SIMREF 2.6

Version 2.6 (1999)

Simultaneous Structure Refinement with
Multiple Powder Diffraction Data Sets

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Last updated: April 12, 1999

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1 New Features

Version 2.3:

The essential changes and extensions of version 2.3 compared with version 2.2 are:

- More than two phases per data set can be refined now. The maximum number of phases is specified in the file "`par.inc`" before compiling the program.
- The background can be fitted by a polynomial with six refinable coefficients (see section 2.9) or entered from the data file. However, the background can also be determined by linear interpolation of values given in a file.
- In addition, a calibration of the 2Θ-axis (peak-shift correction) can be done with a polynomial of second degree in 2θ with three refinable coefficients (see section 2.10). Please note that the zeropoint (first coefficient of the polynomial) has the opposite sign as in older versions of the program. This method now allows to calibrate the powder pattern to a standard material measured simultaneously. For the silicon standard the lattice parameters are built in for temperatures 10 K $<$ T $<$ 1500 K and can be used by the program for the calibration if this is desired. If a substance was measured at different temperatures together with a silicon standard, the data sets can be refined together automatically (see section 12.2).
- The parameter file was revised because of the new parameters and now it is also more compact (see chapter 8).
- The small changes in the input file, which were necessary because of the new parameters, are described in detail in chapter 7.
- The unit cell volume and its standard deviation are calculated after the refinement.
- The parameters of the peak shape function (for example the η parameter of the Pseudo-Voigt function) can be individually refined for each phase.
- The wavelength can be refined. Therefore the wavelength for synchrotron or neutron data can be determined using a standard material.
- The structure factor F_{000} is calculated and written into the output file together with the other structure factors.
- Because the calculation of the individual profile values was optimized, the version 2.3 is clearly faster compared with older versions.
- SIMREF now also runs under Linux (f2c/GNU C) and DOS/Windows (MS-Fortran-Powerstation). Besides, user of the program reported a successfull installations on IBM and Convex computers as well as on HP-Workstations (all with the operating system Unix).
- Removed bugs:
  - The coding of the parameter of the anisotropic temperature factors.
  - Some problems with reading and processing of the parameter files on several Unix computers have been solved.

- In case of unit cell angles (α, β, γ) that differed a lot from 90° it sometimes happened that SIMREF "forgot" some reflections at high diffraction angles. Due to a more accurate calculation of the maximum values h_{max}, k_{max} and l_{max} this error does not occur anymore now.

Version 2.4:

- For modulated structures the displacement vectors and its parameters of each Wyckoff position are given separately in a file. With that the input particularly for special positions becomes clearer.
- A new (hkl) index generator for the reflections of a modulated structure was built in.

Version 2.5:

- The program SIMPRO is built in and can be used with the SIMREF input and parameter file where only a few modifications are necessary (see section 5)
- The space group can be alternatively entered using the complete symbol, the short symbol or the number taken from the *Int. Tables* (see section 7).
- The standard deviations of angular positions can be entered to the program which modify the individual weights of the measured data (see section 2.11).
- The Durbin-Watson statistic is added to the other numerical criteria od fit (see section 2.7.1).
- The Absorption correction for neutron data (Debye-Scherrer geometry) is introduced.
- A SHELX instruction file can be generated.
- The refinement of magnetic structures using magnetic space groups has been realized.
- The relative weight fractions of each phase are calculated automatically after a multiple phase refinement (quantitative phase analysis).

Version 2.6:

- The original Rietveld peak asymmetry correction is replaced by the function of Bérar et al. [1].
- Alternatively the correction for peak asymmetry due to axial divergence worked out by Finger et al. [6] using the subroutine PROFVAL [6] is available.
- The least squares fitting routine is replaced by the modified routine MRQMIN (Levenberg-Marquardt method) [22].
- The preferred orientation correction by Dollase [4] can be used alternatively to the original Rietveld correction.
- The mixing parameter η of the pseudo-Voigt and the exponent μ of the Pearson-VII function can be refined as a function of 2θ.
- The program PROMET which calculates the base vectors of the modes for modulated structure refinements is now available together with the source code of SIMREF.

2 General

SIMREF is a structure refinement program for the simultaneous evaluation of several powder diffraction data sets (fig. 1) and multiple phases per data set. With a structural model all calculated diffraction profiles are fitted to the corresponding observed diffraction profile by the method of least squares. This procedure is called **Rietveld method** (*Rietveld, 1969*). By the simultaneous refinement of several data sets new evaluation techniques are possible:

- Data from neutron and X-ray (home laboratory or synchrotron sources) can be processed simultaneously. Therefore the advantages of each diffraction technique are used within one procedure: high resolution for X-ray and synchrotron diffraction, good localization of light atoms for neutron diffraction.
- Data that have been measured in an experiment with several counters can be treated as multiple data sets. Because of this the merging of the data that has been necessery until now can be avoided. So the resolution of the different counters may be fully exhausted.
- At synchrotron sources diffraction experiments can be carried out at different wavelengths. The wavelength can be chosen near the absorption edge of a particular atom type in the sample, which therefore scatters anomalously. In this way the scattering contrast beween neighbouring elements in the periodic system may be enhanced. With the corresponding anomalous scattering corrections of the atomic form factor $\Delta f'$ and $\Delta f''$ for the relevant atoms, the data sets can be evaluated simoultaneously.
- Diffraction elements are often carried out with limited measuring time. To detect weak superlattice lines, certain small ranges in 2θ can be measured with a much higher measuring time, and then refined together with the whole data set.

Every combination of the possibilities mentioned above is allowed. The only restriction is given by the size of the main memory of the computer used.

In addition to the refinement, the program SIMREF offers options for:

- Calculation of powder patterns
- Calculation of structure factors
- Generation of a reflection list

For structure refinement, according to the Rietveld method, first the so-called residual is calculated:

$$\chi^2(\boldsymbol{\alpha}) = \sum_{i=1}^{N} w_i \left(y_i^{obs} - y_i^{calc}(\boldsymbol{\alpha}) \right)^2 \tag{1}$$

The summation is over all measuring points y_i^{obs} that are used in the refinement. The vector $\boldsymbol{\alpha}$ describes the parameters of the model. With this model the intensity $y_i^{calc}(\boldsymbol{\alpha})$ is calculated. The quantity w_i is a weight for every individual measurement point. Now the program tries to find a new set of parameters $\boldsymbol{\alpha}$, that is a new structure model, fitting the calculated diffraction pattern better to the observed one than

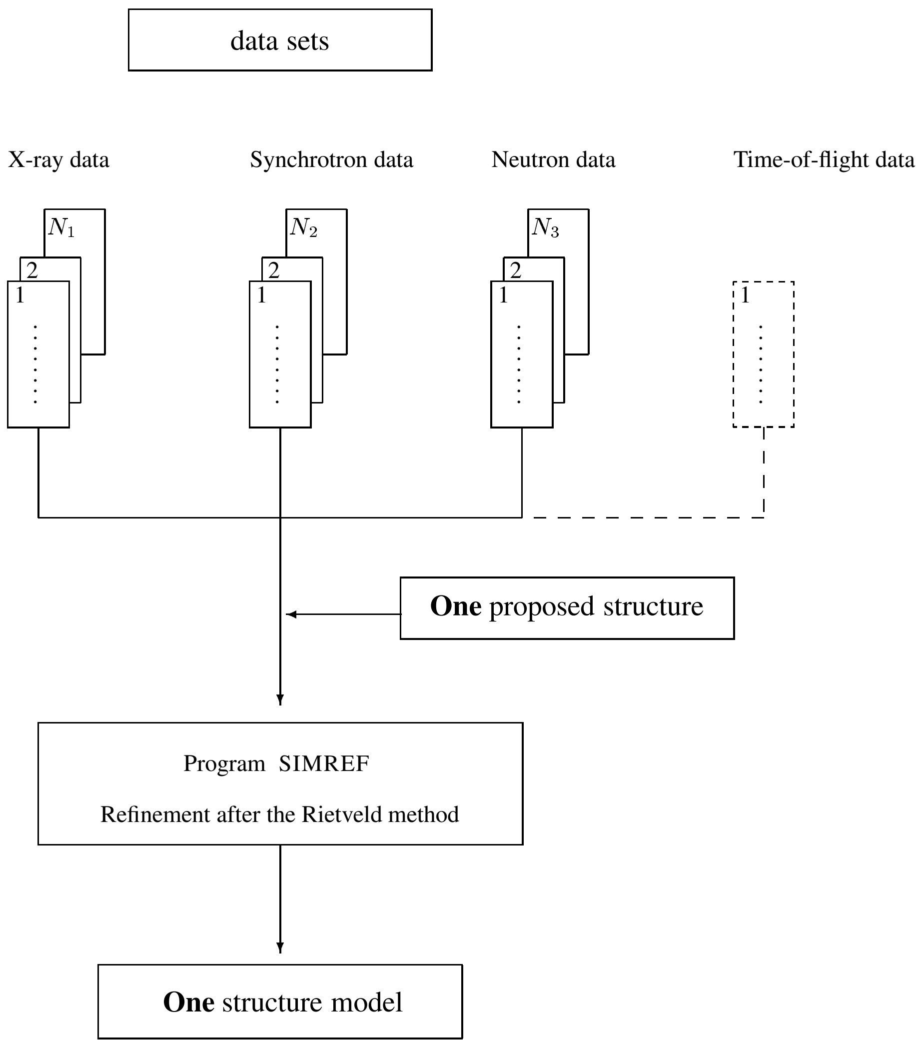

Figure 1: Schematic diagram of the simultaneous structure refinement.

the initial model. For this new set of parameters the residual is minimal. As the parameters $\boldsymbol{\alpha}$ enter non-linearly in (1), the problem is first linearized. Then a set of parameters $\boldsymbol{\alpha}$ is determined with a iterative procedure (in the program SIMREF with the Levenberg-Marquardt method), that minimizes the residual (1).
In principle only the measurements are considered that are inside of a definite area

$$[2\theta_k - \omega \cdot H_k, 2\theta_k + \omega \cdot H_k]$$

around the kth Bragg reflection at $2\theta_k$. H_k is the angle-dependent full-width-of-half-maximum and is described using the three parameters U, V and W according to *Caglioti et al. (1958)*,

$$H_k(\theta_k) = \sqrt{U \tan^2 \theta_k + V \tan \theta_k + W} \quad . \tag{2}$$

ω is entered as a parameter into the program. Depending on the width of the base of a peak ω should be between 1.5 and 10.

2.1 Peak shape functions

The peak shapes of neutron diffraction are well fitted using Gaussian functions. For high resolved X-ray or synchrotron profiles some authors have developed different peak shape functions. In the program SIMREF the following functions are built in. Here the following abbreviations are used:

$$x_{i,k} := 2\theta_i - 2\theta_k \tag{3}$$
$$C_n^2 := 4(2^{\frac{1}{n}} - 1) \tag{4}$$

Gaussian function:

$$G(x_{i,k}) = \frac{2\sqrt{\ln 2}}{H_k\sqrt{\pi}} \exp\left\{-4\ln 2\frac{x_{i,k}^2}{H_k^2}\right\} \tag{5}$$

Lorentzian function:

$$L_n(x_{i,k}) = N_{n,k}\left[1 + \frac{C_n^2}{H_k^2}x_{i,k}^2\right]^{-n} \tag{6}$$

Normalisation for $n = 1$ (simple Lorentzian function):

$$N_{1,k} = \frac{C_1}{\pi H_k} \tag{7}$$

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

$$N_{n,k} = \frac{C_n}{\sqrt{\pi}H_k} \cdot \frac{\Gamma(n)}{\Gamma(n-1/2)} \tag{8}$$

where $\Gamma(n)$ is the Gamma function.
Normalisation for $n = \frac{3}{2}$ (intermediate Lorentzian function):

$$N_{\frac{3}{2},k} = \frac{C_{3/2}}{2H_k} \tag{9}$$

Edgeworth serie [23]:

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

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

Pseudo-Voigt function:

The pseudo-Voigt function is a linear combination of a Gaussian and a Lorentzian, where the sum of the coefficients is always equal to 1. For the Gaussian and the Lorentzian the same full-width-of-half-maximum is used.

$$PV(x_{i,k}) = \eta L_1(x_{i,k}) + (1-\eta)G(x_{i,k}) \tag{11}$$

The mixing parameter η can be refined as a function of 2θ with three parameters:

$$\eta(2\theta) = \eta_0 + \eta_1(2\theta) + \eta_2(2\theta)^2 \tag{12}$$

Pearson-VII function:

$$P^{VII}(x_{i,k}) = \frac{1}{\sqrt{\pi}\sqrt{\mu}a_k} \cdot \frac{\Gamma(\mu)}{\Gamma(\mu-\frac{1}{2})} \cdot \left[1 + \frac{1}{\mu a_k^2} x_{i,k}^2\right]^{-\mu} \tag{13}$$

where a_k is the half width of the height $(1+\frac{1}{\mu})^{-\mu}$. The exponent μ is in the intervall [1,∞] e.g. $\mu \geq 1$, and can be refined as a function of 2θ with three parameters:

$$\eta(2\theta) = \mu_0 + \mu_1/(2\theta) + \mu_2/(2\theta)^2 \tag{14}$$

An alternative formulation is

$$P^{VII}(x_{i,k}) = \frac{C_\mu}{\sqrt{\pi}H_k} \cdot \frac{\Gamma(\mu)}{\Gamma(\mu-\frac{1}{2})} \cdot \left[1 + \frac{C_\mu}{H_k^2} x_{i,k}^2\right]^{-\mu} \tag{15}$$

with the full-width-of-half-maximum H_k.

2.2 Scattering lengths and coefficents

The neutron scattering lengths (*Sears (1984)*) and the coefficients for analytical approximation to scattering factors (*Int. Tables Vol. IV, Table 2.2B, p. 99-101*) are stored in BLOCKDATA statements in the program source code. The atomic scattering amplitudes for X-rays can be calulated by the equation

$$f(u) = c + \sum_{i=1}^{4} a_i \cdot e^{-b_i u^2} \quad \text{with} \quad u = \frac{\sin\theta}{\lambda}. \tag{16}$$

The anomalous scattering factors Δf' and Δf" for X-rays are built into the program for Cr-, Fe-, Cu-, Mo- and Ag-$K_{\alpha 1}$ radiation. (*Cromer & Libermann (1970), Table I*). For other wavelengths the anomalous scattering factors can be calculated using the well-known program "FPRIME" of *Cromer & Liberman (1970)* and entered into the SIMREF input file.

2.3 The preferred orientation correction

The preferred orientation of the powder grains in the sample, which leads to a distortion of the intensities $I_k^{(0)}$, can be corrected using the following factor:

$$I_k = I_k^{(0)} \left[G_2 + (1 - G_2) e^{-G_1 \Phi_k^2} \right] \tag{17}$$

where Φ_k is the angle between the preferred orientation vector and the reciprocal lattice vector $\vec{H}_k$ of the corresponding reflection and G_1 and G_2 are refinable parameters.

Alternatively the correction by Dollase (March-Model) can be applied [4]:

$$I_k = I_k^{(0)} \left[G_1^2 \cos^2 \Phi_k + (1/G_1) \sin^2 \Phi_k \right]^{-3/2} \tag{18}$$

2.4 The asymmetry correction

2.4.1 Asymmetry correction factor

Asymmetric profiles can be fitted with the correction factor of Bérar and Baldinozzi [1]:

$$a_{i,k} = [1 + A(\theta) F_a(x_{i,k}) + B(\theta) F_b(x_{i,k})] \tag{19}$$

where

$$A(\theta) = A_0 / \tan(\theta) + A_1 / \tan(2\theta) \tag{20}$$

and

$$B(\theta) = B_0 / \tan(\theta) + B_1 / \tan(2\theta) \tag{21}$$

with the refinable parameters A_0, B_0, A_1 and B_1. The functions F_a and F_b are defined as

$$F_a(x) = 2x \exp(-x^2) \tag{22}$$

and

$$F_b(x) = (8x^3 - 12x) \exp(-x^2). \tag{23}$$

So the powder pattern at the position $2\theta_i$ can be calculated as

$$y_i^{calc} = \sum_{k=1}^{K} I_k a_{i,k} p(x_{i,k}) \ , \tag{24}$$

where $p(x_{i,k})$ is the peak shape function at the position $2\theta_i$.

2.4.2 Asymmetric pseudo-Voigt function

Finger et al. [5] worked out a correction for peak asymmetry due to axial divergence in terms of finite sample size $2S$ and detector size $2H$, which describes the observed profiles of Bragg-Brentano, synchrotron and neutron diffractometers. This method is implemented to SIMREF using the subroutine PROFVAL [6], where a pseudo-Voigt function (11) with two additional refinable parameters S/L and H/L is introduced. L is the sample-to-detector distance.

2.5 The Lorentz polarisation factor

For the different diffraction geometries the following Lorentz polarisation factors LP are built in:

Neutron diffractometer (Debye-Scherrer geometry):

$$LP = \frac{1}{2\sin\theta\sin 2\theta} \tag{25}$$

Guinier transmission geometry (diffractometer):

$$LP = \frac{1}{2\sin\theta\sin 2\theta} \cdot \frac{(1+\cos 2\theta)^2\cos^2 2\theta_M}{(1+\cos^2 2\theta_M)} \cdot \frac{e^{-0.0633\sin(2\theta+\pi/4)}}{\sin^2(2\theta+\pi/4)} \tag{26}$$

Guinier reflection geometry (diffractometer):

$$LP = \frac{1}{2\sin\theta\sin 2\theta} \cdot \frac{(1+\cos 2\theta)^2\cos^2 2\theta_M}{(1+\cos^2 2\theta_M)} \cdot \frac{e^{-0.0633\sin(\pi-2\theta+\pi/4)}}{\sin^2(\pi-2\theta+\pi/4)} \tag{27}$$

Guinier transmission geometry (film):

$$LP = \frac{1}{2\sin\theta\sin 2\theta} \cdot \frac{(1+\cos 2\theta)^2\cos^2 2\theta_M}{(1+\cos^2 2\theta_M)} \cdot \frac{e^{-0.0633\sin(2\theta+\pi/4)}}{\sin(2\theta+\pi/4)} \tag{28}$$

Bragg-Brentano diffractometer:

$$LP = \frac{1}{2\sin\theta\sin 2\theta} \cdot \frac{(1+\cos 2\theta)^2\cos^2 2\theta_M}{(1+\cos^2 2\theta_M)} \tag{29}$$

3-axes diffractometer at the synchrotron source:

$$LP = \frac{P}{2\sin\theta\sin 2\theta} \tag{30}$$

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.

2.5.1 The polarisation factor at a synchrotron source

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

$$P = (1 - K) + K \cos^2 2\theta \,|\cos 2\theta_A| \quad \text{with} \quad K = \frac{E_\sigma'^2}{E_\sigma'^2 + E_\pi'^2} \tag{31}$$

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* (1992) and *Khan et al.* (1982)

$$P' = 0.5(1 + \cos^2 2\theta) - 0.5\zeta' \sin^2 2\theta \quad \text{with} \quad \zeta' = \frac{E_\sigma'^2 - E_\pi'^2}{E_\sigma'^2 + E_\pi'^2} \tag{32}$$

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 $\cos^2 2\theta_A$, 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 $E_\sigma'^2 \ll E_\pi'^2$, i.e. $K = 0$ and $P = 1$. Experimentally K is approximately 0.05-0.15. P has its largest deviation from 1 at $2\theta = 90°$.

2.6 Absorption correction for neutron data

For a neutron diffractometer with Debye-Scherrer geometry the absorption factor A for a cylindrical sample with the radius R and the linear absorption coefficient μ an analytical approximation is given by *Rouse et al. (1970)* and *Hewat (1979)*:

$$A = \exp\{-(a_1 + b_1 \sin^2\theta)\mu R - (a_2 + b_2 \sin^2\theta)(\mu R)^2\} \;, \tag{33}$$

with the following values for the coefficients:

$$\begin{aligned} a_1 &= 1.7133 \\ b_1 &= -0.0368 \\ a_2 &= -0.0927 \\ b_2 &= -0.3750 \end{aligned}$$

The error of A does not exceed 0.0035 for $\mu R < 1$.

2.7 The definitions of the R-values

These are the definitions of the R-values used in the program:

- "R-pattern":

$$R_p = \frac{\sum\limits_{i=1}^{N} \left| y_i^{obs} - y_i^{back} - y_i^{calc} \right|}{\sum\limits_{i=1}^{N} \left| y_i^{obs} - y_i^{back} \right|} \cdot 100\%$$

- "R-weighted pattern":

$$R_{wp} = \left[\frac{\sum\limits_{i=1}^{N} w_i \left(y_i^{obs} - y_i^{back} - y_i^{calc} \right)^2}{\sum\limits_{i=1}^{N} w_i \left(y_i^{obs} - y_i^{back} \right)^2} \right]^{1/2} \cdot 100\%$$

- "R-expected":

$$R_e = \left[\frac{N - P}{\sum\limits_{i=1}^{N} w_i \left(y_i^{obs} - y_i^{back} \right)^2} \right]^{1/2} \cdot 100\%$$

- The "Goodness-of-fit":

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

- N_σ (*Ihringer, 1995*):

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

- The "R-Bragg factor":

$$R_B = \frac{\sum\limits_{k=1}^{K} \left| I_k^{obs} - I_k^{calc} \right|}{\sum\limits_{k=1}^{K} \left| I_k^{obs} \right|} \cdot 100\%$$

y_i^{obs} and y_i^{calc} 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}:

$$w_i = \frac{1}{\sigma_i^2}$$

The difference $N - P$ between the number of data N and the number of parameters P corresponds to the degrees of freedom. I_k^{obs} and I_k^{calc} are the "observed" and calculated intensities of the k-th peak.

2.7.1 The Durbin-Watson statistic

The weighted form of the Durbin Watson d statistic (*Hill et al. (1987)*) is defined as

$$d = \frac{\sum_{i=2}^{N} \left(\frac{\Delta_i}{\sigma_i} - \frac{\Delta_{i-1}}{\sigma_{i-1}} \right)^2}{\sum_{i=1}^{N} \left(\frac{\Delta_i}{\sigma_i} \right)^2} \qquad \text{with} \qquad \Delta_i = y_i^{obs} - y_i^{calc} \tag{34}$$

The parameter Q for the significance level 0.1% is given by:

$$Q = 2 \left[\frac{N-1}{N-P} - \frac{3.0902}{\sqrt{N-P}} \right] \tag{35}$$

(see *Hill et al. (1987)*

$d < Q < 2$: Successive values of the residuals tends to have the same sign and have **positive serial correlation**.

$d > 4 - Q > 2$: Successive values of the residuals tends to have opposite sign and have **negative serial correlation**.

else : Consecutive residuals are **insignificanty correlated**.

2.8 Anisotropic temperature factors

In Crystallography the anisotropic temperature factors β_{ij}, B_{ij} and U_{ij} are normally used. The relation between the different factors is given:

$$\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\} = \tag{36}$$

$$\exp\{-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + B_{12}a^*b^*hk + B_{13}a^*c^*hl + B_{23}b^*c^*kl)\} = \tag{37}$$

$$\exp\{-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + U_{12}a^*b^*hk + U_{13}a^*c^*hl + U_{23}b^*c^*kl)\} \tag{38}$$

2.9 The background

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

$$y_i^{back} = \sum_{j=0}^{5} c_j \left(\frac{2\theta_i - \theta_{max} - \theta_{min}}{\theta_{max} - \theta_{min}} \right)^j, \tag{39}$$

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.

2.10 Calibration of the 2θ scale

2.10.1 Standard peaks

If a standard material was measured together with the sample as a second phase, its reflections can be taken for scaling. For this the positions of the standard peaks $2\theta_k^{obs}$ have to be determined and together with the positions $2\theta_k^{calc}$ calculated from the lattice constants stored in a file (see section 9.3). The corrected 2θ values can be calculated as

$$2\theta_i^c = 2\theta_k^{calc} + \frac{2\theta_{k+1}^{calc} - 2\theta_k^{calc}}{2\theta_{k+1}^{obs} - 2\theta_k^{obs}} \left(2\theta_i - 2\theta_k^{obs}\right) \tag{40}$$

2.10.2 The peak-shift correction

The measured scattering angles $2\theta_i$ can be corrected using the 2nd-order polynomial in $2\theta_i$

$$2\theta_i^c = 2\theta_i + \sum_{m=0}^{2} t_m (2\theta_i)^m \tag{41}$$

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.

2.10.3 Scaling on the second phase

If a standard material was added to the sample as a second phase, the 2θ scale can be scaled with the peak-shift correction (see section 2.10.2). For that the lattice constants of the standard material have to be fixed during the refinement and the coefficients t_0, t_1 and t_2 of the polynomial (41) have to be refined. If silicon was choosen as the standard material, it is possible to use the built in lattice constants $a_{Si}(T)$ for $0 < T \leq 1500\ K$. In the range of $0 < T < 180\ K$ 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 polynomial given by *Okada et al. (1984)*. The lattice constant a_{Si} will be automatically entered into the input file by the program.

2.10.4 External scaling

If the 2θ values of the measured data are corrected externally, the corrected values can be entered to the program together with the measured data y_i^{obs} in a special data file (see section 9.1).

2.11 The standard deviation of angular positions

The standard deviation of the angular positions σ_a depends on the mechanical precision of the diffractometer. Its influence of the standard deviation of the observed intensity y can be calculated by the law of error propagation (*Rebmann et al. (1997)*):

$$\sigma_t^2 = \sigma_p^2 + \left(\left.\frac{dy}{d(2\theta)}\right|_{2\theta_0} \sigma_a \right) \quad \text{with} \quad \sigma_p = \sqrt{y}\,. \tag{42}$$

σ_a can be entered to the program in the input file and the standard deviation σ_t is calculated with the above equation.

2.12 Quantitative phase analysis

The relative weight fraction of phase i of a mixture of K phases is given by

$$w_i = \frac{S_i Z_i M_i V_i}{\sum\limits_{k=1}^{K} S_k Z_k M_k V_k} \tag{43}$$

where S, Z, M and V are, respectively, the overall scale factor, the number of formula units per unit cell, the mass of the formula unit in atomic mass units and the unit cell volume [10]. SIMREF has built in the atomic mass of all Elements. The number of formula units are calculated using the Wykoff multiplicities of each atom in the asymetric unit given in the input file.

3 Modulated structures

Modulated structures arise from periodic deviations of the crystal lattice. Examples of such deviations are displacements of the atoms and the variation of the occupancy of an atomic position. Commensurate and incommensurate modulations are usually distinguished. For commensurate modulations the wavelength is a rational multiple of a lattice constant (a fraction with an integer numerator and denominator, for example 2 or $\frac{11}{4}$), in the incommensurate case a not-rational (not representable as a fraction, for example: $4.8453456\ldots$). The modulation can be described by a static wave with a wave vector $\vec{q}$, its amplitude $\vec{U}$ is usually given by a Fourier series. However for most cases it is sufficient to consider only the harmonic terms of the series. This is realized with this program.

3.1 The structure factor

In case of a periodic modulation of the displacements of the atoms the amplitude at the position $\vec{r}$ can be written as

$$\vec{U}(\vec{r}) = \vec{u}\cos(\vec{q}\cdot\vec{r}+\phi) \tag{44}$$

In a crystal the atoms are located at discrete positions. So the vector $\vec{r}$ cannot take any values. Furthermore, atoms of the same kind at symmetry equivalent positions are combined in lattice complexes inside the unit cell. Then the atom l of the kth lattice complex in the nth unit cell of the crystal at the position

$$\vec{r}_{kl,n} = \vec{t}_n + \vec{x}_{kl} \tag{45}$$

has the displacement

$$\vec{U}_{kl,n} = a_k \begin{pmatrix} p_{kl,x}\cos(\varphi_{kl,x}+\phi_k+\psi_{kl,n}) \\ p_{kl,y}\cos(\varphi_{kl,y}+\phi_k+\psi_{kl,n}) \\ p_{kl,z}\cos(\varphi_{kl,z}+\phi_k+\psi_{kl,n}) \end{pmatrix}. \tag{46}$$

caused by a harmonic modulation wave. The vector $\vec{t}_n$ is a integer lattice vector and connects the origin of the crystal with the origin of the nth unit cell. The vector $\vec{x}_{kl}$ is the position of the lth atom of the kth lattice complex inside the unit cell. The values a_k and ϕ_k are the absolute value of the maximum amplitude and the phase shift of the wave. The unit vectors $\vec{p}_{kl}$ are the directions of the displacements of the individual atoms of a lattice complex and can be calculated using the projection operater method of *Maradudin et al. (1968)*. Generally the vectors $\vec{p}_{kl}$ are complex with the absolute value $p_{kl,i}$ and the phase $\varphi_{kl,i}$. The phase of the wave at the position $\vec{t}_n + \vec{x}_{kl}$ is given as

$$\psi_{kl,n} = (\vec{g}^1_{kl} + \vec{t}_n + \vec{\nu}_s) \cdot \vec{q} \tag{47}$$

The vector $\vec{\nu}_s$ is the translation part of a symmetry element $S_s = \{\boldsymbol{R}_s|\vec{\nu}_s\}$ with the rotation matrix $\boldsymbol{R}_s$. Applying the symmetry element S_s to the atom j of the kth lattice complex at the position $\vec{x}_{kj}$, another atom l' of the lattice complex is generated:

$$\boldsymbol{R}_s\vec{x}_{kj} + \vec{\nu}_s = \vec{x}_{kl'} \tag{48}$$

If the application of the rotation matrix $\boldsymbol{R}_s$ to the position $\vec{x}_{kj}$ leads out of the cell, then $\vec{g}^1_{kl}$ is the vector between the position $\boldsymbol{R}_s\vec{x}_{kl}$ and the equivalent position inside the cell and otherwise the zero vector. For example, a two-fold axis in the z direction leads from the position $(x, 0, 0)$ to the position $(\bar{x}, 0, 0)$ in the neighbour cell and therefore $\vec{g}^1_{2_z} = (-1, 0, 0)$. To reach from the position $\vec{x}_{kl'}$ outside the unit cell the corresponding atom of the lattice complex inside the unit cell, a lattice vector $\vec{g}^2_{kl}$ has to be applied. So the phase of an atom of the lattice complex can be written as

$$\psi_{kl,n} = (\vec{g}^1_{kl} + \vec{g}^2_{kl} + \vec{\nu}_s + \vec{t}_n) \cdot \vec{q} = (\vec{\tau}_{kl} + \vec{t}_n) \cdot \vec{q}\ . \tag{49}$$

In the example above $\vec{g}^2_{2_z}$ would be $(1, 0, 0)$ and with $\vec{\nu} = (0, 0, 0)$ the translation that affects the phase $\vec{\tau}$ at the position $(1 - x, 0, 0)$ is zero.
If the modulation wave consists of M base vectors the whole displacement of an atom is defined as the sum over the displacements related to the individual base vectors:

$$\vec{U}_{kl,n} = \sum_{m=1}^{M} \vec{U}^{(m)}_{kl,n} \tag{50}$$

A sum of base vectors $\vec{p}_{klm}$ is assigned to each lattice complex k with the refinable parameters a_{km} and ϕ_{km}. These parameters are taken from a seperate file for each lattice complex (see section 9.6).
In the reciprocal space the modulation of the structure generates additional Bragg reflections called satellites. Starting from a basic reflection

$$\vec{H}_0 = \mathrm{h}\vec{a}^* + \mathrm{k}\vec{b}^* + \mathrm{l}\vec{c}^*. \tag{51}$$

the position of any reflection is given by

$$2\pi\vec{H} = 2\pi\vec{H}_0 + \mu\vec{q} \qquad \text{with} \quad \mu = 0, \pm1, \pm2, \pm3, \cdots \tag{52}$$

where μ is called the order of the satellites. The reflections of 0th order are the basic reflections itself. In the incommensurate case each basic reflection leads to an infinite number of satellites. The indexing of the reflections is given by the four indices h, k, l and μ. The corresponding three-dimensional indices H, K and L can be optained according to (52) by:

$$\begin{aligned} \mathrm{H} &= \mathrm{h} + \mu \cdot \delta_1 \\ \mathrm{K} &= \mathrm{k} + \mu \cdot \delta_2 \qquad \text{with} \quad \delta_i = \frac{q_i}{2\pi} \\ \mathrm{L} &= \mathrm{l} + \mu \cdot \delta_3 \end{aligned} \tag{53}$$

The structure factor of a satellite or basic reflection is given by:

$$\boxed{F_\mu(\vec{H}_0, \vec{q}) = \sum_{k=1}^{K} f_k \sum_{l=1}^{L} J_{-\mu}(w_{kl})\ exp\left\{ i \left[2\pi \vec{H} \cdot \vec{x}_{kl} - \mu(\vec{q} \cdot \vec{\tau}_{kl} + \Phi_{kl} + \tfrac{\pi}{2}) \right] \right\}} \tag{54}$$

The argument w_{kl} of the Bessel function $J_{-\mu}$ and the phase Φ_{kl} are defined by the equation

$$w_{kl} e^{i\Phi_{kl}} = z_{kl} + i y_{kl} \tag{55}$$

where z_{kl} and y_{kl} are the scalar product of the reciprocal lattice vectors $2\pi\vec{H} = 2\pi\vec{H}_0 + \mu\vec{q}$ with the modified amplitudes $\vec{u}_{kl}$ or $\vec{v}_{kl}$:

$$y_{kl} = 2\pi\vec{H} \cdot \vec{u}_{kl}\ , \qquad z_{kl} = 2\pi\vec{H} \cdot \vec{v}_{kl}\ . \tag{56}$$

The modified amplitudes can be interpreted as the real and imaginary part of a displacement vector whose phase is independent of any lattice translations:

$$\vec{u}_{kl} = \sum_{m=1}^{M} a_{km} \begin{pmatrix} p_{klm,x} \cos(\varphi_{klm,x} + \phi_{km}) \\ p_{klm,y} \cos(\varphi_{klm,y} + \phi_{km}) \\ p_{klm,z} \cos(\varphi_{klm,z} + \phi_{km}) \end{pmatrix} , \tag{57}$$

$$\vec{v}_{kl} = \sum_{m=1}^{M} a_{km} \begin{pmatrix} p_{klm,x} \sin(\varphi_{klm,x} + \phi_{km}) \\ p_{klm,y} \sin(\varphi_{klm,y} + \phi_{km}) \\ p_{klm,z} \sin(\varphi_{klm,z} + \phi_{km}) \end{pmatrix} . \tag{58}$$

In the commensurate case the satellite systems of the individual basic reflections overlab. So, for example in case of a cell doubling in the a direction in the reciprocal space, superstructure peaks between the basic reflections in the a^* direction appear. The structure factor $F(\vec{H})$ of a reflection at the position $\vec{H}$ (basic or superstructure reflection) has to be understood as a sum over the contributions of satellites of the basic reflections $\vec{H}_{0k}$ in the direction of the q vector of the order μ_k:

$$F(\vec{H}) = \sum_{k=1}^{\infty} F_k^{\mu_k}(\vec{H}) \quad \text{with} \quad 2\pi\vec{H} = 2\pi\vec{H}_{0k} + \mu_k\vec{q} \tag{59}$$

In practice it is sufficient to consider only a finite number of contributions of the satellites, because their absolute values decrease strongly with increasing order μ_k. Giving a maximum order μ_{max}, only the essential contributions are considered for the calculation of the structure factor of the reflection. For incommensurate modulations, μ_{max} restricts the satellites belonging to a basic reflection.

4 Magnetic structures

With the program SIMREF it is possible to refine magnetic spin structures which can be described with magnetic space groups.

4.1 Magnetic space groups

In the program SIMREF the magnetic space group symbols introduced by *W. Opechowski* [20], [20] are used to enter the symmetry of the magnetic lattice. These symbols have the advantage that the space group of the nuclear structure can be easily obtained omitting the primes of the symmetry elements and the subscript part of the centering symbol. All magnetic space groups refering to the space group $Pba2$ are given as an example:

$$\begin{array}{ll} Pba2 & P_{2c}ba2 \\ Pb'a2' & P_{2c}b'a2' \\ Pb'a'2 & P_{2c}b'a'2 \end{array}$$

The first part of the magnetic space group symbol describes the magnetic lattice and is derived from the centering symbol of the "nuclear" space group by an extension which indicates the primitive translations of the magnetic unit cell related to the "nuclear" cell. The different magnetic lattices (36 Bravais classes) are listed in the following table. A brief description is given in reference [20].

system	magnetic lattice symbols
triclinic	P, P_{2a} (P_{2b}, P_{2c})
monoclinic (unique axis b)	P, P_{2a}, P_{2b}, P_C, C, C_{2c}, C_P
monoclinic (unique axis c)	P, P_{2b}, P_{2c}, P_A, C, C_{2a}, C_P
orthorhombic	P, P_{2a}, P_C, P_F, C, C_{2c}, C_P, C_I, F, F_C, I, I_P
tetragonal	P, P_{2c}, P_C, P_I, I, I_P
trigonal and hexagonal	R, R_R, P, P_{2c}
cubic	P, P_F, F, I, I_P

The other parts of the space group symbol are primed and unprimed symmetry elements, which are the generators of the group. Using this set of generators all the symmetry elements of the magnetic space group can be obtained, where the unprimed elements form a subgroup of index 2. Starting with the kth magnetic ion of the asymmetric unit which has the magnetic moment $\vec{m}_k$ at the position $\vec{x}_k$, all the ions of the unit cell at the positions $\vec{r}_{kl}$ are generated by the symmetry elements of the space group:

$$\vec{r}_{kl} = \boldsymbol{R_l}\vec{x}_k + \vec{\tau}_l \qquad \text{with} \quad l = 1, \ldots, L \tag{60}$$

The magnetic moments $\vec{\mu}_{kl}$ are calculated using the symmetry elements of the magnetic space group:

$$\vec{\mu}_{kl} = \boldsymbol{M_{kl}}\vec{m}_k \cdot det(\boldsymbol{R_l}) \qquad \text{with} \quad l = 1, \ldots, L\,, \tag{61}$$

where $\boldsymbol{M_{kl}} = \boldsymbol{R_l}$ for unprimed and $\boldsymbol{M_{kl}} = \boldsymbol{R_l}\boldsymbol{I} = -\boldsymbol{R_l}$ for primed elements. $\boldsymbol{I}$ is the time inversion. The 1421 magnetic space groups are listed in reference [20] and [21], where the settings of the *Int. Tables* are used.

4.2 The form factor

Within the dipole approximation (spherical symmetry) (*Int. Tables*, Vol. C, p. 513) the form factor is given by:

$$f(s) = \langle j_0(s) \rangle + (1 - 2/g) \langle j_2(s) \rangle \qquad \text{with} \quad s = \sin\theta/\lambda \tag{62}$$

where g is the Landé splitting factor. In the program SIMREF the approximation

$$f(s) \approx \langle j_0(s) \rangle \tag{63}$$

is used. An analytical approximation to the $\langle j_0(s) \rangle$ magnetic form factors for the $3d$ and $4d$ transition series, the $4f$ electrons of rare-earth ions and the 5f electrons of some actinide ions has the following form (*Int. Tables*, Vol. C, p. 391):

$$\langle j_0(s) \rangle = A\exp(-as^2) + B\exp(-bs^2) + C\exp(-cs^2) + D \tag{64}$$

Tables 4.4.5.1-4.4.5.4 of the *Int. Tables* Vol. C give the coefficients A, B, C, D, a, b and c. SIMREF use these coefficients, which the program has built in, to calculate the form factors for each magnetic ion. Only the name of the ion has to be entered to the program.

4.3 The structure factor

The intensity of the magnetic reflection $\vec{H}$ can be calculated as:

$$I_M = |\vec{P}_M|^2 - |\vec{h} \cdot \vec{P}_M|^2 \qquad \text{with} \quad \vec{h} = \frac{\vec{H}}{|\vec{H}|}\,. \tag{65}$$

The magnetic structure factor $\vec{P}_M$ is given by:

$$\vec{P}_M = \frac{e^2\gamma}{2mc^2} \sum_k N_k\, f_k(s)\, e^{-B_k s^2} \sum_l \vec{\mu}_{kl}\, e^{2\pi i \vec{H}\cdot\vec{r}_{kl}} \tag{66}$$

where

e = the electronic charge,

m = the mass of an electron,

c = the velocity of light,

γ = the magnetic moment of the neutron in nuclear magnetons,

$\sum_k$ = the summation over all atoms in the asymmetric unit,

$\sum_l$ = the summation over all equivalent positions,

N_k = the site occupation number,

f_k = the magnetic form factor of the kth ion,

B_k = the individual isotropic temperature parameter,

$\vec{r}_{kl}$ = the position of the kth magnetic ion in the lth equivalent position,

$\vec{\mu}_{kl}$ = the magnetic moment of the kth magnetic ion at the lth equivalent position $\vec{r}_{kl}$.

5 Full pattern profile refinement

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 SIMREF, where you fit the whole pattern with the function $y_i^{calc}(a, b, c, \alpha, \beta, \gamma, \ldots)$. with the following parameters:

- Lattice constants a, b, c, α, β, γ, ...
- Halfwidth parameters U, V and W
- Integrated Intensities I_k for each reflection
- Peak shape function parameters
- Peak-shift correction parameters

The lattice constants are the parameters for the peak positions. In the case of a incommensurate or commensurate modulation it is also possible to refine the three components of the wave vector.
The powder pattern at the position $2\theta_i$ can be calculated as a sum of neighbouring Bragg reflections contributing to the point i:

$$\begin{aligned} y_i^{calc} &= s \sum_k m_k \, L_k \, |F_k|^2 \, A_{ik} \, p(x_{ik}, H_k, \eta, \ldots) \; + \; y_i^{back} \\ &= \sum_k I_k \, A_{ik} \, p(x_{ik}, H_k, \eta, \ldots) \; + \; y_i^{back} \end{aligned} \tag{67}$$

where

s is the 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,

$I_k = s\, m_k\, L_k\, |F_k|^2$ is the integrated intensity,

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.

Furthermore the integrated intensities divided by the Lorentz polarisation factor L and multiplicity m of the reflection is proportional to the structure factor $|F|^2$:

$$|F|^2 \sim \frac{I}{L \cdot m} \tag{68}$$

So the refined integrated Intensities can be used to make a structure determination.

6 The different input and output files

The program SIMREF uses several files for the input and output of data:

1. **Initial values for the parameters:** <*Filename*>`.inp`
   This file contains informations about the diffractometer used, the names of the input and output files and the initial values of the parameters for the refinement.

2. **Displacement vectors:** <*Atom*>`.mod`
   These files contain the displacement vectors (base vectors of the irreducible representations) of the certain lattice complexes and the modulation parameters.

3. **Symmetry:** <*Filename*>`.sym`
   This file contains the symmetry informations of the space group.

4. **Parameter:** <*Filename*>`.par`
   Here the coding of the parameters for the refinement is given.

5. **Cycle:** <*Filename*>`.cyc`
   In this output file the course of the refinement is stored in compressed form.

6. **Data:** <*Filename*>`.dat`
   Input file with the measured data.

7. **Background:** <*Filename*>`.bac`
   Background values of the measured data set. In addition, this file contains the regions of the powder pattern which are excluded during the refinement.

8. **Scaling:** <*Filename*>`.eic`
   File with the observed and calculated peak positions of the standard material.

9. **Bragg Intensities:** <*Filename*>`.int`
   File with the refinable Bragg Intensities for profile refinement.

10. **Plot:** <*Filename*>`.plt`
    This file contains the observed and the calculated powder pattern after the refinement, the difference between the observed and calculated values and the background.

11. **(hkl) list:** <*Filename*>`.hkl`
    This file contains a list of all reflections in the given 2θ region with its positions, Lorentz-polarisation factor, etc.

12. **Structure factors:** <*Filename*>`.kof`
    This file contains the structure factors and the observed and calculated Bragg intensities.

13. **SHELX input file:** <*Filename*>`.res`
    This is a input file for the program SHELX or graphic programs, which can read SHELX input files.

7 The input file

All the lines in the input file begin with a key word, which consists of three capital letters followed by a ">" sign. Between the key word and the ">" any text can be included. After the ">" sign follows the input data, where different items are separated by spaces or commas. The values can given in any format. An input line can be broken in several lines: the continuation of the line has to be indicated by a "\" (backslash) at the end of the line before. A complete input line is limited to a maximum of 500 characters. All lines not beginning with one of the key words and all lines, where the ">" sign is missing after the key word, are interpreted as comment lines. The sequence of the input lines is not arbitrary but corresponds to the sequence of the following description of the allowed key words.

7.1 Input for one data set

In the following list, each key word is given together with a description of the parameters to be specified.

`INI:`

1. What SIMREF has to do: 1 $\rightarrow$ Rietveld refinement
   2 $\rightarrow$ Pattern calculation
   3 $\rightarrow$ Calculation of structure factors
   4 $\rightarrow$ Calculation of a (hkl) list
   5 $\rightarrow$ Profile Refinement
2. Number of data sets
3. Output of the symmetry informations of the space group: 1 $\rightarrow$ yes
   0 $\rightarrow$ no
4. Output of the correlation matrix: 1 $\rightarrow$ yes
   0 $\rightarrow$ no
5. Output of Scattering lengths/coefficients: 1 $\rightarrow$ yes
   0 $\rightarrow$ no
6. Create a new input file after the refinement: 1 $\rightarrow$ yes
   0 $\rightarrow$ no
7. Number of columns in the cycle file: 0 $\rightarrow$ 80
   1 $\rightarrow$ 132
8. Generate SHELX input file: 1 $\rightarrow$ yes
   0 $\rightarrow$ no
9. : Preferred orientation correction model: 1 $\rightarrow$ Rietveld
   2 $\rightarrow$ Dollase (March Model)

`FIT:`

1. Maximum number of cycles of the fit
2. ϵ: the refinement will be terminated if $\Delta_n < \epsilon\, \sigma_n\, r_n$,
   where Δ_n is the shift, σ_n the standard deviation and r_n the relaxation factor of the parameter.

3.-10. Relaxation factors for –

3. atomic coordinates x/a, y/b, z/c, isotropic temperature factors B_{iso} and occupancies N
4. anisotropic temperature factors β_{ij} and modulation parameters u_{km} and ϕ_{km}
5. FWHM parameters U, V and W

6. overall scale factor s, overall temperature factor B_0, the parameters of the preferred orientation correction G_1 and G_2 and the integrated Intensities I_k
7. lattice constants a, b, c, α, β, γ and wave vector components δ_1, δ_2, δ_3
8. parameters of the asymmetry correction and of the peak shape function eta_0, η_1, η_2
9. zeropoint t_0, peak-shift correction parameters t_1, t_2 and wavelength λ_1
10. background parameters c_0, ... , c_5

`PAR:` Name of the parameter file

`TIT:` Title of the data set (maximum 70 characters)

`COD:`

1. Number of the diffraction geometry (see section 2.5):
   1 Guinier diffractometer (transmission geometry)
   2 Guinier camera (film)
   3 Bragg-Brentano diffractometer
   4 3-axes diffractometer at synchrotron sources
   5 neutron diffractometer (Debye-Scherrer geometry)
   6 Guinier diffractometer (reflection geometry)
2. Number of phases
3. Number of the peak shape function
   1 Gaussian
   2 Lorentzian
   3 modified Lorentzian
   4 intermediate Lorentzian
   5 Edgeworth serie
   6 Pseudo-Voigt
   7 Pearson-VII
   8 Double Gaussian
   9 asymmetric pseudo-Voigt
4. Output of a reflection list for each phase:
   $0 \rightarrow$ no
   $1 \rightarrow$ yes
5. Output of a merged reflection list: $0 \rightarrow$ no
   $1 \rightarrow$ yes
6. Background: $0 \rightarrow$ Background refinement
   $1 \rightarrow$ Read file with background values
   $2 \rightarrow$ Use background from data file
7. Scaling: (see section 2.10)
   $0 \rightarrow$ Use 2θ values from data file, peak-shift correction **can** be done.
   $1 \rightarrow$ Read file with the standard peaks and scaling of the 2θ scale (see section 9.3).
   $2 \rightarrow$ Scaling on silicon standard using the peak-shift correction (see section 2.10.3)
8. Output of structure factors after the refinement on standard output: $0 \rightarrow$ no
   $1 \rightarrow$ yes
9. Create a file with a merged reflection list: $0 \rightarrow$ no
   $1 \rightarrow$ yes
10. Create a file with structure factors: $0 \rightarrow$ no
    $1 \rightarrow$ yes

11. Generate the reflection list (only for profile refinement) $0 \rightarrow$ no
    $1 \rightarrow$ yes

`DAT:` Name of the data file

`EXC:` Minimum and maximum in 2θ of an excluded region of the powder pattern which is not taken into account during the refinement. This input line will only beread if the background is fitted or the background values from the data file are used.

`BAC:` Name of the file with the background values, alternatively the six background parameters c_i of the polynomial (39).

`SCL:` Name of the file with the standard peaks (see section 9.3)

`WVL:` Wavelengths:

1. λ_1 in Å
2. λ_2 in Å
3. Intensity ratio $I_{\lambda_2}/I_{\lambda_1}$

The wavelength λ_1 can be refined.

`THE:` Parameter of the data set:

1. minimum 2θ value
2. maximum 2θ value
3. stepwidth in 2θ
4. zeropoint t_0
5. peak-shift correction parameter t_1
6. peak-shift correction parameter t_2

In case of a refinement, the 2θ region, which should be used from the data file, can be limited. If the maximum 2θ value is set to zero, the data set will be completely read. In case of the calculation of a powder pattern, a reflection list or structure factors the 2θ region must be chosen. The stepwidth is only needed for a pattern calculation.

`SCA:` Externally entered scattering data: For each atom type where the standard scattering values should not be used, one "`SCA`" line has to be entered.

(a) X-ray diffraction:

1. chemical symbol in capital letters including the charge (e.g. `BA+2`)

2.-3. Resonant (anomalous) corrections $\Delta f'$ and $\Delta f''$ with $f = f_0 + \Delta f' + \Delta f''$ in case of anomalous scattering

4.-12. Nine scattering coefficients for the calculation of the atomic scattering amplitude f_0 in the order a_1, b_1, a_2, b_2, a_3, b_3, a_4, b_4 and c

If only $\Delta f'$ and $\Delta f''$ are entered, the internal coefficients a_i, b_i and c are used

(b) Neutron diffraction:

1. chemical symbol in capital letters without the charge
2. scattering length in 10^{-13}cm

`COR:` Correction parameters:

1. Standard background for pattern calculation
2. Base of peak ω in units of the fwhm
3. The diffraction angle $2\theta_M$ at the monochromator or the polarisation parameter K (only for synchrotron data)
4. $\mu \cdot R$ for the absorption correction of neutron data (Debye-Scherrer geometry), where μ is the linear absorption coefficient and R the radius of the cylindrical sample holder.
5. Maximum angle for asymmetry correction in 2θ
6. Constant background for film data which can be subtracted
7. The diffraction angle at the analyser crystal $2\theta_A$ (only for synchrotron data)
8. The standard deviation of angular positions (see section 2.11)

`PHS:`

1. Name of the phase (maximum 4 characters)
2. Crystal structure type: 0 $\rightarrow$ non-modulated
1 $\rightarrow$ modulated
2 $\rightarrow$ magnetic
3. Number of the Laue group of the ”little group” (1...15) (see section 9.5)
4. Maximum order of the satellites of a modulated structure
5. Anisotropic temperature factors: 0 $\rightarrow$ β_{ij}'s
1 $\rightarrow$ B_{ij}'s
2 $\rightarrow$ U_{ij}'s
6. Maximum atomic distance d_{max} in Ångstrøm for the calculation of atomic distances. If d_{max} is lower or equal to zero no distances will be calculated.

`SPG:` Space group symbol:

“Nuclear” space groups: The space group has to be entered according to the *International Tables* (corrected edition of 1985) Alternatively the **full** (Hermann-Mauguin) symbol, the **short** symbol or the number of the space group can be given using capital letters. The parts of the symbol must be separated by comma or blancks. For space groups with two origin choices this must be entered at the last position of the symbol (see example b). For trigonal space groups with hexagonal or rhombohedral setting the choice of the setting also has to be given at the last position (see example c).

Examples:

a). Space group $I2/m$ (no. 12):
Monoclinic space group with unit axis c:
full: `I,1,1,2/M`
short: `I 2/M 2`
number: `12,6`

b). Space group $Ccca$ (no. 68):
Orthorhombic space group with to possible origin choices (without instruction the origin 1 will be chosen). This example shows the choice of origin 2:
full: `C, 2/C, 2/C,  2/A,  2`
short: `C C C A 2`
number: `68,2`

c). Space group $R32$ (no. 155):
Trigonal space group with hexagonal (H) or rhombohedral (R) setting. In this example the rhombohedral setting will be chosen:
full: `R, 3, 2, , R`
short: `R 3 2 R`
number: `155,2`

d). Cubic space group $Fm\bar{3}m$ (no. 225):
full: `F, 4/M, 3B, 2/M` with `3B` = $\bar{3}$
short: `F M 3B M`
number: `225`

e). Tetragonal space group $P4$ (no. 75):
full: `P, 4, , ,`
short: `P 4`
number: `75`

f). Hexagonal space group $P6_3mc$ (no. 186):
full: `P, 63, M, C` with `63` = 6_3
short: `P 63 M C`
number: `186`

Magnetic space groups: In the case of a magnetic space group the symbols introduced by W. Opechowski (1965) has to be used. This symbols are derived from the short space group symbols of the Int. Tabels. The primed elements are indicated by a "′", for example m'. The Bravais lattice type is given by the centering symbol and a subscript describing primitiv translations of the magnetic lattice. This subscript has to be entered as the second part of the symbol. If there is no suscript, a "1" has to be given.

Examples:

a). Monoclinic space group $C_{2c}2/m'$ (no. 12) with unit axis c:
`C 2c 2/m' C`

b). Orthorhombic space group $C_Pc'ca$ (no. 68) with to possible origin choices (without instruction the origin 1 will be chosen). This example shows the choice of origin 2:
`C P c' c a 2`

c). Trigonal space group $R32'$ (no. 155) with hexagonal (H) or rhombohedral (R) setting. In this example the rhombohedral setting will be chosen:
`R 1 3 2' R`

d). Cubic space group $Fm'3m'$ (no. 225):
`F 1 m' 3 m'`

e). Tetragonal space group P_I4 (no. 75):
`P I 4`

f). Hexagonal space group $P6_3m'c'$ (no. 186):
`P 1 63 m' C'` with `63` = 6_3

`SYM:` Name of the file with the symmetry informations of the space group:
Instead of the input of the space group symbol or number the symmetry informations can be read from a file. (see section 9.5)

`INT:` Name of the file with the refinable Bragg Intensities for profile refinement (see section 9.4)

`MET:` Lattice constants a, b, c, α, β, γ (a, b, c in Å and α, β, γ in degrees)

`WAV:` The three components δ_1, δ_2 and δ_3 of the wave vector in units of the reciprocal lattice constants (only for modulated structures)

`PRO:` Profile parameters:

1. Overall scale factor s
2. Overall temperature factor B_0

3.-5. FWHM parameters U, V and W (Caglioti)

`ETA:` Parameters of the peak shape function:

1. η_0 (pseudo-Voigt) or μ_0 (Pearson-VII) or skewness η_1 (Edgeworth serie)
2. η_1 (pseudo-Voigt) or μ_1 (Pearson-VII) or excess η_2 (Edgeworth serie)
3. η_2 (pseudo-Voigt) or μ_2 (Pearson-VII)

`ASY:` Asymmetry correction parameters (see section 2.4):

1. Parameter A_0 or S/L for the asymmetric pseudo-Voigt function
2. Parameter B_0 or H/L for the asymmetric pseudo-Voigt function
3. Parameter A_1
4. Parameter B_1

`PRE:` Preferred Orientation Correction (see section 2.3)

1. Correction parameter G_1
2. Correction parameter G_2

3.-5. The three components of the preferred orientation vector in units of the reciprocal lattice constants

`ATO:` Atomic parameters:

1. Name of the atom/ion (max. 4 characters)
2. Chemical symbol in capital letters and in case of X-ray diffraction the ionic charge (e.g. `CU+2`)
3. Wyckoff number (see *International Tables* Vol. IV),

4.-6. Coordinates x/a, y/b, z/c,

7. Isotropic temperature factor B_{iso}
8. Occupancy N

9.-14. Six anisotropic temperature factors β_{ij}, B_{ij} or U_{ij} (see section 2.8)

15.-18. Three components of the magnetic moment μ_x, μ_y, μ_z (only for magnetic structures)

For the different types of calculations not all input lines are always needed. For example the line with the fit parameters (`FIT`) is only needed for a refinement, otherwise it can be left out. SIMREF always reads the input lines, which are necessary for the individual types of problems. All other lines are treated as comments. In table 7.4 the input lines for the different types of problems are listed.

7.2 Input for several data sets

For several data sets the instructions `TIT`, `COD`, `DAT`, `(EXC)`, `BAC`, (`SCL`), `WVL`, `THE`, `COR`, (`SCA`), `MET`, (`WAV`), `PRO`, `ETA`, `ASY` and `PRE` are repeated for each data set. For the first data set the atomic parameters have always to be specified. For the following data sets the corresponding parameters are taken from the first data set. If X-ray and neutron data sets are used simultaneously for the refinement, do not forget to enter the element symbol for ions (e.g. `Fe+3`), so that the correct scattering coefficients are used for the X-ray data sets.

7.3 Input for several phases

For several phases the instructions `PHS`, `SPG`/`SYM`, (`INT`), `MET`, (`WAV`), `PRO`, `ETA`, `ASY`, `PRE` and `ATO` are repeated for each phase. Only one phase can have a modulated structure. For the calibration of the 2θ-values on silicon standard, silicon has to be the last phase.

7.4 Input for magnetic structures

Magnetic structures are treated as an additional phase, where only the magnetic ions are given in the input and parameter file. If the magnetic ions have refinable atomic parameters they should be constrained with the “nuclear” phase.

	Type of calculation				
Key word	1	2	3	4	5
`INI`	yes	yes	yes	yes	yes
`FIT`	yes	no	no	no	yes
`PAR`	yes	no	no	no	yes
`TIT`	yes	yes	yes	yes	yes
`COD`	yes	yes	yes	yes	yes
`DAT`	yes	no	no	no	yes
`EXC`	yes[1]	no	no	no	yes[1]
`BAC`	yes[1]	no	no	no	yes[1]
`SCL`	yes[2]	no	no	no	yes[2]
`WVL`	yes	yes	yes	yes	yes
`THE`	yes	yes	yes	yes	yes
`COR`	yes	yes	yes	yes	yes
`SCA`	yes[3]	yes[3]	yes[3]	no	no
`PHS`	yes	yes	yes	yes	yes
`SPG/SYM`	yes[4]	yes[4]	yes[4]	yes[4]	yes[4]
`INT`	no	no	no	no	yes
`MET`	yes	yes	yes	yes	yes
`WAV`	yes[5]	yes[5]	yes[5]	yes[5]	yes[5]
`PRO`	yes	yes	yes	yes	yes
`ETA`	yes	yes	no	no	yes
`ASY`	yes	yes	no	no	yes
`PRE`	yes	yes	yes	no	no
`ATO`	yes[6]	yes[6]	yes[6]	no	no

Table 1: The required instructions of the input file for the differnt types of calculations

[1] The file with the background values is only necessary if the background data from the data file are not used and if a refinement of the background parameters should not be done.

[2] The file with standard peaks is only necessary if a calibration of the 2θ scale shall be done using their theoretical and observed 2θ position.

[3] This instruction has to be repeated for each atom for which scattering data should be entered.

[4] Either the space group symbol can be entered with the instruction `SPG` or the name of a file with the symmetry cards can be used with the instruction `SYM`.

[5] Only for modulated structures

[6] It is repeated for each atom of the phase. For several data sets the input has to be made only for the first data set. For the following data sets the atomic parameters of the corresponding phase of data set 1 are taken. For modulated structures the modulation amplitudes, phases and displacement vectors are given in a separate input file.

7.5 Examples

7.5.1 Input file for two data sets (non-modulated structure)

```
INI>   1    2    0    0    0    1    1    1   1
FIT> 12  0.30  0.20  0.20  0.20  0.20  0.20  0.20  0.20  0.20
PAR> demo2.par

*** data set 1 ***
TIT> Silicon, 300 K, Guinier data, counter 1
COD>  1    1    6    0    0    1    0    0    1    0    0
DAT> si1.dat
BAC> si1.bac
WVL> 1.540600  0.000000  0.000000
THE> 0.00000  0.00000   0.02000   0.00358   0.000   0.000
COR> 10.0000 3.5000  0.0000  0.0000 34.0000  0.0000  0.0000  0.0000

PHS> Si   0   0   0   0   3.2   0.0
SPG>  F, 41/D, 3B, 2/M, 1
MET> 5.47836  5.47836  5.47836 90.00000 90.00000 90.00000
PRO> 0.89E-01 0.00000  0.06427 -0.03707  0.01117
ETA> 0.32100  0.00000  0.00000
ASY> 0.00000  0.00000  0.00000  0.00000
PRE> 0.00000  0.00000   0.00  0.00  0.00
ATO> Si  SI         8 0.00000 0.00000 0.00000 0.95529 1.00000 \
      0.00000 0.00000 0.00000 0.00000 0.00000 0.00000

*** data set 2 ***
TIT> Silicon, 300 K, Guinier data, counter 2
COD>  1    1    6    0    0    1    0    0    1    0    0
DAT> si2.dat
BAC> si2.bac
WVL> 1.540600  0.000000  0.000000
THE> 20.00000  92.00000   0.02000  1.04171   0.000   0.000
COR> 10.0000 3.5000  0.0000  0.0000 34.0000  0.0000  0.0000  0.0000
MET> 5.47836  5.47836  5.47836 90.00000 90.00000 90.00000
PRO> 0.87E-01 0.00000  0.04638 -0.02871  0.01088
ETA> 0.34600  0.00000  0.00000
ASY> 0.00000  0.00000  0.00000  0.00000
PRE> 0.00000  0.00000   0.00  0.00  0.00
```

7.5.2 Input file for one data set and two phases (non-modulated structure)

```
INI>   1    1    0    0     0    1    1    1   1
FIT> 12  0.30  0.20  0.20  0.20  0.20  0.20  0.20  0.20  0.20
PAR> demo3.par

TIT> Si/Ho2O3, 300 K, Guinier data, counter 1
COD>  1    2    6    0    0    1    0    0    1    0    0
DAT> siho2o3.dat
BAC> siho2o3.bac
WVL> 1.540600  0.000000  0.000000
THE> 0.00000  73.00000   0.02000   0.00347   0.000   0.000
COR> 10.0000 3.5000  0.0000  0.0000 34.0000 25.0000  0.0000  0.0000

*** phase 1 ***
PHS> Si  0   0   0   0   2.5   0.0
SPG> F,41/D,3B,2/M,1
MET>  5.47837   5.47837   5.47837  90.00000  90.00000  90.00000
PRO> 0.89E-01 0.00000  0.06475 -0.03749  0.01124
ETA> 0.32100  0.00000  0.00000
ASY> 0.00000  0.00000  0.00000  0.00000
PRE> 0.00000  0.00000   0.00  0.00  0.00
ATO> Si  SI         8 0.00000 0.00000 0.00000 0.95724 1.00000 \
      0.00000 0.00000 0.00000 0.00000 0.00000 0.00000

*** phase 2 ***
PHS> HoO  0   0   0   0   3.2  0.0
SPG> I, 21/A, 3B, ,
MET> 10.60721  10.60721  10.60721  90.00000  90.00000  90.00000
PRO> 0.53E-01 0.00000  0.07463 -0.04020  0.01273
ETA> 0.32100  0.00000  0.00000
ASY> 0.00000  0.00000  0.00000  0.00000
PRE> 0.00000  0.00000   0.00  0.00  0.00
ATO> Ho1 HO+3      8  0.25000 0.25000 0.25000 0.75639 1.00000 \
      0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
ATO> Ho2 HO+3     24 -0.02713 0.00000 0.25000 0.83564 1.00000 \
      0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
ATO> O   O-2      48  0.38841 0.15237 0.38219 1.25837 1.00000 \
      0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
```

7.5.3 Input file for the refinement of a modulated structure

```
INI>   2       1      0      0       0      1     0    0    1
FIT> 15  0.30  0.40  0.40  0.80  0.80  0.80  0.80  0.80  0.80
PAR> knbo3_m.par

TIT> KNbO3, 297 K, Guinier data, counter 2
COD>  1     1     6     0    0    1    0     0     1    0    0
DAT> knbo32.duo
BAC> knbo32.bac
WVL> 1.540600  0.000000  0.000000
THE> 0.00000 0.00000   0.02000   0.80197    0.000    0.000
COR> 10.0000  5.0000  0.0000  0.0000 34.0000  0.0000  0.0000  0.0000

PHS> KNbO   1   3   3   0  3.0  0.0
SYM> P, 4/M, 3B, 2/M
MET> 4.05167  4.05167  3.98879  90.00000  90.00000  90.25703
WAV> 0.00000   0.00000  0.00000
PRO> 0.52E-01 0.00000  0.06982  -0.03204   0.01139
ETA> 0.49900  0.00000  0.00000
ASY> 0.00000  0.00000  0.00000  0.00000
PRE>   0.00000   0.00000  0.00  0.00  0.00
ATO> K    K+1        1  0.50000  0.50000  0.50000  1.83558  1.00000 \
      0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
ATO> Nb   NB+5       1  0.00000  0.00000  0.00000  1.19875  1.00000 \
      0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
ATO> O    O-2        3  0.50000  0.00000  0.00000  1.02369  1.00000 \
      0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
```

8 The parameter file

In this file the parameter which should be refined and possible constraints between two or more parameters can be given. Like the input file, all lines of the parameter file begin with a key word, which consists of three capital letters followed by a “$>$” sign. Between the key word and the “$>$” any signs can be included. After the “$>$” sign follow the input data, which are separated by spaces or commas. The values can be given in any format. An input line can be broken in several lines. The new lines have to be indicated by the “\” sign (backslash) at the end of the line before. A complete input line is limited to a maximum of 500 characters. All lines not beginning with one of the key words and all lines, the “$<$” sign is missing after the key word, are interpreted as comment lines. The sequence of the input lines is not arbitrary, but corresponds to the sequence of the following list, where all allowed key words and its input data values are listed.

8.1 Coding for one data set

In the parameter file for each refinable parameter the code “1” (free for refinement) or “0” (fixed) have to be given in the corresponding input line:

`TIT`: Title

`PAR`: Numbers of the individual model parameters which should be refined

`GLB`: Global parameters (parameters number $1, \ldots, 10$):

- 1. Zeropoint t_0
- 2.-3. Peak-shift parameters t_1 and t_2
- 4.-9. Background parameters $c_0, \ldots, c_5$
- 10. Wavelength λ_1

`PRO`: Profile parameters (parameters $11, \ldots, 25$):

- 11.-13. Parameters of the peak shape function
- 14. Overall scale factor s
- 15. Overall temperature factor B_0
- 16.-17. Parameters of the preferred orientation correction G_1 and G_2
- 18.-20. Halfwidth parameters U, V and W
- 21.-24. Asymmetry parameter A_0 (S/L), B_0 (H/L), A_1 and B_1
- 25. Bragg-Intensities (only for profile refinement)

`MET`: Lattice constants, wave vector and Bragg intensities (parameters $31, \ldots, 39$):

- 31.-36. Lattice constants a, b, c, α, β, γ
- 37.-39. Components of the wave vector δ_1, δ_2 and δ_3

`ATO`: Atomic parameters (parameters $40 + 20(n-1) + 1, \cdots, 40 + 20(n-1) + 11$ with $n = 1, \ldots N$, where N is the number of atoms):
This input line has to be repeated for each atom given in the input file.

1.-3. coordinates x_n/a, y_n/b, z_n/c
4. isotropic temperature factor B_n
5. occupancy N_n
6.-11. six anisotropic temperature factors
12.-14. three components of the magnetic moment (only for magnetic structures)

In addition some simple constraints can be imposed on the refinable parameter. It's a convention that only backward references are allowed, that means to parameters, which are already entered when the reference will be read. Only then the program recognizes the equal sign "=" placed in front of the number of the parameter referenced.

Examples:

a.) Tetragonal space group with $a = b \neq c$
If the lattice constants will be refined, the following coding has to be chosen:

```
MET > 1,=31,1,1,1,1, 1,1,1
```

b.) The coordinates of atom no. 2 should be shifted in the same way as the coordinates of atom no. 1:

```
ATO >   1,  1,  1,1,1, 1,1,1,1,1,1
ATO > =41,=42,=43,1,1, 1,1,1,1,1,1
```

c.) Atom no. 2 should be shifted in the opposite direction of atom no. 1:

```
ATO >    1,   1,   1,1,1, 1,1,1,1,1,1
ATO > =-41,=-42,=-43,1,1, 1,1,1,1,1,1
```

d.) The coordinate x/a of atom no. 2 should be shifted in the opposite direction to the coordinate y/b of atom no. 1, the coordinate y/b of atom no. 2 should be shifted in the opposite direction to the coordinate x/a of atom no. 1:

```
ATO >    1,   1,1,1,1, 1,1,1,1,1,1
ATO > =-42,=-41,1,1,1, 1,1,1,1,1,1
```

e.) The sum of the occupancies of the atoms 1, 2 and 3 should be constant. The shift of the occupancy of atom 1 should change the occupancies of the atoms 2 and 3 in the relation 4:1 :

```
ATO > 1,1,1,1,      1, 1,1,1,1,1,1
ATO > 1,1,1,1,=-45.8, 1,1,1,1,1,1
ATO > 1,1,1,1,=-45.2, 1,1,1,1,1,1
```

8.2 Coding for several data sets

All input lines are repeated for each data set. Only backward references are allowed, which are indicated by a percent sign "%" placed in front of the number of the data set.

Example: The lattice constants of data set k should be equal to the lattice constants of data set 1:

```
MET > %1,%1,%1,%1,%1,%1, %1,%1,%1
```

8.3 Coding for multiple phases

For a data set with multiple phases, the input lines with the key words `TIT>`, `PAR>`, `PRO>`, `MET>` are repeated and for each atom of the phase the input line with the code `ATO>` is needed. Backward references to previous phases are indicated by "&" sign placed in front of the number of the phase.

Example: The Halfwidth parameters U, V and W of the phase n should be equal to the corresponding parameters of the phase 1:

```
PRO > 1, 1, 1, 1, 1, 1, 1, &1, &1, &1, 1, 1, 1, 1, 1
```

8.4 Modulated structures

Refining modulated structure the coordinates of the atoms cannot be refined. The positions are read from the input file (`*.mod`) and are fixed. Furthermore, anisotropic temperature factors cannot be used.

8.5 Examples

8.5.1 Parameter file for two data sets

```
TIT>  Silicon, 300 K, counter 1
PAR> 1, 11,14,18_20, 31_33,   44
            (zero,t1,t2,c0,c1,c2,c3,c4,c5,L1)
GLB [1_10]  >   1 , 1, 1, 1, 1, 1, 1, 1, 1, 0
            (eta0,eta1,eta2,scale,OT,G1,G2,U,V,W,A0,B0,A1,B1, I)
PRO [11_24] >   1,   1,   1,   1,   1, 1, 1,1,1,1, 1, 1, 1, 1, 0
           (a,  b,  c,alpha,beta,gamma,q1,q2,q3)
MET [31_39]> 1,=31,=31,   1,   1,    1,  1, 1, 1
              (x,y,z,B,N, b11,b22,b33,b12,b13,b23)
ATO [41_54] Si > 1,1,1,1,1,  1,  1,  1,  1,  1,  1

TIT>  Silicon, 300 K, counter 2
PAR> 1,   11,14,18_20,   31_33
           (zero,t1,t2,c0,c1,c2,c3,c4,c5,L1)
GLB  [1_10]>   1,  1, 1, 1, 1, 1, 1, 1, 1, 0
           (eta0,eta1,eta2,scale,o-temp,G1,G2,U,V,W,A0,B0,A1,B1, I)
PRO [11_25]>   1,   1,   1,    1,     1,  1, 1,1,1,1, 1, 1, 1, 1, 0
           (a,  b,  c,alpha,beta,gamma,q1,q2,q3)
MET [21_30]> %1,%1, %1,  %1,  %1,   %1,  0, 0, 0
```

8.5.2 Parameter file for two phases

```
TIT>  Silicon, 300 K
PAR> 1, 11,14,18_20,  31_33,   44
            (zero,t1,t2,c0,c1,c2,c3,c4,c5,L1)
GLB  [1_10]>   1,  1, 1, 1, 1, 1, 1, 1, 1,  0
            (eta0,eta1,eta2,scale,o-temp,G1,G2,U,V,W,A0,B0,A1,B1, I)
PRO [11_25]>   1,   1,   1,    1,     1,  1, 1,1,1,1, 1, 1, 1, 1, 0
            (a,  b,  c,alpha,beta,gamma,q1,q2,q3)
MET [31_39]> 1,=31,=31,   1,   1,    1,  1, 1, 1
                (x,y,z,B,N, b11,b22,b33,b12,b13,b23)
ATO [41_54] Si > 1,1,1,1,1,  1,  1,  1,  1,  1,  1

TIT>  Ho2O3, 300 K
PAR> 11,14,18_20, 31_33
            (eta0,eta1,eta2,scale,o-temp,G1,G2,U,V,W,A0,B0,A1,B1, I)
PRO [11_25]>   1,   1,   1,    1,     1,  1, 1,1,1,1, 1, 1, 1, 1, 0
            (a,  b,  c,alpha,beta,gamma,q1,q2,q3)
MET [31_39]> 1,=31,=31,   1,   1,    1,  1, 1, 1
                 (x,y,z,B,N, b11,b22,b33,b12,b13,b23)
ATO [41_54] Ho1 > 1,1,1,1,1,  1,  1,  1,  1,  1,  1
ATO [61_74] Ho2 > 1,1,1,1,1,  1,  1,  1,  1,  1,  1
ATO [81_94] O   > 1,1,1,1,1,  1,  1,  1,  1,  1,  1
```

8.5.3 Parameter file for the refinement of a modulated structure

```
TIT> KNbO3, 297 K
PAR> 1, 11,14,18_20,  31_33,36
            (zero,t1,t2,c0,c1,c2,c3,c4,c5,L1)
GLB  [1_10]>   1,  1, 1, 1, 1, 1, 1, 1, 1, 0
            (eta0,eta1,eta2,scale,o-temp,G1,G2,U,V,W,A0,B0,A1,B1, I)
PRO [11_25]>   1,   1,   1,    1,     1,  1, 1,1,1,1, 1, 1, 1, 1, 0
            (a, b, c,alpha,beta,gamma,q1,q2,q3)
MET [31_39]> 1,=31,1,   1,   1,    1,  1, 1, 1
                (x,y,z,B,N, b11,b22,b33,b12,b13,b23)
ATO [41_54] K  > 1,1,1,1,1,  1,  1,  1,  1,  1,  1
ATO [61_74] Nb > 1,1,1,1,1,  1,  1,  1,  1,  1,  1
ATO [81_94] O  > 1,1,1,1,1,  1,  1,  1,  1,  1,  1
```

9 Data formats

9.1 The file with the measured data

Neutron and X-ray data can be entered to SIMREF with three types of data files with different formats.

1. **Title**: The first lines of the different data files consist of an arbitrary number of comment or title lines.
2. **Header line**: The title is terminated by a line which begins with a key word of three characters. This key word is followed by the specifications of the data separated by blanks or commas:

   code (3 characters),
   measuring time per step (not used),
   minimum 2θ value,
   stepwidth,
   maximum 2θ value,
   temperature,
   block number (not used),
   number of values.

3. **Format for data values**:

   a). **Main data format**: In the main SIMREF data format with the key word "DAT" the data follow separated by blanks or commas in free format. Each line consists of the values:

   $$2\theta_i, \quad y_i^{obs}, \quad \sigma_i, \quad y_i^{back} \quad .$$

   σ_i is the standard deviation of the ith measured value y_i^{obs} and normally equal to the square root of this value. If no background values are available, any values have to be entered for each angle $2\theta_i$ into this column.

   b). **Older data format**: To be compatible with earlier versions of SIMREF, X-ray data files with the so called "DUO" format can also be read in. These files also begin with one or more title lines which are terminated by the line beginning with the key "DUO". It is important to enter the minimum and maximum 2θ value and the stepwidth correctly so that the data can be read in completely. The measured data follow with eight values per line:

   $$y_i^{obs} \qquad \text{in the Fortran format } \texttt{(8(F7.0,X))} \quad .$$

   The measured values are weighted with $w_i = 1/\sigma_i^2 = 1/y_i^{obs}$.

   c). **Neutron data**: For neutron data the title lines are terminated by a line with the key word "NEU". It is also important to enter the 2θ region and the stepwidth correctly. Each data line consists of ten pairs of values

   $$(\,\omega_i,\, y_i^{obs}\,) \qquad \text{in the Fortran format } \texttt{(10(I2,I6))}$$

   ω_i is a weighting factor which is the number of times the multicounter has measured the value y_i^{obs} an the angle $2\theta_i$. It corresponds to the data format of the powder diffractometer of the ILL (Grenoble). Here each value y_i^{obs} is weigthed with $w_i = \omega_i/y_i$.

Example 1: file with the main SIMREF data fomat

```
Silicon standard,  temperature: 299 K,  counter 1
DAT  10.000  0.00000  0.020000  72.0000  299.0000  1  3601
0.000    23.    4.796     0.
0.020    27.    5.196     0.
```

Example 2: X-ray data with the "DUO" format

```
Bi1.5Pb0.5Sr2HoCu2O8, room temperature,  27-APR-1989 10:55:18.36
DUO  20.000     0.00000    0.020000    72.00000     300.0000   1    3601
    28.     33.     23.     29.     26.     24.     23.     10.
    19.     37.     26.     18.     22.     31.     25.     34.
```

Example 3: file with the neutron data format of the ILL (Grenoble)

```
BaPbO3 (Ar), 8 mm,  temperature: 296 K,  wavelength: 1.7058 A
NEU  0.000  3.00000  0.100000  134.90000  296.0000  1  1320
 1  1256 1  1347 1  1427 1  1512 1  1579 1  1588 1  1654 1  1733 1  1729 1  1787
 1  1739 1  1763 1  1701 1  1689 1  1723 1  1789 1  1719 1  1678 1  1711 1  1775
```

9.2 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 of the file si1.duo
  25.407  78.397
  29.629  55.541
  34.521  42.843
  39.412  38.610
  46.227  36.917
  54.521  25.912
  56.333  25.912
  60.163  23.372
  69.550  21.679
  72.716  21.679
EXCLUDED REGIONS
   0.000  25.000
```

9.3 The scale file

This file contains the calculated and observed peak positions of a standard material.

1. line : title
data : calculated peak positions $2\theta_k^{calc}$, observed peak position $2\theta_k^{obs}$, 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
```

9.4 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 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

9.5 The file with the symmetry cards

If a non-standard setting should be used, the symmetry informations of the space group have to be entered into the program using a special file. Like in the file for the parameters, only lines beginnning with a key word and a ">" sign are used. The following input lines are read by the program:

`COD`: 1. symbol for the centering of the unit cell:

- P $\rightarrow$ primitive
- I $\rightarrow$ body-centered
- F $\rightarrow$ face-centered
- A $\rightarrow$ A-centered
- B $\rightarrow$ B-centered
- C $\rightarrow$ C-centered
- H $\rightarrow$ hexagonal setting of a trigonal cell
- R $\rightarrow$ rhombohedral setting of a trigonal cell

2. number of the Laue group (1...15)

   1 triclinic $\bar{1}$
   2 monoclinic $2/m$ ($\alpha = \beta = 90°$, $\gamma \neq 90°$)
   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 cubic $m\bar{3}$ ($a = b = c$, $\alpha = \beta = \gamma = 90°$)
   11 cubic $m\bar{3}m$ ($a = b = c$, $\alpha = \beta = \gamma = 90°$)
   12 monoclinic $2/m$ ($\alpha = \gamma = 90°$, $\beta \neq 90°$)
   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 ($a = b$, $\alpha = \beta = 90°$, $\gamma = 120°$)

3. centrosymmetry: 1 $\rightarrow$ non-centrosymmetric
   2 $\rightarrow$ centrosymmetric

`SYM`: name of the symmetry element followd by the symmetry element with the rotation matrix **R** and the translation $\vec{\nu}$ of the space group in the order: R_{11}, R_{12}, R_{13}, R_{21}, R_{22}, R_{23}, R_{31}, R_{32}, R_{33}, ν_1, ν_2, ν_3.
For a non-modulated structure with a centrosymmetric space groups only the symmetry elements, which together with the additional inversion operator $\bar{1}$ give the whole space group symmetry. The symmetry element 1 has not to be entered for non-modulated structures. This line has to be repeated for each symmetry element.

Example: The file with the symmetry cards of the space group $I2/m$

```
symmetry cards of the space group I 2/M, unit axis C
      Centering, Laue gr., centrosym.
COD>      I          2          2
     Symb.  R11  R12  R13    R21  R22  R23    R31  R32, R33,   t1   t2   t3
SYM>  2z    -1    0    0      0   -1    0      0    0    1    0.0  0.0  0.0
```

9.5.1 Magnetic space groups

Alternatively the symmetry of the magnetic structure can be given in a file instead of the magnetic space group symbol. The file consists of the following input lines:

`COD`:
1. Magnetic Bravais class (see section 4.1)
2. Number of the Laue group
3. Centrosymmetry: all symmetry cards has to be entered also in the case of a centrosymmetric space group. A “1” for non-centrosymmetry has to be chosen.

`SYM`: name of the symmetry element followd by the symmetry element with the rotation matrix **R** and the translation $\vec{\nu}$ of the space group in the order: R_{11}, R_{12}, R_{13}, R_{21}, R_{22}, R_{23}, R_{31}, R_{32}, R_{33}, ν_1, ν_2, ν_3, p. $p \pm 1$ for unprimed/primed symmetry elements. The symmetry element 1 has not to be entered. This line has to be repeated for each symmetry element.

Example: The file with the symmetry elements of the magnetic space group $Pn'ma'$

```
magnetic space group P n' m a'
      Bravais class, Laue gr., centrosym.
COD>       P    1        3          1
     Symb.  R11 R12 R13   R21 R22 R23   R31 R32  R33   t1   t2   t3     p
SYM>  1       1   0   0     0   1   0     0   0    1   0.   0.   0.     1
SYM>  n      -1   0   0     0   1   0     0   0    1   0.5  0.5  0.5   -1
SYM>  m       1   0   0     0  -1   0     0   0    1   0.   0.5  0.     1
SYM>  a       1   0   0     0   1   0     0   0   -1   0.5  0.   0.5   -1
SYM>  1b     -1   0   0     0  -1   0     0   0   -1   0.   0.   0.     1
SYM>  21      1   0   0     0  -1   0     0   0   -1   0.5  0.5  0.5    1
SYM>  21     -1   0   0     0   1   0     0   0   -1   0.   0.5  0.    -1
SYM>  21     -1   0   0     0  -1   0     0   0    1   0.5  0.   0.5    1
```

9.6 Files with the displacements of the atoms

The input of the displacement vectors, amplitudes and phases of the atoms of a modulated structure are entered in a special file for each lattice complex, of which atoms are displaced. The filename consists the name of the name of the lattice complex in the input file and the extention "`.mod`". For example, the filename for the lattice complex O2 in the input file is `O2.mod`.
These are the possible input key words and its values:

`TIT`: Title

`BAS`: Numbers of the base vectors which should be taken into account

`PAR`: Parameters which should be refined. If the amplitude u_{kl} should be refined, the number of the corresponding base vector has to be entered here. If the phase ϕ_{kl} should be refined, the number of the base vector with a minus sign has to be entered.

`POS`: Positions of the lattice complex and translation vector of the phase factor: no., x/a, y/b, z/c, t_x/a, t_y/b, t_z/c
This line has to be repeated for each position of the lattice complex.

`MOD`: The exact description of the base vector.
Each input of a base vector begins with this line with the following values:

1. name of the irreducible representation (e.g. B_u)
2. matrix element (e.g. 11 for the matrix element $A_{g,11}$ of a representation A_g)
3. number of the base vector concerning the irreducible representation
4. serial number (all base vectors of a lattice complex are numbered beginning with "1")
5. amplitude u_{kl}
6. phase ϕ_{kl}

`VEC`: displacement vector (base vector) of an atom of a lattice complex:

1. number of the atom of the lattice complex
2. absolute value of the displacement vector in the direction of the a axis
3. absolute value of the displacement vector in the direction of the b axis
4. absolute value of the displacement vector in the direction of the c axis
5. phase of the displacement vector in the direction of the a axis
6. phase of the displacement vector in the direction of the b axis
7. phase of the displacement vector in the direction of the c axis

This input line is repeated for each atom of the lattice complex. The part of the phase which is due to the propagation of the modulation wave has to be left out, because this part is added by the program.

These files can be generated by the program PROMET.

Example: File `O.mod` of the Oxygen atom O of $KNbO_3$

```
TIT> space group Pm3bm, Perovskite, Oxygen ion, q=(0,0,0)
BAS> 1_6
PAR> 1_6

Atom  no.   x/a      y/b      z/c       tx/a     ty/b     tz/c
POS>   1  0.50000  0.00000  0.00000   0.00000  0.00000  0.00000
POS>   2  0.00000  0.50000  0.00000   0.00000  0.00000  0.00000
POS>   3  0.00000  0.00000  0.50000   0.00000  0.00000  0.00000

MOD> T1u  11  1      1          -0.05304   0.00000
VEC>   1  1.00000  0.00000  0.00000     0.00     0.00     0.00
VEC>   2  0.00000  0.00000  0.00000     0.00     0.00     0.00
VEC>   3  0.00000  0.00000  0.00000     0.00     0.00     0.00
MOD> T1u  11  2      2           0.07912   0.00000
VEC>   1  0.00000  0.00000  0.00000     0.00     0.00     0.00
VEC>   2  0.50000  0.00000  0.00000     0.00     0.00     0.00
VEC>   3  0.50000  0.00000  0.00000     0.00     0.00     0.00
MOD> T1u  22  1      3          -0.01903   0.00000
VEC>   1  0.00000  0.50000  0.00000     0.00     0.00     0.00
VEC>   2  0.00000  0.00000  0.00000     0.00     0.00     0.00
VEC>   3  0.00000  0.50000  0.00000     0.00     0.00     0.00
MOD> T1u  22  2      4          -0.04621   0.00000
VEC>   1  0.00000  0.00000  0.00000     0.00     0.00     0.00
VEC>   2  0.00000  1.00000  0.00000     0.00     0.00     0.00
VEC>   3  0.00000  0.00000  0.00000     0.00     0.00     0.00
MOD> T1u  33  1      5          -0.01745   0.00000
VEC>   1  0.00000  0.00000  0.50000     0.00     0.00     0.00
VEC>   2  0.00000  0.00000  0.50000     0.00     0.00     0.00
VEC>   3  0.00000  0.00000  0.00000     0.00     0.00     0.00
MOD> T1u  33  2      6          -0.00340   0.00000
VEC>   1  0.00000  0.00000  0.00000     0.00     0.00     0.00
VEC>   2  0.00000  0.00000  0.00000     0.00     0.00     0.00
VEC>   3  0.00000  0.00000  1.00000     0.00     0.00     0.00
MOD> T2u  11  1      7           0.02421   0.00000
VEC>   1  0.00000  0.00000  0.00000     0.00     0.00     0.00
VEC>   2  0.50000  0.00000  0.00000     0.00     0.00     0.00
VEC>   3  0.50000  0.00000  0.00000   180.00     0.00     0.00
MOD> T2u  22  1      8          -0.04386   0.00000
VEC>   1  0.00000  0.50000  0.00000     0.00     0.00     0.00
VEC>   2  0.00000  0.00000  0.00000     0.00     0.00     0.00
VEC>   3  0.00000  0.50000  0.00000     0.00   180.00     0.00
MOD> T2u  33  1      9           0.03277   0.00000
VEC>   1  0.00000  0.00000  0.50000     0.00     0.00     0.00
VEC>   2  0.00000  0.00000  0.50000     0.00     0.00   180.00
VEC>   3  0.00000  0.00000  0.00000     0.00     0.00     0.00
```

9.7 File with the fitted profile values

This output file contains the observed and calculated profile values, the difference $y_i^{obs} - y_i^{calc}$ and the background at the position $2\theta_i$. The data are given in the following order in the Fortran format (F8.4,4(X,12.0)):

$$2\theta_i, \quad y_i^{obs}, \quad y_i^{obs} - y_i^{calc}, \quad y_i^{back} \quad .$$

The first line is the title line taken from the input file. The second line consists of the code "SIM", the first 2θ value, the stepwidth, the last 2θ value, the temperature and the number of data values.

Example:

```
Silicon,   299 K,   Guinier data, counter 1
SIM   0.000    0.020    72.000    297.0    3601
  0.0000          23.          24.          23.          23.
```

9.8 File with the reflection list

This file contains the data of the reflections, for all phases and wavelengths in the given 2θ region. The following columns are given:

1. line: the title from the input file
2. line: the caption of the columns

next lines: the data in the Fortran format (2x,3i4,3f12.4,4x,4i4,i8):

1. number of the reflection
2. number of the phase
3. number of the wavelength
4. peak position in 2θ
6. Lorentz-Polarisation factor
7. Full-width-of-half-maximum (fwhm)
4. Miller indices h, k , l and n (n only for modulated structures
5. multiplicity

Example: file with a (hkl)-list of Silicon at 300 K

```
Silicon, 300K, Guinier diffr., counter 1
   No. Ph. Co.     2-Theta       Lopo        Fwhm        h   k   l    Mult
     1   1   1     28.1875      4.0236      0.0769       1   1   1       8
     2   1   1     32.6620      2.8273      0.0763       0   0   2       6
     3   1   1     46.8652      1.2380      0.0847       0   2   2      12
     4   1   1     55.5908      0.8839      0.0974       1   1   3      24
     5   1   1     58.2940      0.8149      0.1024       2   2   2       8
     6   1   1     68.4446      0.6622      0.1252       0   0   4       6
```

9.9 File with the structure factors

This file can be used to calculate for Fourier maps and difference Fourier plots. The filename has the extention "`.kof`". The data are given as follows:

1. line:	title
2. line:	caption of the columns
next lines:	data values in the Fortran format `(X,3I4,3X,3I4,F8.3,4F10.2)`:
	1. number of the data set
	2. number of the reflection
	3. number of the wavelength
	4. Miller indices h, k, l and n (n only for modulated structures)
	5. peak position in 2θ
	6. calculated real part of the structure factor (`A`)
	7. calculated imaginary part of the structure factor (`B`)
	8. square of the calculated absolute value of the structure factor (`FF(calc)`)
	9. square of the observed absolute value of the structure factor (`FF(obs)`)

Attention: For two or more phases the data are written in only **one** file!!!

Example: file with the structure factors (`*.kof` file)

```
Silicon, 300 K, Guinier diffr., counter 2
  No. Co.      h   k   l   n    Pos.        A         B    FF(calc)   FF(obs)
    0   1      0   0   0   0   0.000    113.93      2.64  12987.65      0.00
    1   1      1   1   1   0  28.189     43.57    -40.99   3578.22   3580.73
    2   1      0   2   2   0  46.865     67.70      2.48   4589.19   4661.27
    3   1      1   1   3   0  55.590     29.85     32.28   1933.19   1905.35
    4   1      2   2   2   0  58.293      0.00      0.00      0.00      0.00
    5   1      0   0   4   0  68.443     55.18      2.34   3049.98   3157.61
    6   1      1   3   3   0  75.592     26.99    -24.71   1339.29   1464.43
    7   1      2   2   4   0  87.068     46.60      2.20   2176.60   2311.37
    8   1      1   1   5   0  93.868     23.00    -20.85    964.00    821.79
    9   1      3   3   3   0  93.868     20.85     23.00    963.99    821.79
```

9.10 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 1).

10 Program ProMet

This program calculates all base vectors of a lattice complexe of any space group using the projection operator method described by *Maradudin and Vosko* [18]. The input of the program is given as a file, where

1. a title,
2. the coordinates of the lattice complex (x/a, y/b, z/c),
3. the commponents of the wave vector (δ_1, δ_2, δ_3),
4. the space group symbol

have to be entered with the key words `TIT>`, `ATO>`, `WAV>` and `SPG>`.

Example: input file of the program PROMET

```
TIT> Space group Pm3bm, Perovskite KNdO3, Oxygen-Ion

Lattice complex:
ATO> 0.5  0.  0.

Wave vector:
WAV> 0.  0.  0.

Space group:
SPG>  P,4/M,3B,2/M
```

The output is written in the file `<filename>.mod` which can be used as a input file for SIMREF. An example is shown in section 9.6. In addition the file `<filename>.sym` with all symmetry elements of the space group is generated.

11 Building SIMREF from the source code

11.1 The archive file

At first the file `simref.tar.gz` has to be decompressed with

```
$ gzip -d simref.tar.gz
```

Then all files from the decompressed archive file `simref.tar` has to be extracted with

```
$ tar -xvf simref.tar
```

In the following table all files from `simref.tar.gz` are listed with a short description:

file	description
`demo`	directory with sample files
`daten.f`	source code
`datum.c`	source code to create date and time (C routine)
`datum.f`	source code to create date and time for Ultrix and VMS
`datum_MS.for`	source code to create date and time for DEC Visual Fortran
`install.com`	command file to compile and link for DEC VMS
`makefile.Ultrix`	makefile for DEC Ultrix and other Unix systems
`makefile.f2c`	makefile for Linux with f2c and gcc
`makefile.g77`	makefile for Linux with g77
`mettab.f`	source code for multiple data refinement
`promet10.f`	source code of the program PROMET
`sim_MS.for`	source code of the main program for DEC Visual Fortran
`simref.bash`	bash shellscript file
`simref.csh`	csh shellscript file
`simref26.f`	source code

Attention: The source code of the programs (`simref26.f`, `promet10.f` contains some double backslashes “\\”, which represent **one** backslash in the in- and output of the programs using a Linux operating system. On other systems like Windows 95/NT or VMS, they have to be replaced by only one backslash “\” in the source code.

11.2 Building the program

On the different systems the following commands have to be typed to build the program:

Linux using `f2c` (AT&T Bell Laboratories Fortran-to-C Converter) and gcc (GNU project C Compiler):

```
$ make -f makefile.f2c
```

Linux using `g77` (GNU project F77 Compiler):

```
$ make -f makefile.g77
```

DEC Ultrix:

```
$ make -f makefile.Ultrix
```

DEC VMS:

```
$ @install.com
```

On other Unix systems the makefile `makefile.g77` has to be modified. On Computers with Windows 3.x, Windows 95 and Windows NT *Microsoft Fortran Powerstation* or *DIGITAL Visual Fortran* can be used to build the program. Then the following files are needed:

```
simref26.f, daten.f, datum_MS.for, sim_MS.for
```

At least on Unix systems one of the shellscript files has to be renamed to `simref`:

If a csh shell is used type:

```
$ mv simref.csh simref
```

If a bash shell is used type:

```
$ mv simref.bash simref
```

The shellscript file `simref` is used to start the program (see the following section).

12 How to start SIMREF

SIMREF can be started with the following command:

```
$ simref26
```

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

12.1 How to start SIMREF on Unix systems

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

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

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

- `-r` simple Rietveld refinement (default)
- `-m` automatic refinement of several data sets at different temperatures (e.g. film-lift data).

Example:

```
$ simref -r demo1.inp
```

If no option is used, the simple Rietveld refinement will be executed.
Shell script for the *bash* and the *csh* shell are available. (files `simref.bash` and `simref.csh`)

12.2 Refinement of several data sets at different temperatures

If SIMREF is started with the option -m, the shell script `simref` expects an arbitrary number of data sets, which are measured at different temperatures (e.g. the different lines of a film-lift) where silicon powder has been measured together with the sample as a second phase. The names of the data files have to be in the following form:

`name`*z*`.duo`

The data sets should be ordered in ascending or descending temperature order indicated by the number *z* of the filename. *z* must consist of the same number of digits for all filenames. 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 SIMREF reads it from this file to do the scaling on silicon standard. In the input file the following settings have to be chosen (see section 7):

1. two phases: 1. phase = the sample to be analysed
   2. phase = silicon standard
2. background fitting with the polynomial (see section 2.9)
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.dat`.

The parameter file has to be prepared for two phases.

When the shell script `simref` is started, for each data set the data file `name`*z*`.duo` will be copied to `sim.dat`, because the main refinement program `simref26` always reads the data file `sim.dat`, which is given in the input file. After the refinement of one data set 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 and the atomic parameters with their standard deviations for all temperatures will be stored in the file `<filename>.met` and `<atom>.ato` in tabular form.

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