# *FOX:*
# *Modular Approach to Crystal Structure Determination from Powder Diffraction*

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# Global Optimization in Direct Space

***Direct space methods*** : locating building units (molecules, polyhedrons, atoms) in the cell.
***Global Optimization*** : evaluating a ***Cost*** of the structural model in parameter space.

***Monte-Carlo based Optimization***

Explore parameter space and generate “all” possible configurations with a Boltzmann-type distribution

Markov chain

Random configuration → Random move → Evaluate configuration → Metropolis: Is configuration “better” ?

yes → Keep configuration → Random move

no → Keep configuration with probability :

$$P = \exp(-\Delta CF / T)$$

→ Random move

***Cost Function*** **(CF)**

***Annealing temperature***

***Available computer programs:***
- optimized for specific material (organics, zeolithes…)
- customization of Cost Functions ?
- handling of special positions ?

# *FOX: Free Objects for Xtallography*

(i) The crystal structure can be described using ***any*** combination of ***building blocks***: isolated atoms, molecules, polyhedrons.

(ii) The correct structure can be found without ***any*** assumption on the actual ***connectivity*** between building blocks, nor ***any*** *a priori* knowledge about atoms on ***special positions***.

(iii) Several ***optimization algorithms*** can be used, with ***easy*** path from one to another and with ***easy*** upgrade of algorithm. All optimized objects (crystal structure, powder pattern) can define their ***Cost Function*** (CF) and ***any*** combination of CF can be used as a criterion.

(iv) It is possible to use ***jointly*** all available diffraction data sets.

(v) Any modification or upgrade of the program is ***easy***.

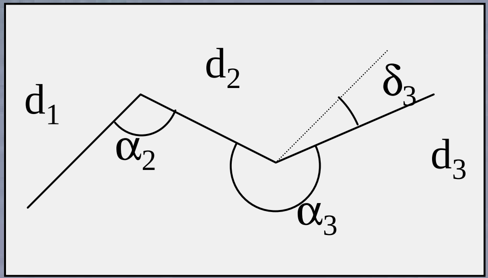
***Graphical User Interface***

***ObjCryst++***

***Crystallographic Library***

***Algorithms***

# *Building Blocks :*
# *Polyhedrons, Molecules described by Z-matrix*

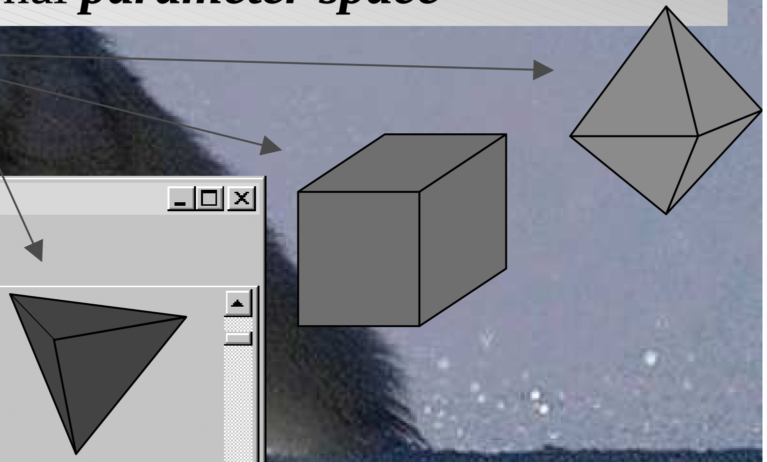


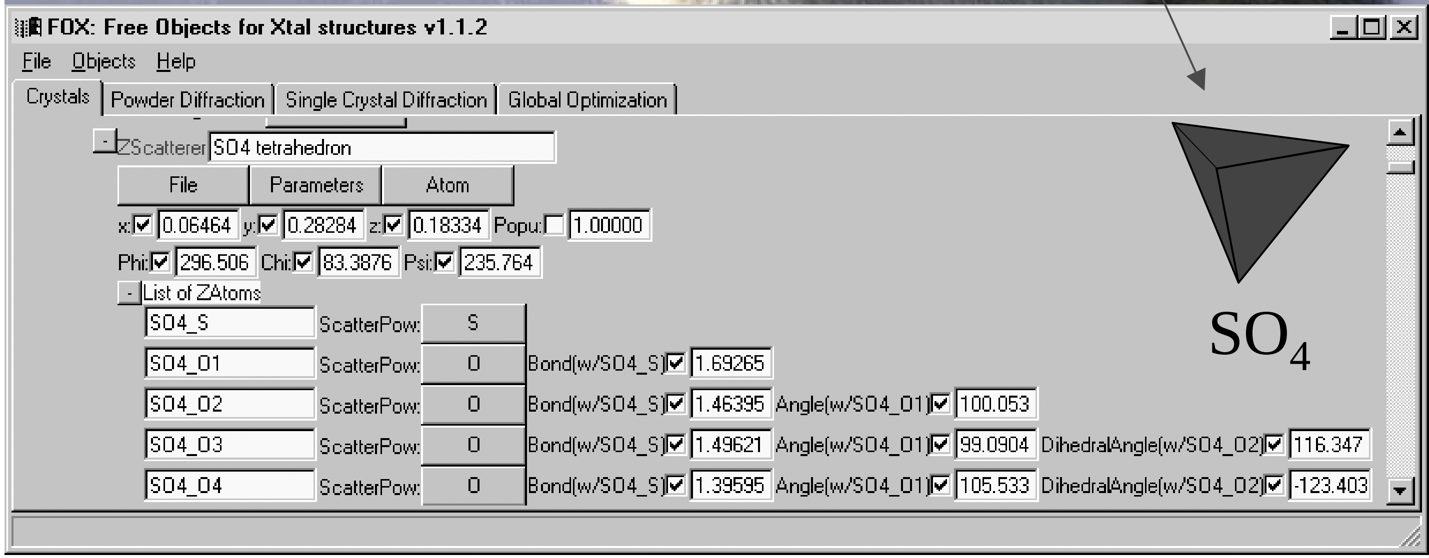

***Z-Matrix:*** describe atom positions using ***relevant*** parameters:

*Bond lengths*, *bond angles* and *dihedral angles*

- give ***'natural' constraints*** to the model
- keep some ***flexibility*** (limit parameters)
- reduce the *n*-dimensional ***parameter space***

Describing crystal from 'known' *building blocks* :





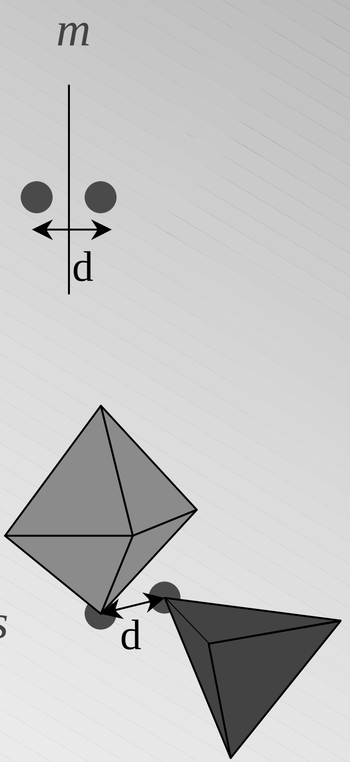

$SO_4$

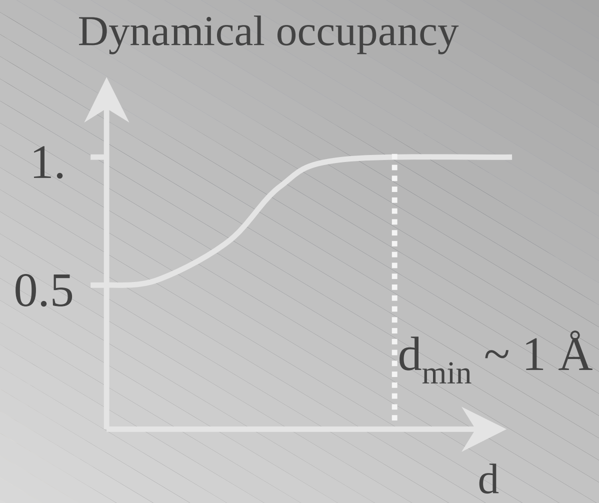
# *Special Positions and Connectivity : Dynamical Occupancy Correction*

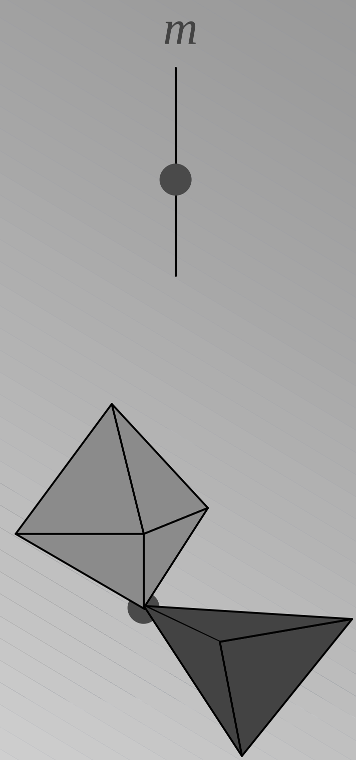
$$\text{Occupancy}^{-1} = 1 + \Sigma_{\text{neighbours closer then } d_{min}} |d_{min} - d_i|$$

*Symmetry*

*Shared atoms*



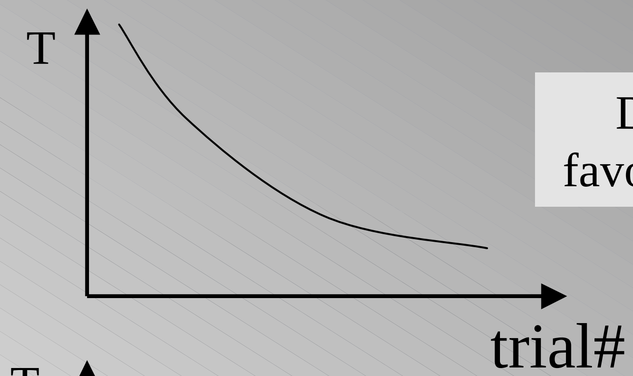

- ***Smooth** correction*
- ***Merging** of identical atoms*

# Algorithms and Cost Functions

***Cost Functions*** are defined for each kind of object : R, $R_w$, AntiBump, …

Use a ***weighted sum*** of Cost Functions: $\boldsymbol{f} = w_1 R_1 + w_2 R_2 + w_3$ AntiBump+…

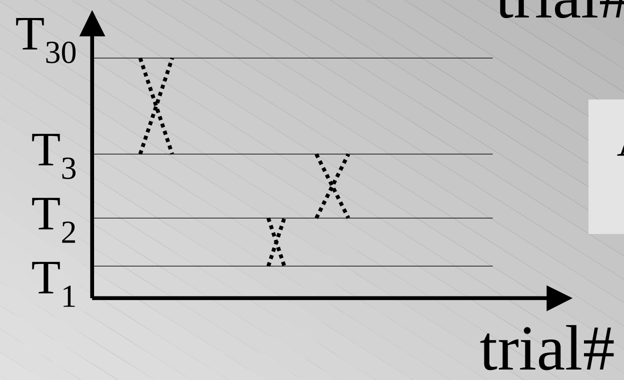
***Simulated Annealing*** :



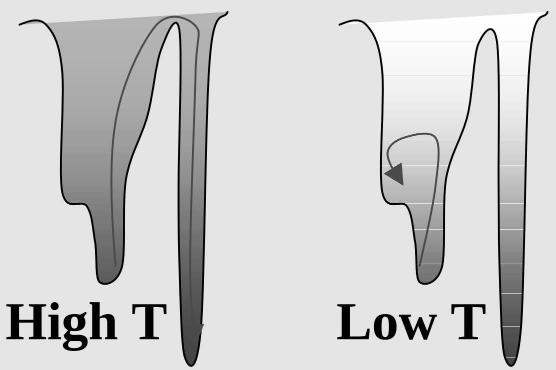

Decrease temperature:
favorize best configurations

***Parallel Tempering*** :

$$P = e^{-\frac{\Delta CF}{T}}$$




Allow to get out of local
minimas at all times



# Tuned for Global Optimization

***Avoid useless recalculations*** (auto. store profiles, scattering factors, …)

***Performance*** : up to 5000 trial structures / s (Athlon 1.4 Ghz, Linux)

*Cimetidine* : *up to 2500 trials/s for 150 reflections in single-crystal mode,*

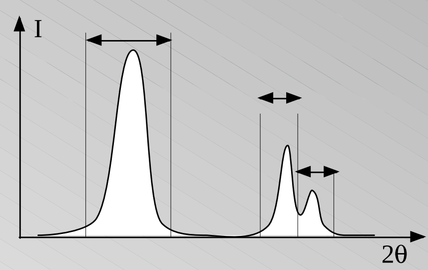
*40 % slower in powder-mode.*

***'Smart' annealing temperature*** : automatic adaptative tuning of the temperature to keep the acceptance rate between 10 and 30 %

***'Smart' moves for molecules*** : local minimization after a random move, increase the success rate

*Cimetidine* : *success increases from 80 to 90 %*

***Integrated R-factor*** : summing more than 90% of intensity around each peak using full observed and calculated patterns :



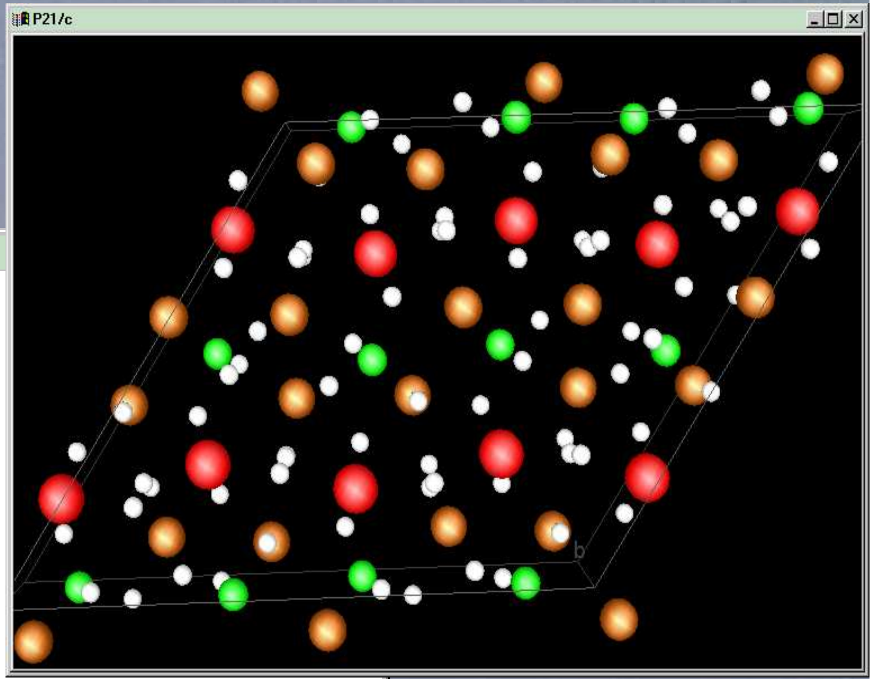
# Applications

| Compound | Atoms[c] | Space group | DOF | Modelization | Data[d] | Cost Function[e] | Success [%] | Trials×$10^3$ (time [s]) |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| $PbSO_4$[b] | 5 | *Pnma* | 18 | free atoms (6) | Xl+N | $iR_{wp}$ | 100 | <40(<30) |
| | | | 9 | Pb + ($SO_4$) | Xl+N | $iR_{wp}$ | 100 | <50(<30) |
| $CsOH{\cdot}H_2O$[a] | 2 | *$I4_1/amd$* | 9 | free atoms (3) | Xl | $iR_{wp}$ | 100 | <20(<30) |
| $LiBH_4$ - RT[a] | 5 | *Pnma* | 9 | Li + ($BH_4$) | Xs | $iR_{wp}$ + AB | 100 | <50(<30) |
| $LiBH_4$ - HT[a] | 4 | *$P6_3mc$* | 9 | Li + ($BH_4$) | Xs | $iR_{wp}$ + AB | 100 | <50(<30) |
| $NdNi_4MgD_{3.6}$[a] | 5M, | *$Pmn2_1$* | 15, | free atoms (5M) | Xs, | $iR_{wp}$ + AB | 100 | 100(60) |
| | 3D | | 15 | free atoms (5D) | N | $iR_{wp}$ | 100 | 100(60) |
| $Zr_3NiO_{0.6}D_{6.32}$[a] | 4D | *Cmcm* | 15 | free atoms (5D) | N | $iR_{wp}$ | 100 | 100(60) |
| $LaNi_2Mn_3D_{5.5}$[a] | 5D | *P6/mmm* | 15 | free atoms (5D) | N | $iR_{wp}$ | 100 | 100(60) |
| $ErFe_2D_{4.72}$ | 10D | *$Pmn2_1$* | 60 | free atoms (20D) | N | $iR_{wp}$ + AB | 100 | 500(300) |
| $LaMg_2NiD_7$[a] | 8M, | *$P2_1/c$* | 24, | free atoms (8M) | Xs, | $iR_{wp}$ | 100 | 100(60) |
| | 14D | | 42 | free atoms (14D) | N | $iR_{wp}$ + AB | 100 | 400(900) |
| MgIr[a] | 23 | *Cmca* | 69 | free atoms (23) | Xs+N | $iR_{wp}$ + AB | 50 | 500(12000) |
| | | | 20 | $4[Ir(Ir,Mg)_{12}]$ | Xs+N | $iR_{wp}$ | 75 | 100(7000) |
| K-tartrate | 11 | *$P2_12_12_1$* | 14 | K + ($C_4O_6$) | Xl | $iR_{wp}$ | 95 | 1200(720) |
| Cimetidine[b] | 17 | *$P2_1/c$* | 14 | ($C_{10}N_6S$) | Xs | $iR_{wp}$ | 90 | 4000(2800) |
| $Al_2(CH_3PO_3)_3$[a] | 26 | *P*-1 | 24 | 2Al + $3H_3CPO_3$ | Xl | $iR_{wp}$ +AB | 100 | 750(750) |

[a] new crystal structure; [b] test data available on web; [c] M=metal atom, D=deuterium
[d] Xl=laboratory X-ray, Xs=synchrotron, N=neutron, Xl(s)+N=joint use, Xl(s),N=successive use
[e] $iR_{wp}$ (weighted, integrated profile), AB (anti-bump)

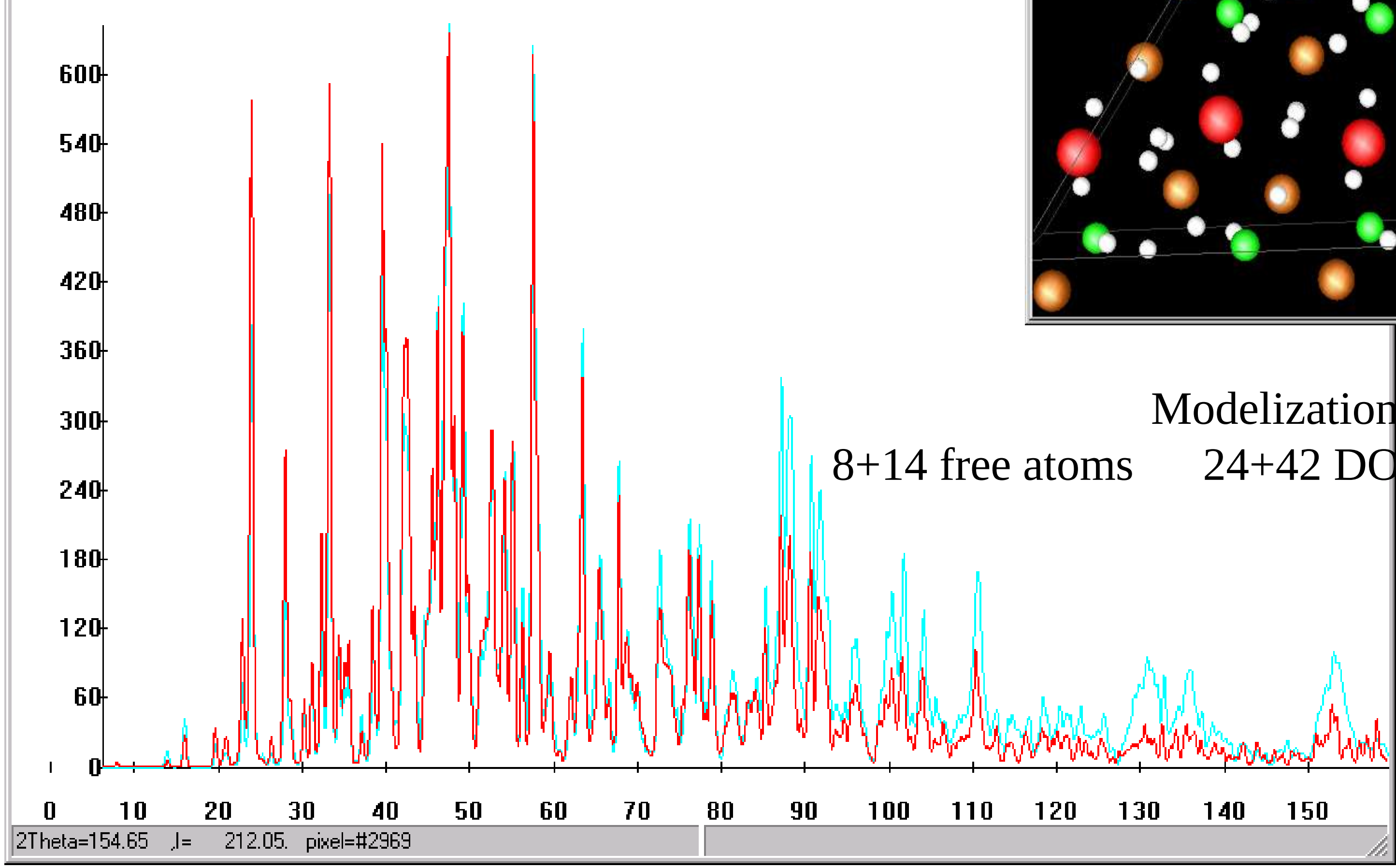
# *Isolated atoms : $LaMg_2NiD_7$*

***a*** = 13.9785 ***b*** = 4.7025 ***c*** = 16.0244 **β** = 125.238,
**sg** *P*2$_1$/*c*, metal atoms pseudosymmetry *Cmcm*
8 metal and 14 deuterium atoms




P21/c

*Neutron pattern (ILL-D2B), λ = 1.594 Å*




Modelization:

8+14 free atoms 24+42 DOF solution in 60+900 s

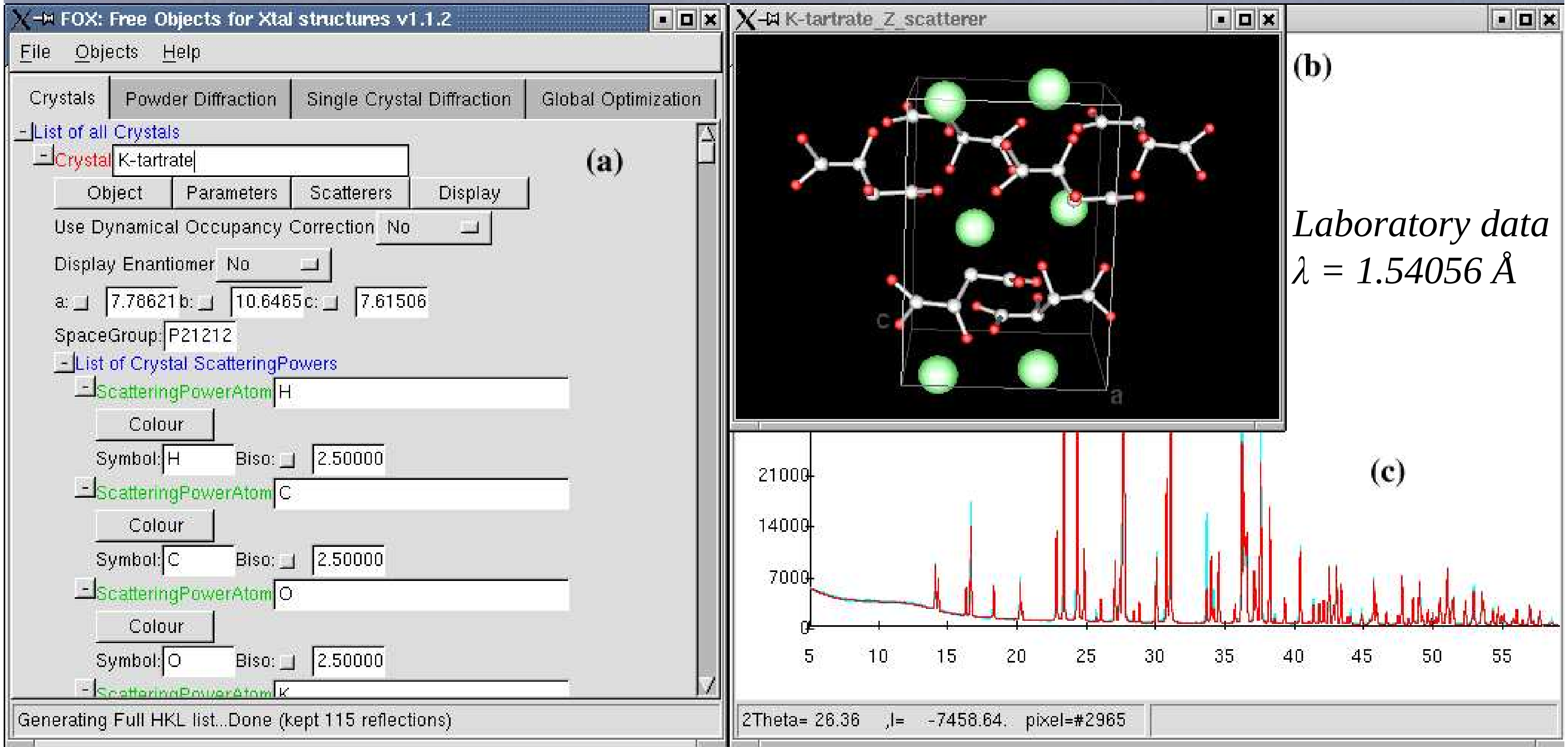
# *Molecule : Potassium Hydrogen 2R, 3R (+) Tartrate ($C_4 H_5 O_6 K$)*

***a*** = 7.7864 ***b*** = 10.6516 ***c*** = 7.6166 **sg** $P2_12_12_1$

Modelization: K + ($C_4O_6$)

11 non-hydrogen atoms

14 DOF solution in 720 s

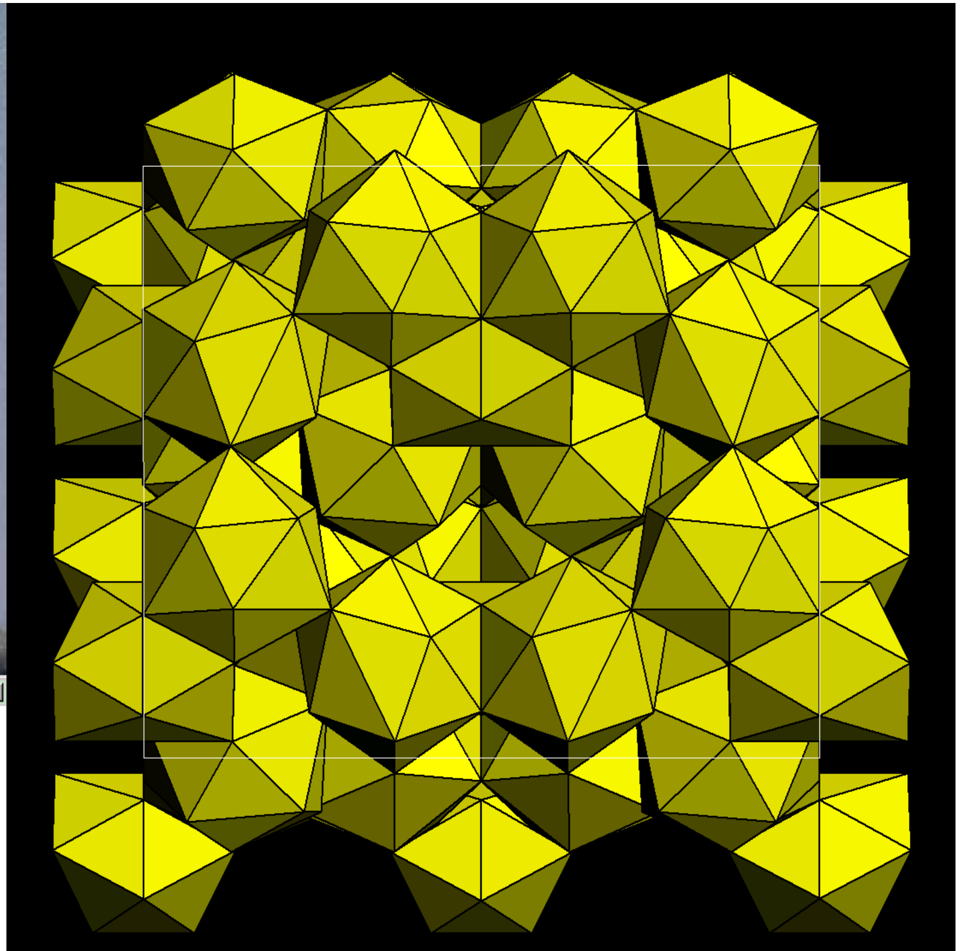


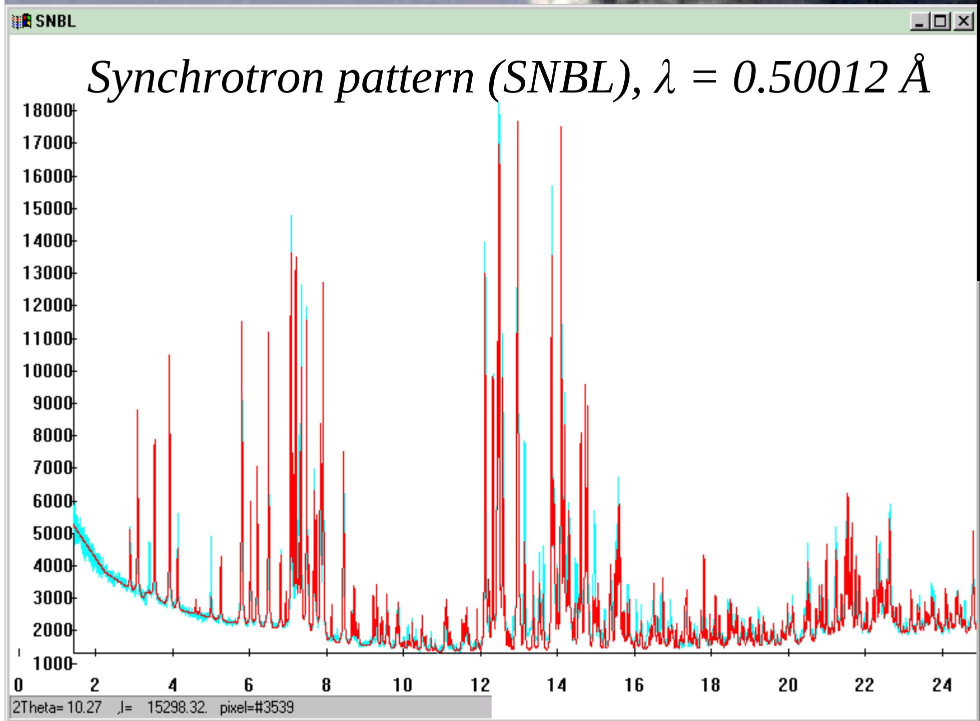
# *Polyhedrons : MgIr*

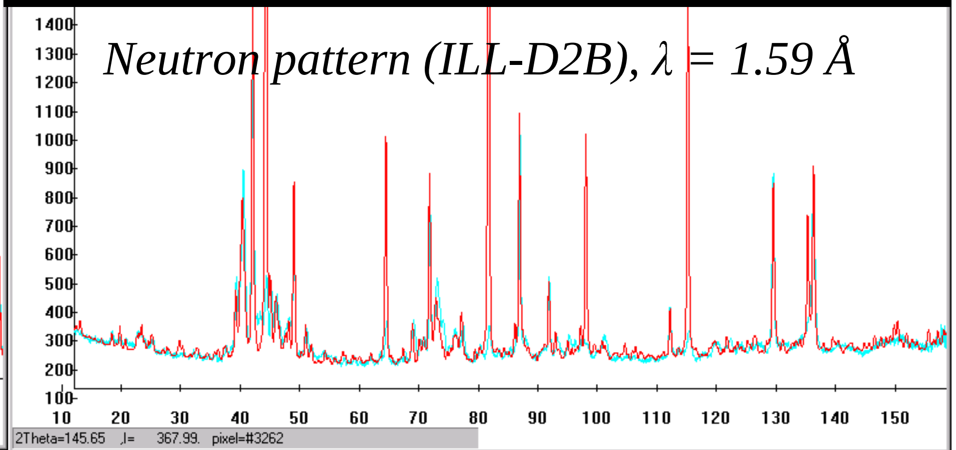
***a*** = 18.4648 ***b*** = 16.1701 ***c*** = 16.8175, **sg** *Cmca*
11 Ir and 12 Mg atoms
Frank-Kasper intermetallic compound

Modelization:

| | | |
|---|---|---|
| 23 free atoms | 69 DOF | solution in 12000 s |
| 4 icosahedrons | 20 DOF | solution in 7000 s |



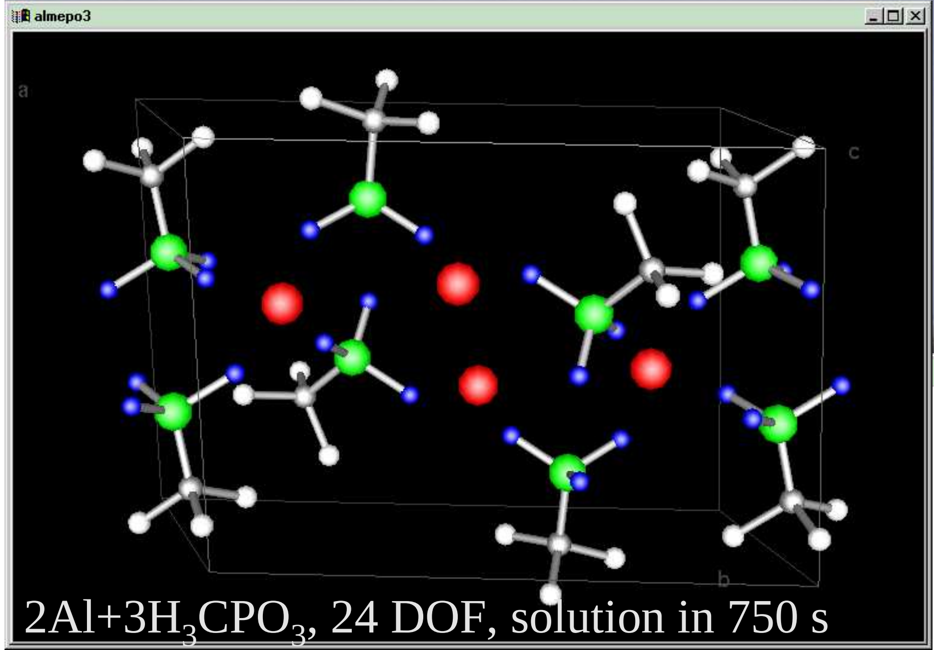


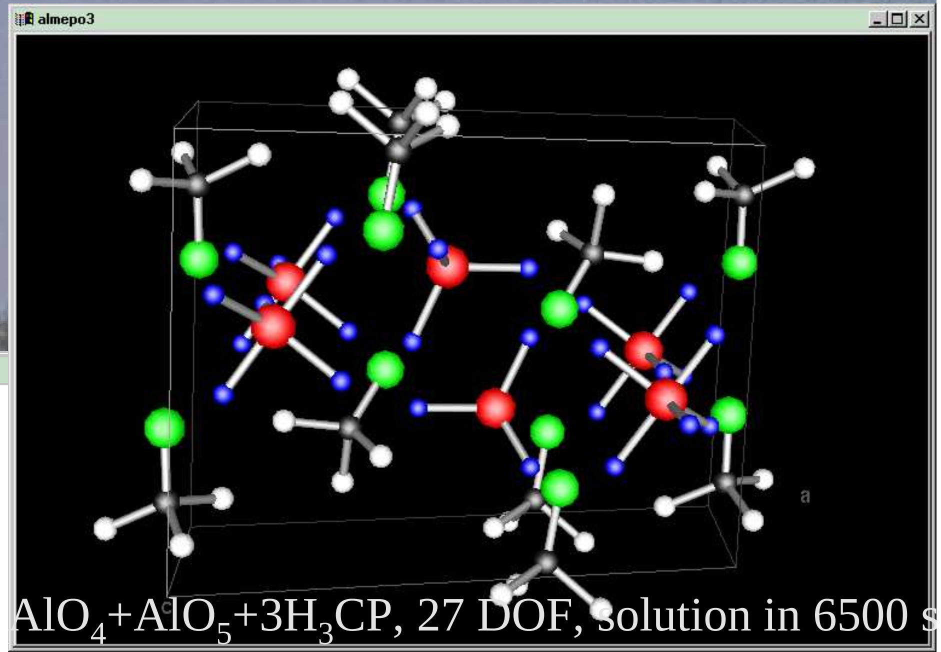
# *Hybrid* : $Al_2(CH_3PO_3)_3$

**Edgar *et al.* (2002) submitted to *Chem. Commun.***

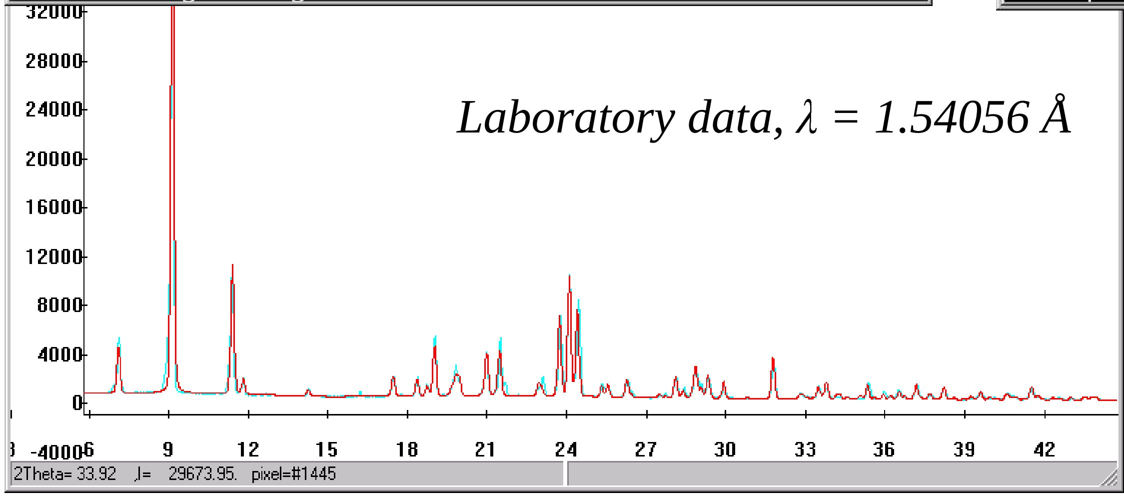
***a*** = 13.2979 ***b*** = 9.6570 ***c*** = 5.0725 **α** = 89.601 **β** = 111.242 **γ** = 92.088, **sg** *P* $\bar{1}$ , 26 atoms




$2Al+3H_3CPO_3$, 24 DOF, solution in 750 s




$AlO_4+AlO_5+3H_3CP$, 27 DOF, solution in 6500 s




*Laboratory data, λ = 1.54056 Å*

Buildings blocks deduced from $_{27}Al$, $_{13}C$ and $_{31}P$ NMR spectra :

3 C-PO3 units and 2 Al atoms

# *Conclusions*

**ObjCryst++**

***versatile***, ***expandable*** Crystallographic library
*not* a "finished" product (add your code!)

**FOX**

program for the global optimization of crystal structures (powder diffraction)

- ***any*** combination of ***building blocks*** : isolated atoms, molecules, polyhedrons
- **no** assumption on the actual ***connectivity***
- **no** *a priori* knowledge about ***special positions***
- ***joint*** use of diffraction data sets
- ***easy*** modifications

***Future developments*** :
- ***smart modelization*** of molecules (restraints)
- ***new*** Cost Functions (energy, atomic coordination)
- ***guided optimization*** (structure envelope , parameter space modification)
- ***other algorithms*** (genetic)

Availability (Windows, Linux): ***http://objcryst.sourceforge.net***

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## *Samples or powder patterns*

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## *Development*

Global Optimization: **Yu. Andreev** (Uni. of St. Andrews)

SpaceGroup & element library : **R. Grosse-Kunstleve** (L. Berkeley N. Lab)

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