text{STR}_{13}klh^2 + \text{STR}_{14}hkl^2 + \text{STR}_{15}khl^2)]/10000$$

The term *Fder* responsible for the selective anisotropic broadening due to structural defects is calculated as described in ref [Solovyov L.A. *J. Appl. Cryst.* (2000) 338]. Its calculation involves the structure factor derivative with respect to a refinable parameter responsible for the defects (pseudo-position occupancy, for instance). The codeword number of the defect-responsible parameter is specified in the variable NDPAR (Line 13.2). If NDPAR=0, no broadening related to defects is considered.

The background intensity Yb_i at the i^{th} 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 3 of the Parameters file. The choices are: (1) an operator-supplied file with background intensities Ib_i (NBCKGD = 1), or (2) linear interpolation between operator-selected points in the pattern (NBCKGD = n, where n is the number of points), or (3) the background function (NBCKGD = 0):

$$Yb_i = Ib_i + \sum_{m=0}^5 B_m \left(\frac{2\theta_i}{BKPOS} - 1 \right)^m$$

where *BKPOS* is user-specified in Line 5 of the Parameters file. Note that the operator-supplied background intensities Ib_i are optional; they are added to the background function when NBCKGD = 1.

The diffraction peak asymmetry is allowed for by giving the left side of a peak an additional broadening:

$$\text{FWHM}_{\text{left}} = \text{FWHM}_{\text{right}} + 2P_1 \exp(-2\theta * 0.084) + P_2 \tan \theta,$$

where P_1 and P_2 are refinable parameters.

The angular dependent absorption correction for a flat sample is

$$Sa = 1 + \text{ABSORP}_1 \exp(-\text{ABSORP}_2 / \sin \theta)$$

where ABSORP_1 and ABSORP_2 are adjustable parameters. $\text{ABSORP}_1 = -1$ holds for the finite sample thickness effect and $\text{ABSORP}_1 > 0$ holds for the surface roughness effect (equivalent to the Suortti model [Suortti P. *J. Appl. Cryst.* (1972) 325]). For a cylindrical sample:

$$Sa = \exp[-(1.7133 - 0.0368 \sin^2 \theta) \text{ABSORP}_3 + (0.0927 + 0.375 \sin^2 \theta) \text{ABSORP}_3^2]$$

The preferred orientation function may be chosen in three different forms, depending on IPREF flag:

- (1) Rietveld-Toraya model: $P_k = G_2 + (1 - G_2) \exp(-G_1 \alpha^2)$
- (2) March-Dollase model: $P_k = (G_1^2 \cos^2 \alpha + \sin^2 \alpha / G_1)^{-3/2}$
- (3) Ellipsoidal model: $P_k = [1 + d^2(\text{EPR}_1 h^2 + \text{EPR}_2 k^2 + \text{EPR}_3 l^2 + \text{EPR}_4 2hk + \text{EPR}_5 2hl + \text{EPR}_6 2kl)/100]^{-3/2}$

where G_1 , G_2 , and $\text{EPR}_1 \dots \text{EPR}_6$ are refinable parameters, α is the acute angle between the scattering vector and the preferred orientation direction in reciprocal space, and d is the reflection d-spacing. When all six EPR coefficients are refined without restraints, the scale-factor SF should be fixed.

3. Size-strain calculations

When the **TCH** profile function is used (NPROF = 7), the crystallite size and micro-strain calculations are performed based on the refined FWHM parameters. The estimated size and strain values are written to the Output file. The volume-weighted and area-weighted domain sizes D_V and D_A , and the maximum (upper limit) of strain e are calculated as:

$$D_V = 1/\beta_S, \quad D_A = 1/2\beta_{SL}, \quad e = \beta_D/4,$$

$$\beta_S = [2\beta_{SL} + (\beta_{SL}^2 + 9\beta_{SG}^2)^{1/2}]/3, \quad \beta_D = [2\beta_{DL} + (\beta_{DL}^2 + 9\beta_{DG}^2)^{1/2}]/3,$$

$$\beta_{SL} = (Y - Y_s)\pi^2/360\lambda, \quad \beta_{DL} = (X - X_s)\pi^2/360,$$

$$\beta_{SG} = [(Z - Z_s)/\pi \ln 2]^{1/2} \pi^2/360\lambda, \quad \beta_{DG} = [(U - U_s)/\pi \ln 2]^{1/2} \pi^2/360,$$

where β_s and β_D are the approximations of the integral breadth of the size- and strain-broadened profiles derived from their Gaussian and Lorentzian components, Y , Z , X and U are the refinable parameters of the FWHM components H_L and H_G of the **TCH** function, Y_s , Z_s , X_s and U_s are the respective FWHM parameters for an instrumental broadening standard (entered in Line 12 of the Parameters file), and λ is the wavelength. An estimation of the average crystallite diameter $\langle D \rangle$ and its distribution dispersion $\sigma \langle D \rangle$ is done using equations

$$\langle D \rangle = D_A + (D_A D_V)^{1/2} / 4 \quad \text{and} \quad \sigma \langle D \rangle = \langle D \rangle (D_V / D_A - 1/2) / 2$$

found empirically from fitting **TCH** function to simulated profiles for the model of spherical crystallites with different size distribution dispersions. The anisotropic diameter $\langle D \rangle^{\text{aniso}}$ and strain e^{aniso} are calculated similarly, but the Lorentzian breadth components are given by:

$$\beta_{SL}^{\text{aniso}} = (Y - Y_s + Aniso_1^{1/2}) \pi^2 / 360 \lambda, \quad \beta_{DL}^{\text{aniso}} = (X - X_s + Aniso_2^{1/2}) \pi^2 / 360.$$

4. Quantitative phase analysis calculations

In a mixture of N crystalline phases the weight fraction W_j of phase j is given by:

$$W_j = S_j Z_j M_j V_j / t_j \sum (S_i Z_i M_i V_i / t_i),$$

where S_j is the scale factor of phase j , Z_j is the number of formula units per unit cell for phase j , M_j is the mass of the formula unit, V_j is the unit cell volume, t_j is the Brindley particle absorption contrast factor for phase j (parameter SAQF in Line 13.2). In the program code the weight fraction is additionally multiplied by squared multiplicity of the symmetry group due to a specific way of the structure factor calculation.

The Brindley parameter t accounts for microabsorption effects that become important when the compounds of the powder have essentially different linear absorption coefficients. Values of t as a function of the product $(m_j - \mu)R$ have been tabulated by Brindley [Brindley G.W., Phil. Mag. (1945) 347] and are reproduced in the table below. Here m_j is the particle linear absorption coefficient and μ is the mean linear absorption coefficient of the solid material of the powder.

$(m_j - \mu)R$	$t, 2\theta = 90$	$(m_j - \mu)R$	$t, 2\theta = 90$
-0.50	2.036	0.01	0.986
-0.40	1.807	0.02	0.973
-0.30	1.573	0.03	0.960
-0.20	1.353	0.04	0.946
-0.10	1.162	0.05	0.933
-0.09	1.143	0.06	0.919
-0.08	1.125	0.07	0.906
-0.07	1.108	0.08	0.893
-0.06	1.091	0.09	0.879
-0.05	1.073	0.10	0.866
-0.04	1.058	0.20	0.753
-0.03	1.042	0.30	0.653
-0.02	1.027	0.40	0.569
-0.01	1.014	0.50	0.496
0.00	1.000		