Ab initio structure determination using powder diffraction

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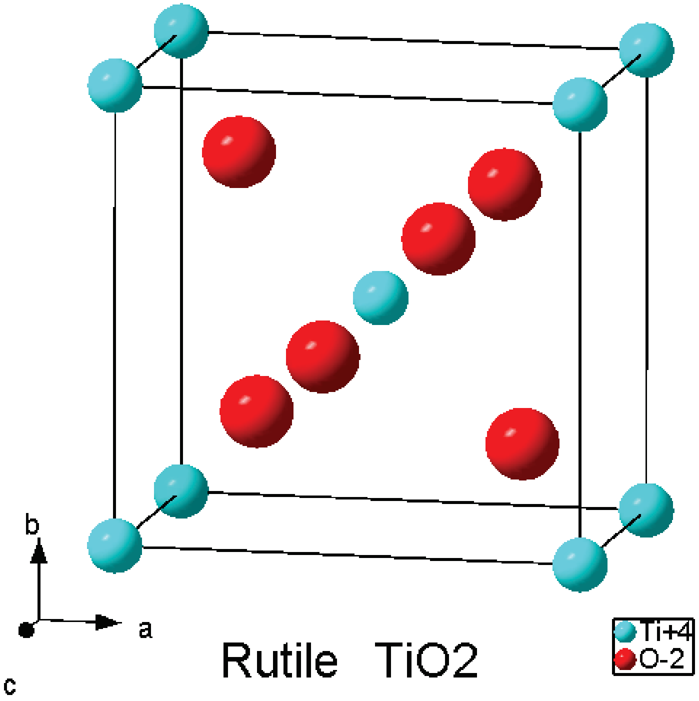
Description of the Crystal Structure

The crystal structure is completely determined by the knowledge of

- ***the unit cell***
- ***the space group***
- ***the asymmetric unit***

To solve the structure, these three components must be determined



Crystal data

Formula sum	O2 Ti
Crystal system	tetragonal
Space group	*P* 42/m n m (no. 136)
Unit cell dimensions	a = 4.5937 Å c = 2.9587 Å
Cell volume	62.40 Å3
Z	2

Atomic coordinates

Atom	**Ox.**	**Wyck.**	**x**	**y**	**z**
Ti	+4	2*a*	0	0	0
O	-2	4*f*	0.30469	0.30469	0

Selected geometric parameters (Å, °)

Ti—O	1.949(0)	Ti1—Ti1ii	2.959
O—O	2.959	Ti1—Ti1iii	3.569

A crystal can be described as the convolution of an atomic motif $M(\vec{r})$ and a lattice $R(\vec{r})$

$$\boxed{C(\vec{r}) = R(\vec{r}) * M(\vec{r})}$$

The scattered amplitude corresponds to the Fourier transform of the scattering object

$$\boxed{C(\vec{h}) = TF\{C(\vec{r})\} = TF\{R(\vec{r}) * M(\vec{r})\} = R(\vec{h}) x F(\vec{h})}$$

The Fourier space is called **reciprocal space**

$R(\vec{h})$ = Fourier transform of the (direct) lattice : **Reciprocal Lattice**

$F(\vec{h})$ = Fourier transform of the atomic motif : **Structure factor**

Knowing the reciprocal lattice and the structure factors is equivalent to knowing the structure in real space

That is the aim of the diffraction experiments (RX, neutrons, electrons)

Structure Factors

F_{hkl} : structure factor for reflexion (hkl) = TF{ $M(\vec{r})$ }, atomic motif

Fhkl : Fourier transform of the scattering density of the the crystal

$$\boxed{F_{hkl} = \sum_{j \subset cell} f_j T_j \exp(2i\pi(hx_j + ky_j + lz_j))}$$

f_j : scattering factor for atom j with coordinates (x_j, y_j, z_j). FT of its scattering density

For x-rays, $\boldsymbol{f_j}$ is the atomic form factor,
For neutrons, $\boldsymbol{f_j = b_j}$ is the Fermi length.

T_j = **Debye-Waller** factor related to atomic displacements (thermal, static…).
In an isotropic, harmonic approximation one has :

$$\boxed{T_j = \exp\{-B_j(\sin^2\theta)/\lambda^2\}} \quad \text{with} \quad B_j = 8\pi^2\langle U_j^{\,2}\rangle$$

$\langle U_j^{\,2}\rangle$ is the *root mean square displacement* of atom j.

Extinction Conditions :

If the crystal contains symmetry elements with translations, some categories of reflexions will have zero intensity by symmetry. One speaks of **systematic extinctions**

Example : body centered lattice I : translation $(\vec{a}+\vec{b}+\vec{c})/2$

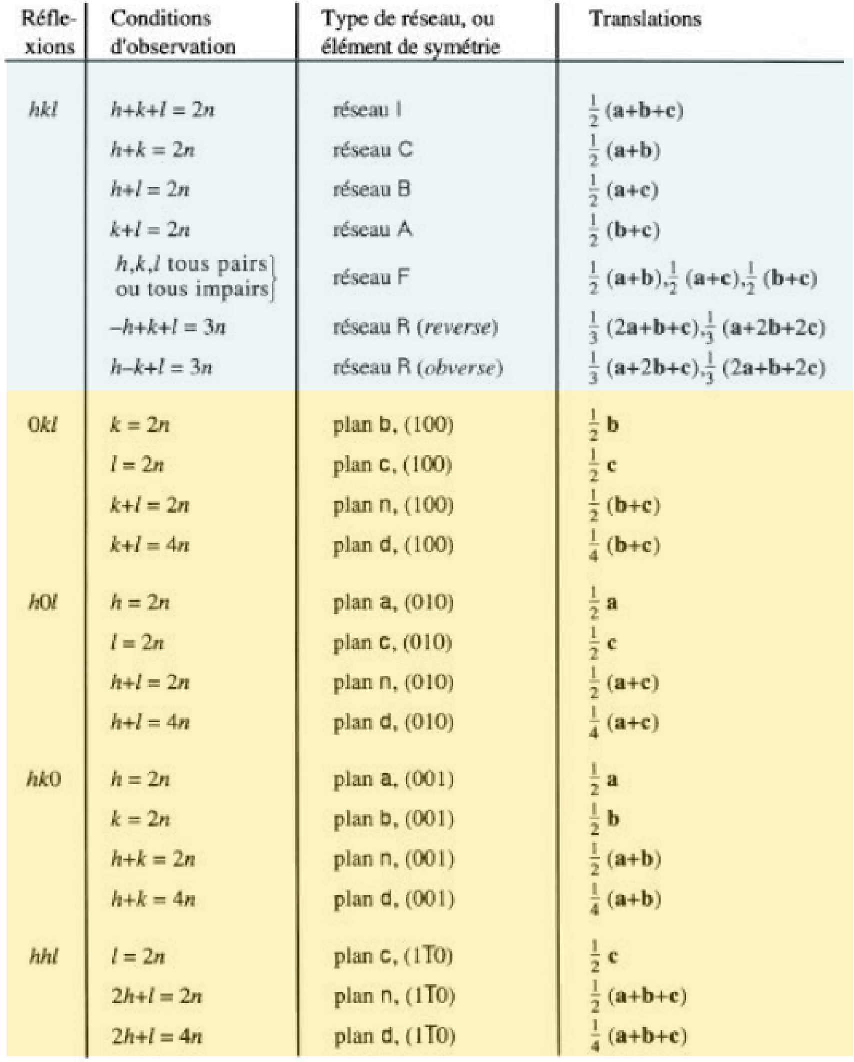
For every atom at (x_j, y_j, z_j) there an equivalent atom at $(x_j+1/2, y_j+1/2, z_j+1/2)$

$$F_{hkl} = \sum_{j \subset cell} f_j \exp(2i\pi(hx_j + ky_j + lz_j))$$

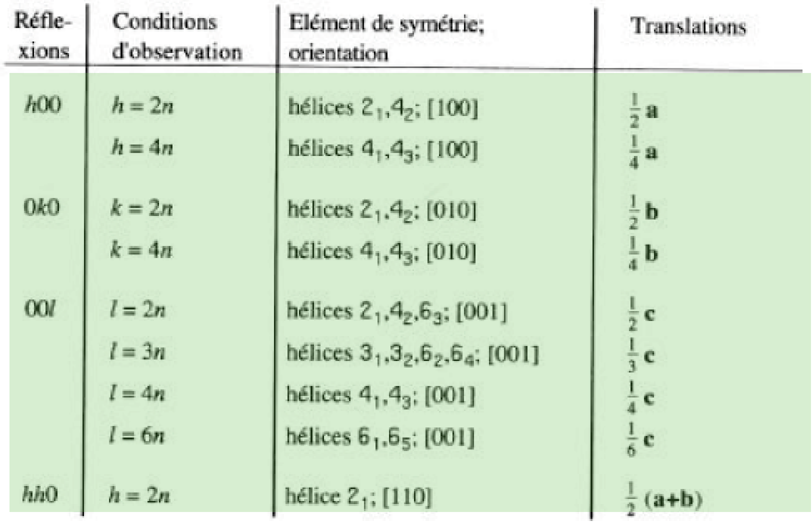
$$F_{hkl} = \sum_{j \subset 1/2 cell} f_j \exp(2i\pi(hx_j + ky_j + lz_j))\{1 + \exp(i\pi(h+k+l))\}$$

=> The lattice is I ⇔ $F_{hkl}=0$ *for every odd* $(h+k+l)$

This is used to detect symmetry-translation elements and restrict the space group choice



Réflexions	Conditions d'observation	Type de réseau, ou élément de symétrie	Translations
hkl	$h+k+l = 2n$	réseau I	$\frac{1}{2}(\mathbf{a}+\mathbf{b}+\mathbf{c})$
	$h+k = 2n$	réseau C	$\frac{1}{2}(\mathbf{a}+\mathbf{b})$
	$h+l = 2n$	réseau B	$\frac{1}{2}(\mathbf{a}+\mathbf{c})$
	$k+l = 2n$	réseau A	$\frac{1}{2}(\mathbf{b}+\mathbf{c})$
	h,k,l tous pairs ou tous impairs	réseau F	$\frac{1}{2}(\mathbf{a}+\mathbf{b}),\frac{1}{2}(\mathbf{a}+\mathbf{c}),\frac{1}{2}(\mathbf{b}+\mathbf{c})$
	$-h+k+l = 3n$	réseau R (*reverse*)	$\frac{1}{3}(2\mathbf{a}+\mathbf{b}+\mathbf{c}),\frac{1}{3}(\mathbf{a}+2\mathbf{b}+2\mathbf{c})$
	$h-k+l = 3n$	réseau R (*obverse*)	$\frac{1}{3}(\mathbf{a}+2\mathbf{b}+\mathbf{c}),\frac{1}{3}(2\mathbf{a}+\mathbf{b}+2\mathbf{c})$
$0kl$	$k = 2n$	plan b, (100)	$\frac{1}{2}\mathbf{b}$
	$l = 2n$	plan c, (100)	$\frac{1}{2}\mathbf{c}$
	$k+l = 2n$	plan n, (100)	$\frac{1}{2}(\mathbf{b}+\mathbf{c})$
	$k+l = 4n$	plan d, (100)	$\frac{1}{4}(\mathbf{b}+\mathbf{c})$
$h0l$	$h = 2n$	plan a, (010)	$\frac{1}{2}\mathbf{a}$
	$l = 2n$	plan c, (010)	$\frac{1}{2}\mathbf{c}$
	$h+l = 2n$	plan n, (010)	$\frac{1}{2}(\mathbf{a}+\mathbf{c})$
	$h+l = 4n$	plan d, (010)	$\frac{1}{4}(\mathbf{a}+\mathbf{c})$
$hk0$	$h = 2n$	plan a, (001)	$\frac{1}{2}\mathbf{a}$
	$k = 2n$	plan b, (001)	$\frac{1}{2}\mathbf{b}$
	$h+k = 2n$	plan n, (001)	$\frac{1}{2}(\mathbf{a}+\mathbf{b})$
	$h+k = 4n$	plan d, (001)	$\frac{1}{4}(\mathbf{a}+\mathbf{b})$
hhl	$l = 2n$	plan c, $(1\bar{1}0)$	$\frac{1}{2}\mathbf{c}$
	$2h+l = 2n$	plan n, $(1\bar{1}0)$	$\frac{1}{2}(\mathbf{a}+\mathbf{b}+\mathbf{c})$
	$2h+l = 4n$	plan d, $(1\bar{1}0)$	$\frac{1}{4}(\mathbf{a}+\mathbf{b}+\mathbf{c})$



Réflexions	Conditions d'observation	Elément de symétrie; orientation	Translations
$h00$	$h = 2n$	hélices $2_1,4_2$; [100]	$\frac{1}{2}\mathbf{a}$
	$h = 4n$	hélices $4_1,4_3$; [100]	$\frac{1}{4}\mathbf{a}$
$0k0$	$k = 2n$	hélices $2_1,4_2$; [010]	$\frac{1}{2}\mathbf{b}$
	$k = 4n$	hélices $4_1,4_3$; [010]	$\frac{1}{4}\mathbf{b}$
$00l$	$l = 2n$	hélices $2_1,4_2,6_3$; [001]	$\frac{1}{2}\mathbf{c}$
	$l = 3n$	hélices $3_1,3_2,6_2,6_4$; [001]	$\frac{1}{3}\mathbf{c}$
	$l = 4n$	hélices $4_1,4_3$; [001]	$\frac{1}{4}\mathbf{c}$
	$l = 6n$	hélices $6_1,6_5$; [001]	$\frac{1}{6}\mathbf{c}$
$hh0$	$h = 2n$	hélice 2_1; [110]	$\frac{1}{2}(\mathbf{a}+\mathbf{b})$

Integral Extinctions :
3 indices, due to lattice

Zonal Extinctions :
2 indices, due to glide mirrors

Serial Extinctions :
1 index, due to screw axes

This can be performed using ***CheckGroup*** within the **Fullprof Suite toolbar**

Diffracted Intensity

The diffracted intensity is the quantity accessible in a diffraction experiment
(proportional to the number of diffracted particles reaching the detector)

In the kinematic approximation (neglecting double diffraction), one has :

$$\boxed{I_{hkl} = S.C_{hkl}.\left|F_{hkl}\right|^2}$$

S : scale factor
C_{hkl} : experimental corrections
instrument *(Lorentz, polarization, diffraction geometry…)*
sample *(multiplicity, absorption, preferred orientation, extinction…)*

$$\boxed{F_{hkl} = \sum_{j \subset cell} f_j T_j \exp(2i\pi(hx_j + ky_j + lz_j))}$$

F_{hkl} : complex number => the **phase of F_{hkl} is not measured**. The information is incomplete

To solve the structure, one must retrieve the phases of F_{hkl} , one way or another…

Ab initio experimental détermination of crystal structure using powder diffration and the *Fullprof Suite*

… can be a difficult matter (even with FPS !)

One needs a **high quality sample** already well characterized (composition, density, dimension…)

Carry out one or more ***well adapted*** **diffraction experiments**
(x-ray and/or neutrons and/or electrons, choice of resolution, wavelength, etc…)

Find the unit cell and **index Bragg reflexions**
Using WinplotR + Dicvol04, Treor, Ito, etc…

Obtain the **intensities of Bragg reflexions** and **determine the space group**
Using Fullprof in LeBail mode + CheckGroup

Find an **approximate starting structural model of the atomic motif *ab initio***
Using Direct methods , simulated annealing (Fullprof, GloPSAnn), Charge flipping (superflip)

Refinement and Fourier recycling to obtain a complete and accurate structure
Rietveld Refinement using Fullprof, Fourier using GFour

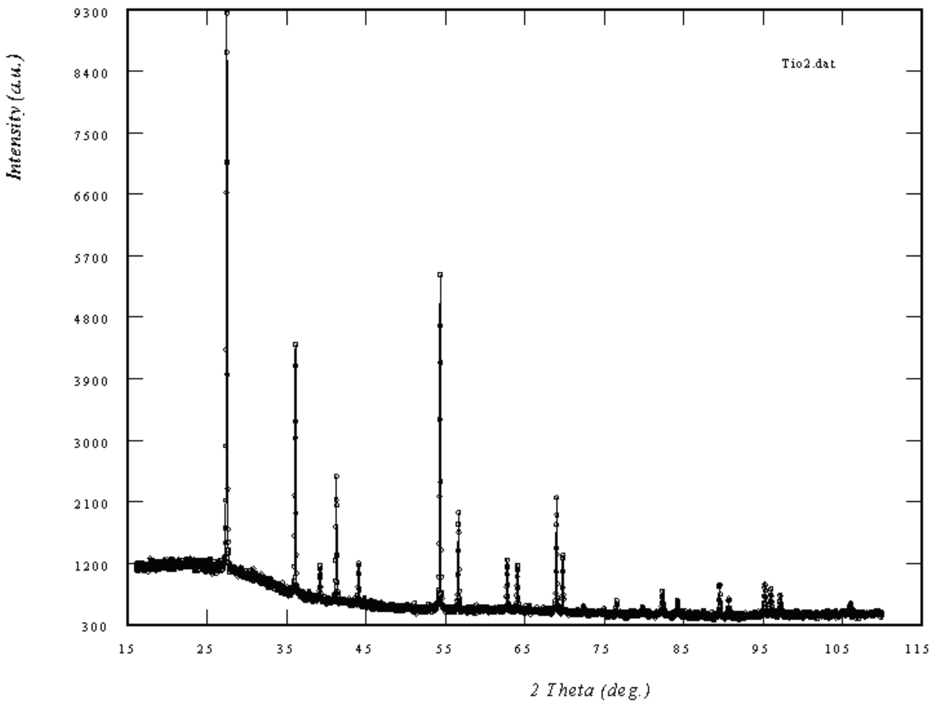
Determining the space group :

Example : TiO_2 rutile, x-ray powder diffraction, $\lambda=1.54Å$

TETRAGONAL SYSTEM

a= 4.59349, c= 2.95862

H	K	L	2TH.OBS	2TH.CAL	DIF
1	1	0	27.435	27.437	-.002
1	0	1	36.075	36.081	-.006
2	0	0	39.197	39.192	.005
1	1	1	41.241	41.241	.000
2	1	0	44.051	44.046	.005
2	1	1	54.320	54.323	-.003
2	2	0	56.631	56.629	.002
0	0	2	62.765	62.760	.005
3	1	0	64.051	64.051	.000
3	0	1	68.998	69.007	-.009
1	1	2	69.792	69.804	-.012
2	0	2	76.554	76.541	.013
3	2	1	82.335	82.341	-.006
4	0	0	84.250	84.254	-.004
4	1	1	95.260	95.261	-.001
3	1	2	96.013	96.011	.002
4	2	0	97.179	97.172	.007



Presence Conditions :

$0kl$, $k+l=2n$

$h00$, $h=2n$

$00l$, $l=2n$

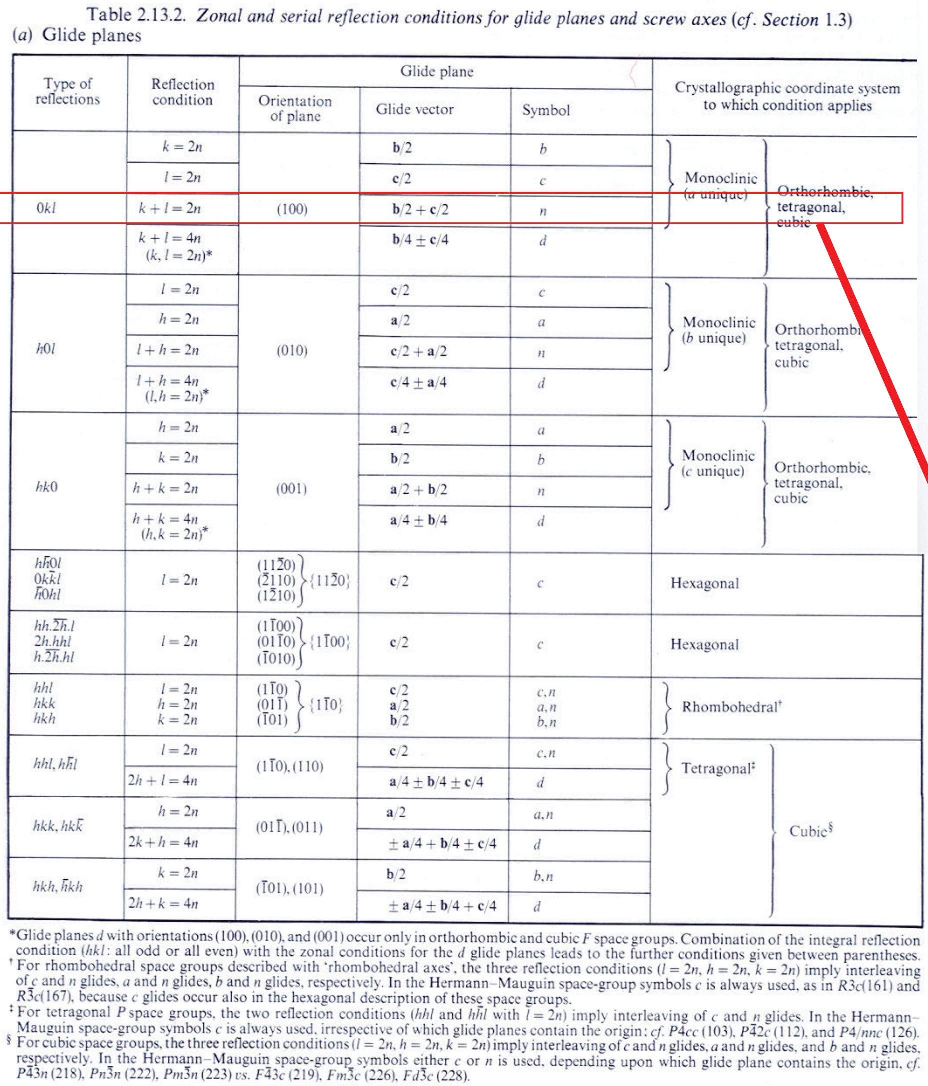


Table 2.13.2. *Zonal and serial reflection conditions for glide planes and screw axes* (*cf*. *Section* 1.3)

(*a*) Glide planes

Type of reflections	Reflection condition	Glide plane: Orientation of plane	Glide plane: Glide vector	Glide plane: Symbol	Crystallographic coordinate system to which condition applies
$0kl$	$k=2n$	(100)	$\mathbf{b}/2$	b	Monoclinic (*a* unique) Orthorhombic, tetragonal, cubic
	$l=2n$		$\mathbf{c}/2$	c	
	$k+l=2n$		$\mathbf{b}/2+\mathbf{c}/2$	n	
	$k+l=4n$ $(k,l=2n)$*		$\mathbf{b}/4\pm\mathbf{c}/4$	d	
$h0l$	$l=2n$	(010)	$\mathbf{c}/2$	c	Monoclinic (*b* unique) Orthorhombic, tetragonal, cubic
	$h=2n$		$\mathbf{a}/2$	a	
	$l+h=2n$		$\mathbf{c}/2+\mathbf{a}/2$	n	
	$l+h=4n$ $(l,h=2n)$*		$\mathbf{c}/4\pm\mathbf{a}/4$	d	
$hk0$	$h=2n$	(001)	$\mathbf{a}/2$	a	Monoclinic (*c* unique) Orthorhombic, tetragonal, cubic
	$k=2n$		$\mathbf{b}/2$	b	
	$h+k=2n$		$\mathbf{a}/2+\mathbf{b}/2$	n	
	$h+k=4n$ $(h,k=2n)$*		$\mathbf{a}/4\pm\mathbf{b}/4$	d	
$h\bar{h}0l$ $0k\bar{k}l$ $\bar{h}0hl$	$l=2n$	$(11\bar{2}0)$ $(\bar{2}110)$ $(1\bar{2}10)$ $\{11\bar{2}0\}$	$\mathbf{c}/2$	c	Hexagonal
$hh.\overline{2h}.l$ $2h.hhl$ $h.\overline{2h}.hl$	$l=2n$	$(1\bar{1}00)$ $(01\bar{1}0)$ $(\bar{1}010)$ $\{1\bar{1}00\}$	$\mathbf{c}/2$	c	Hexagonal
hhl hkk hkh	$l=2n$ $h=2n$ $k=2n$	$(1\bar{1}0)$ $(01\bar{1})$ $(\bar{1}01)$ $\{1\bar{1}0\}$	$\mathbf{c}/2$ $\mathbf{a}/2$ $\mathbf{b}/2$	c,n a,n b,n	Rhombohedral†
$hhl,\ h\bar{h}l$	$l=2n$	$(1\bar{1}0),(110)$	$\mathbf{c}/2$	c,n	Tetragonal‡ Cubic§
	$2h+l=4n$		$\mathbf{a}/4\pm\mathbf{b}/4\pm\mathbf{c}/4$	d	
$hkk,\ hk\bar{k}$	$h=2n$	$(01\bar{1}),(011)$	$\mathbf{a}/2$	a,n	
	$2k+h=4n$		$\pm\mathbf{a}/4+\mathbf{b}/4\pm\mathbf{c}/4$	d	
$hkh,\ \bar{h}kh$	$k=2n$	$(\bar{1}01),(101)$	$\mathbf{b}/2$	b,n	
	$2h+k=4n$		$\pm\mathbf{a}/4\pm\mathbf{b}/4+\mathbf{c}/4$	d	

*Glide planes *d* with orientations (100), (010), and (001) occur only in orthorhombic and cubic *F* space groups. Combination of the integral reflection condition (*hkl*: all odd or all even) with the zonal conditions for the *d* glide planes leads to the further conditions given between parentheses.

† For rhombohedral space groups described with 'rhombohedral axes', the three reflection conditions ($l=2n$, $h=2n$, $k=2n$) imply interleaving of *c* and *n* glides, *a* and *n* glides, *b* and *n* glides, respectively. In the Hermann–Mauguin space-group symbols *c* is always used, as in $R3c$(161) and $R\bar{3}c$(167), because *c* glides occur also in the hexagonal description of these space groups.

‡ For tetragonal *P* space groups, the two reflection conditions (hhl and $h\bar{h}l$ with $l=2n$) imply interleaving of *c* and *n* glides. In the Hermann–Mauguin space-group symbols *c* is always used, irrespective of which glide planes contain the origin: *cf*. $P4cc$ (103), $P\bar{4}2c$ (112), and $P4/nnc$ (126).

§ For cubic space groups, the three reflection conditions ($l=2n$, $h=2n$, $k=2n$) imply interleaving of *c* and *n* glides, *a* and *n* glides, and *b* and *n* glides, respectively. In the Hermann–Mauguin space-group symbols either *c* or *n* is used, depending upon which glide plane contains the origin, *cf*. $P\bar{4}3n$ (218), $Pn\bar{3}n$ (222), $Pm\bar{3}n$ (223) *vs*. $F\bar{4}3c$ (219), $Fm\bar{3}c$ (226), $Fd\bar{3}c$ (228).

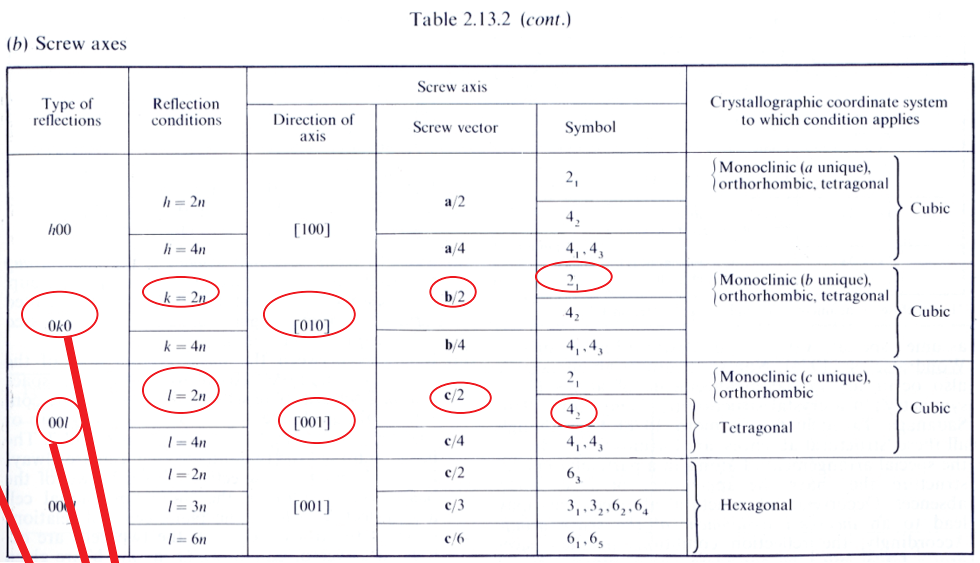


Table 2.13.2 (*cont*.)

(*b*) Screw axes

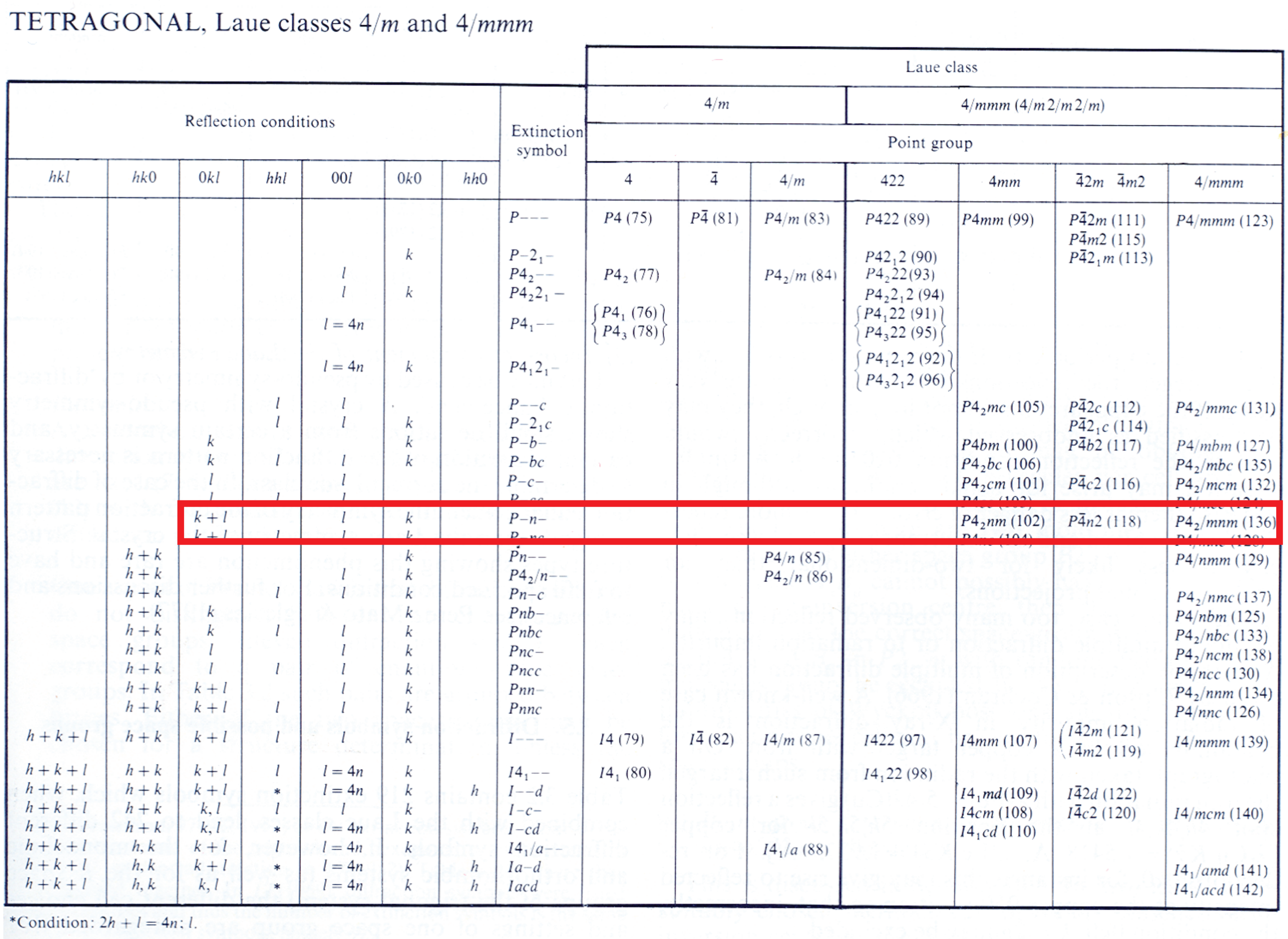
Type of reflections	Reflection conditions	Screw axis: Direction of axis	Screw axis: Screw vector	Screw axis: Symbol	Crystallographic coordinate system to which condition applies
$h00$	$h=2n$	[100]	$\mathbf{a}/2$	2_1	Monoclinic (*a* unique), orthorhombic, tetragonal Cubic
				4_2	
	$h=4n$		$\mathbf{a}/4$	$4_1, 4_3$	
$0k0$	$k=2n$	[010]	$\mathbf{b}/2$	2_1	Monoclinic (*b* unique), orthorhombic, tetragonal Cubic
				4_2	
	$k=4n$		$\mathbf{b}/4$	$4_1, 4_3$	
$00l$	$l=2n$	[001]	$\mathbf{c}/2$	2_1	Monoclinic (*c* unique), orthorhombic Cubic
				4_2	Tetragonal
	$l=4n$		$\mathbf{c}/4$	$4_1, 4_3$	
$000l$	$l=2n$	[001]	$\mathbf{c}/2$	6_3	Hexagonal
	$l=3n$		$\mathbf{c}/3$	$3_1, 3_2, 6_2, 6_4$	
	$l=6n$		$\mathbf{c}/6$	$6_1, 6_5$	

Axis 4_2 parallel to c *(consequence)*

Axis 2_1 parallel to b (resp. a) *(consequence)*

Mirror n perp. to a (resp. b)

=> Extinction symbol = P . n .



TETRAGONAL, Laue classes $4/m$ and $4/mmm$

Reflection conditions							Extinction symbol	Laue class						
								$4/m$			$4/mmm$ $(4/m\,2/m\,2/m)$			
								Point group						
hkl	$hk0$	$0kl$	hhl	$00l$	$0k0$	$hh0$		4	$\bar{4}$	$4/m$	422	$4mm$	$\bar{4}2m$ $\bar{4}m2$	$4/mmm$
							$P---$	$P4$ (75)	$P\bar{4}$ (81)	$P4/m$ (83)	$P422$ (89)	$P4mm$ (99)	$P\bar{4}2m$ (111) $P\bar{4}m2$ (115)	$P4/mmm$ (123)
					k		$P-2_1-$				$P42_12$ (90)		$P\bar{4}2_1m$ (113)	
				l			$P4_2--$	$P4_2$ (77)		$P4_2/m$ (84)	$P4_222$ (93)			
				l	k		$P4_22_1-$				$P4_22_12$ (94)			
				$l=4n$			$P4_1--$	$P4_1$ (76) $P4_3$ (78)			$P4_122$ (91) $P4_322$ (95)			
				$l=4n$	k		$P4_12_1-$				$P4_12_12$ (92) $P4_32_12$ (96)			
			l	l			$P--c$					$P4_2mc$ (105)	$P\bar{4}2c$ (112)	$P4_2/mmc$ (131)
			l	l	k		$P-2_1c$						$P\bar{4}2_1c$ (114)	
		k			k		$P-b-$					$P4bm$ (100)	$P\bar{4}b2$ (117)	$P4/mbm$ (127)
		k	l	l	k		$P-bc$					$P4_2bc$ (106)		$P4_2/mbc$ (135)
		l		l			$P-c-$					$P4_2cm$ (101)	$P\bar{4}c2$ (116)	$P4_2/mcm$ (132)
		l	l	l			$P-cc$					$P4cc$ (103)		$P4/mcc$ (124)
		$k+l$		l	k		$P-n-$					$P4_2nm$ (102)	$P\bar{4}n2$ (118)	$P4_2/mnm$ (136)
		$k+l$	l	l	k		$P-nc$					$P4nc$ (104)		$P4/mnc$ (128)
	$h+k$				k		$Pn--$			$P4/n$ (85)				$P4/nmm$ (129)
	$h+k$			l	k		$P4_2/n--$			$P4_2/n$ (86)				
	$h+k$		l	l	k		$Pn-c$							$P4_2/nmc$ (137)
	$h+k$	k			k		$Pnb-$							$P4/nbm$ (125)
	$h+k$	k	l	l	k		$Pnbc$							$P4_2/nbc$ (133)
	$h+k$	l		l	k		$Pnc-$							$P4_2/ncm$ (138)
	$h+k$	l	l	l	k		$Pncc$							$P4/ncc$ (130)
	$h+k$	$k+l$		l	k		$Pnn-$							$P4_2/nnm$ (134)
	$h+k$	$k+l$	l	l	k		$Pnnc$							$P4/nnc$ (126)
$h+k+l$	$h+k$	$k+l$	l	l	k		$I---$	$I4$ (79)	$I\bar{4}$ (82)	$I4/m$ (87)	$I422$ (97)	$I4mm$ (107)	$I\bar{4}2m$ (121) $I\bar{4}m2$ (119)	$I4/mmm$ (139)
$h+k+l$	$h+k$	$k+l$	l	$l=4n$	k		$I4_1--$	$I4_1$ (80)			$I4_122$ (98)			
$h+k+l$	$h+k$	$k+l$	*	$l=4n$	k	h	$I--d$					$I4_1md$ (109)	$I\bar{4}2d$ (122)	
$h+k+l$	$h+k$	k, l	l	l	k		$I-c-$					$I4cm$ (108)	$I\bar{4}c2$ (120)	$I4/mcm$ (140)
$h+k+l$	$h+k$	k, l	*	$l=4n$	k	h	$I-cd$					$I4_1cd$ (110)		
$h+k+l$	h, k	$k+l$	l	$l=4n$	k		$I4_1/a--$			$I4_1/a$ (88)				
$h+k+l$	h, k	$k+l$	*	$l=4n$	k	h	$Ia-d$							$I4_1/amd$ (141)
$h+k+l$	h, k	k, l	*	$l=4n$	k	h	$Iacd$							$I4_1/acd$ (142)

*Condition: $2h+l=4n$; l.

3 choices of possible space groups ! ***$P4_2nm$, P-$4n2$, $P4_2/mnm$***

Or use CheckGroup to select the most probable Space Groups

- Use DicVol/Treor… to find the unit cell and create a starting .pcr file
- Make a LeBail type refinement to generate a .hkl file

```
Pattern#  1 Phase No:   1  phase 1: Myphase
1366        0  293.00    <-- The number of effective reflections may be lower
   2   0   0    4        18.884         0.801       5.1224       0.0138
   1   1   2    8        27.160         0.473       5.4115       0.0138
   2   0   1    8       403.671         1.470       5.5030       0.0138
   2   1   0    8         4.917         0.551       5.7275       0.0139
  . . . . . . . . . . . . . .
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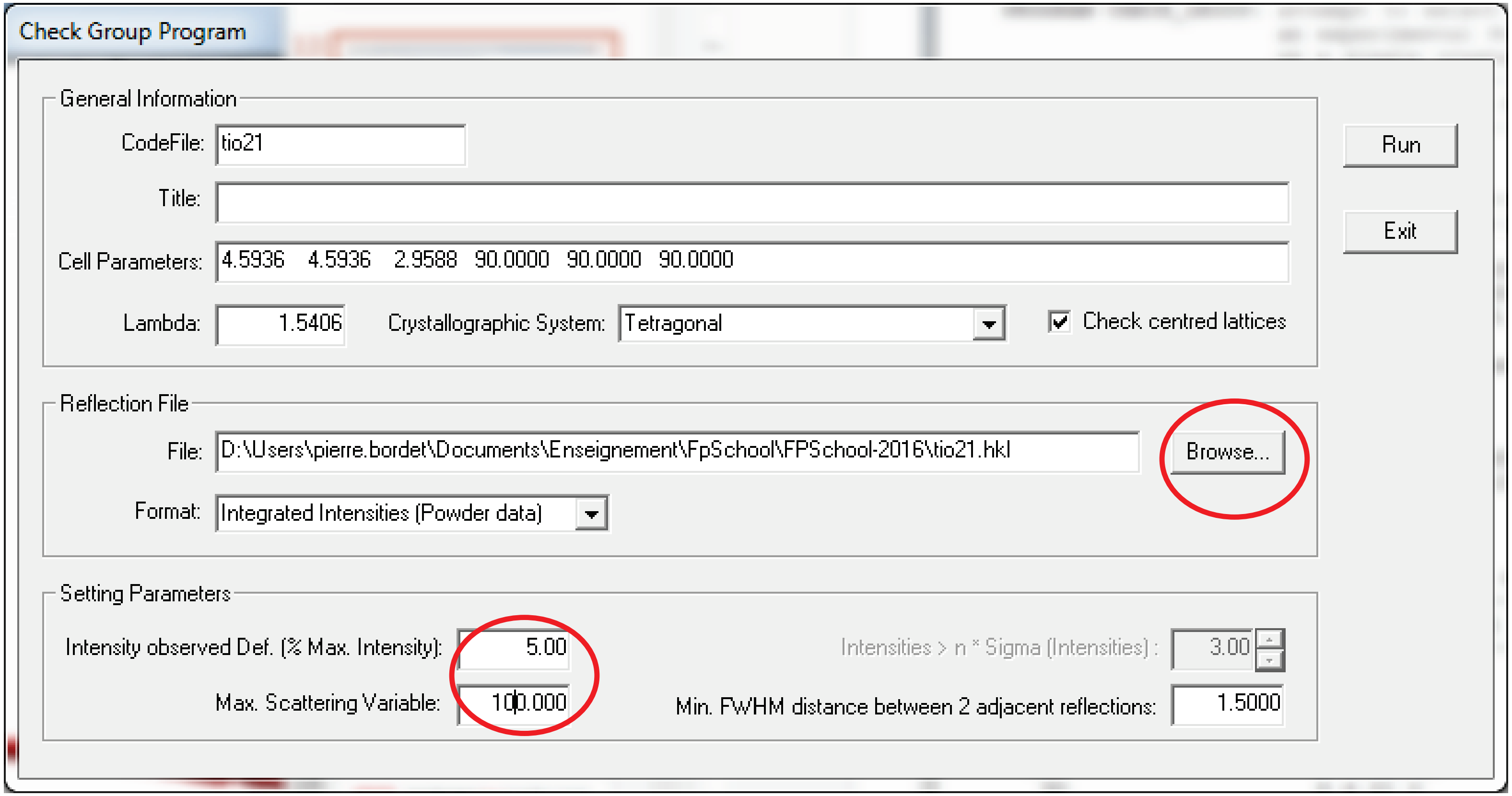
- Use CheckGroup from the FPSuite toolbar



Check Group Program

General Information

CodeFile: tio21

Title:

Cell Parameters: 4.5936 4.5936 2.9588 90.0000 90.0000 90.0000

Lambda: 1.5406

Crystallographic System: Tetragonal

☑ Check centred lattices

Reflection File

File: D:\Users\pierre.bordet\Documents\Enseignement\FpSchool\FPSchool-2016\tio21.hkl

Format: Integrated Intensities (Powder data)

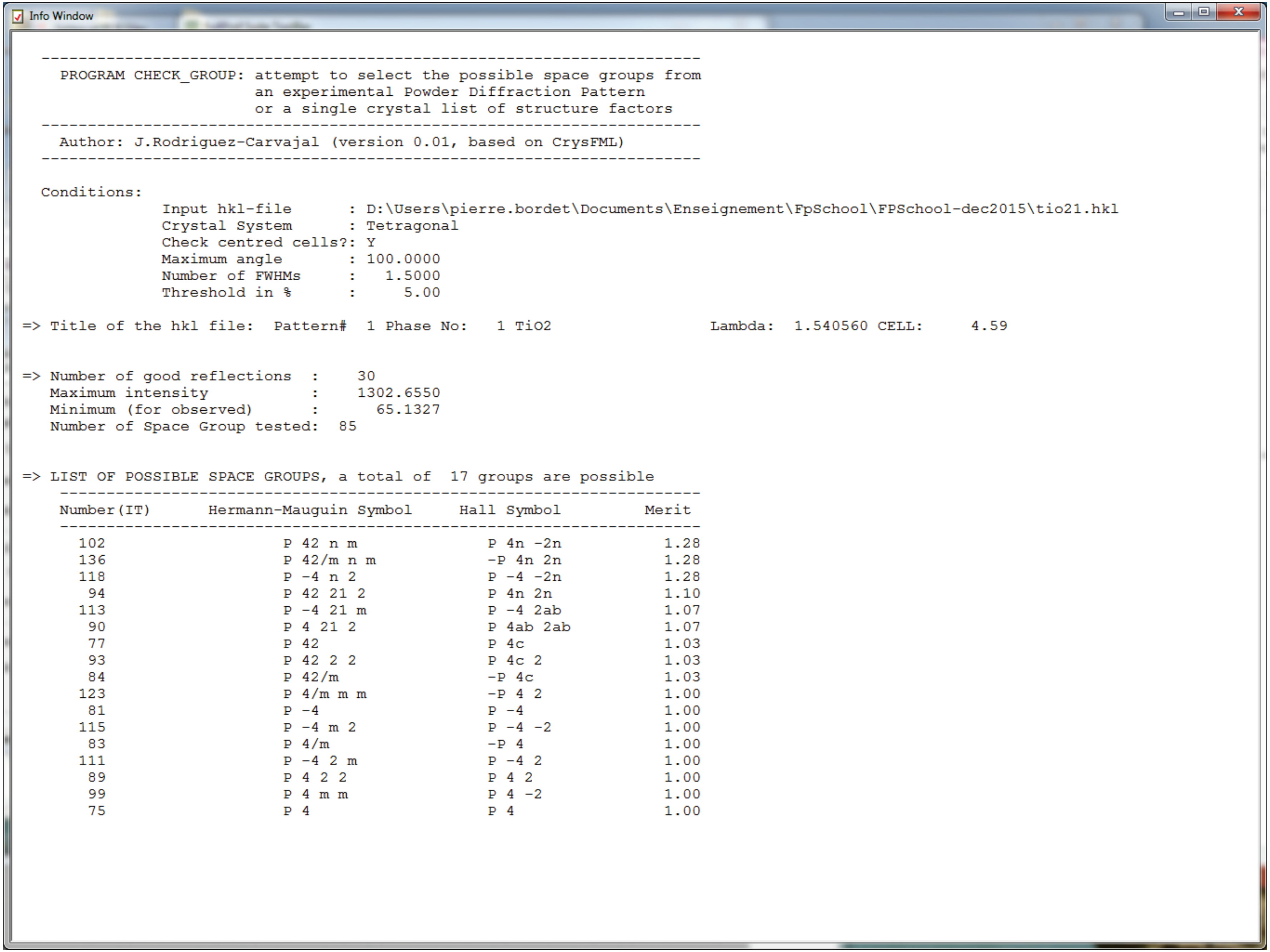
Setting Parameters

Intensity observed Def. (% Max. Intensity): 5.00

Max. Scattering Variable: 100.000

Intensities > n * Sigma (Intensities) : 3.00

Min. FWHM distance between 2 adjacent reflections: 1.5000



```
  ----------------------------------------------------------------------
    PROGRAM CHECK_GROUP: attempt to select the possible space groups from
                         an experimental Powder Diffraction Pattern
                         or a single crystal list of structure factors
  ----------------------------------------------------------------------
    Author: J.Rodriguez-Carvajal (version 0.01, based on CrysFML)
  ----------------------------------------------------------------------

  Conditions:
               Input hkl-file      : D:\Users\pierre.bordet\Documents\Enseignement\FpSchool\FPSchool-dec2015\tio21.hkl
               Crystal System      : Tetragonal
               Check centred cells?: Y
               Maximum angle       : 100.0000
               Number of FWHMs     :   1.5000
               Threshold in %      :     5.00

=> Title of the hkl file:  Pattern#  1 Phase No:   1 TiO2                Lambda:  1.540560 CELL:     4.59


=> Number of good reflections  :    30
   Maximum intensity           :    1302.6550
   Minimum (for observed)      :      65.1327
   Number of Space Group tested:  85


=> LIST OF POSSIBLE SPACE GROUPS, a total of  17 groups are possible
    ---------------------------------------------------------------------
    Number(IT)      Hermann-Mauguin Symbol     Hall Symbol          Merit
    ---------------------------------------------------------------------
      102                   P 42 n m             P 4n -2n             1.28
      136                   P 42/m n m           -P 4n 2n             1.28
      118                   P -4 n 2             P -4 -2n             1.28
       94                   P 42 21 2            P 4n 2n              1.10
      113                   P -4 21 m            P -4 2ab             1.07
       90                   P 4 21 2             P 4ab 2ab            1.07
       77                   P 42                 P 4c                 1.03
       93                   P 42 2 2             P 4c 2               1.03
       84                   P 42/m               -P 4c                1.03
      123                   P 4/m m m            -P 4 2               1.00
       81                   P -4                 P -4                 1.00
      115                   P -4 m 2             P -4 -2              1.00
       83                   P 4/m                -P 4                 1.00
      111                   P -4 2 m             P -4 2               1.00
       89                   P 4 2 2              P 4 2                1.00
       99                   P 4 m m              P 4 -2               1.00
       75                   P 4                  P 4                  1.00
```

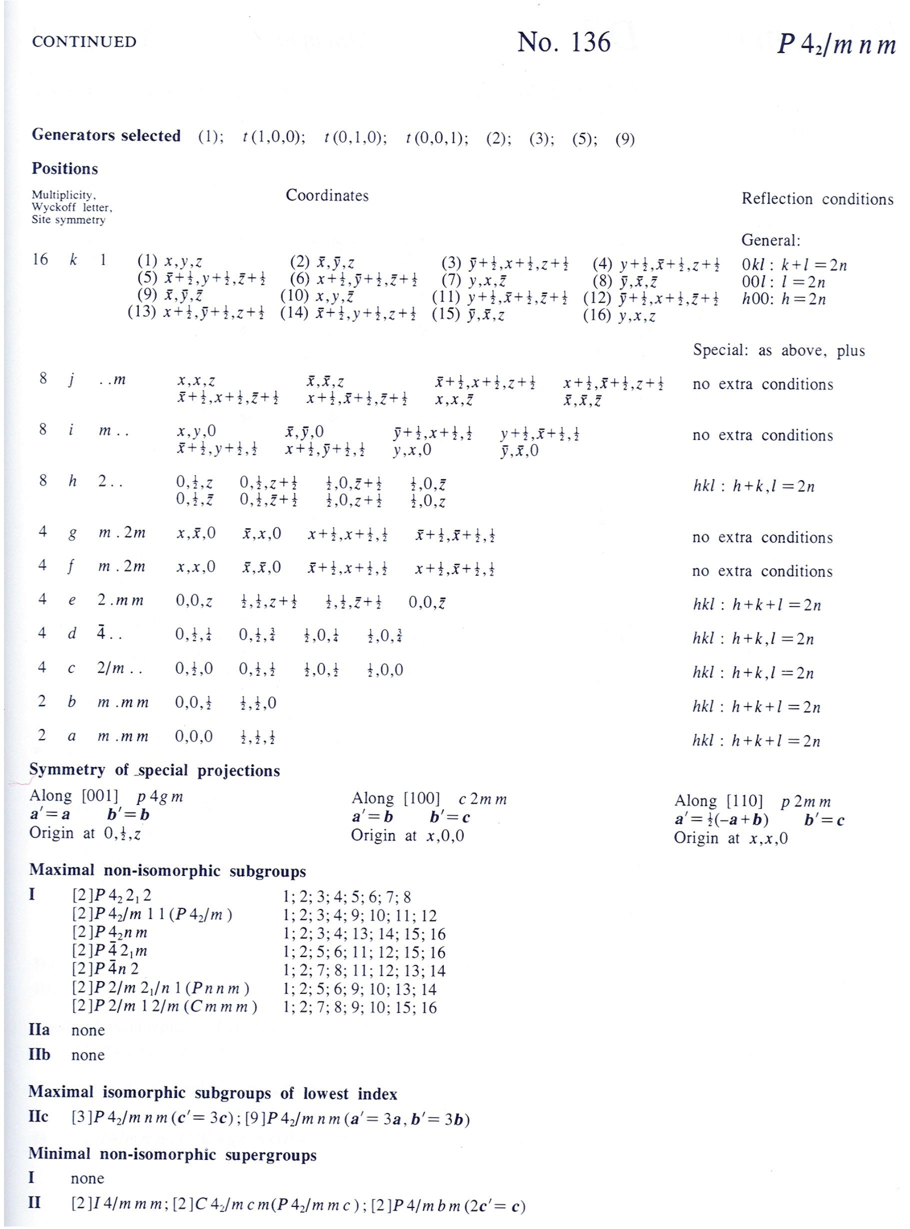
Mesure of density TiO_2 :

⇒Z=2

⇒2 Ti and 4 O per cell

⇒One can almost solve the structure
Just by knowing the cell and space group

…and a bit of crystal-chemistry…



CONTINUED No. 136 $P\,4_2/m\,n\,m$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5); (9)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates	Reflection conditions
				General:
16	k	1	(1) x,y,z (2) $\bar{x},\bar{y},z$ (3) $\bar{y}+\tfrac12,x+\tfrac12,z+\tfrac12$ (4) $y+\tfrac12,\bar{x}+\tfrac12,z+\tfrac12$ (5) $\bar{x}+\tfrac12,y+\tfrac12,\bar{z}+\tfrac12$ (6) $x+\tfrac12,\bar{y}+\tfrac12,\bar{z}+\tfrac12$ (7) $y,x,\bar{z}$ (8) $\bar{y},\bar{x},\bar{z}$ (9) $\bar{x},\bar{y},\bar{z}$ (10) $x,y,\bar{z}$ (11) $y+\tfrac12,\bar{x}+\tfrac12,\bar{z}+\tfrac12$ (12) $\bar{y}+\tfrac12,x+\tfrac12,\bar{z}+\tfrac12$ (13) $x+\tfrac12,\bar{y}+\tfrac12,z+\tfrac12$ (14) $\bar{x}+\tfrac12,y+\tfrac12,z+\tfrac12$ (15) $\bar{y},\bar{x},z$ (16) y,x,z	$0kl$: $k+l=2n$ $00l$: $l=2n$ $h00$: $h=2n$
				Special: as above, plus
8	j	$..m$	x,x,z $\bar{x},\bar{x},z$ $\bar{x}+\tfrac12,x+\tfrac12,z+\tfrac12$ $x+\tfrac12,\bar{x}+\tfrac12,z+\tfrac12$ $\bar{x}+\tfrac12,x+\tfrac12,\bar{z}+\tfrac12$ $x+\tfrac12,\bar{x}+\tfrac12,\bar{z}+\tfrac12$ $x,x,\bar{z}$ $\bar{x},\bar{x},\bar{z}$	no extra conditions
8	i	$m..$	$x,y,0$ $\bar{x},\bar{y},0$ $\bar{y}+\tfrac12,x+\tfrac12,\tfrac12$ $y+\tfrac12,\bar{x}+\tfrac12,\tfrac12$ $\bar{x}+\tfrac12,y+\tfrac12,\tfrac12$ $x+\tfrac12,\bar{y}+\tfrac12,\tfrac12$ $y,x,0$ $\bar{y},\bar{x},0$	no extra conditions
8	h	$2..$	$0,\tfrac12,z$ $0,\tfrac12,z+\tfrac12$ $\tfrac12,0,\bar{z}+\tfrac12$ $\tfrac12,0,\bar{z}$ $0,\tfrac12,\bar{z}$ $0,\tfrac12,\bar{z}+\tfrac12$ $\tfrac12,0,z+\tfrac12$ $\tfrac12,0,z$	hkl : $h+k,l=2n$
4	g	$m.2m$	$x,\bar{x},0$ $\bar{x},x,0$ $x+\tfrac12,x+\tfrac12,\tfrac12$ $\bar{x}+\tfrac12,\bar{x}+\tfrac12,\tfrac12$	no extra conditions
4	f	$m.2m$	$x,x,0$ $\bar{x},\bar{x},0$ $\bar{x}+\tfrac12,x+\tfrac12,\tfrac12$ $x+\tfrac12,\bar{x}+\tfrac12,\tfrac12$	no extra conditions
4	e	$2.mm$	$0,0,z$ $\tfrac12,\tfrac12,z+\tfrac12$ $\tfrac12,\tfrac12,\bar{z}+\tfrac12$ $0,0,\bar{z}$	hkl : $h+k+l=2n$
4	d	$\bar{4}..$	$0,\tfrac12,\tfrac14$ $0,\tfrac12,\tfrac34$ $\tfrac12,0,\tfrac14$ $\tfrac12,0,\tfrac34$	hkl : $h+k,l=2n$
4	c	$2/m..$	$0,\tfrac12,0$ $0,\tfrac12,\tfrac12$ $\tfrac12,0,\tfrac12$ $\tfrac12,0,0$	hkl : $h+k,l=2n$
2	b	$m.mm$	$0,0,\tfrac12$ $\tfrac12,\tfrac12,0$	hkl : $h+k+l=2n$
2	a	$m.mm$	$0,0,0$ $\tfrac12,\tfrac12,\tfrac12$	hkl : $h+k+l=2n$

Symmetry of special projections

Along [001] $p\,4g\,m$	Along [100] $c\,2m\,m$	Along [110] $p\,2m\,m$
$\mathbf{a}'=\mathbf{a}$ $\mathbf{b}'=\mathbf{b}$	$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}$	$\mathbf{a}'=\tfrac12(-\mathbf{a}+\mathbf{b})$ $\mathbf{b}'=\mathbf{c}$
Origin at $0,\tfrac12,z$	Origin at $x,0,0$	Origin at $x,x,0$

Maximal non-isomorphic subgroups

I	[2] $P\,4_2 2_1 2$	1; 2; 3; 4; 5; 6; 7; 8
	[2] $P\,4_2/m\,1\,1$ ($P\,4_2/m$)	1; 2; 3; 4; 9; 10; 11; 12
	[2] $P\,4_2 n\,m$	1; 2; 3; 4; 13; 14; 15; 16
	[2] $P\,\bar{4}\,2_1 m$	1; 2; 5; 6; 11; 12; 15; 16
	[2] $P\,\bar{4}n\,2$	1; 2; 7; 8; 11; 12; 13; 14
	[2] $P\,2/m\,2_1/n\,1$ ($P\,n\,n\,m$)	1; 2; 5; 6; 9; 10; 13; 14
	[2] $P\,2/m\,1\,2/m$ ($C\,m\,m\,m$)	1; 2; 7; 8; 9; 10; 15; 16
IIa	none	
IIb	none	

Maximal isomorphic subgroups of lowest index

IIc [3] $P\,4_2/m\,n\,m$ ($\mathbf{c}'=3\mathbf{c}$); [9] $P\,4_2/m\,n\,m$ ($\mathbf{a}'=3\mathbf{a}$, $\mathbf{b}'=3\mathbf{b}$)

Minimal non-isomorphic supergroups

I none

II [2] $I\,4/m\,m\,m$; [2] $C\,4_2/m\,c\,m$ ($P\,4_2/m\,m\,c$); [2] $P\,4/m\,b\,m$ ($2\mathbf{c}'=\mathbf{c}$)

Solving crystal structures by direct methods

Phases of strong reflections are obtained *directly* from the structure factor moduli

Based on few simple properties of scattering density functions :

- **scattering density is always positive** (not always true for neutrons)
- scattering density is **a strongly peaked function at atomic positions**

Sophisticated mathematical developments based on simple concepts.

Requires the **space group symmetry** and a **somewhat relaxed knowledge of the cell content**

For powder data, the indexed peak intensity list must be obtained using LeBail fitting.
Overlapping reflections must be taken care of.

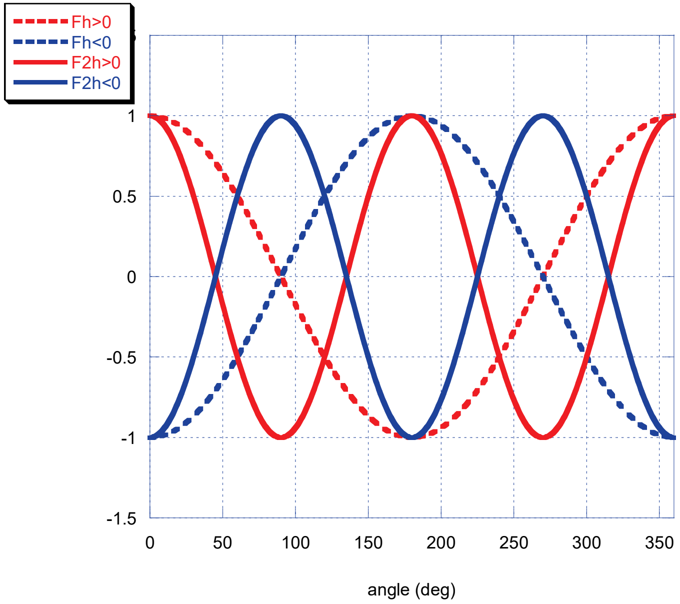
Example at 1D

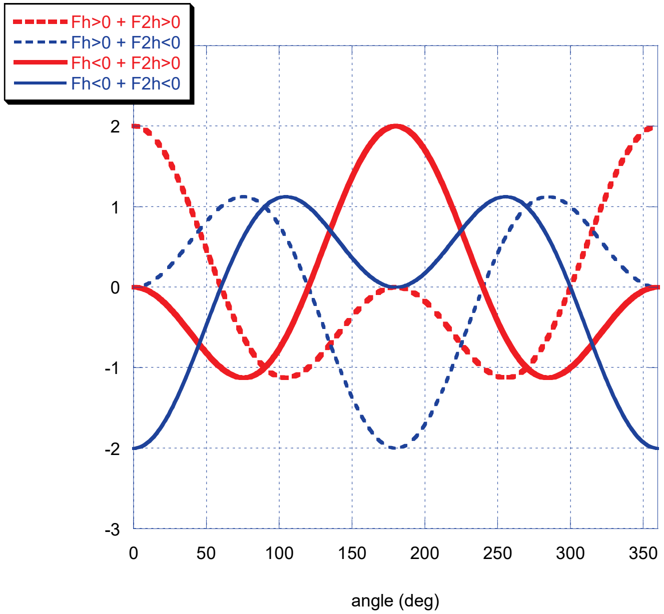
Structure 1D centrosymmetric. *Suppose* |Fh| and |F2h| are strong enough so that they dominate the calculation of the scattering density :

$$\boxed{\rho(x) = \frac{1}{a}\sum_h F_h \cos 2\pi .h.x \approx F_h \cos 2\pi .h.x + F_{2h} \cos 2\pi .2h.x}$$

=> 4 possibilities according to the signs of F_h ad F_{2h}

We look for a function with localized (positive) peaks !!

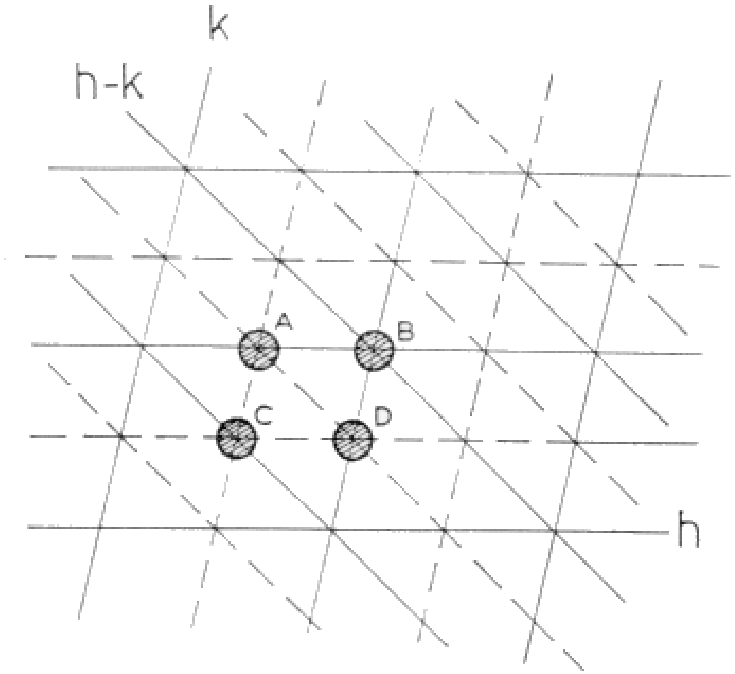




Since ρ(x) > 0, if |Fh| and |F2h| are strong,
|F2h| is *probably* positive, whatever the sign of |Fh|.

Example at 3D

Structure 3D centrosymmetric, $|F_h|$, $|F_k|$ and $|F_{h-k}|$ (called structure invariant triplet)are strong : they have a dominant contribution to the overall scattering density



$$\rho(r) = \frac{1}{V}\sum_h F_h \cos 2\pi h.r$$

Full lines : maxima of

$|F_h| \cos 2\pi h.r$

$|F_k| \cos 2\pi k.r$

$|F_{h-k}| \cos 2\pi (h-k).r$

Broken lines : minima .

A, B, C, D : regions of probably strong scattering density

If $|Fh|$, $|Fk|$ and $|Fh\text{-}k|$ are strong, the Fourier terms must add to yield a positive, peaked scattering density

=> $\cos 2\pi h.r = +1$ *if $Fh>0$*, $\cos 2\pi h.r = -1$ *if $Fh<0$*.

These conditions are satisfied at A, B, C, D only if :

Region	**S(h)**	**S(k)**	**S(h-k)**
A	+	-	-
B	+	+	+
C	-	-	+
D	-	+	-

=> **le product *S(h).S(k).S(h-k)* is always positive**

=> if $|F_h|$, $|F_k|$ and $|F_{h-k}|$ are large enough and if 2 signs are known, the 3rd can be determined with a good (and calculable) probability.

Structure invariants

The amplitudes of the structure factors do not depend on the celle origin, but their phases do. So from the amplitudes, one can only obtain information about linear combinations of phases hich do not depend on the choice of the origin: the strucure invariants. The most general s.i. is :

$$F_{h1}.F_{h2}\ldots F_{hn} = \left|F_{h1}.F_{h2}\ldots F_{hn}\right| \exp(i(\varphi_1 + \varphi_2 + \ldots + \varphi_n))$$

with $\boldsymbol{h1} + \boldsymbol{h2} + \ldots + \boldsymbol{hn} = 0$

The multiplet of reciprocal space vectors make a close loop.

The most currently used s.i. are invariant triplets of Miller indices:

h1,***h2***,***h3*** (***h1*** : (h1,k1,l1), ***h2*** : (h2,k2,l2), ***h3*** : (h3,k3,l3))
With ***h1***+***h2***+***h3***=0

They are said to obey a ***Σ2 relation.***

Sayre's Equation :

By applying the convolution theorem to ρ^2.

$$E_h = T\sum_k E_k E_{h-k}$$

E_{hkl} is the normalized structure factor defined as:

$$E_h^2 \approx \frac{|F_h|^2}{\sum_{cell} f_j^2}$$

To calculate the normalized structure factor, one must know the chemical content of the cell

By multi plying Sayre's equation on both sides by $\boldsymbol{E_{-h}}$, one gets:

$$|E_h|^2 = T\sum_k E_{-h} E_k E_{h-k} \qquad |E_h|^2 = T\sum_k |E_h.E_k.E_{h-k}| \exp(i(\varphi_{-h} + \varphi_k + \varphi_{h-k}))$$

The left side is a positive real number. If it is large, the terms of the sum on the right must also be positive real numbers.

So, if $|E_k|$ and $|E_{h-k}|$ are large too, one gets :

$$\varphi_{-h} + \varphi_k + \varphi_{h-k} \approx 0$$

where ≈ means « probably equal"

In the centrosymmetric case, the structure factors are real, the phase problem is just a sign problem

The equation becomes: $\boldsymbol{S(-h).S(k).S(h-k)} \approx +$

The ***probability*** for this equation to hold can be calculated using the tangent formula:

centro
$$p = 1/2 + (1/2)\tanh\left[\frac{1}{\sqrt{N}}\left|E(-h)E(k)E(h-k)\right|\right]$$

Non centro
$$\tan\varphi(h3) = \frac{\sum_{h1}\left|E(h1)E(h2)\right|\sin\left[\varphi(h1)+\varphi(h2)\right]}{\sum_{h1}\left|E(h1)E(h2)\right|\cos\left[\varphi(h1)+\varphi(h2)\right]}$$

with $h1+h2+h3=0$

N is the number of atoms in the cell.
The probability increases wit the reflexion intensities.

Knowing the phase (sign) of 2 reflexions, the phase (sign) of the 3rd one in a invariant triplet can be obtained with a known probability

The phases of a set of starting strong reflexions (<=2) must be chosen to fix the origin.
***This can be done using the space group symmetry*.**

Additional phases (signs) in selected s.i. are obtained with a known probability using the tangent formula.

A FT is calculated using the phases and moduli (*E*) of the reflexions for the most probable set (*E-MAP*)

Practical Use

Expo .exp file : unit cell, space group, cell content

Expo does :

- **pattern decomposition to generate .*hkl* file if required (or use LeBail fit in Fullprof)**
- **structure factor normalization**
- **Wilson plot to get scale factor and B$_{\text{overall}}$**

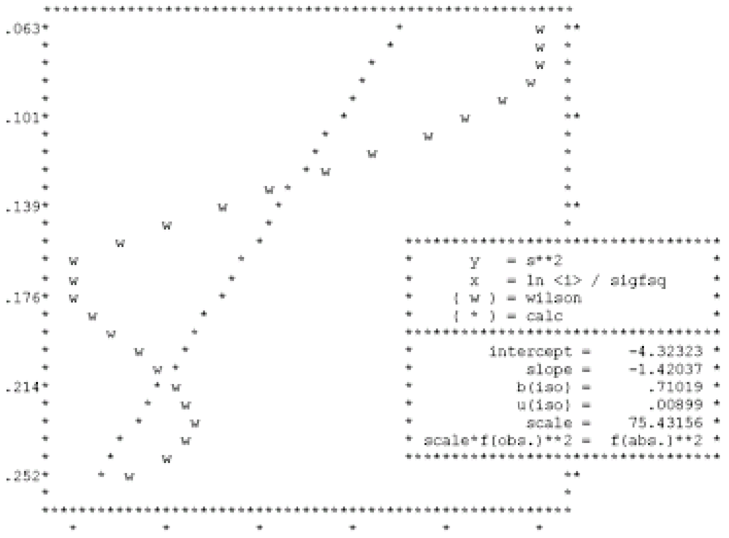
$$I_{hkl} = E.\left|F_{hkl}\right|^2.\exp(-(2B\sin^2\theta)/\lambda^2) \quad \text{with } s=\sin\theta/\lambda,$$

In a small s interval, one gets :

$$E.\exp(-2Bs^2) = \frac{\langle I_{hkl}\rangle}{\langle\left|F_{hkl}\right|^2\rangle} = K(s) \quad \text{and} \quad \langle\left|F_{hkl}\right|^2\rangle = \sum_{maille} f_j^2$$

$$\ln E - 2Bs^2 = \ln K(s)$$

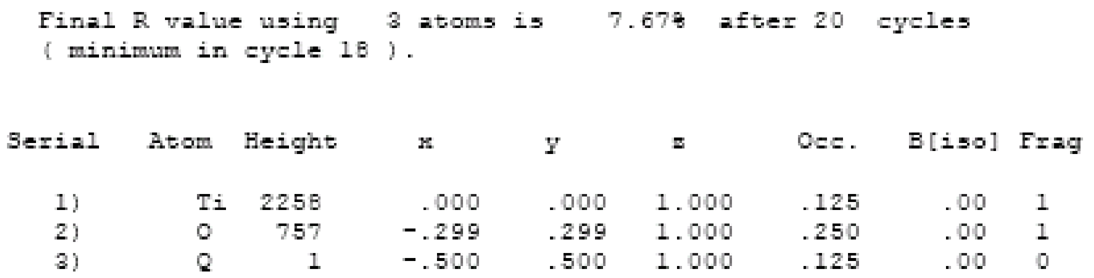
E and B are obtained from a linear fit of *K(s)* vs s^2.



```
   y   = s**2
   x   = ln <i> / sigfsq
 ( w ) = wilson
 ( * ) = calc

        intercept =    -4.32323
            slope =    -1.42037
           b(iso) =      .71019
           u(iso) =      .00899
            scale =    75.43156
 scale*f(obs.)**2 =  f(abs.)**2
```

- **determination of origin fixing reflexions**
- **search of usable s.i. (strongest reflexions)**
- **phase expansion**
- **Fourier (E-map) yields the structural model (atom positions)**



```
   Final R value using   3 atoms is    7.67%  after 20  cycles
   ( minimum in cycle 18 ).


 Serial    Atom  Height      x         y         z        Occ.    B[iso] Frag

    1)       Ti   2258      .000      .000     1.000      .125      .00    1
    2)       O     757     -.299      .299     1.000      .250      .00    1
    3)       Q       1     -.500      .500     1.000      .125      .00    0
```

Practical Use:

For powder diffraction, a list of (hkl I sigma) must be provided to an external direct methods program (e.g. ***Expo***, *Bari team)*. ***Expo*** can also perform the LeBail fit, for a single phase only.

⇒ In case of single phase, use Expo for LeBail intensity extraction and direct method solution
⇒ In case of multi-phase, use FP for LeBail fit of phase of interest (others=Rietveld), create input data files in a suitable format for Expo *(hkl=2).* Run Expo for direct method structure solution using the created *.hkl* file (*CodFil.hkl*) and prepare an *.exp* expo file.
⇒ Run Expo. Transfer the result to FullProf (use *.ins* file)
⇒ Then, Rietveld refinement/Fourier recycling with Fullprof/GFourier

.exp file with extraction in Expo

```
%window
%struct TiO2
%job TiO2
%init
%data
pattern TiO2.pow
range  20.000 109.98 0.03
format (15x,f12.0)
record 1
wave 1.540598
space P 42/M N M
cell      4.5937  4.5937  2.9589  90.0    90.0   90.0
cont Ti 2 O 4
%extract
%continue
```

.exp file with extraction in Fullprof

```
%window
%struct TiO2
%job TiO2
%init
%data
ref2 TiO2.hkl
wave 1.540598
space P 42/M N M
cell      4.5937  4.5937  2.9589  90.0    90.0   90.0
cont Ti 2 O 4
%continue
```

Methods for ab initio structure solution in direct space

Principle :

Plausible structure model are randomly generated by moving atoms or groups of atoms. The calculated diagram is compared to the observed one

Difficulties :

avoid a priori impossible configurations (too small distances, etc.) not always necessary/useful
avoid to get blocked in a local minimum
sensitivity to the algorithm parameters.

Example : **simulated annealing**

Originally, a method to *predict* structures ab initio (without experimental data).
For each configuration, one calculates a ***cost function***, based on a pseudo-potential energy to minimize, and on the agreement between experiment and model :

$$C=\alpha Epot+(1-\alpha)R$$

Epot may depend on the bond type (ionic, covalent, intermetallic…), Lennard-Jones, coulomb, …

$$R = 100\sum_{2\theta}\left|I_{\exp}(2\theta) - I_{calc}(2\theta)\right| / \sum_{2\theta} I_{\exp}(2\theta)$$

One goes from config. Ci to Ci+1 following a **Monte-Carlo** type algorithm,
If Ci+1 < Ci, move accepted
If Ci+1 > Ci, move accepted with probability : ***exp[-(Ci+1-Ci)/K]***

K≈ temperature, decreases slowly during search following a predefined “temperature program”.

Interests of simulated annealing

May not be necessary to know the space group (may work in P1, but it is still better to know it)
May not be necessary to know the composition (atoms may move on top of each other and merge, but no new atom can be created, so it is still better to know it)
Flexibility to define the parameters in the minimization process (not necessarily atomic positions)

- structural rigid groups (tetrahedra, octahedra…)
- rigid molecular groups, in cartesian, spherical, Z-matrix coordinates
- unknown structure fragments, beside already known ones
- magnetic moments orientations and moduli (solving magnetic structures)
- amplimodes, starting from a (hypothetical) higher symmetry structure

⇒Reduction of the number of parameters
⇒More stable minimization procedure
⇒Adapted to the geometrical/crystallo-chemical specificities of a given problem

Preparing your data file in FullProf:

Do a LeBail fit with More=1, Jvi=11. Produces the *_ctrl.int* file containing single crystal-like intensities
If Ipr=-1 (line 2) a pseudo-profile data file *.spr* is produced for using pseudo-profiles in the SAN search.

Then use these data for the SAN search with a single crystal structure description in the .pcr file.
Cry=3, Nre=number of variables, Ipr=-1 if you want to use profile data, 0 if not, Irf=4

Simulated annealing can be used directly in Fullprof

*for solving crystal and magnetic structures
*on integrated intensities or profile data

```
COMM Ab initio structure solution of PbSO4 (Simulated Annealing, data D1A-ILL)
! Files => DAT-file: pb_san,  PCR-file: pb_san
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
  1   0   1   0   0   0   0   0   0   0   0   0   0  12   3   0   0   0   1
!
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
  0   0   1   0   1   0   5   0   0   1   0   0   0   0   0   0   0
!
!NCY  Eps  R_at  R_an  R_pr  R_gl     Thmin       Step       Thmax    PSD    Sent0
  1  0.10  1.00  1.00  1.00  1.00     15.0000   0.020000  120.0400   0.000   0.000
!
!
      12    !Number of refined parameters
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:    36.73
!-------------------------------------------------------------------------------
 PbSO4
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
  5   0   0  0.0 0.0 1.0  0   4   0   0    0        2426.060  0   7   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind   RMua    RMub    RMuc   Jtyp  Nsp_Ref Ph_Shift
  3   0   0   0   0   0  1.0000  1.0000  0.0000  0.0000    1    0    0      0
!
P n m a                  <--Space group symbol
!Atom Typ       X        Y        Z      Biso       Occ     In Fin N_t Spc /Codes
Pb    PB      0.31294  0.25806  0.82424  1.42124   0.50000   0   0   0    0
                11.00    21.00    31.00     0.00      0.00
S     S       0.28429  0.25806  0.89134  0.41603   0.50000   0   0   0    0
                41.00    21.00    51.00     0.00      0.00
O1    O       0.59101  0.25806  0.40489  1.99182   0.50000   0   0   0    0
                61.00    21.00    71.00     0.00      0.00
O2    O       0.81205  0.25806  0.03500  1.47906   0.50000   0   0   0    0
                81.00    21.00    91.00     0.00      0.00
O3    O       0.58159  0.95861  0.77608  1.33000   1.00000   0   0   0    0
               101.00   111.00   121.00     0.00      0.00
```

…

Nre=nb of parameters

Cry=3: single crystal data

Ipr=0 : no profile (spr) used

Ipr=-1 : profile (spr) used, generated with previous LeBail with Ipr=-1 and Cry=0

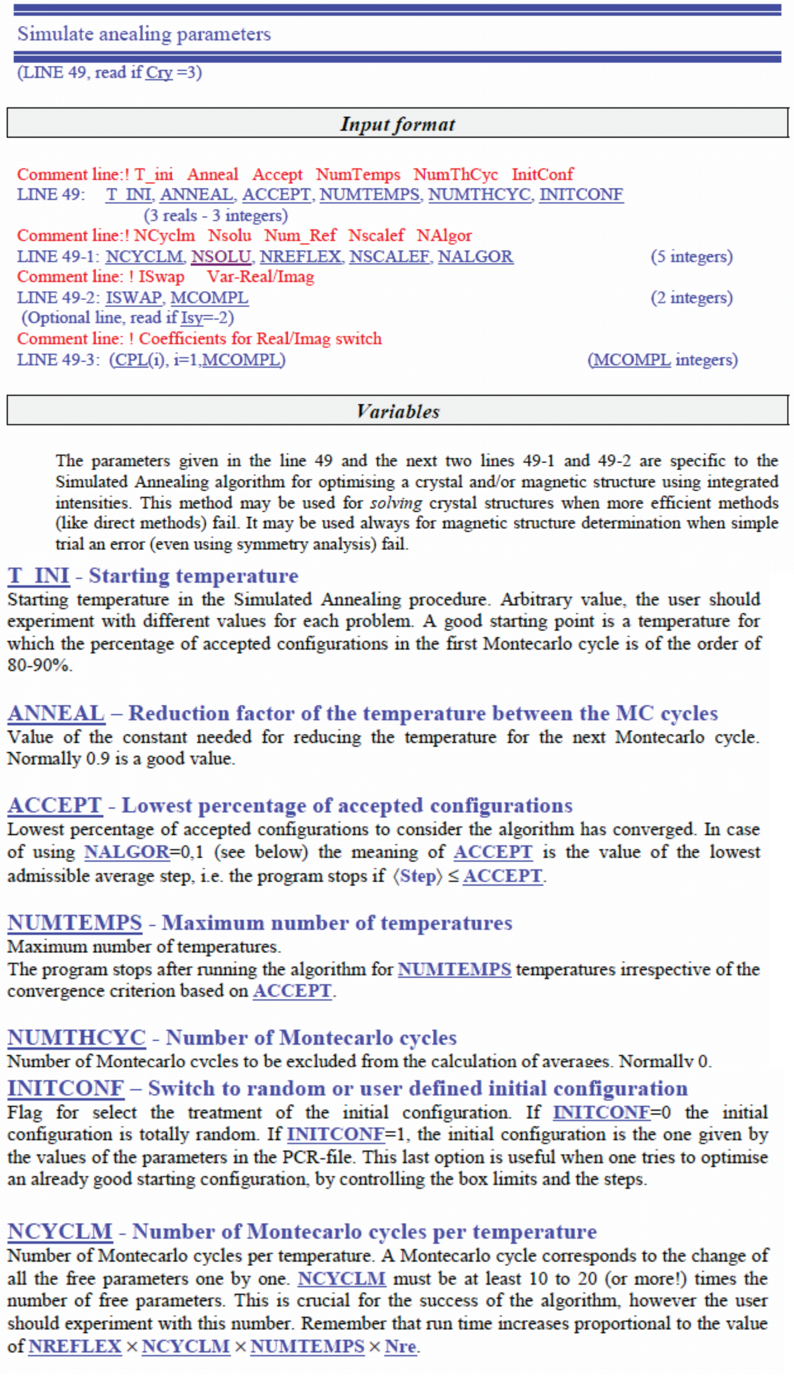
Irf=4 powder treated as single crystal

Ls2=5 & Jvi=3 : real time view of structure in fp-studio

Simulated annealing can be used directly in Fullprof

*for solving crystal and magnetic structures
*on integrated intensities or profile data

```
!  Scale Factors
!   Sc1        Sc2         Sc3         Sc4         Sc5         Sc6
   1.354      .0000       .0000       .0000       .0000       .0000
    0.00       0.00        0.00        0.00        0.00        0.00
!  Extinction Parameters
! Ext1       Ext2       Ext3       Ext4       Ext5       Ext6       Ext7   Ext-Model
 .0000      .0000      .0000      .0000      .0000      .0000      .0000       0
  0.00       0.00       0.00       0.00       0.00       0.00       0.00
!     a          b         c        alpha      beta       gamma      #Cell Info
   8.485130   5.402066   6.964059  90.000000  90.000000  90.000000
    0.00000    0.00000    0.00000    0.00000    0.00000    0.00000
! x-Lambda/2  +          Not yet used parameters
    0.00000     0.00000     0.00000     0.00000     0.00000
       0.00        0.00        0.00        0.00        0.00
! Limits for selected parameters (+ steps & BoundCond for SA):
   1       0.0000      1.0000      0.0033    1      X_Pb
   2       0.0000      1.0000      0.0064    1      Y_Pb
   3       0.0000      1.0000      0.0092    1      Z_Pb
   4       0.0000      1.0000      0.0084    1       X_S
   5       0.0000      1.0000      0.0140    1       Z_S
   6       0.0000      1.0000      0.0051    1      X_O1
   7       0.0000      1.0000      0.0131    1      Z_O1
   8       0.0000      1.0000      0.0090    1      X_O2
   9       0.0000      1.0000      0.0075    1      Z_O2
  10       0.0000      1.0000      0.0029    1      X_O3
  11       0.0000      1.0000      0.0084    1      Y_O3
  12       0.0000      1.0000      0.0042    1      Z_O3
! T_ini   Anneal  Accept NumTemps NumThCyc InitConf
   6.000   0.950   0.003       80        0        0
! NCyclM   Nsolu Num_Ref Nscalef  NAlgor
     240         1      71        1       0
! ISwap     Var-Real/Imag
       0       0
```



Simulate anealing parameters

(LINE 49, read if Cry =3)

Input format

Comment line:! T_ini Anneal Accept NumTemps NumThCyc InitConf
LINE 49: T_INI, ANNEAL, ACCEPT, NUMTEMPS, NUMTHCYC, INITCONF
(3 reals - 3 integers)
Comment line:! NCyclm Nsolu Num_Ref Nscalef NAlgor
LINE 49-1: NCYCLM, NSOLU, NREFLEX, NSCALEF, NALGOR (5 integers)
Comment line: ! ISwap Var-Real/Imag
LINE 49-2: ISWAP, MCOMPL (2 integers)
(Optional line, read if Isy=-2)
Comment line: ! Coefficients for Real/Imag switch
LINE 49-3: (CPL(i), i=1,MCOMPL) (MCOMPL integers)

Variables

The parameters given in the line 49 and the next two lines 49-1 and 49-2 are specific to the Simulated Annealing algorithm for optimising a crystal and/or magnetic structure using integrated intensities. This method may be used for *solving* crystal structures when more efficient methods (like direct methods) fail. It may be used always for magnetic structure determination when simple trial an error (even using symmetry analysis) fail.

T_INI - Starting temperature

Starting temperature in the Simulated Annealing procedure. Arbitrary value, the user should experiment with different values for each problem. A good starting point is a temperature for which the percentage of accepted configurations in the first Montecarlo cycle is of the order of 80-90%.

ANNEAL – Reduction factor of the temperature between the MC cycles

Value of the constant needed for reducing the temperature for the next Montecarlo cycle. Normally 0.9 is a good value.

ACCEPT - Lowest percentage of accepted configurations

Lowest percentage of accepted configurations to consider the algorithm has converged. In case of using NALGOR=0,1 (see below) the meaning of ACCEPT is the value of the lowest admissible average step, i.e. the program stops if $\langle \text{Step} \rangle \leq$ ACCEPT.

NUMTEMPS - Maximum number of temperatures

Maximum number of temperatures.
The program stops after running the algorithm for NUMTEMPS temperatures irrespective of the convergence criterion based on ACCEPT.

NUMTHCYC - Number of Montecarlo cycles

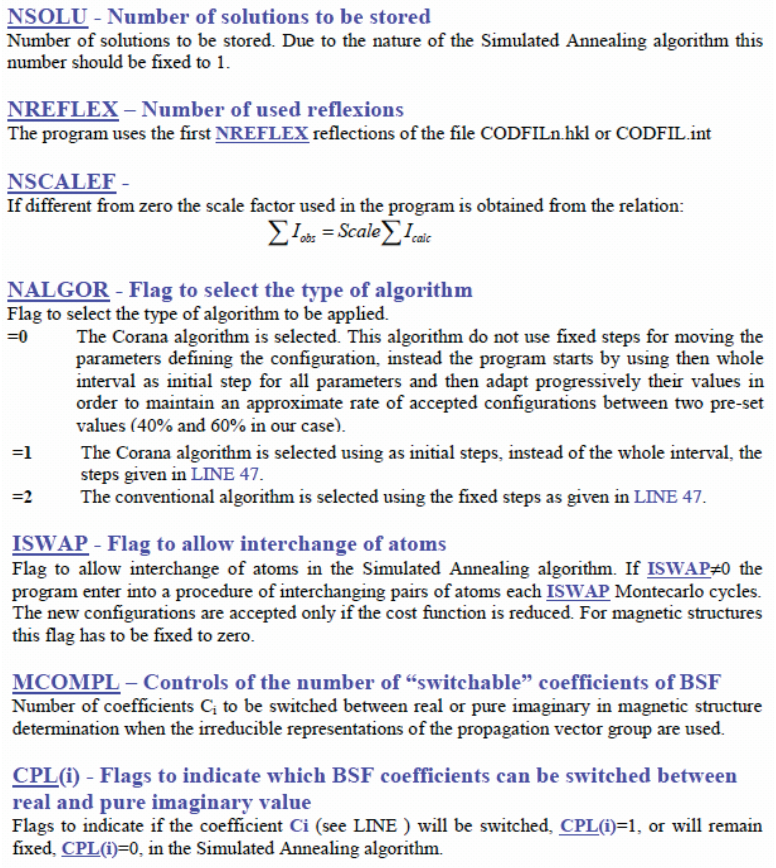
Number of Montecarlo cycles to be excluded from the calculation of averages. Normally 0.

INITCONF – Switch to random or user defined initial configuration

Flag for select the treatment of the initial configuration. If INITCONF=0 the initial configuration is totally random. If INITCONF=1, the initial configuration is the one given by the values of the parameters in the PCR-file. This last option is useful when one tries to optimise an already good starting configuration, by controlling the box limits and the steps.

NCYCLM - Number of Montecarlo cycles per temperature

Number of Montecarlo cycles per temperature. A Montecarlo cycle corresponds to the change of all the free parameters one by one. NCYCLM must be at least 10 to 20 (or more!) times the number of free parameters. This is crucial for the success of the algorithm, however the user should experiment with this number. Remember that run time increases proportional to the value of NREFLEX × NCYCLM × NUMTEMPS × Nre.



NSOLU - Number of solutions to be stored

Number of solutions to be stored. Due to the nature of the Simulated Annealing algorithm this number should be fixed to 1.

NREFLEX – Number of used reflexions

The program uses the first NREFLEX reflections of the file CODFILn.hkl or CODFIL.int

NSCALEF -

If different from zero the scale factor used in the program is obtained from the relation:

$$\sum I_{obs} = Scale \sum I_{calc}$$

NALGOR - Flag to select the type of algorithm

Flag to select the type of algorithm to be applied.

=0 The Corana algorithm is selected. This algorithm do not use fixed steps for moving the parameters defining the configuration, instead the program starts by using then whole interval as initial step for all parameters and then adapt progressively their values in order to maintain an approximate rate of accepted configurations between two pre-set values (40% and 60% in our case).

=1 The Corana algorithm is selected using as initial steps, instead of the whole interval, the steps given in LINE 47.

=2 The conventional algorithm is selected using the fixed steps as given in LINE 47.

ISWAP - Flag to allow interchange of atoms

Flag to allow interchange of atoms in the Simulated Annealing algorithm. If ISWAP≠0 the program enter into a procedure of interchanging pairs of atoms each ISWAP Montecarlo cycles. The new configurations are accepted only if the cost function is reduced. For magnetic structures this flag has to be fixed to zero.

MCOMPL – Controls of the number of "switchable" coefficients of BSF

Number of coefficients C_i to be switched between real or pure imaginary in magnetic structure determination when the irreducible representations of the propagation vector group are used.

CPL(i) - Flags to indicate which BSF coefficients can be switched between real and pure imaginary value

Flags to indicate if the coefficient Ci (see LINE) will be switched, CPL(i)=1, or will remain fixed, CPL(i)=0, in the Simulated Annealing algorithm.

CRY=3, Nre = nb of relations

```
Monte Carlo Parameters
! T_ini   Anneal  Accept NumTemps NumThCyc InitConf
   6.000    0.950    0.003        80            0              0
! NCyclM   Nsolu   Num_Ref   Nscalef    NAlgor
    240          1           71            1           0
! ISwap     Var-Real/Imag
     0            0
```

To display live structure : Jvi=3, Ls2=5 creates simann.fst.
Run FP, (Ls2=>4) creates simann.fst.
Start FPStudio with simann.fst, select read continuous, start FP.

GLOpSAnn Simulated Annealing to solve crystal structures with CrysFML

Similar to SAN in Fullprof + large choice of cost functions and combinations of them.
Magnetic structure and rigid groups are not available (but can use dist+angle restraints).

```
"F2obs-F2cal"       Cost(F2obs-F2cal)       : Optimization of C0 =Sum|F2obs-F2cal|/Sum|F2obs|
"Fobs-Fcal"         Cost(Fobs-Fcal)         : Optimization of C1 =Sum|Fobs-Fcal|/Sum|Fobs|
"dis-restr"         Cost(dis-restr)         : Optimization of C2 =Sum{w(dobs-dcal)^2}, w=1/var(d)
"Ang-restr"         Cost(Ang-restr)         : Optimization of C3 =Sum{w(Ang_obs-Ang_cal)^2}, w=1/var(Ang)
"Tor-restr"         Cost(Tor-restr)         : Optimization of C4 =Sum{w(Tor_obs-Tor_cal)^2}, w=1/var(Tor)
"bond-valence"      Cost(bond-valence)      : Optimization of C5 =Sum{|q-BVS|/tot_Atoms}
"bvs_coulomb"       C5 + Cost(Coulomb)      : Optimization of C6 =Sum{qi qj/dij}
"FoFc-Powder"       Cost(FoFc-Powder)       : Optimization of C7 =Sum|Gobs-Sum(Fcal)|/Sum|Gobs|
"Coordination"      Cost(Coordination)      : Optimization of C8 =Sum|Coord-Efcn|/Sum|Coord|
"Anti_Bump"         Cost(Anti_Bump)         : Optimization of C9 =Sum{(dmin/d)**power}
"Powder_Profile"    Cost(Powder_Profile)    : Optimization of C10=Sum{|yiobs-yicalc|/|yiobs|}
"Powder_WProfile"   Cost(Powder_WProfile)   : Optimization of C11=Sum{w{yiobs-yicalc}^2/(N-P)} Equivalent to Chi2
```

Works with LeBail extracted single crystal-like data (*.int*) or pseudo-profile data (*.spr*),
as for simulated annealing in fullProf.

Need to create a *.cfl* control file with starting structure and minimization commands

Input .cfl file for GLOpSAnn

```
Title  PbSO4 (experimental Jvi=-11 |F|) Neutrons
!        a            b          c      alpha    beta   gamma
Cell   8.485454   5.402319   6.964360  90.000  90.000  90.000
!     Space Group
Spgr  P n m a
!                  x        y        z        B        occ    Spin Charge
Atom  Pb   PB   0.18797  0.25000  0.16754  1.35290   0.50000   0.0   2.0      #color 0 0 1 1
Atom  S    S    0.06467  0.25000  0.68300  0.89361   0.50000   0.0   6.0      #color 1 1 0 1
Atom  O1   O    0.90712  0.25000  0.59675  0.57221   0.50000   0.0  -2.0      #color 0 1 1 1
Atom  O2   O    0.18635  0.25000  0.54278  0.99996   0.50000   0.0  -2.0      #color 1 0 1 1
Atom  O3   O    0.08021  0.02965  0.81211  1.07399   1.00000   0.0  -2.0      #color 1 0 0 1

! Codes for refinement
Vary xyz 0  1  0  1
!
HKL-OBS  pb_neu.int
MIN-DSPACING   1.5
WAVE  1.912
RADIATION NEUTRONS
FST_CMD  conn S O 0.0 1.8

OPTIMIZE    bond-valence 0.15  FoFc-Powder 0.85
LOCAL_OPTIMIZATION

SIM_ANN! Simulated Annealing conditions


!       Name of the cost function
CostNam  FoFc_Pow+BVS

!         T_ini     anneal     num_temps
TemParM     3.0       0.95       80

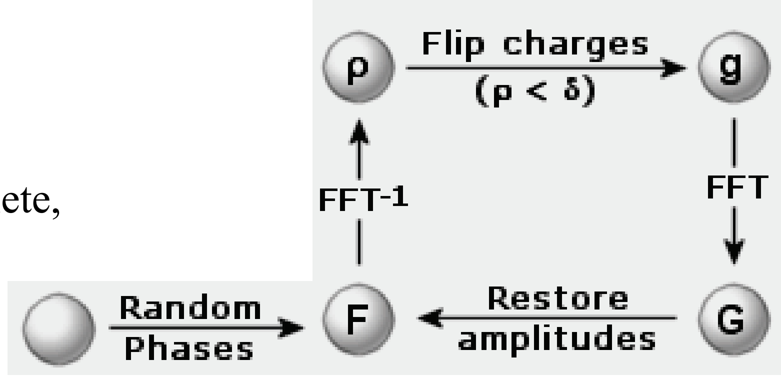
!         Nalgor  Nconf nm_cycl   num_therm   accept%
Algor_T     0       6   120        0        10.0

!         Value of Seed (if SeedVAL = 0, random seed)
SeedVAL     0
!
Threshold   25.0
!         Treatment of initial configuration
InitCON    RAN
```

A mixed Method : charge flipping *(Oszlani & Süto, Acta Cryst A60, **2004**)*

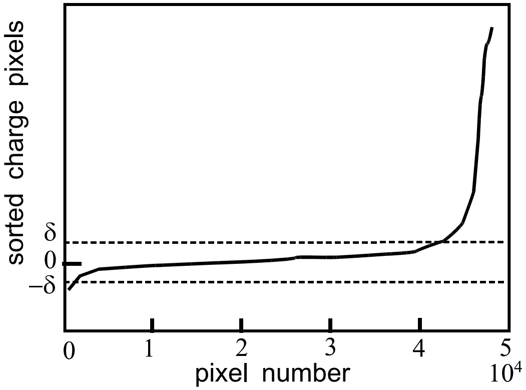
Principle :

One works *alternately in direct and reciprocal space.*
Based on image analysis techniques.
requires a list of *hkl I sig(I)*, i.e. LeBail extraction.
Works in P1.
Don't need to know anything about cell content
Data : a set of │Fobs(hkl)│, may be noisy, incomplete,
but with atomic resolution …



Algorithm :

Start, **φ** random + │**Fobs(hkl)**│ => **F(hkl)**
ρ =FFT^{-1}(**F**) (calculated on a pixel grid in direct space)
flip the signs of **ρ** for every pixels where │**ρ**│<δ => **ρ'**



One calculates **G**= FFT(**ρ'**)
For each (hkl), one keeps the phases of **G**, with │**Fobs(hkl)**│=>**F** ,
Loop observing RBragg…. And it works !

May be limited for powders by deconvolution/resolution problems…

Java Applet from the Lausanne group (G. Chapuis et al.)

flip.jar

In FullProf, make LeBail refinement + FOU=7, => SuperFlip *(Palatinus et al.)*

my_code.spf ---- Contains the input parameters for SuperFlip
my_code.fou ---- Contains the reflection file in SHELX format as extracted from a Le Bail fit.
edma.input ---- Input file for the program EDMA (analysis of SuperFlip results)