SHORT REFERENCE GUIDE

****
Powder Diffraction Structure Analysis Program
DDM
Version 1.95
****

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

Update/Download:
http://www.icct.ru/eng/content/persons/Sol_LA/ddm.html
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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 refinemet 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:

$$x: \quad 31.00$$
$$y: \quad 30.50$$
$$z: \quad 41.00$$

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:

$$sign(A)*(10P + |A|)$$

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.**

1. *Refinement method*

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

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

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

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

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

where Y_i and Yc_i are the observed and calculated profile intensities at the ith 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 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 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 < WDDM < 3 and -1.7 < WDDM < -1.3.

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

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

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

The standard uncertainties of the variable parameters are estimated from the diagonal elements of a residual-related variance-covariance matrix $\mathbf{V}_x$. In the Rietveld refinement $\mathbf{V}_x$ is calculated as

$$\mathbf{V}_x = k_R \mathbf{A}^{-1} \mathbf{C} \mathbf{A}^{-1}, \qquad C_{ij} = \sum_n \frac{\partial Y_n}{\partial x_i} \frac{\partial Y_n}{\partial x_j} w_n^2 \Delta_n^2 , \qquad k_R = \frac{\sum \Delta_n^2 w_n}{\sum \Delta_n^2 w_n - \sum_i \sum_j A_{ij}^{-1} C_{ij}} ,$$

where $\mathbf{A}$ is the inverted normal matrix, Δ_n is the residual (Y_n - Yc_n), and x is the variable parameter. In the DDM mode the matrix $\mathbf{V}_x$ is derived as follows:

$$\mathbf{V}_x = k_D \mathbf{B}^{-1} \mathbf{D} \mathbf{B}^{-1},$$

$$D_{ij} = \sum_n V_{ynn} \sum_i \sum_j L_{ni} L_{nj} , \qquad V_{ynn} = k_D \frac{\Delta_n^{"2}}{\sigma_{yn}^{"2}} \sigma_{yn}^2 , \qquad L_{ni} = \sum_l (c_{m_k, n-l}' J_{li}' w_l' + c_{m_k, n-l}'' J_{li}'' w_l'') ,$$

$$B_{ij} = \sum_n (J'_{ni} J'_{nj} w'_n + J''_{ni} J''_{nj} w''_n), \qquad J'_{ni} = \sum_{k=-m_n}^{m_n} c'_{m_n k} \frac{\partial Y_{n+k}}{\partial x_i}, \qquad J''_{ni} = \sum_{k=-m_n}^{m_n} c''_{m_n k} \frac{\partial Y_{n+k}}{\partial x_i}$$

$$k_D = \frac{\sum \Delta''^2_n / \sigma''^2_{yn}}{\sum \Delta''^2_n / \sigma''^2_{yn} - \sum_i \sum_j A^{-1}_{ij} \sum_n \frac{\partial Y_n}{\partial x_i} \frac{\partial Y_n}{\partial x_j} \frac{\Delta''^2_n}{\sigma^2_{yn} \sigma''^2_{yn}}}, \qquad \Delta''_n = \sum_{k=-m_n}^{m_n} c''_{m_n k} \Delta_{n+k}, \qquad \sigma''^2_{yn} = \sum_{k=-m_n}^{m_n} c''^2_{m_n k} \sigma^2_{y,n+k},$$

where $c'_{m_n k}$ and $c''_{m_n k}$ are the SG coefficients, and the summation in the expression for L_{ni} is done for all the profile points whose convolution interval $[-m, m]$ includes the nth point.

 The refinement reliability factors are calculated as:

$R_p = 100 \, \Sigma|Y_i - Yc_i| / \Sigma(Y_i - Yb_i)$,   the profile R-factor;

$R_{wp} = 100 \, [\Sigma w_i (Y_i - Yc_i)^2 / \Sigma w_i (Y_i - Yb_i)^2]^{1/2}$,   the weighted profile R-factor;

$R_{exp} = 100 \, [(N - P + C) / \Sigma w_i (Y_i - Yb_i)^2]^{1/2}$,   the expected weighted R-factor;

$R_B = 100 \, \Sigma|I - Ic| / \Sigma Io$,   the Bragg R-factor;

where Yb_i is the background intensity at the ith step, I and Ic are the "observed" (estimated from the observed profile) and the calculated integral reflection intensities;

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

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

2. *Calculated profile*

 The profile intensities Yc_i are calculated by summing the contributions from neighboring Bragg reflections, k, for all phases, p, plus the background, Yb_i:

$$Yc_i = \Sigma_p \, s_p \, \{ \Sigma_k \, [\, |F_k|^2 f(2\theta_i - 2\theta_k) \, L_k \, P_k \, Sa \,] \}_p + Yb_i,$$

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, 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)	$\exp[-C_o(2\theta_i - 2\theta_k)^2 / H_k^2] \, \sqrt{C_o} / H_k \sqrt{\pi}$	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)	$[1 + C_3(2\theta_i - 2\theta_k)^2 / H_k^2]^{-1.5} \, \sqrt{C_3} / 2 H_k$	Lorentzian Mod 2
(5)	$n\mathbf{L} + (1 - n)\mathbf{G}$, $n = NA + NB*2\theta$	pseudo-Voigt ('pV')
(6)	$(C_4 / H_k) \, [1 + 4(2^{1/m} - 1) \, (2\theta_i - 2\theta_k)^2 / H_k^2]^{-m}$,	Pearson VII (`PVII')

$$m = NA + NB/2\theta + NC/(2\theta)^2$$

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) $n\mathbf{L} + (1 - n)\mathbf{G}$,   Thompson-Cox-Hastings (**TCH**) pseudo-Voigt

$n = 1.36603q - 0.47719q^2 + 0.1116q^3$ [Thompson P., Cox D.E., Hastings J.B.

q = H_L / H_k,   *J. Appl. Cryst.* (1987) 79]

$H_k = (H_G^5 + 2.69269H_G^4 H_L + 2.42843H_G^3 H_L^2 + 4.47163H_G^2 H_L^3 + 0.07842H_G H_L^4 + H_L^5)^{0.2}$,

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: $H_L = X\tan\theta + (Y + Aniso_1^{1/2}Fder)/\cos\theta$,

$H_G = [(U + Aniso_2)\tan^2\theta + V\tan\theta + W + Z/\cos^2\theta]^{1/2}$,

where H_k is the full-width-at-half-maximum (FWHM) of the kth Bragg reflection, *NA, NB, NC, U, V, W, Z, X,* and *Y* are refinable parameters, and

$C_o = 4\ln2$, $C_1 = 4$, $C_2 = 4(\sqrt2 - 1)$, $C_3 = 4(2^{2/3} - 1)$, and $C_4 = 2\Gamma(m)(2^{1/m} - 1)^{1/2}/\Gamma(m - 0.5)\sqrt\pi$.

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,

if IAN3=1, $Aniso_2 = d^2(STR_1 h^2 + STR_2 k^2 + STR_3 l^2 + STR_4 2hk + STR_5 2hl + STR_6 2kl)/100$

if IAN3=2, $Aniso_2 = d^4[STR_1 h^4 + STR_2 k^4 + STR_3 l^4 + 3(STR_4 h^2 k^2 + STR_5 h^2 l^2 + STR_6 k^2 l^2) +$
$+ 2(STR_7 kh^3 + STR_8 hl^3 + STR_9 lk^3 + STR_{10} hk^3 + STR_{11} lh^3 + STR_{12} kl^3) +$
$+ 4(STR_{13} klh^2 + STR_{14} hlk^2 + STR_{15} khl^2)]/10000$

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 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 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):

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

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:

FWHM_left = FWHM_right + $2P_1\exp(-2\theta*0.084) + P_2\tan\theta$,

where P_1 and P_2 are refinable parameters. Additionally, the peak asymmetry may be introduced by the approach of Finger, Cox & Jephcoat (1994) J. Appl. Cryst. 892. The respective refinable parameter FCJ (Line 13.8) is related to an effective slit_height/diffractometer_radius ratio that is considered to be equal to the sample_height/diffractometer_radius ratio.

The absorption and microabsorption correction for a flat sample is

$Sa_k = \mu/\mu_k + (1 - \mu/\mu_k)\exp(-0.0002PARS_k\mu_k/3) + ABSORP_1\exp[-0.0002PARS_k(\mu - \mu_k)/3 - ABSORP_2/\sin\theta]$

where ABSORP$_1$ and ABSORP$_2$ are adjustable parameters, μ and μ_k are the linear absorption coefficients of the sample and the kth phase, and PARS$_k$ is the particle size [um]. ABSORP$_1$ = -1 holds for the finite sample

thickness effect and $ABSORP_1 > 0$ holds for the surface roughness effect (equivalent to the Suortti model [Suortti P. *J.Appl. Cryst.* (1972) 325]). For a cylindrical sample:

$$Sa = \exp[-(1.7133 - 0.0368\sin^2\theta)ABSORP_3 + (0.0927 + 0.375\sin^2\theta)ABSORP_3^2]$$

The preferred orientation function is:

$$P_k = G_2 + (1-G_2)P[1 + d^2(EPR_1h^2 + EPR_2k^2 + EPR_3l^2 + EPR_42hk + EPR_52hl + EPR_62kl)/100]^{-3/2},$$

with $P = G_2 + (1-G_2)(G_1^2\cos^2\alpha + \sin^2\alpha/G_1)^{-3/2}$ (March-Dollase model chosen by IPREF=1)

or $P = G_2 + (1-G_2)\exp(-G_1\alpha^2)$ (Rietveld-Toraya model chosen by IPREF=0)

where G_1, G_2, and EPR_1...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 the EPR coefficients are refined without restraints, the scale-factor SF is 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:

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

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

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

$$\beta_{SG} = [(Z - Z_s)/\pi\ln2]^{1/2}\pi^2/360\lambda, \qquad \beta_{DG} = [(U - U_s)/\pi\ln2]^{1/2}\pi^2/360,$$

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 $<D>$ and its distribution dispersion $\sigma<D>$ is done using equations

$$<D> = D_A + (D_AD_V)^{1/2}/4 \qquad \text{and} \qquad \sigma<D> = <D>(D_V/D_A - 1/2)/2$$

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

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

4. *Quantitative phase analysis calculations*

In a mixture of N crystalline phases the net weight fraction W_i of phase i is given by:

$$W_i = S_iM_iV_iN_i^2 / \Sigma(S_jM_jV_jN_j^2) \qquad (4.1)$$

where S is the scale factor, M and V are the unit cell mass and volume, N is the space group multiplicity.
If the internal standard with the weighted fraction W_s is used, the phase fractions are corrected:

$$W_i^* = W_iW_s / W_0, \qquad W_R = 1 - \Sigma W_i^* \qquad (4.2)$$

where W_0 is the standard fraction calculated from (4.1), and W_R is the residual "amorphous" fraction.
The external standard based calculations are performed as follows:

$$W_i^* = \mu S_iM_iV_iN_i^2 / CT, \quad W_R = 1 - \Sigma W_i^* \qquad (4.3)$$

where μ is the sample mass absorption coefficient, C is the diffractometer constant (DIFC) determined from the external standard measurement, and T is the counting time of the current scan (TPS).

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.

Line	Par.N	Description
1.		Title – any 70 characters to be used to label the printout.
2.		Data file name
3.	1	JOBTYP – 0 – X-ray case
		1 – Neutron case(nuclear scattering only)
	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 in the sample
	4	NBCKGD – background correction control
		0 – polynomial background
		-1 – background to be estimated by weighted difference smoothing (see BKCURV, Line 5.10). The resultant curve is output to ddm_bckgr file
	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 θ-2θ X-ray data, or single detector neutron data (the Data file contains only profile intensities, see section B.)
		1 – the Data file contains profile intensities and squared variances
		2 – PANalytical XRDML data (multi-scans are summed)
		3 – XY (2Theta Intensity) format
		4 – XYE (2Theta Intensity Sigma) format
	8	IPREF – preferred orientation function type
		0 – Rietveld-Toraya function
		1 – March-Dollase 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 output
	5	NXT =1: parameters file is updated after the last cycle
	6	LST1 number of last refinement cycles to output
	7	LST2 not used
	8	LST3 not used
	9	LST4 not used

Line	Par.N	Description
5.	1	Lamda(1) – Wavelength1
	2	Lamda(2) – Wavelength2

	3	RATIO – Alpha2/Alpha1 intensity ratio
	4	BKPOS – origin of background polynomial (in °2θ)
	5	WDT – range of calculated peak profile in units of FWHM (beyond this the calc. profile is set to zero)
	6	CTHM – monochromator coefficient in polarization correction $[1 + CTHM*(\cos 2\theta)^2]/[\sin 2\theta \sin\theta]$
	7	TMR – convolution interval for R-Bragg calculation and profile decomposition in units of FWHM
	8	RLIM – peaks below this angle (2θ) are corrected for asymmetry by the Finger, Cox & Jephcoat model
	9	SAMPLE – angle (2θ) 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: $Icor=I/(1+(.0128+.0106*(SAMPLE-2\theta))*(SAMPLE-2\theta))$
	10	BKCURV – number of <FWHM> values in the weighted difference smoothing estimation of the background curve
6.	1	MCYCLE – number of refinement cycles (starting from 0)
	2	EPS – refinement convergence precision: run terminates when all parameter shifts are < EPS*e.s.u.
		RELAX – relaxation factors for parameter shifts
	3	(1) – coordinates & isotropic displacement factors
	4	(2) – anisotropic displacement parameters
	5	(3) – profile, asymmetry, overall atomic displacement and preferred orientation parameters
	6	(4) – peak shift and lattice parameters, overall scale factor, site occupancies
7.	1	NDEC – number of cycles for profile decomposition run (either DDM or Le Bail methods depending on CDDM) If NDEC > 0, the structure model is ignored and the squared structure factors F^2 are read from ddm_ffobs file which is overwritten with the refined F^2s after the final run cycle. If ddm_ffobs is absent, a set of equal F^2 is applied at the first decomposition cycle. If both MCYCLE and NDEC > 0, the refinement of profile parameters is 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 (optimal WDDM=3) 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 2θ **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 – zero-point for 2θ (in degrees)
	2	DISP – sample displacement 2θ correction parameter
	3	SHASM – asymmetry-related peak shift correction parameter
	4	ABSORP1,
	5	ABSORP2 – absorption correction coeffs. for flat sample: $Icor=I*[1 + ABSORP1*\exp(-ABSORP2/\sin\theta)]$ 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: $Icor = I*\exp[-(1.7133 - 0.0368*\sin^2\theta)* ABSORP3 +$

```
                                    + (0.0927 + 0.375*sin²θ)*ABSORP3²]
```
$$+ (0.0927 + 0.375*\sin^2\theta)*ABSORP3^2]$$

```
  8.2              Codewords for ZER, DISP, SHASM, ABSORP
  8.3              BACK  - polynomial background coefficients (six values)
  8.4              FBACK - codewords for background coefficients


 *9.               Not used

*10.               If NEXCRG > 0, there are NEXCRG lines
                   ALOW - 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, 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, AMAC – mass absorption coefficient
*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 = sinθ/lambda 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, there are instrumental broadening parameters
                   US, ZS, XS, YS for size-strain calculations (only for NPROF=7).


************************************************************************************
At this point optional code-lines may be added beginning from $ symbol followed
by the line-code and parameters:
          $QPA  SWT DIFC TPS OMAC – quantitative phase analysis constants
                SWT  – internal standard weight percent
                DIFC – diffractometer constant derived from external standard
                TPS  – counting time of current data scan
                OMAC – overall sample mass absorption coefficient (if known)
                If SWT>0, the 1st phase is assumed as the internal standard
                If DIFC=0, TPS>0, the DIFC constant will be calculated
                If OMAC=0, the MAC will be derived from the atomic composition
          $BFILE Filename – background curve file name
                The program will read the background point positions and
                intensities in free format from the specified file.
************************************************************************************


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        PARS  - Particle size [um] for the microabsorption correction


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
```

```
Line              Description
******************************* NATOM line sets *******************************
13.4        4 lines for each of the N atoms
13.41             LABEL - identification characters for atom (4 characters)
                  NTYP  - 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 GEOMETRY output
                       If ADIST<0, ANGLES will not be output to CIF for this atom
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, CBQ  - codewords for SF and BQ
13.6
13.61             U,V,W,Z,X,Y - FWHM ("H") parameters
                          For NPROF = 0...6
```

$$H^2 = U*\tan^2\theta + V*\tan\theta + W + Z/\cos^2\theta$$

```
                          X & Y are used only when NPROF = 7, where
```

$$HGauss = [U*\tan^2\theta + V*\tan\theta + W + Z/\cos^2\theta]^{0.5}$$

$$HLorentz = X*\tan\theta + Y/\cos\theta$$

```
13.62             CU,CV,CW,CZ,UX,UY - codewords for FWHM parameters
13.7
13.71             A, B, C, Alpha, Beta, Gamma - lattice parameters
                  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 - lattice parameters codewords
13.8
13.81             G1, G2 - preferred orientation parameters,
                       PO = G2 + (1 - G2)* PrefCorrr(G1)
                          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
                  P1, P2, FCJ - peak asymmetry parameters
                  P1 and P2 are the split-FWHM asymmetry parameters:
                    FWHM_left  = FWHM_right + 2P1*EXP(-2θ*0.084) + P2tanθ
                  FCJ is an effective slit_height/diffractometer_radius ratio in
                  the Finger, Cox & Jephcoat asymmetry model. The convergence of
                  FCJ refinement may be slow and/or unstable for strongly
                  overlapped and noisy data. Use an appropriate starting value
```

```
                       (0.01-0.02), RLIM (Line 5) and relaxation factors (Line 6)
13.82                  CG1, CG2, CP1, CP2, CFCJ - codewords for G1, G2, P1, P2, FCJ


Line                   Description


13.9                      Profile Shape parameters
13.91                  NA, NB, NC
```

For the usual pseudo-Voigt (NPROF=5) the Shape parameter
$$n = NA + NB*2\theta$$
For the Pearson VII (NPROF=6) the Shape parameter
$$m = NA + NB/2\theta + NC/(2\theta)^2$$
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:
$$Aniso2 = (STR1*h^2 + STR2*k^2 + STR3*l^2 + STR4*2hk +$$
$$+ STR5*2hl + STR6*2kl)*0.001*d^2$$
= 2 or –2 indicates 4th rank anisotropy tensor:
$$Aniso2 = [STR1*h^4 + STR2*k^4 + STR3*l^4 +$$
$$+ 3(STR4*h^2k^2 + STR5*h^2l^2 + STR6*k^2l^2) +$$
$$+ 2(STR7*kh^3 + STR8*hl^3 + STR9*lk^3 +$$
$$+ STR10*hk^3 + STR11*lh^3 + STR12*kl^3) +$$
$$+ 4(STR13*klh^2 + STR14*hlk^2 + STR15*khl^2)]*0.00001*d^4$$
For NPROF < 7, $H(a)^2 = H^2 + Aniso2*\tan^2\theta$
For NPROF = 7 only:
 if IAN3 > 0, $HLorentz(a) = HLorentz + Aniso2^{1/2}*\tan\theta$
 if IAN3 < 0, $HGauss(a) = HGauss + Aniso2*\tan^2\theta$

```
13.11
13.111                 EPR(6) - six preferred orientation coefficients for the
                               Ellipsoidal IPREF = 2) function:
```
$$Icorr = Iobs[1 + (EPR1*h^2 + EPR2*k^2 + EPR3*l^2 +$$
$$+ EPR4*2hk + EPR5*2hl + EPR6*2kl)*0.001d\hat{}2]^{-1.5}$$
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:
$$Aniso1 = (SIZ1*h^2 + SIZ2*k^2 + SIZ3*l^2 + SIZ4*2hk +$$
$$+ SIZ5*2hl + SIZ6*2kl)*0.001*d^2$$
For NPROF < 7, $H(a)^2 = H^2 + Aniso1/\cos^2\theta$
For NPROF = 7, $HLorentz(a) = HLorentz + Aniso1^{1/2}/\cos\theta$
```
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 2θ
  STEP   - step size in degrees 2θ
  STOP   - last angle in degrees 2θ
  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_ffobs', and 'ddm_fwobs'

  These files, if used, should be placed to the same folder from which the program was run.
  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 2θ).

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.