First FullProf School 2025:

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

Elementary Description of a Crystal Structure

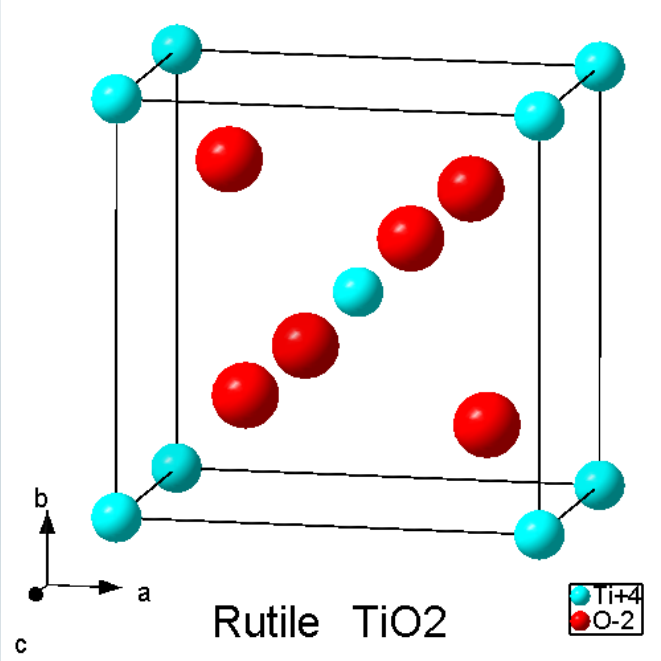
The crystal structure is completely determined by the knowledge of

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	

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:

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

S : scale factor

C_{hkl} : experimental corrections

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

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

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

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} ,**

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

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

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

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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 (e.g. EXPO) , 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

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)

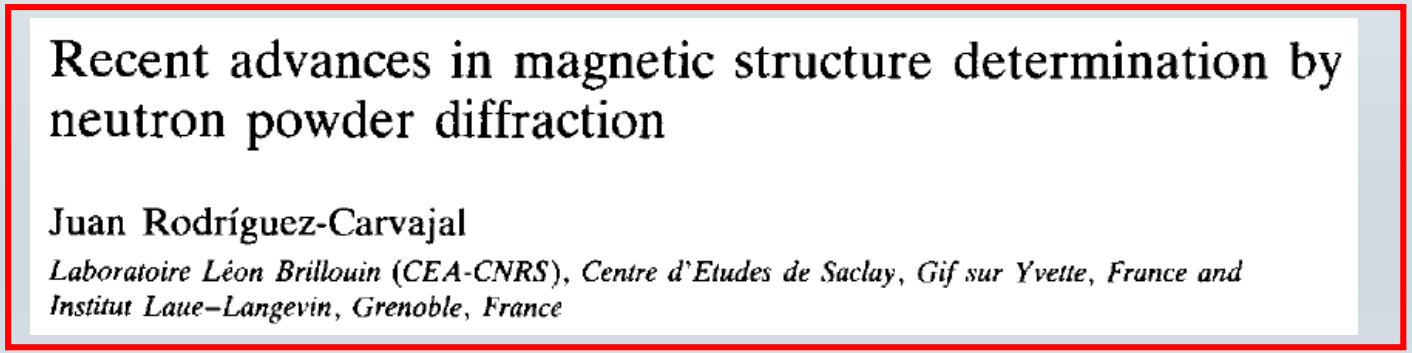
Algorithm trying to mimic the process of annealing a sample to obtain a good crystalline state (ground state):

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

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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`**

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