First FullProf School 2026:

Diffraction data analysis of energy materials

Solving structures in real space: Simulated Annealing

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Outline

1. **Ab initio crystal structure determination from powder diffraction**

2. **Introduction to the program GLOpSAnn**

Talks-1-4.zip https://cloud.ill.fr/index.php/s/CDfrgkDfPOPjxwV
Demos-1.zip https://cloud.ill.fr/index.php/s/h57Km6IVuEqtIoi

(Many slides come from presentations by Pierre Bordet)

Elementary Description of a Crystal Structure

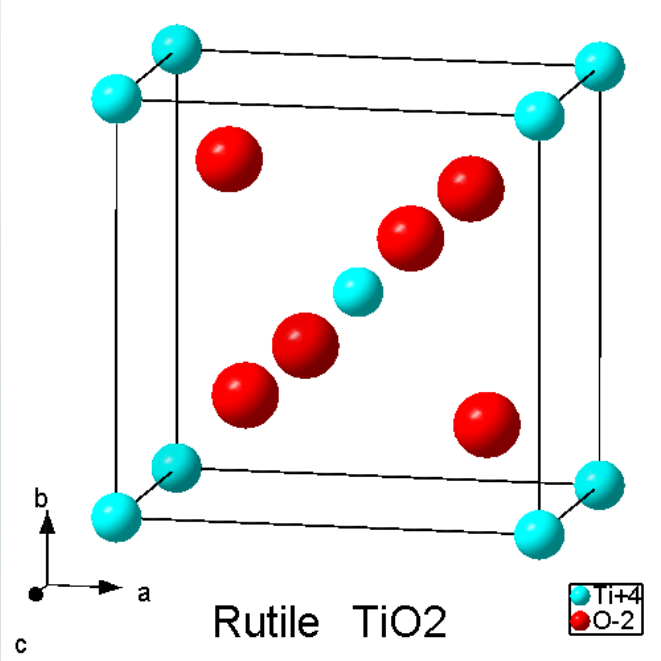
The crystal structure is completely determined by the knowledge of

the unit cell

the space group

the asymmetric unit

To solve a crystal structure, these three components must be determined



Crystal data

Chemical Formula	O2 Ti
Crystal system	tetragonal
Space group	$P\,4_2/m\,n\,m$ (no. 136)
Unit cell dimensions	a = 4.5937 Å c = 2.9587 Å
Cell volume	62.40 Å^3
Number of formula units 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	

A crystal can be described as the convolution of an atomic motif $\rho(\mathbf{r})$ and a lattice $L(\mathbf{r})$

$$C(\mathbf{r}) = L(\mathbf{r}) * \rho(\mathbf{r})$$

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

$$C(\mathbf{h}) = FT\{C(\mathbf{r})\} = FT\{L(\mathbf{r}) * \rho(\mathbf{r})\} = \Lambda(\mathbf{h}).F(\mathbf{h})$$

The Fourier space is called **reciprocal space**

$$\rho(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{h}} F(\mathbf{h}) \exp\{-2\pi i \mathbf{hr}\}$$

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

$F(\mathbf{h})$ = Fourier transform of the atomic motif (scattering density) : **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 reflection **h**=(*hkl*) $\quad F(\mathbf{h}) = FT\{\rho(\mathbf{r})\}$

$F_{hkl} \rightarrow$ *Fourier transform of the scattering density of the crystal*

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

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

For x-rays, f_j is the atomic form factor,

For neutrons, $f_j = b_j$ is the Fermi length.

T_j = **Debye-Waller** factor related to atomic displacements (thermal, static…).

In an isotropic, harmonic approximation one has :

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

$\left\langle U_j^{\,2}\right\rangle^{1/2}$ is the *root mean square displacement* of atom *j*.

Extinction Conditions:

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

Example : body centered lattice I : translation

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 $\Leftrightarrow$ $F_{hkl}=0$ *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	$\frac{1}{2}$ (a+b+c)
	$h+k=2n$	réseau C	$\frac{1}{2}$ (a+b)
	$h+l=2n$	réseau B	$\frac{1}{2}$ (a+c)
	$k+l=2n$	réseau A	$\frac{1}{2}$ (b+c)
	h,k,l tous pairs ou tous impairs	réseau F	$\frac{1}{2}$ (a+b), $\frac{1}{2}$ (a+c), $\frac{1}{2}$ (b+c)
	$-h+k+l=3n$	réseau R (*reverse*)	$\frac{1}{3}$ (2a+b+c), $\frac{1}{3}$ (a+2b+2c)
	$h-k+l=3n$	réseau R (*obverse*)	$\frac{1}{3}$ (a+2b+c), $\frac{1}{3}$ (2a+b+2c)
0kl	$k=2n$	plan b, (100)	$\frac{1}{2}$ b
	$l=2n$	plan c, (100)	$\frac{1}{2}$ c
	$k+l=2n$	plan n, (100)	$\frac{1}{2}$ (b+c)
	$k+l=4n$	plan d, (100)	$\frac{1}{4}$ (b+c)
h0l	$h=2n$	plan a, (010)	$\frac{1}{2}$ a
	$l=2n$	plan c, (010)	$\frac{1}{2}$ c
	$h+l=2n$	plan n, (010)	$\frac{1}{2}$ (a+c)
	$h+l=4n$	plan d, (010)	$\frac{1}{4}$ (a+c)
hk0	$h=2n$	plan a, (001)	$\frac{1}{2}$ a
	$k=2n$	plan b, (001)	$\frac{1}{2}$ b
	$h+k=2n$	plan n, (001)	$\frac{1}{2}$ (a+b)
	$h+k=4n$	plan d, (001)	$\frac{1}{4}$ (a+b)
hhl	$l=2n$	plan c, (1$\bar{1}$0)	$\frac{1}{2}$ c
	$2h+l=2n$	plan n, (1$\bar{1}$0)	$\frac{1}{2}$ (a+b+c)
	$2h+l=4n$	plan d, (1$\bar{1}$0)	$\frac{1}{4}$ (a+b+c)

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

$$I_{hkl} = S.C_{hkl}.|F_{hkl}|^2$$

S : scale factor

C_{hkl} : experimental corrections

instrument *(Lorentz, polarization, diffraction geometry…)*

sample *(multiplicity, absorption, preferred orientation, extinction…)*

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

$$\rho(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{h}} F(\mathbf{h}) \exp\{-2\pi i \mathbf{hr}\} = \frac{1}{V}\sum_{\mathbf{h}} |F(\mathbf{h})| \exp\{-2\pi i(\mathbf{hr}+\phi_{\mathbf{h}})\}$$

For centrosymmetric structures $\phi_{\mathbf{h}} = 0, \frac{1}{2}$ $\rightarrow$ *only need the sign (positive or negative)*

$$s_{\mathbf{h}} = 1, -1 \quad \rightarrow \quad \rho(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{h}} s_{\mathbf{h}} |F(\mathbf{h})| \exp\{-2\pi i \mathbf{hr}\}$$

Ab initio determination of crystal structures using powder diffraction and the *FullProf Suite*

1: One needs a **high quality sample** already well characterized (composition, density)

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

3: **Find the unit cell** and **index Bragg reflections**
Using WinPLOTR + Dicvol04, Treor, Ito, etc…

4: Obtain the **intensities of Bragg reflections** and **determine the space group**
Using FullProf in Le Bail mode + CheckGroup

5: Find an **approximate starting structural model of the atomic motif *ab initio***
Using Direct methods , simulated annealing (FullProf, GLOpSAnn),
Charge flipping (Superflip), or in simple cases, chemical knowledge

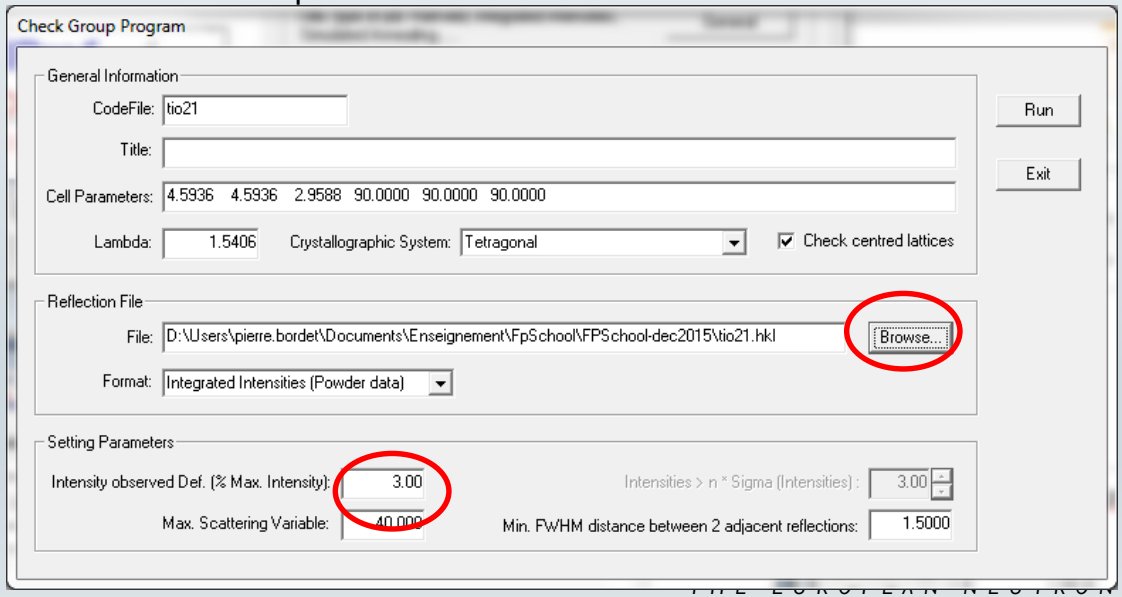
6: **Refinement and Fourier recycling** to obtain a complete and accurate structure
Rietveld Refinement using FullProf, Fourier using GFourier

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
  . . . . . . . . . . . . . . . .
```

- Use CheckGroup from the FPSuite toolbar



Info Window

```
  ------------------------------------------------------------------------
    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
```

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 Le Bail fitting. Overlapping reflections must be taken care of.

Practical Use

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

Expo does :

- **pattern decomposition to generate *.hkl* file if required (or use Le Bail fit in FullProf)**
- **structure factor normalization**
- **Wilson plot to get scale factor and $B_{overall}$**

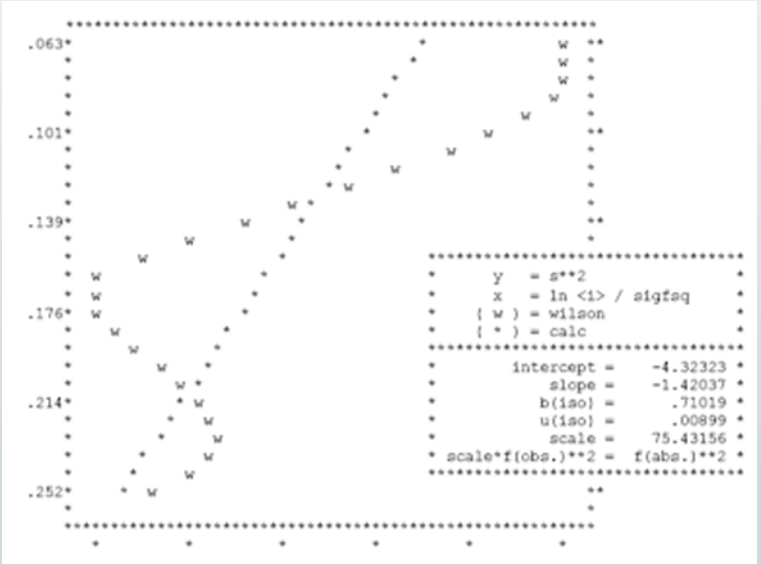
$$I_{hkl} = E.|F_{hkl}|^2.\exp(-(2B\sin^2\theta)/\lambda^2) \quad \text{with s=sin}\theta/\lambda,$$

In a small s interval, one gets :

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

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

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



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

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 Le Bail fit, for a single phase only.

⇒In case of single phase, use Expo for Le Bail intensity extraction and direct method solution

⇒In case of multi-phase, use FP for Le Bail 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
```

What is Simulated Annealing?

Simulated Annealing:

The SA method is a general purpose optimisation technique
for large combinatorial problems introduced by:

Kirpatrick, Gelatt and Vecchi, *Science* **220**, 671-680 (1983).

Minimize a cost function, energy E(ω), with respect to the configuration vector ω.

Origin: Monte Carlo methods for simulating properties of liquids (Metropolis algorithm)

Algorithm trying to mimic the process of annealing a sample to obtain a good crystalline state (ground state):

A temperature schedule (starting high temperature + cooling rate) is needed.

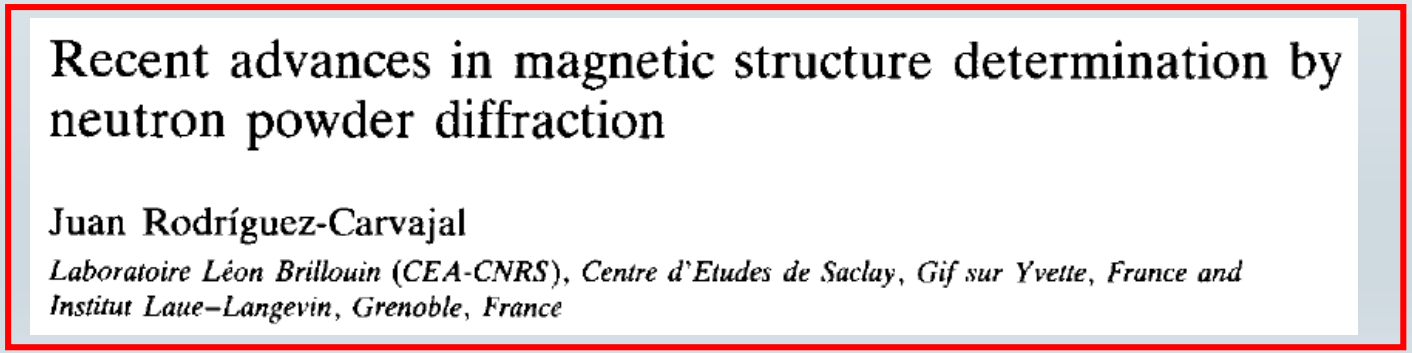
Procedure to generate new configurations (Markov chains) and a Boltzmann probability to explore the phase space (importance sampling)

Simulated Annealing for magnetic structures

The Simulated Annealing method applied to magnetic structural problems from experimental data was treated for the first time in 1993

J. Rodríguez-Carvajal, Physica B **192**, 55-69 (1993)

(program MAGSAN)



Recent advances in magnetic structure determination by neutron powder diffraction

Juan Rodríguez-Carvajal

Laboratoire Léon Brillouin (CEA-CNRS), Centre d'Etudes de Saclay, Gif sur Yvette, France and Institut Laue–Langevin, Grenoble, France

Simulated Annealing for Crystal And Magnetic Structures

Minimize a reliability factor with respect to the "configuration vector"

$$\boldsymbol{\omega} = \left| C_1, C_2, C_3, C_4, C_5, \ldots C_m \right\rangle$$

$$R_m(\boldsymbol{\omega}) = c \sum_{r=1}^{N} \left| G^2_{obs}(\mathbf{h}_r) - G^2_{calc}(\mathbf{h}_r, \boldsymbol{\omega}) \right|$$

The "configuration vector" is formed by the free parameters of the structure that may be: (1)atom positions, (2) occupation factors, (3) thermal parameters, (4) magnetic moments, (5) amplitudes of symmetry modes, (6) rigid body parameters, (7) amplitude of modulation functions, (8) coefficients of the linear combination of basis functions of irreducible representations, etc.

The Simulated Annealing Algorithm

begin

Initialise (set to zero useful quantities, do preliminary calculations)

$\tau = 1$

do

do

Perturb the system:

$\omega_{old} \rightarrow \omega_{new}$, $\Delta = E(\omega_{new}) - E(\omega_{old})$

if $\Delta \leq 0$ **then accept**, **else**

if $\exp(-\Delta/T_\tau) >$ **random[0,1] then accept**

if accept then **Update** (**replace** ω_{old} **by** ω_{new})

until equilibrium is approached closely enough (Ncyc)

$T_{\tau+1} = f(T_\tau)$ **(decrease temperature, usually** $T_{\tau+1} = q\, T_\tau$, $q \approx 0.9$)

$\tau = \tau + 1$

until stop criterion is true (maximum τ, **convergence, low % accepted...)**

end

Interests of simulated annealing

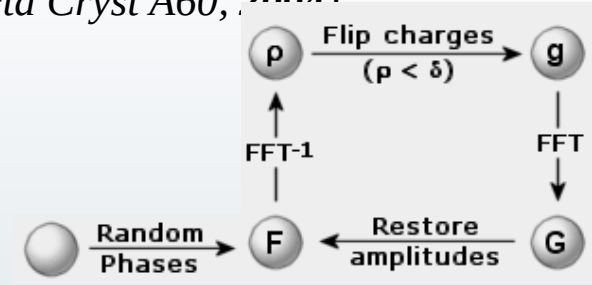
May not be necessary to know the space group (may work in P1, but it is still better to know it)
May not be necessary to know the composition (atoms may move on top of each other and merge, but no new atom can be created, so it is still better to know it)
Flexibility to define the parameters in the minimization process (not necessarily atomic positions)
⇒Reduction of the number of parameters
⇒More stable minimization procedure
⇒Adapted to the geometrical/crystal-chemical specificities of a given problem

Preparing your data file in FullProf:

Do a Le Bail 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 SAnn search.

Then use these data for the SAnn 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`**

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

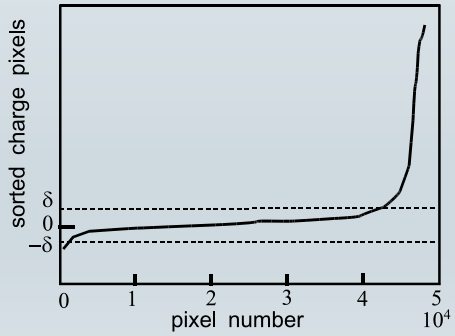


Principle :

One works *alternately in direct and reciprocal space.*
Based on image analysis techniques.
requires a list of *hkl I sig(I)*, i.e. Le Bail 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 + $|\mathbf{Fobs(hkl)}|$ => **F(hkl)** $\rho = FFT^{-1}(\mathbf{F})$ (calculated on a pixel grid in direct space)
flip the signs of **ρ** for every pixels where $|\rho| < \delta$ => **ρ'**



One calculates **G**= FFT(**ρ'**)
For each (hkl), one keeps the phases of **G**, with $|\mathbf{Fobs(hkl)}|$ =>**F** ,
Loop observing R-Bragg…. And it works !
May be limited for powders by deconvolution/resolution problems…
Java Applet from the Lausanne group (G. Chapuis et al.)
The reference software for charge flipping is Superflip (Lucas Palatinus)

Web site of Superflip

http://superflip.fzu.cz/

Superflip is a computer program for application of the charge-flipping algorithm to structure solution of crystal structures from diffraction data. Superflip works in arbitrary dimension and can be therefore used for solution of normal periodic structures, modulated structures and also quasicrystals.

Superflip is written in Fortran 90 and it uses the mathematical library FFTW3 for making the fast Fourier transform. This library must be installed on your system if you want to compile the program from the source code. Superflip also makes use of the subroutine SGELSY (+ dependencies) from the mathematic library LAPACK. This routine is included in the installation package of Superflip, and the LAPACK library neednot be installed on your system. Superflip also contains part of the code adapted from the program ECALC (Ian Ticke), and symmetry library symlib.info, both being a part of the project CCP4. The program package contains the source code, the Makefile, sample input file and user manual.

If you want to use the precompiled executable, just download the appropriate file from the table below and follow the instructions. If you want to compile the program from the source code, please follow the notes in the user manual.

In the following table click download to download the particular item, or click instructions to view the instructions for installation (see license agreement):

Current version: 03/15/13 12:43

complete package with source code, user manual and sample file	download	instructions
zipped exectutable for Windows	download	instructions
zipped executable for MacOS X intel	download	instructions
zipped executable for MacOS X ppc (not updated anymore)	download	instructions
RPM for Linux (Centos 5)	external link	instructions
Documentation	download	
Sample input files		instructions

FullProf can create a list of (hkl Int sigma) using Le Bail fitting procedure that are adapted to **Superflip**

By putting **Fou=7** in the PCR file, **FullProf** produces files for the programs Superflip and EDMA (http://superflip.fzu.cz).

The generated files corresponding to the PCR file "my_code.pcr" are the following:

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

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

```
!  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
   . . . . . .
  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
```

Simulated in FullProf

Outline

1. Live presentation: The programs WinPLOTR and WinPLOTR-2006 for visualizing powder diffraction patterns, peak search, background determination, peak fitting, etc.

2. Indexing powder patterns. Le Bail Fit of powder patterns.

3. Ab initio crystal structure determination from powder diffraction

4. **Introduction to the program GLOpSAnn**

GLOpSAnn Simulated Annealing to solve crystal structures with CrysFML

Similar to SAnn in FullProf + large choice of cost functions and combinations of them. Magnetic structure and rigid groups are not yet 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)} Similar to Chi2
```

Works with Le Bail 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
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
CostNam  FoFc_Pow+BVS
TemParM     3.0       0.95       80    ! T_ini     anneal     num_temps
Algor_T     0  6  120 0 10.0           ! Nalgor  Nconf nm_cycl   num_therm   accept%
SeedVAL     0
Threshold   25.0
InitCON   RAN
```

Live presentation of GLOpSAnn