SIMPRO

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Contents

1 Introduction

Today, structure determination from powder diffraction data is well established and lots of crystal structures especially of inorganic compounds, where the High-T_C superconductors are the most prominent, have been solved. The Rietveld method (*Rietveld, 1969*) is the most common method to get structure and profile data from the powder pattern. But this method only works if there is a structure model of the compound. If the lattice and the Laue group is known, there are two ways to refine the lattice parameters from the powder pattern. The first one is a two-step method: At first the single peaks are fitted and then the lattice parameters are refined using the fitted peak positions. The second way is to do both in one step. This is realized with the program SIMPRO, where you fit the whole pattern with function $y_i^{calc}(a, b, c, \alpha, \beta, \gamma, \ldots)$. The lattice constants are the parameters for the peak positions. The additional variables are the profile and full-width-of-half-maximum parameters.
SIMPRO is not only a refinement program for the lattice constants, it is also possible to refine the three components of the wave vector of a incommensurate or commensurate modulation. Furthermore you obtain the intensities I' of each reflection with $I' \sim |F|^2$, because the Lorentz polarisation factors for different X-ray, neutron and synchrotron powder diffractometers are built in. So, these intensity data can be used to make a structure determination. Finally, the full-width-of-half-maximum parameters indicate the resolution of your diffractometer or line broadening caused by strain or grain size of the sample.
Some other important features of the program should be mentioned: One can refine up to two phases and if the second phase is a standard material like silicon, it can serve to scale the 2Θ values of the data set. It is possible to scale manually or automatically by fitting. Like the scaling on standards, the background can be fitted or determined manually and will be fixed during the refinement.
SIMPRO is written in FORTRAN 77 and tested on DECstations 5000 with Ultrix 4.3A.

2 The powder pattern

The powder pattern at the position $2\Theta_i$ can be calculated as a sum of neighbouring Bragg reflections contributing to the point i:

$$y_i^{calc} = s \sum_k m_k \, L_k \, |F_k|^2 \, A_{ik} \, p(x_{ik}, H_k, \eta, \ldots) \; + \; y_i^{back} \tag{1}$$

where

s is a scale factor,

k represents the Miller indices, h, k, l for a Bragg reflection

m_k is the multipicity of the kth Bragg reflection,

L_k is the Lorentz polarisation factor,

F_k is the structure factor for the kth Bragg reflection,

A_{ik} is the asymmetry correction,

$p(x_{ik}, H_k, \eta, \ldots)$ is the reflection profile function with $x_{ik} = 2\Theta_i - 2\Theta_k$, the full-width-of-half-maximum H_k and the profile function parameter η,

y_i^{back} is the background intensity at the ith step.

If there is no structure model for the measured powder diffraction pattern, it will be impossible to calculate $|F_k|^2$ like in the Rietveld method, where F_k is given by the atomic parameters. In order to fit the Bragg intensities I_k, the product $s \cdot |F_k|^2$ can be taken as a fitting parameter. So, each Bragg reflection has a individual parameter I_k' for its intensity:

$$I_k' = s \cdot |F_k|^2 \tag{2}$$

In the least squares refinement the residual χ^2 is minimized:

$$\chi^2(z_1, \ldots, z_P) = \sum_{i=1}^{N} w_i \left(y_i^{obs} - y_i^{calc}(z_1, \ldots, z_P) \right)^2 \tag{3}$$

where

$w_i = 1/\sigma_i^2 = 1/y_i^{obs}$ is the weight,

y_i^{obs} is the observed profile at $2\Theta_i$,

y_i^{calc} is the calculated profile at $2\Theta_i$,

$z_1, \ldots, z_P$ are the refinable parameters,

and the sum is over all data points N.

3 Program features

3.1 The profile functions

The following profile shape functions can be used with SIMPRO:

1. **Gaussian**:

$$G(x_{i,k}) = \frac{2\sqrt{\ln 2}}{H_k\sqrt{\pi}} \exp\left\{-4\ln 2\frac{x_{i,k}^2}{H_k^2}\right\} \tag{4}$$

2. **Lorentzian**:

$$L_n(x_{i,k}) = N_{n,k}\left[1 + \frac{C_n^2}{H_k^2}x_{i,k}^2\right]^{-n} \qquad \text{with} \quad C_n^2 := 4(2^{\frac{1}{n}} - 1) \tag{5}$$

Normalisation for $n = 1$ (Lorentzian):

$$N_{1,k} = \frac{C_1}{\pi H_k} \tag{6}$$

Normalisation for $n \geq 2$ (modified Lorentzian):

$$N_{n,k} = \frac{C_n}{\sqrt{\pi}H_k} \cdot \frac{\Gamma(n)}{\Gamma(n-1/2)} \qquad \text{with the Gamma function } \Gamma(n) \tag{7}$$

Normalisation for $n = \frac{3}{2}$ (intermediate Lorentzian):

$$N_{3/2,k} = \frac{C_{3/2}}{2H_k} \tag{8}$$

3. **Edgeworth serie:**

$$E(x_{ik}) = G(x_{ik}) - \frac{1}{3!}\eta_1\frac{\partial^3}{\partial x_{ik}^3}G(x_{ik}) + \frac{1}{4!}\eta_2\frac{\partial^4}{\partial x_{ik}^4}G(x_{ik}) + \frac{10}{6!}\eta_1^2\frac{\partial^6}{\partial x_{ik}^6}G(x_{ik}) + \cdots \tag{9}$$

with the parameters η_1 (skewness) and η_2 (excess)

4. **Pseudo-Voigt**:
The pseudo-Voigt function is a simple linear combination of a Gaussian and a Lorentzian, where the sum of the coefficients is equal 1. The Gaussian and the Lorentzian have the same full-width-of-half-maximum.

$$PV(x_{i,k}) = \eta\, L_1(x_{i,k}) + (1-\eta)\, G(x_{i,k}) \tag{10}$$

where the mixing parameter η is refinable.

5. **Pearson-VII**:

$$P^{VII}(x_{i,k}) = \frac{C_\mu}{\sqrt{\pi}H_k} \cdot \frac{\Gamma(\mu)}{\Gamma(\mu - \frac{1}{2})} \cdot \left[1 + \frac{C_\mu}{H_k^2} x_{i,k}^2\right]^{-\mu} \quad \text{with} \quad C_\mu^2 := 4(2^{\frac{1}{\mu}} - 1) \tag{11}$$

The refinable parameter μ is defined in the intervall $[1, \infty]$. For $\mu = 1$ the Pearson-VII ist equal to the simple Lorentzian an for $\mu \to \infty$ it is equal to the Gaussian.

6. **Double Gaussian**:

$$D(x_{i,k}) = \frac{4\sqrt{\ln 2}}{5\tilde{H}_k\sqrt{\pi}} \left(2\exp\left\{-4\ln 2 \frac{x_{i,k}^2}{\tilde{H}_k^2}\right\} + \exp\left\{-16\ln 2 \frac{x_{i,k}^2}{\tilde{H}_k^2}\right\}\right) \tag{12}$$

with $\tilde{H}_k = H_k/0.7786267$

The argument of the profile functions $x_{i,k}$ is defined as

$$x_{i,k} := 2\Theta_i - 2\Theta_k \ ,$$

where $2\Theta_k$ is the peak position of the kth peak. H_k is is the full-width-of-half-maximum of this peak.

3.2 The asymmetry correction

Asymmetric profiles can be fitted with the correction factor

$$A_{ik} = 1 - \mathrm{sign}(x_{ik}) P x_{ik} / \tan\Theta_k \tag{13}$$

with the parameter P. So, the powder pattern at the position $2\Theta_i$ can be calculated after

$$y_i^{calc} = \sum_{k=1}^{K} I_k \, A_{ik} \, p(x_{ik}) \ , \tag{14}$$

where $p(x_{ik})$ is the profile function at the position $2\Theta_i$.

3.3 The full-width-of-half-maximum (FWHM)

The angle dependence of the breadth of the peaks after *Caglioti et al. (1958)*:

$$\mathrm{H}(\Theta) = \sqrt{U\tan^2\Theta + V\tan\Theta + W}. \tag{15}$$

where U, V and W are refinable parameters.

3.4 The Lorentz polarisation factors

For the differnt diffraction geometries the following Lorentz polarisation factors L are built in:

1. **Neutron diffractometer (Debye-Scherrer geometry):**

$$L = \frac{1}{2\sin\Theta\sin 2\Theta} \tag{16}$$

2. **Guinier transmission geometry (diffractometer):**

$$L = \frac{1}{2\sin\Theta\sin 2\Theta} \cdot \frac{(1+\cos 2\Theta)^2\cos^2 2\Theta_M}{(1+\cos^2 2\Theta_M)} \cdot \frac{e^{-0.0633\sin(2\Theta+\pi/4)}}{\sin^2(2\Theta+\pi/4)} \tag{17}$$

3. **Guinier reflection geometry (diffractometer):**

$$L = \frac{1}{2\sin\Theta\sin 2\Theta} \cdot \frac{(1+\cos 2\Theta)^2\cos^2 2\Theta_M}{(1+\cos^2 2\Theta_M)} \cdot \frac{e^{-0.0633\sin(\pi-2\Theta+\pi/4)}}{\sin^2(\pi-2\Theta+\pi/4)} \tag{18}$$

4. **Guinier transmission geometry (film):**

$$L = \frac{1}{2\sin\Theta\sin 2\Theta} \cdot \frac{(1+\cos 2\Theta)^2\cos^2 2\Theta_M}{(1+\cos^2 2\Theta_M)} \cdot \frac{e^{-0.0633\sin(2\Theta+\pi/4)}}{\sin(2\Theta+\pi/4)} \tag{19}$$

5. **Bragg-Brentano diffractometer:**

$$L = \frac{1}{2\sin\Theta\sin 2\Theta} \cdot \frac{(1+\cos 2\Theta)^2\cos^2 2\Theta_M}{(1+\cos^2 2\Theta_M)} \tag{20}$$

6. **The 3 axes diffractometer at the synchrotron source:**

$$L = \frac{P}{2\sin\Theta\sin 2\Theta} \tag{21}$$

The **polarisation factor** P is for Bragg-Brentano parallel-beam geometry at a synchrotron (e. g. HASYLAB) given by

$$P = (1-K) + K\cos^2 2\Theta\,|\cos 2\Theta_A| \quad \text{with} \quad K = \frac{E_\sigma'^2}{E_\sigma'^2 + E_\pi'^2} \tag{22}$$

with the parameters K, which is the fraction of the intensity of the "wrongly" polarised radiation of the total intensity reaching the sample. θ_A is the Bragg-reflection angle at the analysator crystal in front of the detector. Another formulation is the one of *Giacovazzo et al. (1992)* and *Khan et al. (1982)*

$$P' = 0.5(1+\cos^2 2\Theta) - 0.5\zeta'\sin^2 2\Theta \quad \text{with} \quad \zeta' = \frac{E_\sigma'^2 - E_\pi'^2}{E_\sigma'^2 + E_\pi'^2} \tag{23}$$

where ζ' describes the polarisation of the radiation incident on the sample. The relation is $\zeta' = 2K-1$. The factor $|\cos 2\Theta_A|$ is correct for a perfect analyser-crystal and is often neglected. For a (ideal) mosaic crystal it has to be replaced by $\cos^2\Theta_A$, and real crystals

could be somewhere intermediate.
E'_σ and E'_π are the electrical field vectors of the components oszillating parallel and perpendicular to the (vertical) scattering plane. At a synchrotron with its strongly polarised radiation, ideally $E'^2_\sigma \ll E'^2_\pi$, i.e. $K \approx 0$ and $P \approx 1$. Experimentally K is $\approx 0.05 - 0.15$. P has its largest deviation from 1 at $2\Theta = 90°$.

The angle Θ_M is the diffraction angle of the monochromator. For the Guinier geometry an angle of 45° ($\pi/4$) between the sample and the incident beam is assumed.

3.5 The background

The background intensity can be fitted with the function y_i^{back} which has six refinable parameters c_0, ..., c_5:

$$y_i^{back} = \sum_{j=0}^{5} c_j \left(\frac{2\Theta_i - \Theta_{max} - \Theta_{min}}{\Theta_{max} - \Theta_{min}} \right)^j, \tag{24}$$

where Θ_{max} and Θ_{min} are respectively maximum and minimum Θ_i's.
Alternatively a fixed background can be used, calculated from some background values determined manually or read from the data file.

3.6 The peak-shift correction

The measured scattering angles $2\Theta_i$ can be corrected by

$$2\Theta_i^c = 2\Theta_i + \sum_{m=0}^{2} t_m (2\Theta_i)^m \tag{25}$$

where $2\Theta_i^c$ is the corrected angle and t_0, t_1 and t_2 are refinable parameters. The parameter t_0 is the zeropoint of the 2Θ scale.

3.6.1 Scaling on silicon standard

If silicon standard is measured with the sample, which has to be analysed, the silicon peaks can be treated as a second phase to scale on it. SIMPRO has built in the well known lattice constant a_{Si} in the temperature whole range up to 1500 K. In the range of $0\ K < T < 180\ K$ a_{Si} is taken from a tabular given by *Lyon et al. (1977)*. For $180\ K \leq T \leq 1500\ K$ a_{Si} is calculated with a formula given by *Okada et al. (1984)*. During the refinement the lattice parameter a_{Si} has to be fixed and so the refinement of the parameters t_i scales the whole pattern on silicon standard.

3.7 Modulated structures

The wave vector of the modulation is given as

$$\vec{q}/2\pi = \delta_1\vec{a}^* + \delta_2\vec{b}^* + \delta_3\vec{c}^* \tag{26}$$

where δ_1, δ_2 and δ_3 are refinable parameters. The reziprocal lattice vector can be written as

$$2\pi\vec{H} = 2\pi\vec{H}_0 + n\vec{q} \quad \text{with} \quad n = 0, \pm 1, \pm 2, \dots\ , \tag{27}$$

where n is the order of the satellite peaks and $\vec{H}_0$ is the basic peak:

$$\vec{H}_0 = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*. \tag{28}$$

So, all reflections can be indexed by four integer numbers h, k, l and n.

3.8 The definitions of the R-values

- "R-pattern":

$$R_p = \frac{\sum\limits_{i=1}^{N} \left| y_i^{obs} - y_i^{back} - y_i^{calc} \right|}{\sum\limits_{i=1}^{N} \left| y_i^{obs} - y_i^{back} \right|}$$

- "R-weigthed pattern":

$$R_{wp} = \left[\frac{\sum\limits_{i=1}^{N} w_i \left(y_i^{obs} - y_i^{back} - y_i^{calc} \right)^2}{\sum\limits_{i=1}^{N} w_i \left(y_i^{obs} - y_i^{back} \right)^2} \right]^{1/2}$$

- "R-expected":

$$R_e = \left[\frac{N - P}{\sum\limits_{i=1}^{N} w_i \left(y_i^{obs} - y_i^{back} \right)^2} \right]^{1/2}$$

- The "R-Bragg factor":

$$R_B = \frac{\sum\limits_{k=1}^{K} \left| I_k^{obs} - I_k^{calc} \right|}{\sum\limits_{k=1}^{K} \left| I_k^{obs} \right|}$$

- The "Goodness-of-fit":

$$S = \left[\frac{\chi^2}{N-P}\right]^{1/2} = R_{wp}/R_e$$

- The N_σ (*Ihringer, 1995*):

$$N_\sigma = \frac{\chi^2 - (N-P)}{\sqrt{2(N-P)}}$$

y_i^{obs} and y_i^{obs} are the observed and calculated pattern and y_i^{back} is the background at the position $2\Theta_i$. The weights w_i can be calculated from the standard deviation σ_i of y_i^{obs}:

$$w_i = \frac{1}{\sigma_i^2} = \frac{1}{y_i^{obs}} \qquad \text{with} \quad \sigma_i = \sqrt{y_i^{obs}}$$

The difference $(N-P)$ between the number of data N an the number of parameters P corresponds to the degrees of freedom. I_k^{obs} and I_k^{calc} are the "observed" and calculated intensity of the kth peak.

4 The different input and output files

4.1 The parameter input file

The parameters, SIMPRO needs to calculate y_i^{calc} are read from a special file. All lines of this input file which are read begin with a code like "`THE>`". All other lines are not read and treated as comments. The code always consists of three letters and the "`>`" sign after which the data begin. The different codes and the parameters belonging to them are listed in the following:

`COD:`

1. number of the diffraction geometry:
   - 1 Guinier diffractometer (transmission)
   - 2 Guinier film camera (transmission)
   - 3 Bragg-Brentano diffractometer
   - 4 3 axes synchrotron diffractometer
   - 5 neutron diffractometer (Debye-Scherrer)
   - 6 Guinier diffractometer (reflection)
2. number of the profile function:
   - 1 Gaussian
   - 2 Lorentzian
   - 3 Intermediate Lorentzian
   - 4 Modified Lorentzian
   - 5 Edgeworth serie
   - 6 Pseudo-Voigt
   - 7 Pearson-VII
   - 8 Double Gaussian
3. print (hkl)-list for each phase: $1 \rightarrow$ yes
   $0 \rightarrow$ no
4. print merged (hkl)-list: $1 \rightarrow$ yes
   $0 \rightarrow$ no
5. number of columns in the cycle file: $1 \rightarrow 132$
   $0 \rightarrow 80$
6. background: $0 \rightarrow$ background fitting (see section 3.5)
   $1 \rightarrow$ read background data file (see section 4.3)
   $2 \rightarrow$ use background data from data file (see section 4.2)
7. scaling: $0 \rightarrow$ no scaling or peak-shift correction (see section 3.6)
   $1 \rightarrow$ read scale data file (see section 4.4)
   $2 \rightarrow$ scaling on silicon standard (see section 3.6.1)
8. generate reflections: $1 \rightarrow$ yes
   $0 \rightarrow$ no
9. print "observed" and calculated intensities: $1 \rightarrow$ yes
   $0 \rightarrow$ no

`FIT:`

1. maximum number of cycles of the fit
2. ϵ: the refinement will be terminated if

   $$\Delta_n < \epsilon \cdot \sigma_n \cdot r_n$$

   where Δ_n, σ_n and r_n are the shift, the standard deviation and the relaxation factor of the parameter.

relaxation factors for –

3. profile parameters
4. halfwidth parameters
5. wave vector components
6. lattice constants
7. intensities
8. zeropoint and peak-shift parameters
9. background parameters
10. Wavelength λ_1

`DAT:` the name of the data file

`EXC:` minimum and maximum in 2Θ of an excluded region of the powder pattern, which are not taken into account during the refinement.

`BAC:` the 6 background parameters $c_0, \ldots, c_5$ or
the name of the background data file (only for fixed background).

`SCL:` the name of the file with the theoretical and observed peak positions of the standard material for scaling.

`WVL:`
1. Wavelength λ_1
2. Wavelength λ_2
3. ratio $I(\lambda_2)/I(\lambda_1)$

The wavelength λ_1 can be refined.

`THE:`
1. the 2Θ begin
2. the 2Θ end
3. the zeropoint t_0
4. the peak-shift parameter t_1
5. the peak-shift parameter t_2

`COR:`
1. base of peak w
2. maximum angle for asymmetry correction in 2Θ
3. The diffraction angle $2\Theta_M$ at the monochromator or the polarisation parameter K for synchrotron data
4. The diffraction angle at the analyser crystal $2\Theta_A$ (only for synchrotron data)

`GLB:` This line contains the coding of the global parameters. For the 10 global parameters the order is: the zeropoint, the 2 peak-shift parameters, the 6 background parameters, the wavelength λ_1. The codes which are allowed are "0", "1". "0" means that the parameter is fixed, "1" means that it should be refined: 1 $\rightarrow$ refine
0 $\rightarrow$ fixed

`PHS:`

1. name of the phase (maximum 4 characters are read)
2. centering of the unit cell (P, I, F, A, B, C, R)
3. number of the Laue group:
   - 1 triclinic $\bar{1}$
   - 2 monoclinic $2/m$ ($\alpha = \beta = 90°$, $\gamma \neq 90°$), unique axis c
   - 3 orthorhombic mmm ($\alpha = \beta = \gamma = 90°$)
   - 4 tetragonal $4/m$ ($a = b$, $\alpha = \beta = \gamma = 90°$)
   - 5 tetragonal $4/mmm$ ($a = b$, $\alpha = \beta = \gamma = 90°$)
   - 6 trigonal $\bar{3}$, hexagonal axes ($a = b$, $\alpha = \beta = 90°$, $\gamma = 120°$)
   - 7 trigonal $\bar{3}m1$, hexagonal axes ($a = b$, $\alpha = \beta = 90°$, $\gamma = 120°$)
   - 8 hexagonal $6/m$ ($a = b$, $\alpha = \beta = 90°$, $\gamma = 120°$)
   - 9 hexagonal $6/mmm$ ($a = b$, $\alpha = \beta = 90°$, $\gamma = 120°$)
   - 10 kubic $m\bar{3}$ ($a = b = c$, $\alpha = \beta = \gamma = 90°$)
   - 11 cubic $m\bar{3}m$ ($a = b = c$, $\alpha = \beta = \gamma = 90°$)
   - 12 monoclinic $2/m$ ($\alpha = \gamma = 90°$, $\beta \neq 90°$), unique axis b
   - 13 trigonal $\bar{3}$, rhombohedral axes ($a = b = c$, $\alpha = \beta = \gamma \neq 90°$)
   - 14 trigonal $\bar{3}m$, rhombohedral axes ($a = b = c$, $\alpha = \beta = \gamma \neq 90°$)
   - 15 trigonal $\bar{3}1m$, hexagonal axes ($a = b$, $\alpha = \beta = 90°$, $\gamma = 120°$)
4. structure type: 0 → non-modulated
1 → modulated
5. maximum order of the satellite peaks for modulated structures
6. default value of the Bragg intensities, if the program will be started and there still isn't an intensity file

`INT:` the file with the Bragg intensities (see section 4.5)

`MET:` the 6 lattice constants ($a, b, c, \alpha, \beta, \gamma$)

`WAV:` the 3 components of the wave vector $\vec{q}/2\pi$ in units of the reziprocal lattice constants (only for modulated structures)

`PRO:` the profile parameters

1. the skewness parameters of the edgeworth serie (5), the mixing parameter η of the pseudo-Voigt function (6) or the parameter μ of the Pearson-VII function (7)
2. the excess parameter of the edgeworth serie (5)
3. the asymmetry correction parameter P

`HWB:` the 3 halfwidth parameters U, V and W after *Caglioti et al. (1958)*

`PAR:` This line contains the coding of the parameters for each phase. For the 15 parameters and the intensities the order is: the 3 profile parameters, the 3 halfwidth parameters, the 3 wave vector components, the lattice parameters and the intensities (16 codes). The codes which are allowed are "0", "1" or "%n". "0" means that the parameter is fixed, "1" means that it should be refined and "means that the parameter should be refined like the same parameter of phase n: 1 → refine
0 → fixed
%n → refine like the same parameter of the phase n

For a two phase refinement the input lines with the codes

`PHS, INT, HWB, PRO, MET, PAR`

have to be repeated for the second phase.

Input file for one phase of a non-modulated structure:

```
TIT> Silicon (NBS standard), 300 K, Guinier data, counter 1
COD>   1     6      1     0    0     0     0      1    0
FIT>  30  0.3    0.2  0.2  0.2  0.4  0.2  0.2  0.4  0.8
DAT> si.duo
EXC> 0. 10.
BAC>     31.89    -22.18     -9.67      8.73     48.48    -35.25
WVL>   1.540600   0.000000   0.00000
THE>  22.00000  73.00000  -0.02878  0.1016E-01  -.2793E-05
COR>   3.5000   34.000   0.000   0.000
             (t0,t1,t2,c0,c1,c2,c3,c4,c5,L1)
GLB [1_10] >   1, 1, 1, 1, 1, 1, 1, 1, 1, 0

PHS> SI  F  11   0   3    20.
INT> si.int
MET>    5.43094   5.43094   5.43094  90.00000  90.00000  90.00000
PRO>    0.31921   0.00000   2.99005
HWB>    0.04477  -0.02235   0.00891
           (e1,e2,As, U, V, W,q1,q2,q3, a, b, c,al,be,ga, I)
PAR [1_16]>  1, 0, 1, 1, 1, 1, 0, 0, 0, 1, 1, 1, 1, 1, 1, 1
```

4.2 The data files

The first lines of a data file can be a title. The number of the lines are not limited. The title is terminated by a line which begins with a code of three characters. This code is followed by the specifications of the data separated by blanks:

1. code (3 characters)
2. measuring time t (not used by SIMPRO)
3. 2Θ begin
4. stepwidth in 2Θ
5. 2Θ end
6. temperature T
7. block number (not used by SIMPRO)
8. number of values

Example:

```
DAT   10.000   0.00000    0.020000    73.00000    300.0000   1    3651
```

The three allowed codes indicate the different file formats:

1. `DAT`: The **standard data file** with four columns: $2\Theta_i$, y_i^{obs}, σ_i, y_i^{back}; (values separated by blanks):

```
Si (NBS standard), 300 K, 50kV/150mA, counter 1,  22-AUG-1989 17:48:34.80
DAT   10.000   0.00000    0.020000    73.00000    300.0000   1    3651
10.00     6.      2.45     0.
10.02     6.      2.45     0.
10.04     3.      1.73     0.
10.06     5.      2.24     0.
10.08     3.      1.73     0.
10.10     6.      2.45     0.
10.12     8.      2.83     0.
10.14     6.      2.45     0.
10.16     8.      2.83     0.
10.18     4.      2.00     0.
```

2. `DUO`: The DUO-**Format** with 8 columns of y_i^{obs}: FORTRAN format code: `8(f7.0,1x)`

```
Si (NBS standard), 300 K, 50kV/150mA, counter 1,  22-AUG-1989 17:48:34.80
DUO   10.000   0.00000    0.020000    73.00000    300.0000   1    3651
     6.      6.      3.      5.      3.      6.      8.      6.
     8.      4.      4.      4.     10.      8.      3.      9.
     2.      2.      0.      7.      2.      5.      4.      9.
     6.      7.      6.      6.      5.      8.      6.      2.
     2.      7.      9.      6.      4.      1.      4.      4.
     8.      4.      3.      7.      5.      2.      3.      4.
     7.      6.      3.      3.      1.      7.      3.      4.
     7.      4.      4.      6.      5.      8.      9.      7.
     2.      4.      2.      7.      5.      8.      7.      1.
     7.      4.      6.     11.      3.      5.      3.      8.
     5.     11.      3.      3.      7.      5.      2.      5.
     8.      3.      4.      5.      3.      4.      6.      4.
     8.      8.      7.      5.      3.      3.      8.     12.
```

3. `NEU`: The **neutron data format** of the ILL (Grenoble):
FORTRAN format code: `10(i2,i6)`

```
Pb5Al3F19, 330K, HMI Berlin, 700000 Monitor
NEU   0.000   4.00000    0.100000     83.900     330.000    1    800
 1   352 1   358 1   395 1   428 1   486 1   487 1   439 1   499 1   504 1   553
 1   554 1   583 1   583 1   588 1   473 1   504 1   671 1   595 1   676 1   701
 1   682 1   668 1   825 1   813 1   790 1   866 1   835 1   834 1   801 1   819
 1   834 1   806 1   789 1   758 1   852 1   781 1   767 1   767 1   780 1   775
 1   766 1   798 1   748 1   805 1   828 1   813 1   840 1   789 1   771 1   796
 1   803 1   798 1   838 1   803 1   735 1   728 1   883 1   796 1   799 1   847
 1   821 1   832 1   865 1   814 1   874 1   845 1   810 1   777 1   833 1   827
 1   825 1   819 1   815 1   736 1   772 1   827 1   814 1   892 1   755 1   800
 1   786 1   742 1   830 1   789 1   813 1   777 1   749 1   787 1   810 1   787
 1   867 1   761 1   809 1   792 1   680 1   693 1   804 1   832 1   811 1   833
 1   814 1   789 1   881 1   925 1   953 1   888 1   863 1   833 1   894 1   924
```

4.3 The background data file

1. line:	title
data:	$2\Theta_u$, y_u^{back}, separated by blanks
excluded regions:	introduced by "`EXCLUDED REGIONS`"
	$2\Theta_{beg}$, $2\Theta_{end}$, separated by blanks

If no excluded regions are required, the file ends with the last pair of background data and not with "`EXCLUDED REGIONS`"!

Example: Background data file

```
Background data of file si1.duo
  25.407  78.397
  27.593  69.932
  28.834  62.313
  29.629  55.541
  29.927  61.466
  32.559  57.234
  34.521  42.843
  39.412  38.610
  40.391  36.917
  46.227  36.917
  47.021  36.917
  54.521  25.912
  56.333  25.912
  59.537  23.372
  60.163  23.372
  68.004  23.372
  69.550  21.679
  72.716  21.679
EXCLUDED REGIONS
   0.000  25.000
```

4.4 The scale file

This file contains calculated and observed peak positions in 2Θ of a standard material.

1. line :	title
data :	calculated peak positions $2\Theta_k^c$, observed peak positions, $2\Theta_k^o$ separated by blanks

Example: file with the peak positions of silicon standard

```
silicon standard at room temperature, Guinier diffr., counter 1
     28.4424      28.1864
     47.3028      46.8600
     56.1225      55.5987
     69.1301      68.4705
```

4.5 The file with the Bragg intensities

File with the Bragg intensities for a single phase including the 2Θ positions the Lorentz polarisation factors and the multiplizities. The number of the wavelength is given in the second column. In the last column the intensity parameter can be fixed with a "0" or refined with a "1". This file is created by default, if it does not exist, but it can also be created by the user (see section 4.1).

Example: file with the Bragg intensities of silicon:

```
No. Co.     h    k    l  Mult     2-Theta        Lopo     Intensity     I_sigma     R
  1   1     1    1    1     8     28.4424      3.9387       20.6927      0.1532     1
  2   1     0    0    2     6     32.9588      2.7677        0.0000      0.0000     0
  3   1     0    2    2    12     47.3028      1.2141       27.1533      1.5354     1
  4   1     1    1    3    24     56.1225      0.8692       11.3334      0.5366     1
  5   1     2    2    2     8     58.8564      0.8024        0.0000      0.0000     0
  6   1     0    0    4     6     69.1301      0.6567       17.4380      0.7401     1
```

4.6 The cycle file

This file contains a commpressed summary of the refinement with the parameters, the shifts, the standard deviations and the R-values of each cycle. It is possible to choose a file either with 80 or 132 columns (see section 4.1).

4.7 The plot file

File with the fitted data, the corrected 2Θ scale and the background values. The first line is the title from the input file and the second line consists of the code "`SIM`", 2Θ begin, stepwidth, 2Θ end, the temperature and the number of values. The data follows in free format only separated by blanks: $2\Theta_i^c$, y_i^{obs}, y_i^{calc}, $y_i^{obs} - y_i^{calc}$, y_i^{back}.

```
Silicon (NBS standard), 300 K, Guinier data, counter 1
SIM        22.1935      0.0200        73.6984         300.00      2551
     22.1935         118.         119.          -1.         119.
     22.2137         117.         119.          -2.         119.
     22.2339         117.         119.          -2.         119.
     22.2541         132.         119.          13.         119.
     22.2743          96.         118.         -22.         118.
     22.2945         104.         118.         -14.         118.
     22.3147         122.         118.           4.         118.
     22.3349         120.         118.           2.         118.
     22.3551         120.         117.           3.         117.
     22.3753          99.         117.         -18.         117.
     22.3955         103.         117.         -14.         117.
     22.4157          98.         116.         -18.         116.
```

4.8 The (hkl)-file

File with a list of the Bragg reflection in the given 2Θ region including the Lorentz polarisation factor, the fwhm and the multiplicity. The number of the phase and the wavelength is given in the second and third column:

```
Silicon (NBS standard), 300 K, Guinier data, counter 1
   No. Ph. Co.      2-Theta       Lopo         Fwhm        h   k   l    Mult
     1   1   1      28.4424      3.9387       0.0782       1   1   1       8
     2   1   1      32.9588      2.7677       0.0788       0   0   2       6
     3   1   1      47.3028      1.2141       0.0878       0   2   2      12
     4   1   1      56.1225      0.8692       0.0986       1   1   3      24
     5   1   1      58.8564      0.8024       0.1027       2   2   2       8
     6   1   1      69.1301      0.6567       0.1215       0   0   4       6
```

5 How to start SIMPRO

SIMPRO can be started with the following command:

`$ simpro11`

Immediately after SIMPRO is started, it asks for the name of the input file and waits until the name is entered. Then the program begins to work.

5.1 How to start SIMPRO on Unix systems

On Unix systems it is possible to start SIMPRO with a shell script program with the following command:

`$ simpro [-option] <filename>.inp`

`simpro` is the name of the shell script and `<filename>.inp` is the name of the input file. The allowed options `-option` are:

-r simple profile refinement (default)

-f automatic refinement of several datasets at different temperatures (eg film-lift data).

Example:

`$ simpro -r demo.inp`

If no option is used, the simple profile refinement will be executed.
Shell script for the bash and the csh shell are available.

5.2 Refinement of several datasets at different temperatures

If SIMPRO is started with the option `-f`, the shell script `simpro` expects an arbitrary number of datasets, which are measured at different temperatures (eg the different lines of a film-lift) where silicon powder has to be measured with the sample as a second phase. The names of the data files have to be the following form:

name$z$.duo

The datasets should be ordered in ascending or descending temperature which have to be done with the number z of the filename. The following tabular shows an example:

temperature/K	filename	temperature/K	filename
300	test01.duo	200	test07.duo
290	test02.duo	150	test08.duo
280	test03.duo	100	test09.duo
270	test04.duo	50	test10.duo
260	test05.duo	25	test11.duo
250	test06.duo	10	test12.duo

The temperature has to be correctly entered in the data file, because SIMPRO reads it from this file to do the scaling on silicon standard.

In the input file the following settings has to be choosen (see chapter 4.1):

1. two phases: 1. phase = the sample to be analysed
2. phase = silicon standard
2. background fitting (see section 3.5)
3. scaling of the 2Θ values on silicon standard, which was measured together with the sample as a second phase.
4. the name of the data file has to be sim.duo.

The parameter file has to be prepared for two phases.

When the shell script simpro is started, for each dataset the data file namez.duo will be copied to sim.dat, because the real refinement program simpro12 always read the data file sim.dat, which is given in the input file. After the refinement of one dataset the created cycle file <filename>.cyc will be renamed to <filename>z.cyc. All the other output files will not be saved. In addition the lattice constants with their standard deviations for all temperatures will be stored in the file <filename>.met in tabular form.

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