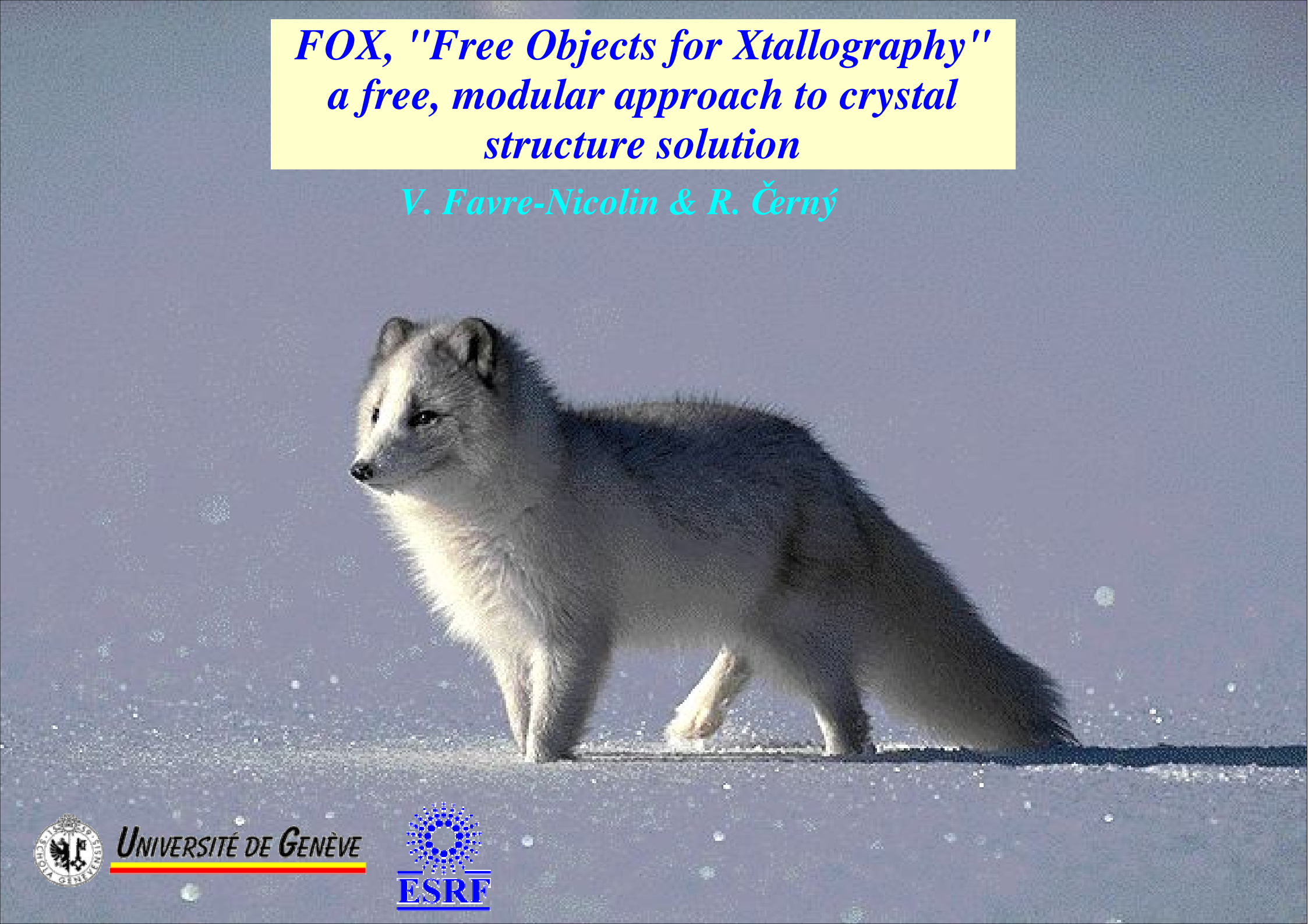
FOX, "Free Objects for Xtallography" a free, modular approach to crystal structure solution

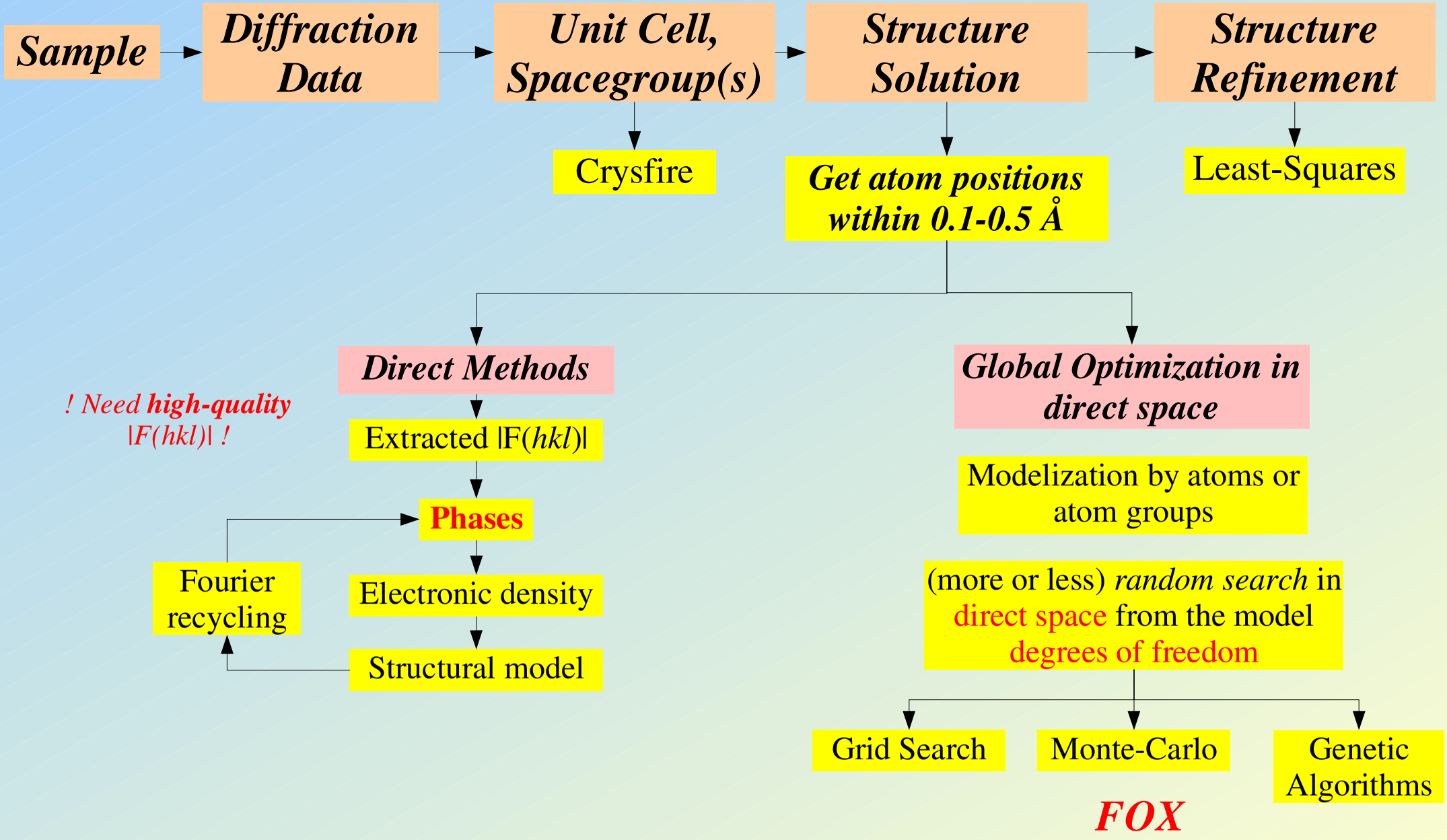
V. Favre-Nicolin & R. Černý



UNIVERSITÉ DE GENÈVE

ESRF

Structure Determination Overview



FOX Overview

Parametrization

- inorganic or organic materials
- description using atoms or building blocks
- automatic, smooth correction of special positions

Data

- powder pattern (X-Ray, neutron, multi-phase)
- (pseudo-) single crystal
- joint optimization with several data sets

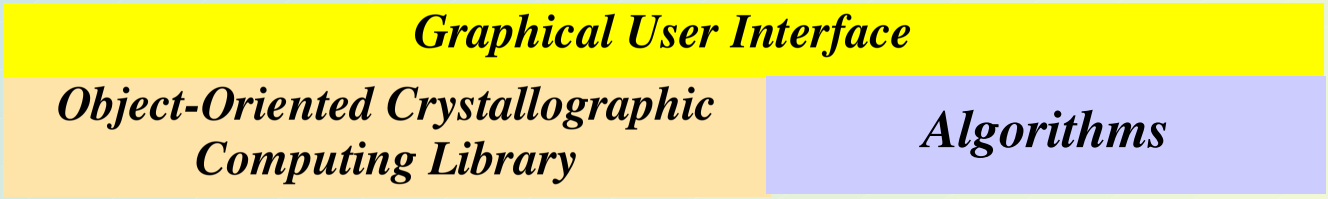
Algorithms

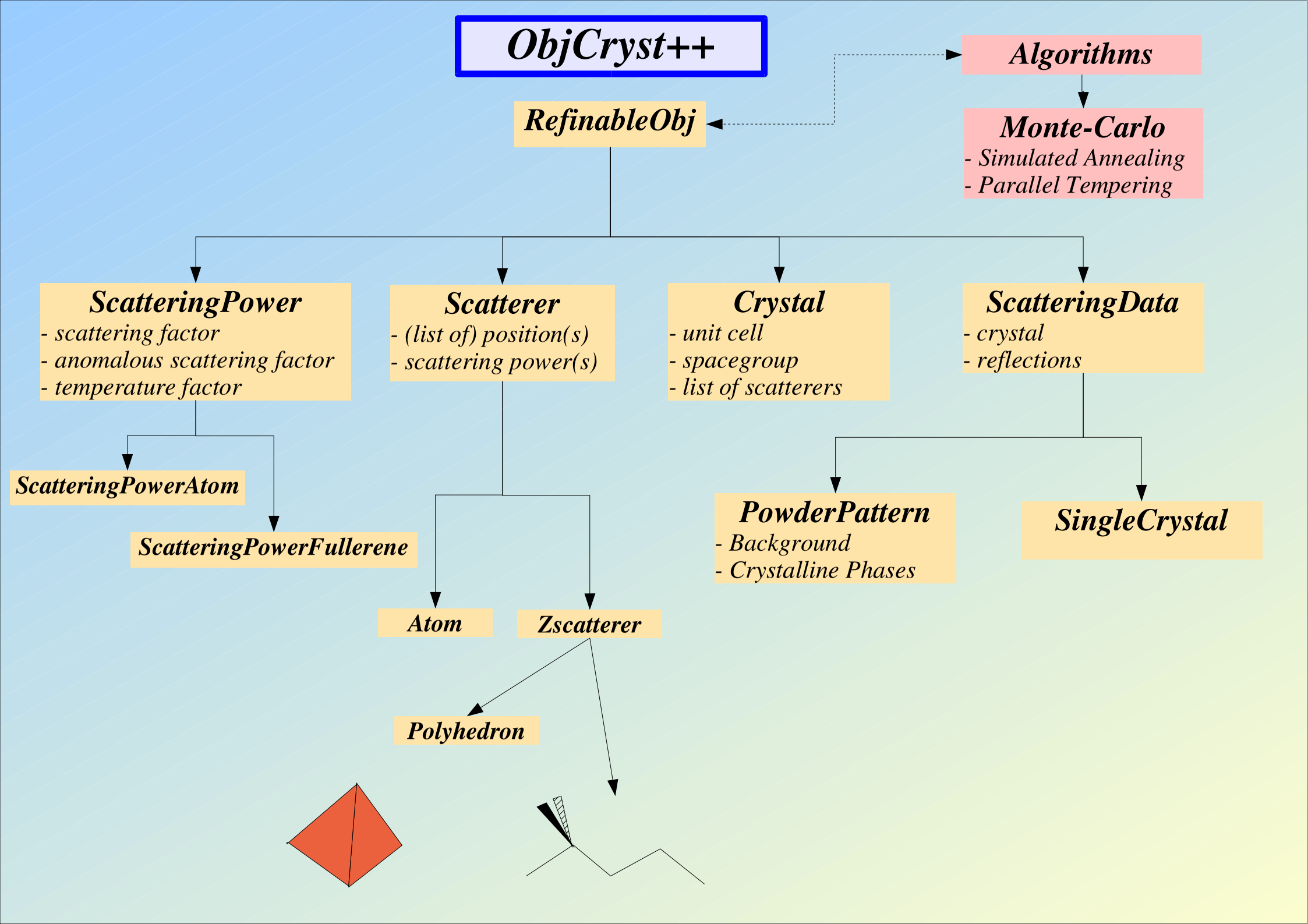
- Parallel Tempering (Simulated Annealing)
- expandable to new algorithms

Availability

- free (http://objcryst.sourceforge.net and CCP14)
- open source
- available for *Linux* and *windows*

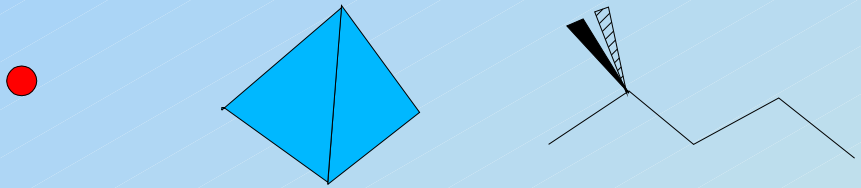
Organization




ObjCryst++
Algorithms
RefinableObj
Monte-Carlo
- Simulated Annealing
- Parallel Tempering
ScatteringPower
- scattering factor
- anomalous scattering factor
- temperature factor
Scatterer
- (list of) position(s)
- scattering power(s)
Crystal
- unit cell
- spacegroup
- list of scatterers
ScatteringData
- crystal
- reflections
ScatteringPowerAtom
ScatteringPowerFullerene
Atom
Zscatterer
PowderPattern
- Background
- Crystalline Phases
SingleCrystal
Polyhedron

Modelization

***Building blocks* for the crystal structure**



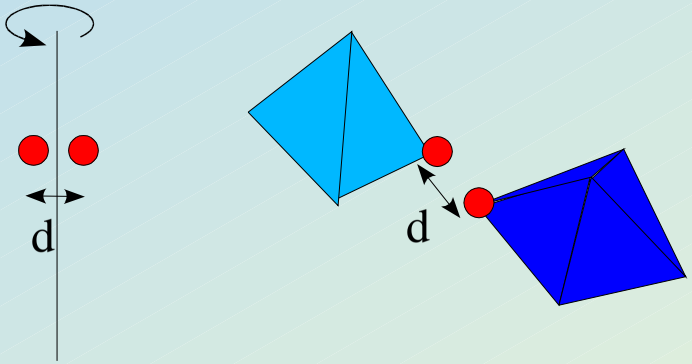
Atom ***Polyhedron*** ***Molecule***

Description from bond lengths, bond angles and dihedral angles : Z-matrix

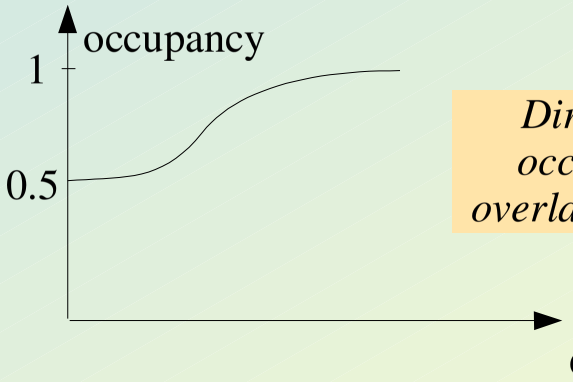
⇒ Use the maximum *a priori* information about the atoms coordination

Less degrees of freedom
⇒ More efficient search

***Special positions* & Shared atoms**

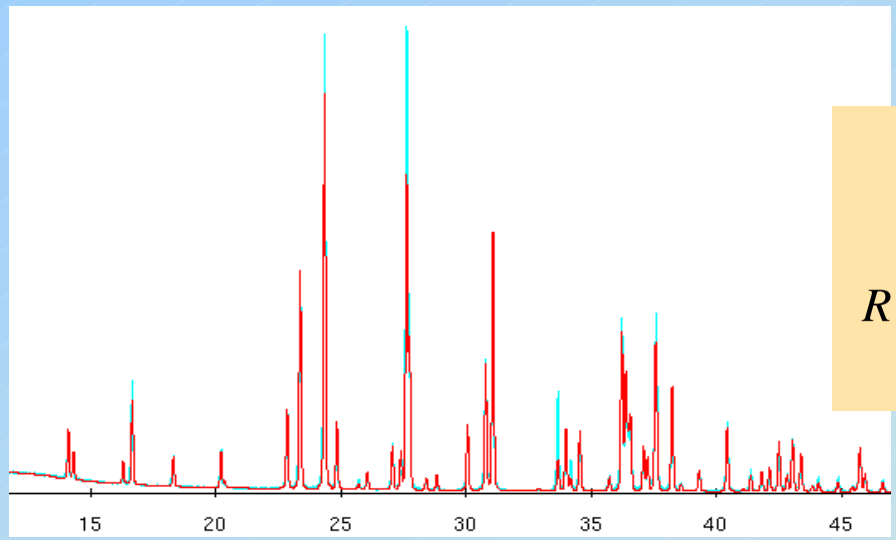


Overlap of identical atoms using a ***Dynamical Occupancy Correction***



Diminish the occupancy of overlapping atoms

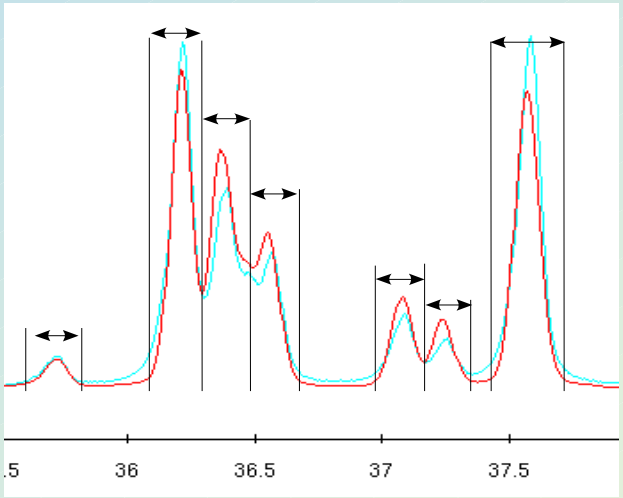
Evaluation of Trial Configurations



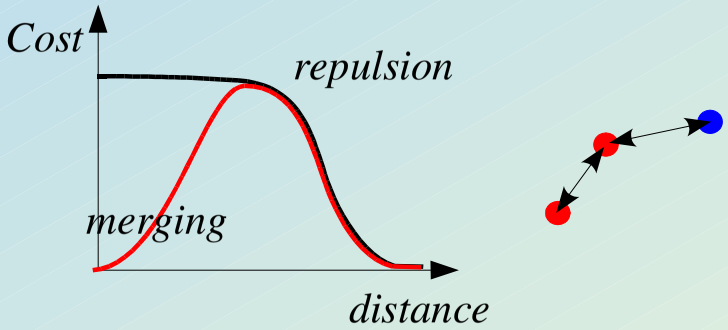
full profile R-factor

$$R_{wp} = \sqrt{\frac{\sum w_i (I_i^{obs} - I_i^{calc})^2}{\sum w_i (I_i^{obs})^2}}$$

***integrated* full profile R-factor**
iR_{wp}



Anti-bump



Use any combination of criteria

$$Cost = \sum w_j C_j$$

Monte-Carlo Algorithm

Parametrization
-> Degrees Of Freedom

keep configuration

yes

starting sonfiguration

random change of parameters

evaluation of the new configuration:
Cost (C)

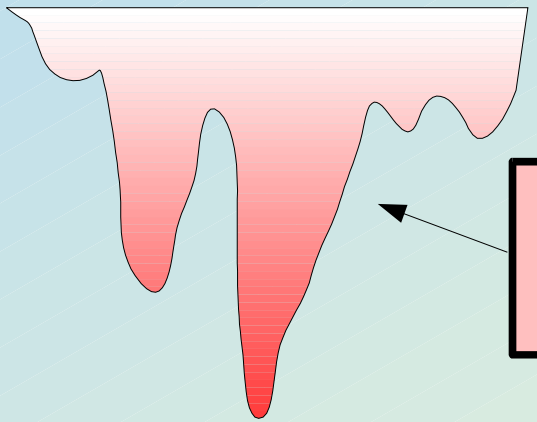
is configuration better ?
$C_n < C_{n-1}$

no

keep configuration with probability:
$P = e^{\frac{-\Delta C}{T}}$

Temperature of the algorithm

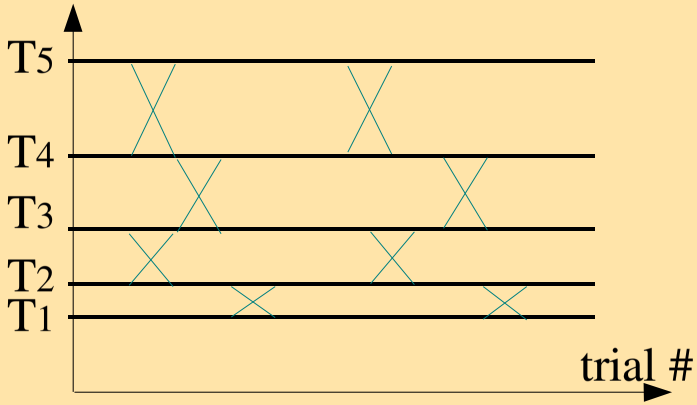
Hypersurface
Cost = f (DOF)



Generate a distribution of configurations following ***Boltzmann****'s law*

Parallel Tempering

simultaneous optimization at different temperatures
⇒ explore entire hypersurface
More efficient than Simulated Annealing

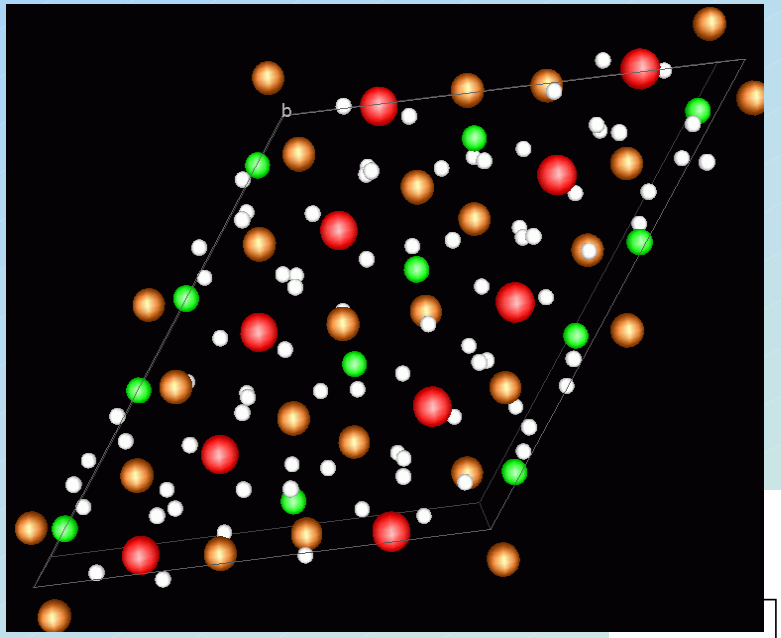


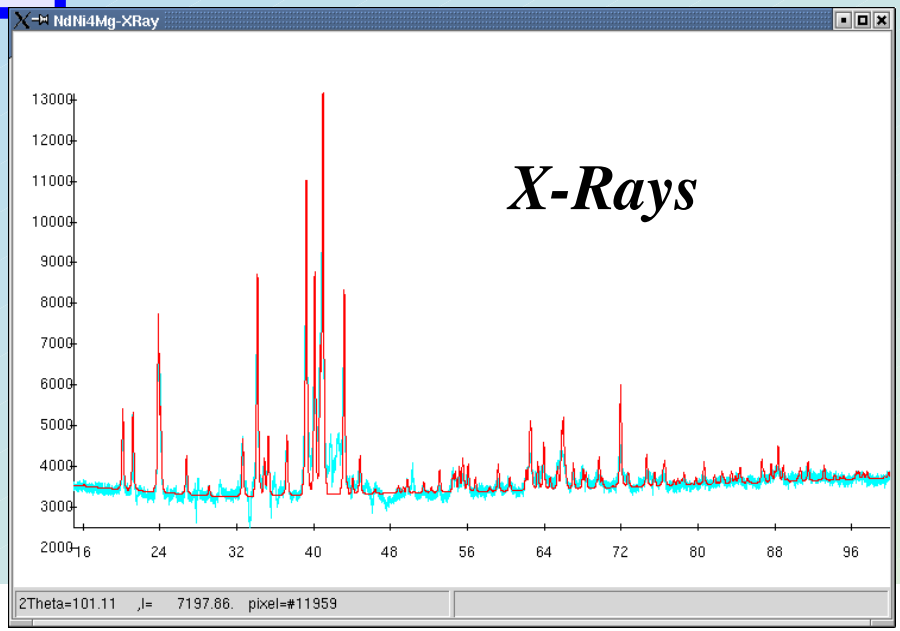
Hydrides Solved Using Fox

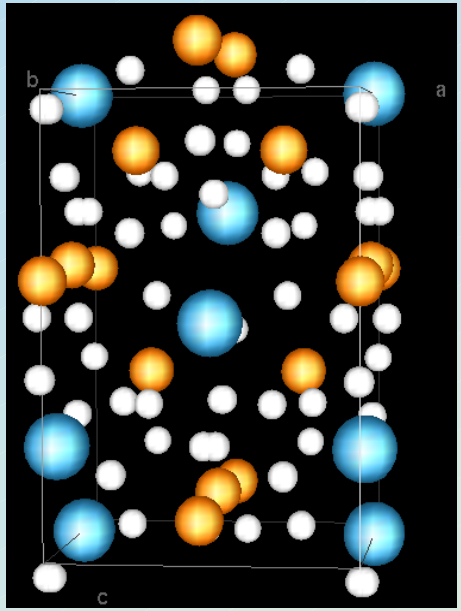
Inorganic

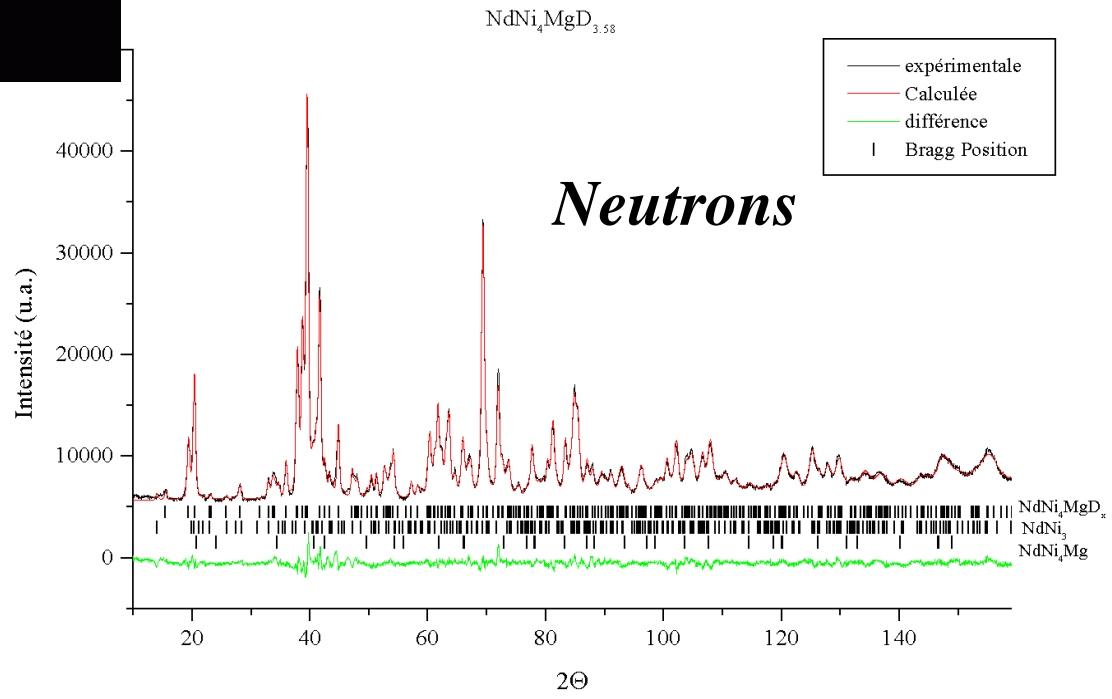
- $NdNi_4MgD_{3.6}$
- $Zr_3NiO_{0.6}D_{6.32}$
- $LaNi_2Mn_3D_{5.5}$
- $LaMg_2NiD_7$

...









M. Edgar (St Andrews, Scotland)
Chem. Commun. **8** (2002) 808

Hybrid Structure : $Al_2(H_3CPO_3)_3$

a=13.297 b=9.657 c=5.072 (89.6° 111.2° 92.1°) ***P-1***
17 atoms + 9 H

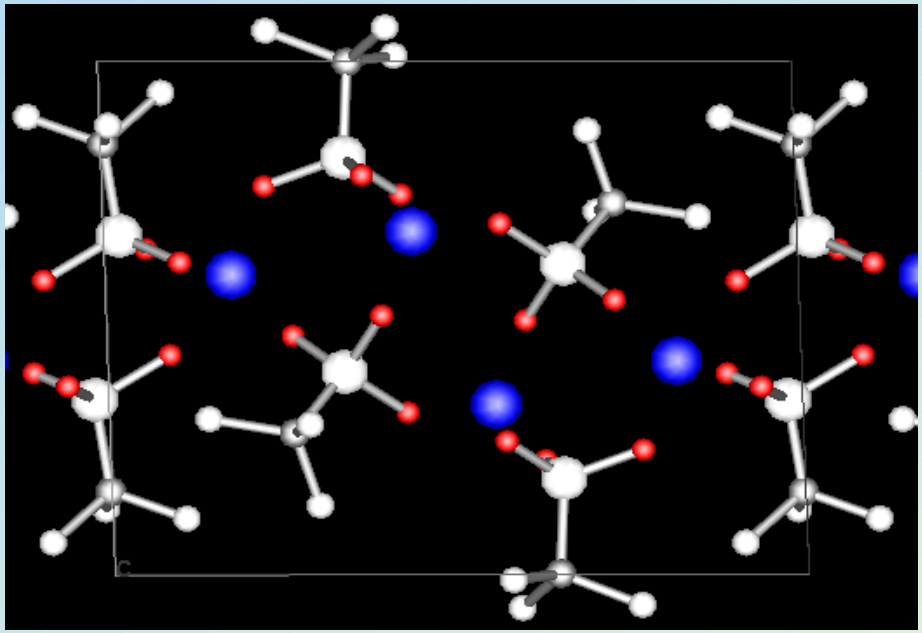
Solving through direct methods : failed

RMN ^{13}C ^{27}Al ^{31}P : identification of 5 building blocks
- 3 non-equivalent H_3C-PO_3 fragments
- 2 Al non-equivalent, one in tetrahedral and one in trigonal bypiramid

2 possible modelization in Fox

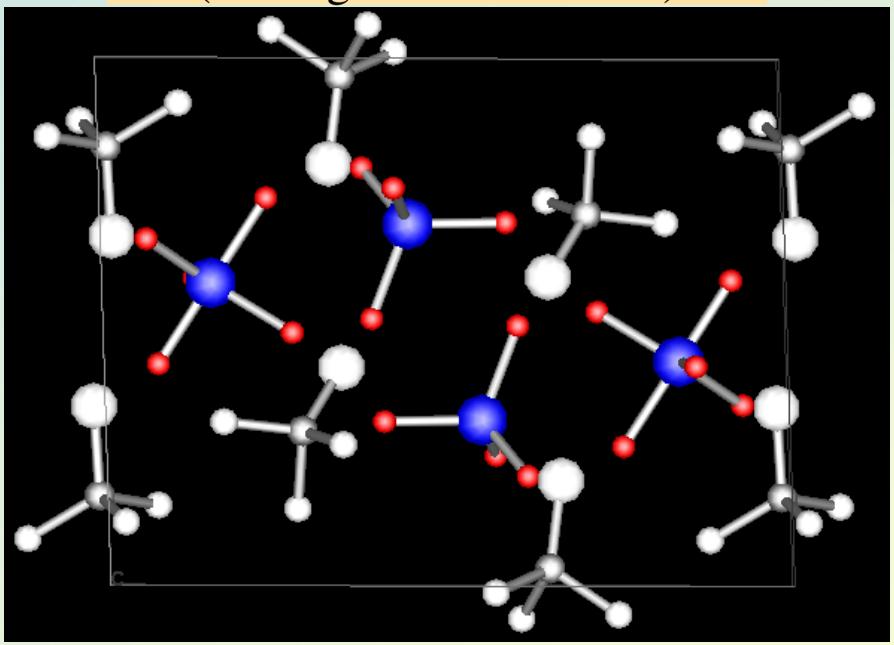
including the hydrogens improves the search, by steric effect

3 H_3C-PO_3 + 2 Al atoms
(24 Degrees of Freedom)



750.000 trials /12 min

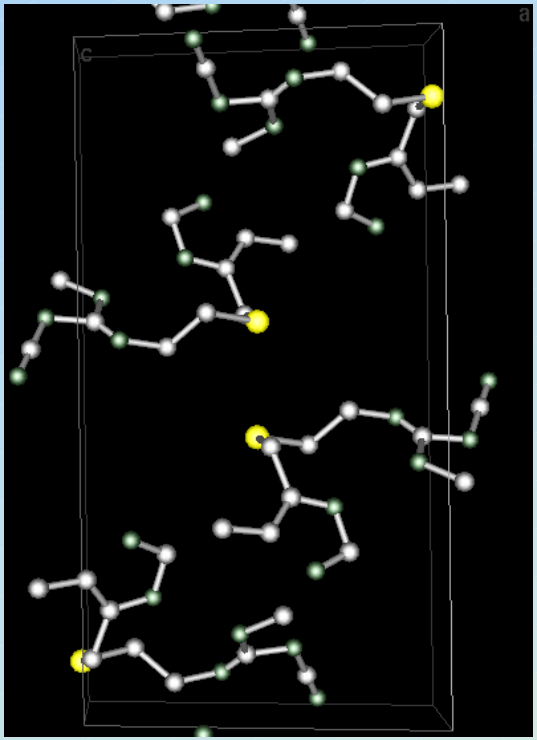
3 H_3C-P + AlO_4 + AlO_5
(27 Degrees of Freedom)



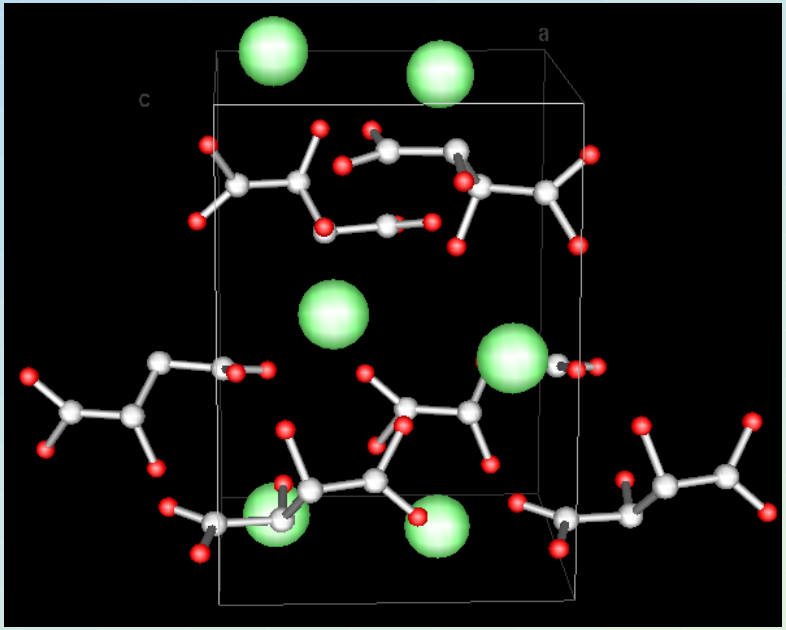
6.5 million trials /160 min

Tests on Organic Compounds

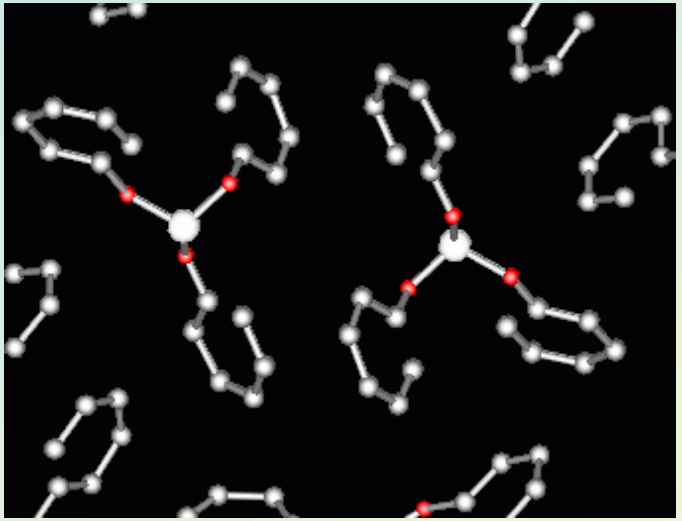
Cimetidine
14 DOF (8 torsion)
90% success after 4 million trials
(25 mn single, 45 mn powder)



K-Tartrate
14 DOF (5 torsion)
95% success after 1.2 million trials
12 mn powder



Triphenyl Phosphite
in R-3 : 12 DOF (6 torsion)
(a few 100.000 trials)
in R3 : 23 DOF (6+6 torsion)
(20 million trials or more...)



Conclusion

FOX : J. Appl. Cryst 35 (2002), 734

- modelize structure from any combination of building blocks *(use chemist's* a priori *knowledge)*
- automatic handling of special positions and building blocks connectivity
- multi-pattern joint optimization & multi-phase powder data
- new version with search of preferred orientation
- does not require individual structure factor extraction

- expandable (new algorithms, structure modelization, criteria...) : object-oriented library ObjCryst++
- fast

- Free for Linux & windows

- not a "black box"

Future of FOX :

- more friendly to organic compounds
- more intelligent algorithms

-User-friendliness and forgiveness still to be improved !
Depends on user feedback !!! Send user reports, feature requests !
open-source project => add your contribution
=> help by testing "development" versions

Get FOX at http://objcryst.sourceforge.net and from CCP14 mirrors

Acknowledgements

Samples & data:

- *L. Guénée*, *G. Renaudin*, *B. Bertheville* (University of Geneva, Switzerland)
- *V. Paul-Boncour* (CNRS Thiais, France)
- *M. Edgar* (St Andrews, Scotland)

Fox Development & ideas:

- *Yu. Andreev*
- Spacegroup & element info library: *R. Grosse-Kunstleve* (LBL)
- *A. Markvardsen & W. David*

CCP14:

- *L. Cranswick*

Project Supported by the *Swiss National Science Foundation*

Future Developments

Improve Molecule Modelization

Z-matrix approach is too “rigid” : diminishes the advantages of reducing the number of DOF

-> Use a description from *individual atoms*, plus *restraints* (bond lengths, angles, dihedral angles)

Use Maximum Likelihood

- more general approach than current cost functions
- the likelihood takes into account the imperfections of the model => better convergence ?
- can handle partially disordered structures

New Restraints (?)

- Chemical composition
- Density
- Atom Coordination
- Energy minimization (??)
- Use Calculated Enveloppe ?

Introduce Derivative Calculations

-> New Algorithms (Hybrid MC)

YOU Can Help !

*-> Get **development versions** of Fox and test !*

-> Supply code !

Fox is not my main research project any more