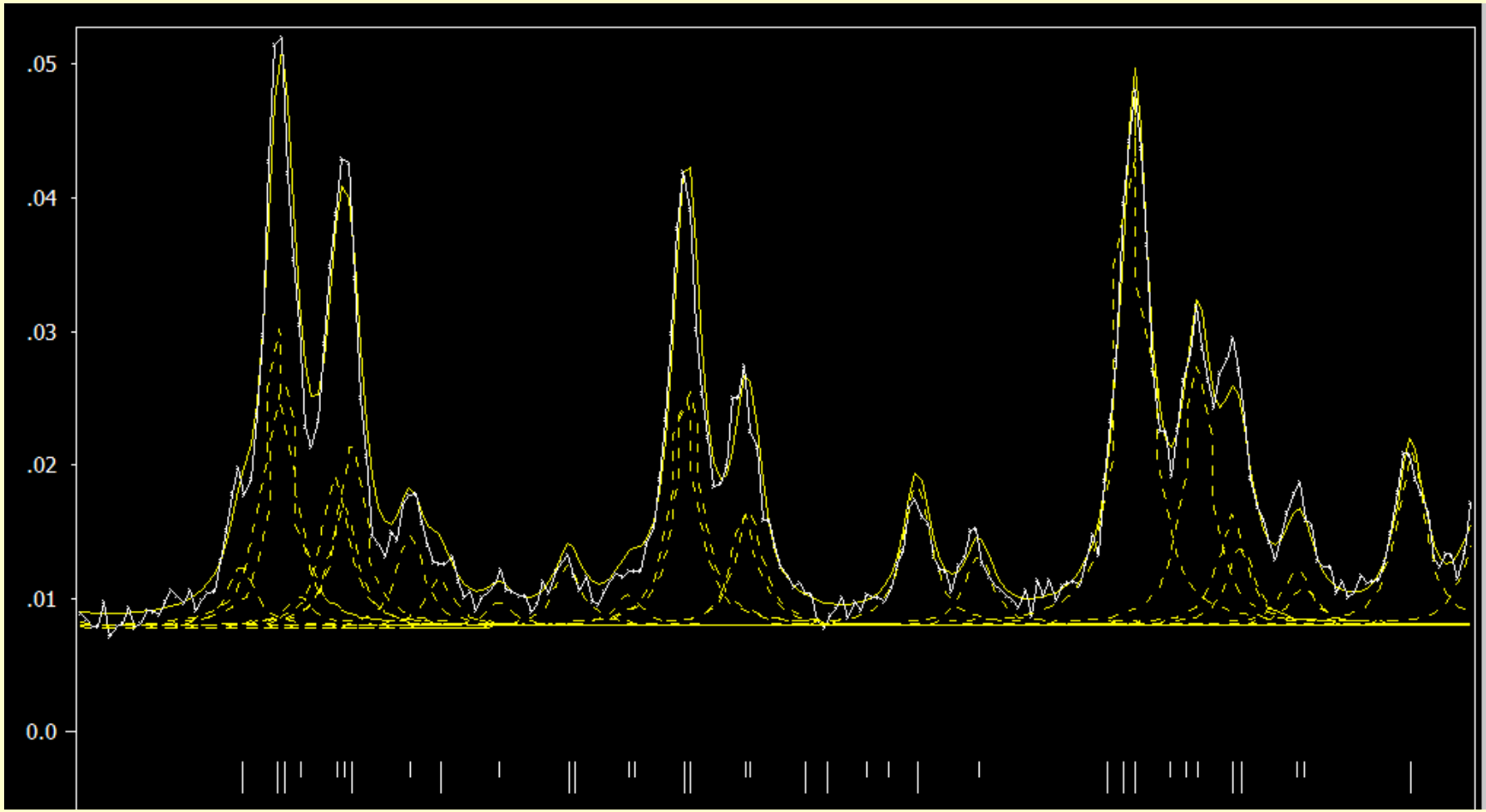
Le Bail and Rietveld refinement



The powder diffraction option (Rietveld refinement + leBail technique) was implemented in 2001:

Dušek,M., Petříček,V., Wunschel,M., Dinnebier,R.,E. & Van Smaalen,S. (2001). J.Appl.Cryst. 34,398-404.

Main powder characteristics

Profile functions: Gauss, Lorentz and pseudo-Voigt

Background corrections: Legendre, Chebyshev polynomials, “cos” functions

Peak asymmetry: Simpson, Berar-Baldinozzi, Finger-Cox-Jephcoat

fundamental approach (Cheary-Coelho)

Preferred orientation: March-Dollase, Sasa-Uda

Roughness: Pitchke-Hermann-Matter, Suorti

Anisotropic line-broadening according to Stephens modified by Leineweber and Petricek to include modulated phases

Powder profile parameters and correction

Profile functions:

Gaussian: $G(b_G, x) = \frac{1}{\sqrt{2\pi b_G}} \exp\left(-x^2 / 2b_G^2\right)$ $\qquad b_G^2 = \frac{H_G^2}{8 \ln 2}$

where H_G is Full-Width at Half-Maximum

Lorentzian: $L(b_L, x) = \frac{2}{\pi b_L} \frac{1}{1 + \left(2x / b_L\right)^2}$ $\qquad b_L = H_L$

where H_L is Full-Width at Half-Maximum

Voigt function: $V(b_G, b_L, x) = \int_{-\infty}^{+\infty} G(b_G, x') L(b_L, x - x') dx'$

is a convolution of Gaussian and Lorentzian function. For powder profile we use a simpler analytical approximation of the Voigt function called pseudo-Voigt function:

$$pV(H, x) = \eta L(H, x) + (1 - \eta) G(H, x)$$

the parameters η and H are functions of H_G and H_L

$$H^5 = H_G^5 + 2.69269 H_G^4 H_L + 2.42843 H_G^3 H_L^2 + 4.47163 H_G^2 H_L^3 + 0.07842 H_G H_L^4 + H_L^5$$

$$\eta = 1.36603 \frac{H_L}{H} - 0.47719 \left(\frac{H_L}{H} \right)^2 + 0.11116 \left(\frac{H_L}{H} \right)^3$$

The diffraction line broadening induced by the sample is usually divided into to crystalline size effect T and microstrain Y. In a first approximation they have the following angular dependence:

$$H_L = b_L = X_L/\cos\theta + Y_L \tan\theta \qquad X_L = 180\lambda/\pi T$$

Similar equations are valid for Gaussian distribution but then an additional factor $8\ln 2$ is to be applied to get b_G from H_G.

$$H_G^2 = 8\ln 2 b_G^2 = X_G^2/\cos^2\theta + Y_G^2 \tan^2\theta$$

These ideal equations are valid only if broadening , induced by experimental parameters are neglected. This means we can use the refined values to make conclusions about crystalline size and microstrain only if some type of fundamental approach is used.

But usually we are using an additional terms to take into account other experimental effects.

For the Gaussian term the formula Cagliotti, Pauletti & Ricci, 1958 (Nucl.Instrum., **3**, 223) is used:

$$b_G^2 = U\tan^2\theta + V\tan\theta + W + \frac{P}{\cos^2\theta}$$

In the original formula only three first terms were used. The last one was introduced later as a Scherrer term and it is connected with crystalline size. But from the fact that:

$$\tan^2\theta + 1 = \frac{1}{\cos^2\theta}$$

follows that only two of three coefficients U, W, P can be refined simultaneously.

For the Lorentzian part we use the same terms as for pure crystal broadening but, as mentioned above, they cannot be used directly to find sample characteristics.

$$b_L = X_L/\cos\theta + Y_L\tan\theta$$

Stephens model for anisotropic broadening

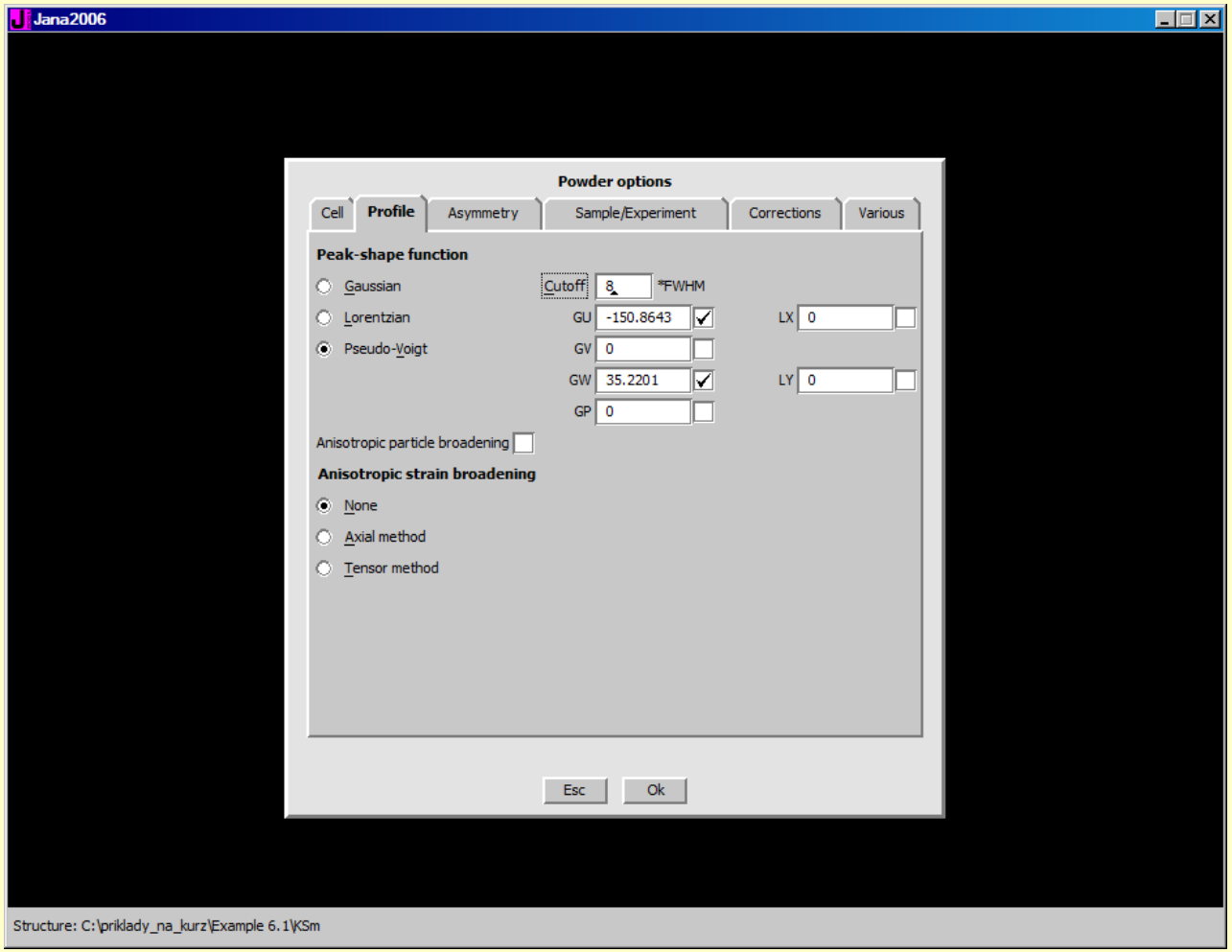
This phenomenological model is based on a general tensor expression in which the anisotropic strain is described by a symmetrical 4th order tensor:

$$\sigma^2(hkl) = D^{ijmn} h_i h_j h_m h_n = \sum_{H,K,L} S_{HKL} h^H k^K l^L$$

The first term is just a general tensor expression where Landau summation convention is used and which allows a simple derivation of symmetry restrictions similar to those for 4th order ADP parameters. The second term has an explicit form as used by Stephens in which summation is restricted to $H + K + L = 4$

This term is used to modify equations for b_G and b_L

For modulated structures this method has been generalized by A.Leineweber and V.Petříček, (2007). J.Appl.Cryst. ,**40**, 1027-1034.



The angular parameters (LX, LY,…) are measured in 0.01 deg, the squared ones in 0.0001 deg^2.

Asymmetry options in Jana2006

Simpson's method – Peak is combined with several shifted peaks having the identical shape according to the formula:

$$P_{corr}[2\theta] = \frac{1}{6n}\sum_{i=1}^{2n+1} k_i P\left[2\theta + a\left(\frac{i-1}{2n}\right)^2 \cot 2\theta\right]$$

$$k_i = 1 \quad \text{for} \quad i = 1 \text{ or } i = 2n+1$$

$$k_i = 4 \quad \text{for} \quad i = 2m$$

$$k_i = 2 \quad \text{for} \quad i = 2m+1 \quad m \neq 0 \quad m \neq n$$

a is the only parameter to be refined

Asymmetry options in Jana2006

Berar-Baldinozzi method –

$$P_{corr}(2\theta) = P(2\theta)\left(1 + \frac{p_1 F_1(z) + p_2 F_2(z)}{\tan\theta} + \frac{p_3 F_1(z) + p_4 F_2(z)}{\tan 2\theta}\right)$$

where $F_1(z) = H_1(2z)\exp(-z^2)$ $\quad z = \frac{\theta - \theta_0}{FWHM}$

$F_2(z) = H_3(2z)\exp(-z^2)$

$H_n(z)$ stand for Hermit polynomials

Asymmetry options in Jana2006

By axial divergence – according to Finger, Cox and Jephcoat, (1994) J.Appl.Cryst. **27**, 892-900.

Two parameters are used: H/L S/L "height" and "sample"

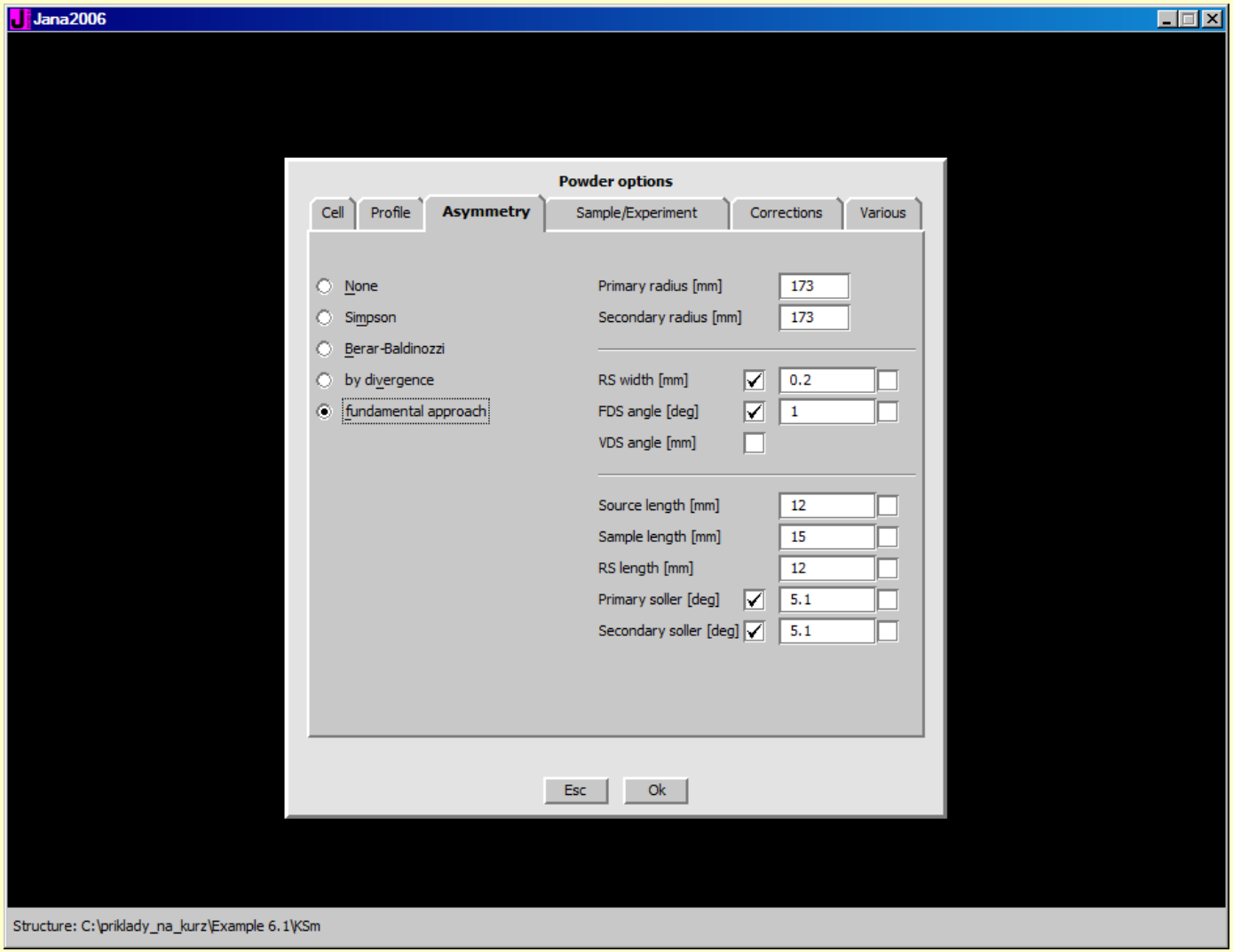
These parameters are strongly correlated. Our recommendation is to estimate their ratio and keep it as a restriction during the refinement.

Asymmetry options in Jana2006

Fundamental approach – it follows the method introduced by Cheary and Coelho, (1998), J.Appl.Cryst. **31**, 851-861.

This method can estimate the profile asymmetry just on the base of experimental parameters. For Bragg-Brentano geometry it works very nicely.

The method makes multiple convolution of several functions.


Jana2006
Powder options
Cell
Profile
Asymmetry
Sample/Experiment
Corrections
Various
None
Simpson
Berar-Baldinozzi
by divergence
fundamental approach
Primary radius [mm]
173
Secondary radius [mm]
173
RS width [mm]
0.2
FDS angle [deg]
1
VDS angle [mm]
Source length [mm]
12
Sample length [mm]
15
RS length [mm]
12
Primary soller [deg]
5.1
Secondary soller [deg]
5.1
Esc
Ok
Structure: C:\priklady_na_kurz\Example 6.1\KSm

Background correction

Legendre polynomials – set of orthonormal polynomials defined on the interval $\langle -1,+1 \rangle$ The measured interval have to be first linearly projected into this interval. Then their orthonormality considerably suppress their mutual correlations.

Chebyshev polynomials – they are also orthogonal but in difference sense

$$\int_{-1}^{1} w(x) p_i(x) p_j(x) = \delta_{ij}$$

Legendre polynomials: $w(x) = 1$

Chebyshev polynomials: $w(x) = 1/\sqrt{1-x^2}$

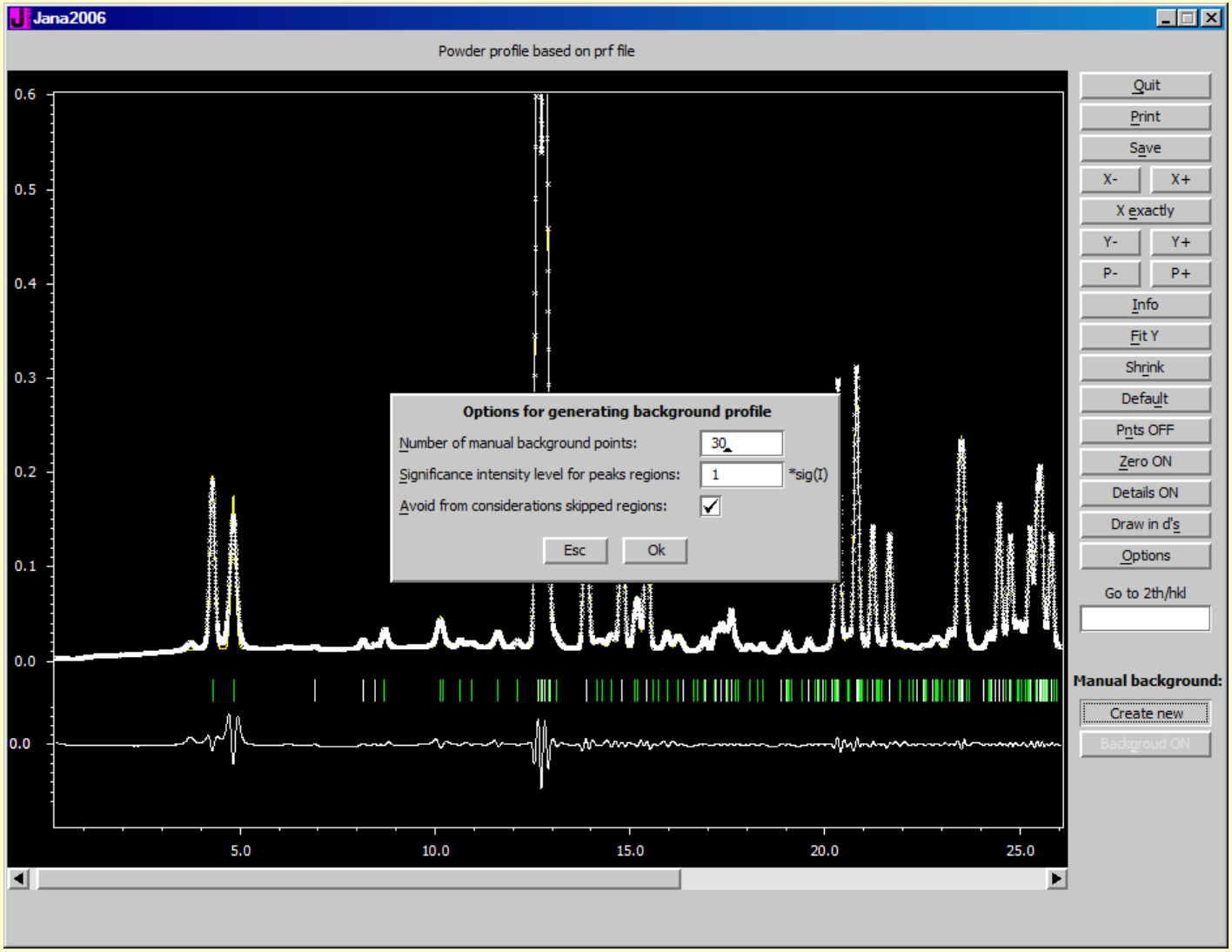
$w(x) = \sqrt{1-x^2}$

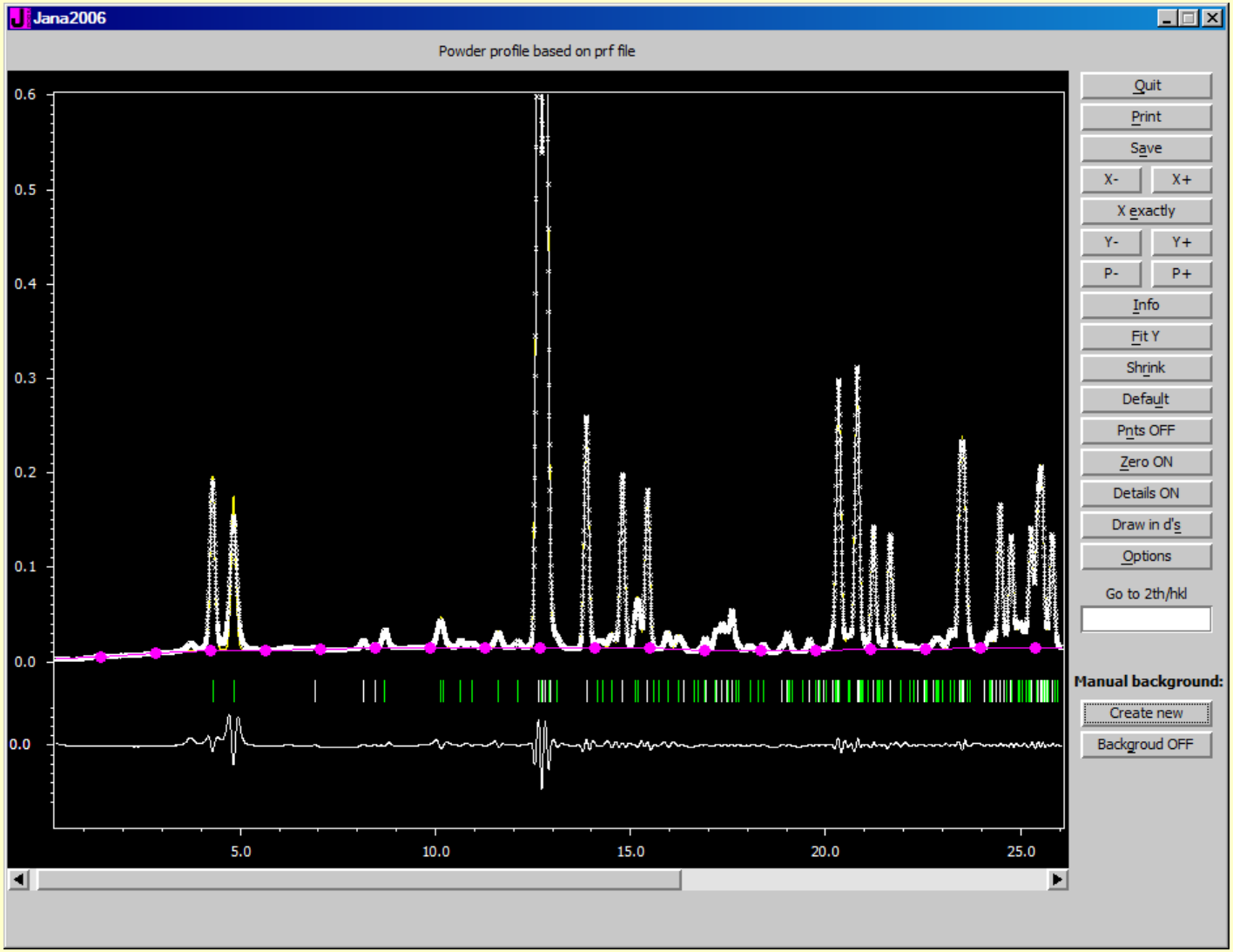
For data collected uniformly along diffraction interval we should preferably use the unique weight.

Background correction

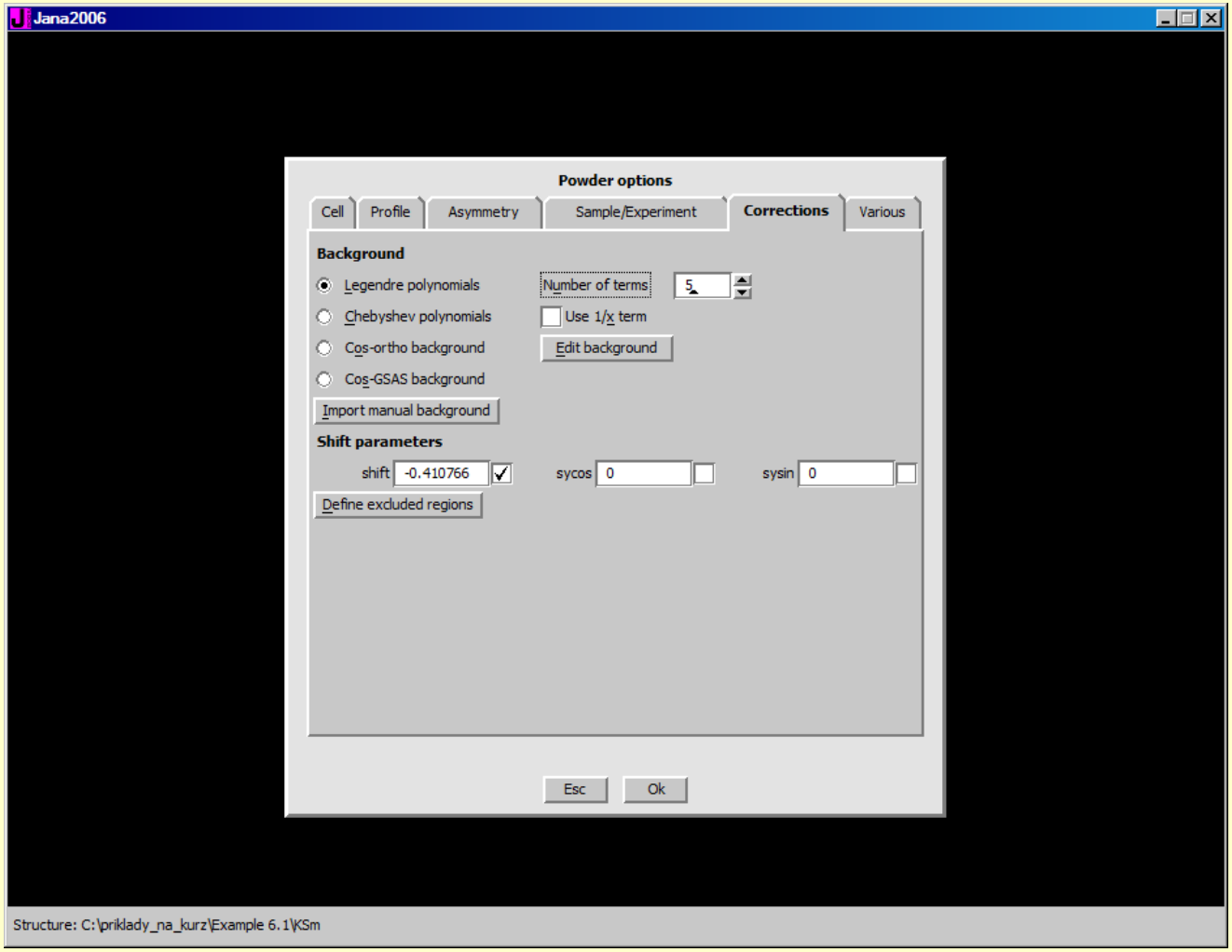
Manual background – the background is expressed as a set of background intensities over the diffraction interval. The actual value is calculated by a linear interpolation. This method is can very effectively describe even very complicated background profiles. But it need some user assistance to select it properly. Moreover this first background estimation can be combined with some of previous continuous functions.

In the program Jana2006 there is a tool to select a first estimation of manual background but then you can interactively modify it.


Jana2006
Powder profile based on prf file
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
5.0
10.0
15.0
20.0
25.0
Options for generating background profile
Number of manual background points:
30
Significance intensity level for peaks regions:
1
*sig(I)
Avoid from considerations skipped regions:
Esc
Ok
Quit
Print
Save
X-
X+
X exactly
Y-
Y+
P-
P+
Info
Fit Y
Shrink
Default
Pnts OFF
Zero ON
Details ON
Draw in d's
Options
Go to 2th/hkl
Manual background:
Create new
Backgroud ON


Jana2006
Powder profile based on prf file
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
5.0
10.0
15.0
20.0
25.0
Quit
Print
Save
X-
X+
X exactly
Y-
Y+
P-
P+
Info
Fit Y
Shrink
Default
Pnts OFF
Zero ON
Details ON
Draw in d's
Options
Go to 2th/hkl
Manual background:
Create new
Backgroud OFF

Shift parameters



Shift parameters

Shift – it defines the zero shift (again in units of 0.01 deg). This value is to be added to the theoretical peak position to get a position in experimental profile

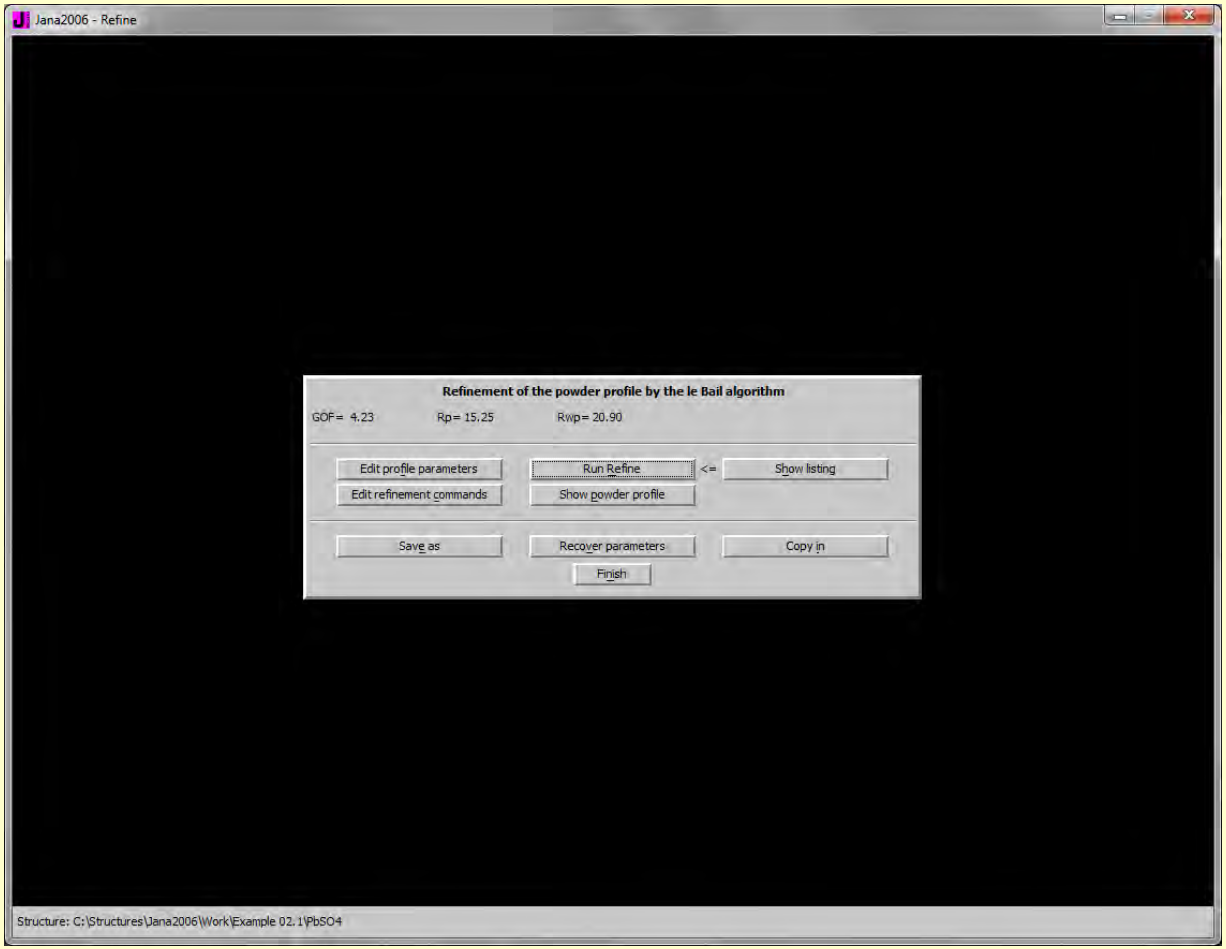
sycos – in analogy with the Fullprof: $\Delta 2\theta = \mathrm{c}.\cos\theta$
is connected with a specimen displacement

sysin – in analogy with the Fullprof: $\Delta 2\theta = \mathrm{s}.\sin 2\theta$
is connected with a transparency correction

These three corrections are combined together to the actual peak position.

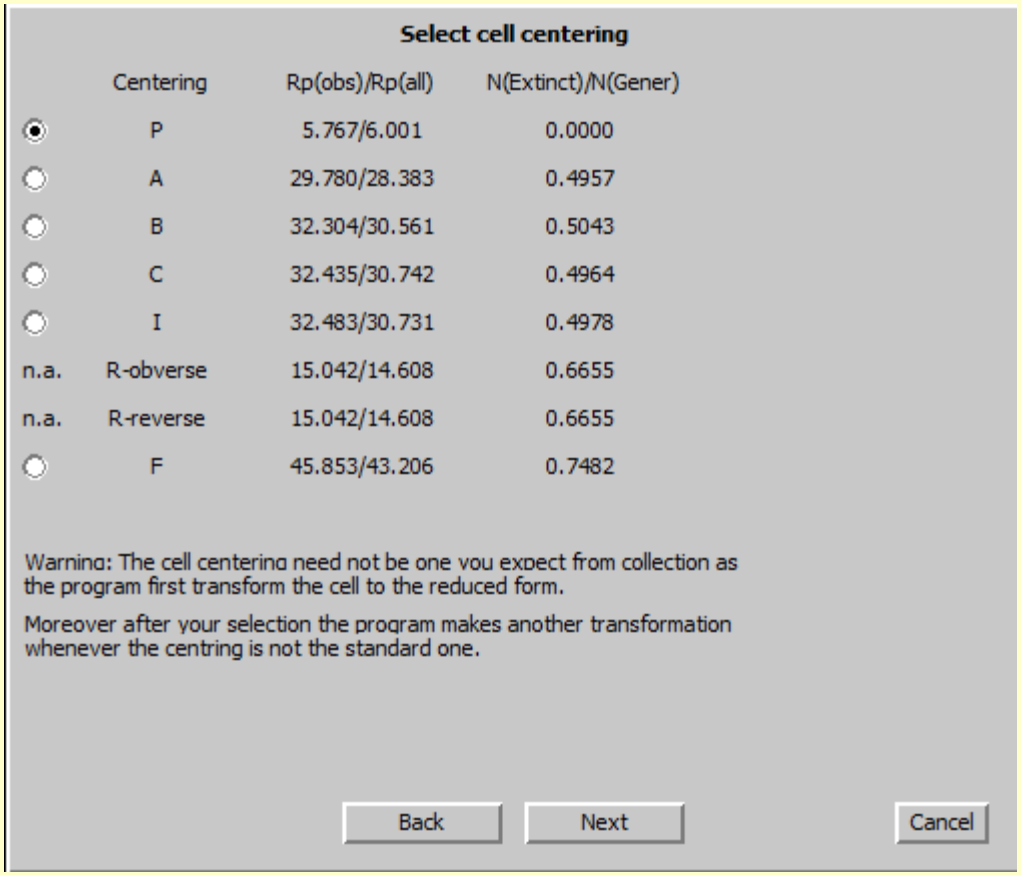
Profile refinement – le Bail technique

Based on a peak decomposition and subsequent refinement of profile parameters.



Profile refinement – le Bail technique

In Jana2006 is also used to predict symmetry by comparing of profile fits for different space groups:



Profile refinement – le Bail technique

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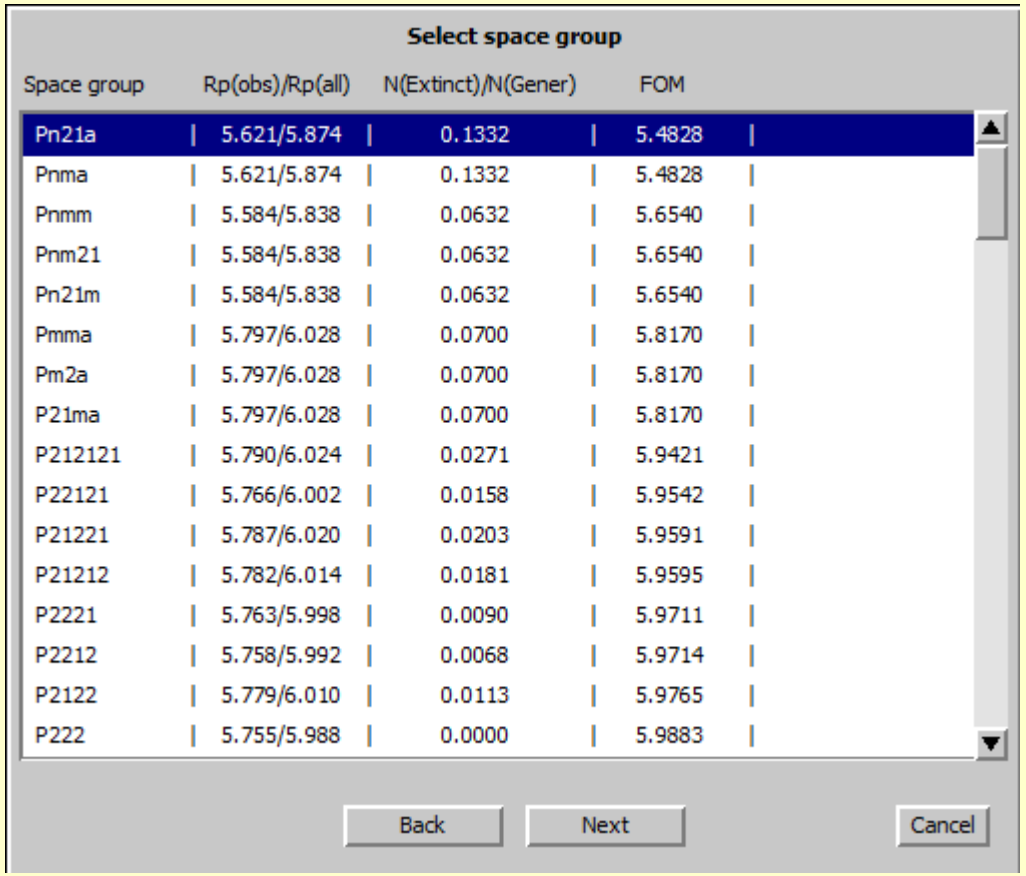
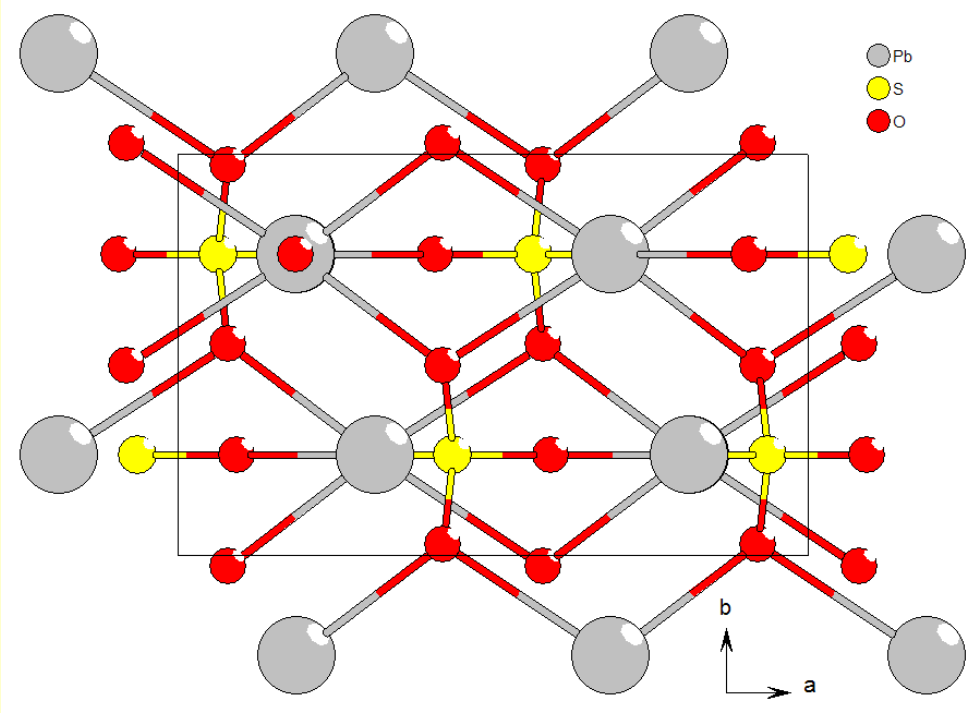
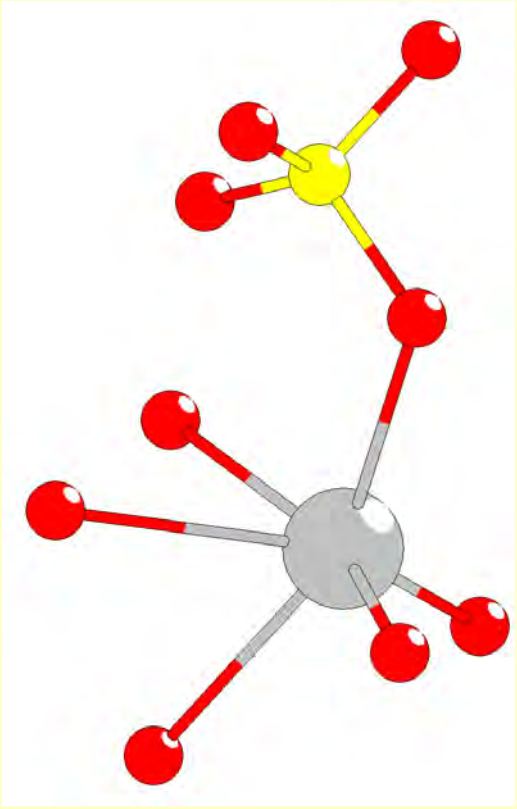


Example 2.1: $PbSO_4$

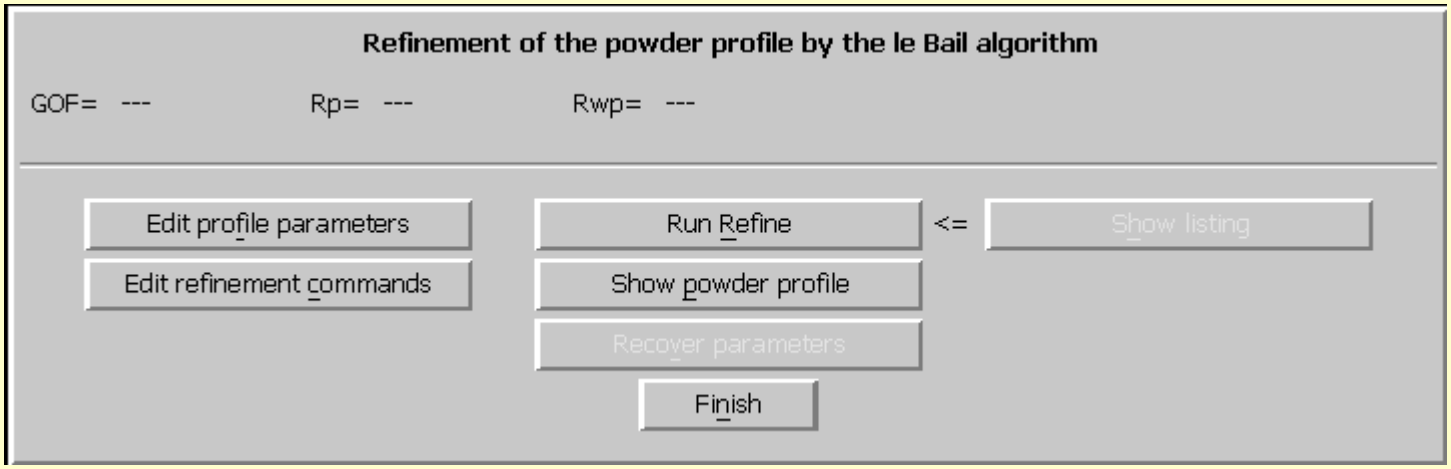
Application of Jana2006 to simple structure from powder data. Ideal case where determination of symmetry and structure solution are simple.

Powder data measured with laboratory diffractometer
Input files:
PbSO4.mac (powder profile data)
PbSO4.txt (additional information)

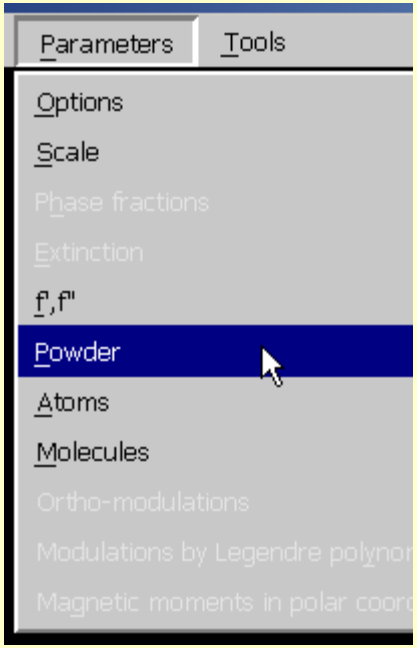


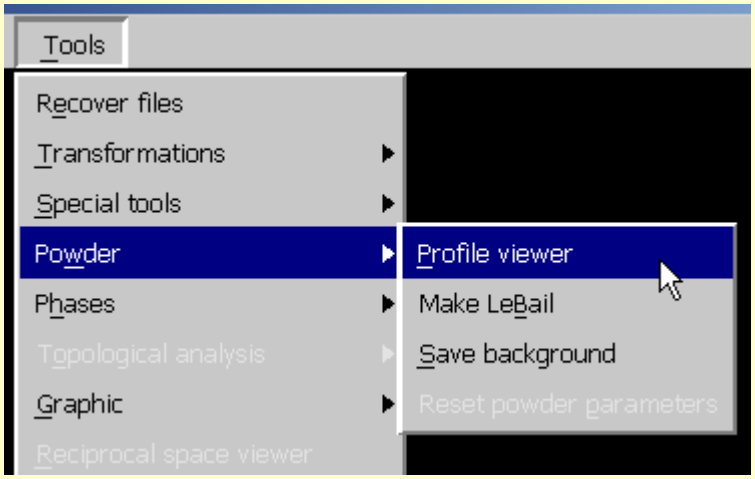


Step 1: profile fitting



Wizard for profile fitting connects tools, which can be also started separately from the main Jana window





Step 2: symmetry determination

Select cell centering

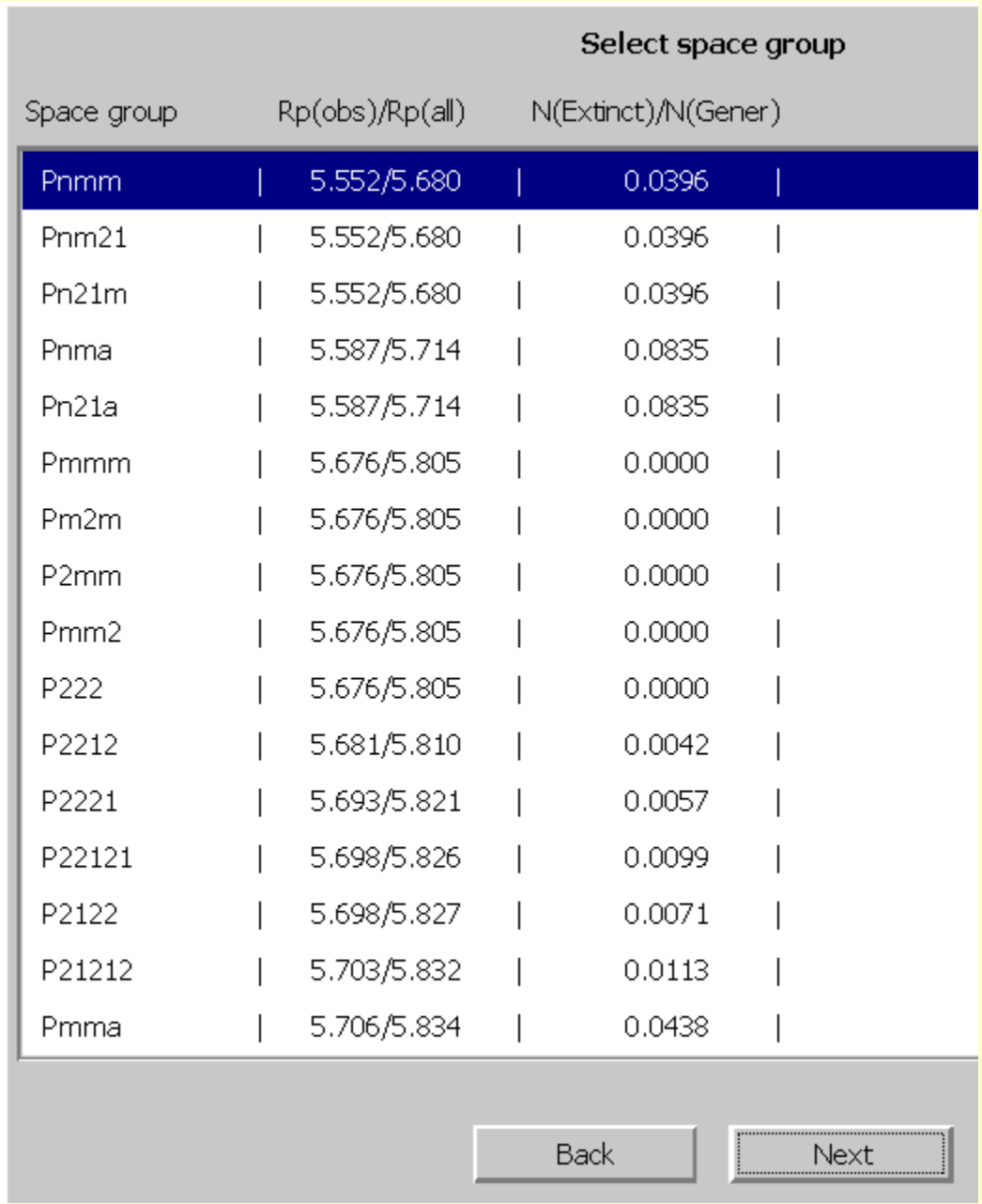
	Centering	Rp(obs)/Rp(all)	N(Extinct)/N(Gener)
◉	P	5.576/5.771	0.0000
○	A	29.593/28.232	0.4957
○	B	32.060/30.362	0.5043
○	C	32.228/30.595	0.4964
○	I	32.291/30.585	0.4978
n.a.	R-obverse	14.822/14.378	0.6655
n.a.	R-reverse	14.822/14.378	0.6655
○	F	45.678/43.136	0.7482

Each line contains ratio of extinct and all reflections and R_p corresponding to a profile with discarded extinct reflections. Thus we are looking for case where number of extinct reflections is large without serious impact on R_p .

$$R_p = \frac{\sum |y(obs) - y(calc)|}{\sum y(obs)} \cdot 100$$

$$R_{wp} = \sqrt{\frac{\sum w(y(obs) - y(calc))^2}{\sum wy(obs)^2}} \cdot 100$$

Data import
Refinement of profile parameters (with symmetry P1)
Determination of symmetry
Charge flipping (based on Bragg intensities calculated from the profile)
Rietveld refinement



Step 3: structure solution

Superflip uses intensities from profile decomposition

Step 4: Rietveld refinement
Instead of Le Bail fit the intensities are calculated from the structure.

```
R factors : [384=383+1/14]
R(obs)=   5.91     Rw(obs)=   7.45     R(all)=   5.94     Rw(all)=   7.45
================================================
Profile R factors :[5769/13+14],   Damping factor:  1.0000
GOF  =  2.59 Rp  =  9.98 Rwp   = 12.78
Last Rwp: 18.59 14.86 12.93 12.79 12.78 12.78 12.78 12.78
Maximum change/s.u. :  -0.0485 for x[S1]
```

Step 4: Completing the structure from difference Fourier map