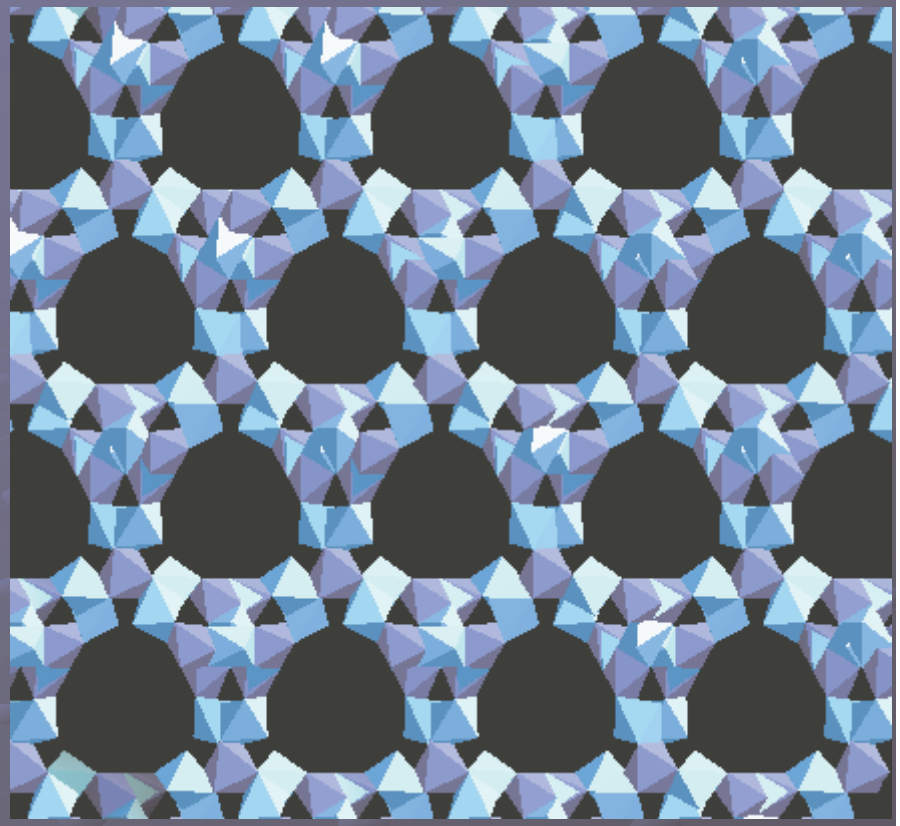
Université de Versailles

Institut Lavoisier

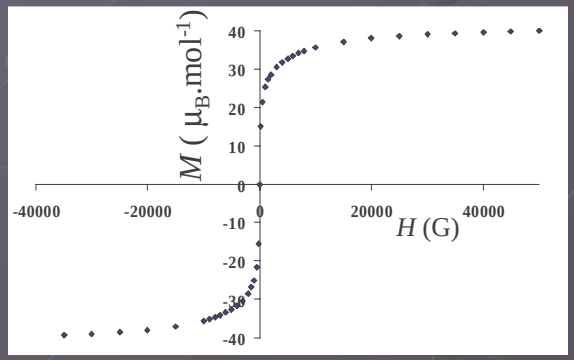
Résolutions structurales complexes à partir de données synchrotron : des méthodes "classiques" vers une approche dans l'espace direct

Nathalie Guillou

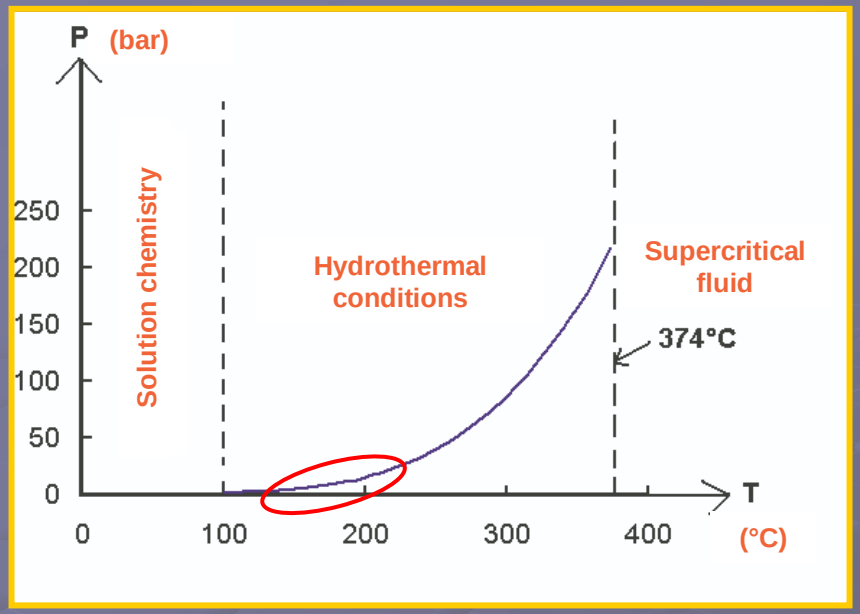
- **Zeolitic Properties**
  - Ion Exchange
  - Catalysis
  - Sorption
- **Organic Properties**
  - Diversity
  - functionality
  - chirality
- **Transition Metal Properties**
  - Magnetic, electronic, spectroscopic
  - Uncoordinated metal sites
  - redox centers



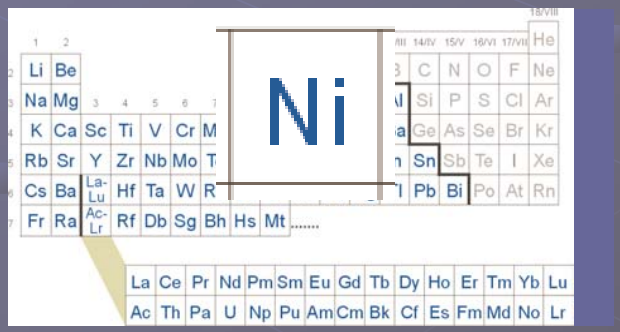
Mil77 is a pure cooperative ferromagnet



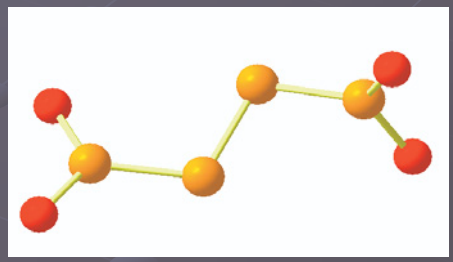
N. Guillou, C. Livage, M. Drillon, G. Férey, *Angew. Chem. Int. Ed.*, **42**, 5314 (2003)

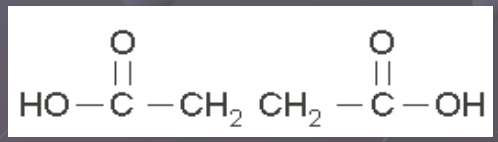


Inorganic condensation



Organic to avoid formation of simple dense oxides





$Ni_7[(C_4H_4O_4)_4(OH)_6(H_2O)_3].7H_2O$ or MIL-73

High-resolution synchrotron data collection on the Swiss-Norwegian Beamline at the ESRF (λ = 0.7999 Å)

Indexing – (DICVOL91)

monoclinic solution $P2_1/c$
a = 7.8597(1) Å
b = 18.8154(3) Å β = 92.0288(9)°
c = 23.4377(4) Å
M_{20} = 34 and F_{20} = 210 (0.0026, 36)

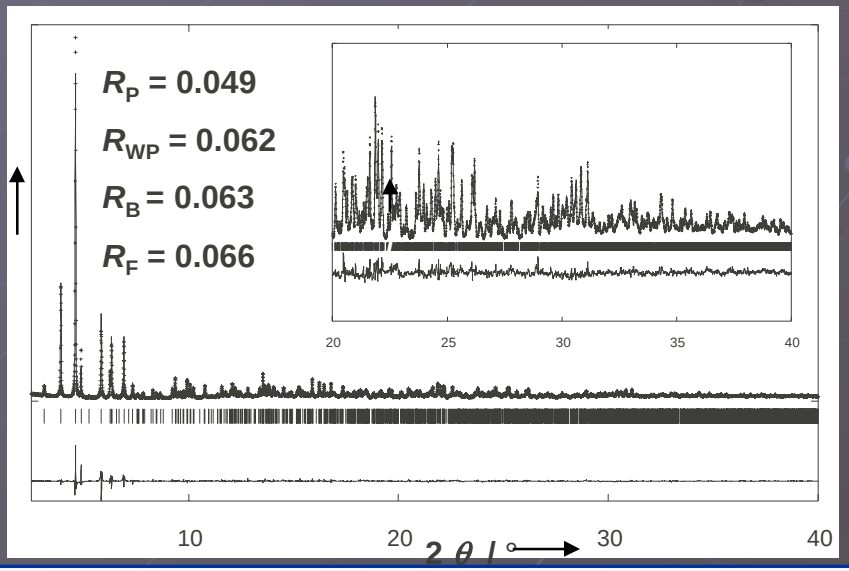
Structural determination : SHELXTL
2921 reflections extracted (FullProf)
Direct methods calculations (SHELXS)

location of:
- the 7 independent Ni atoms
- 17 surrounding oxygens
- few carbons

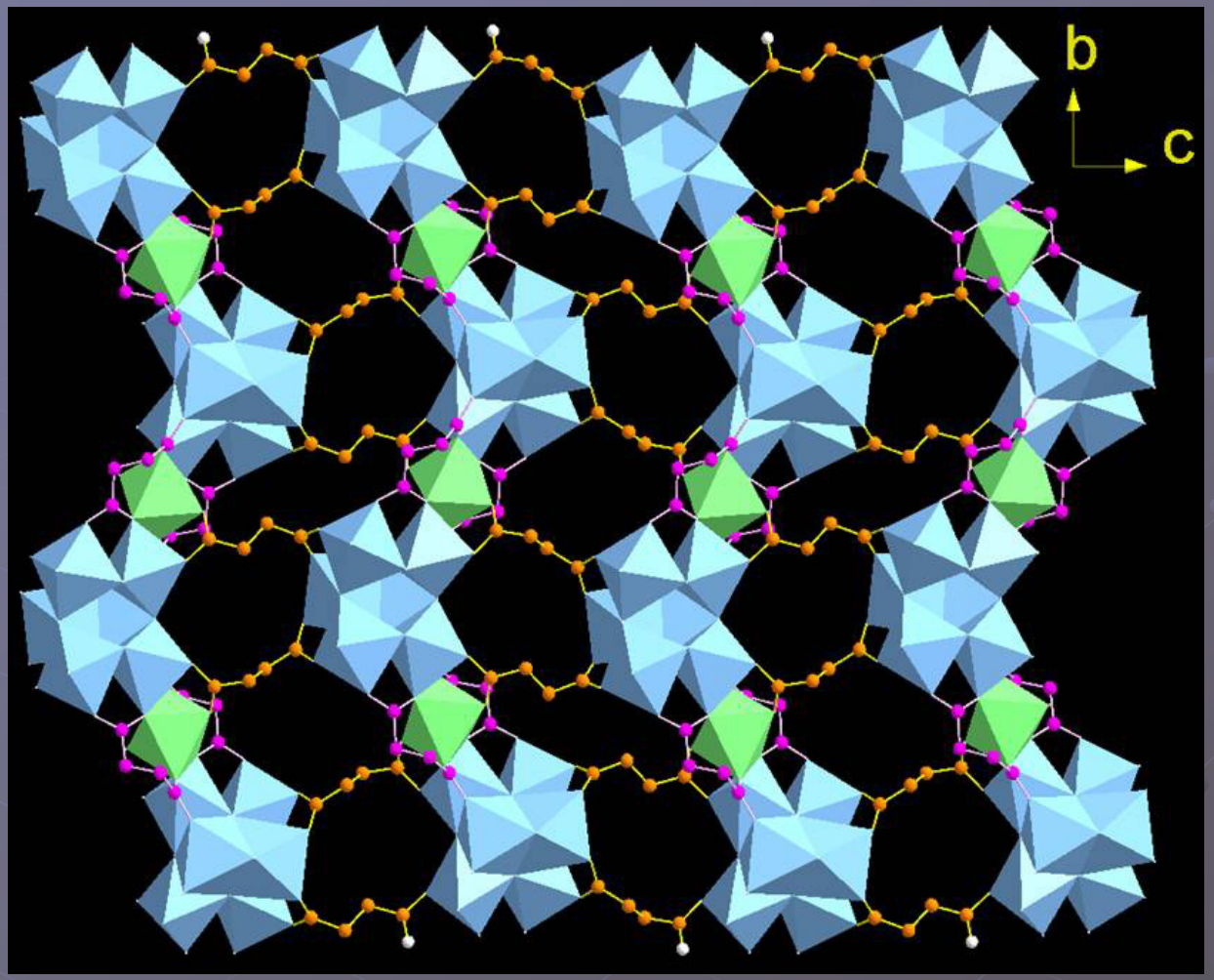
Rietveld refinement (FullProf - WinPLOTR)
R_B = 0.30 R_F = 0.20

Difference Fourier calculation (SHELXL)

Rietveld refinement

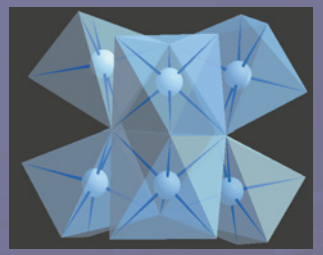


$Ni_7[(C_4H_4O_4)_4(OH)_6(H_2O)_3].7H_2O$ or MIL73



N. Guillou, C. Livage, W. van Beek, M. Noguès, G. Férey, *Angew. Chem. Int. Ed.,* **42**, 644 (2003)

$Ni_7[(C_4H_4O_4)_4(OH)_6(H_2O)_3].7H_2O$ or MIL73



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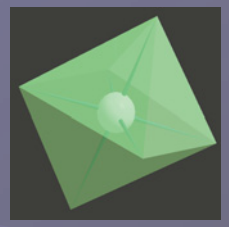

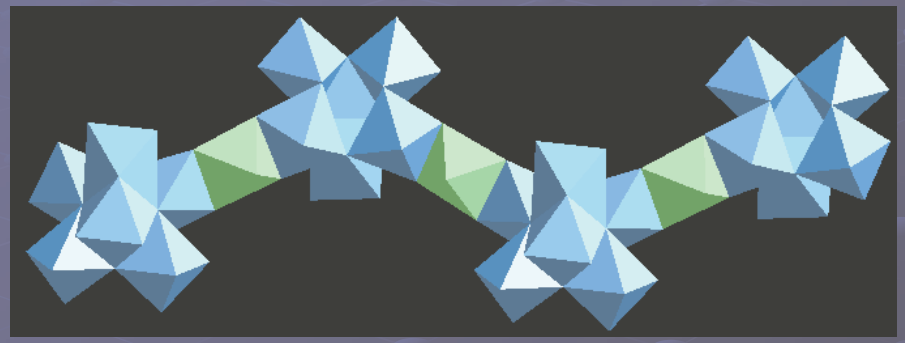

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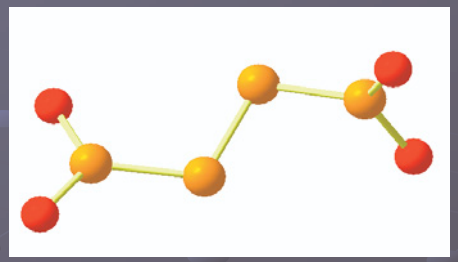
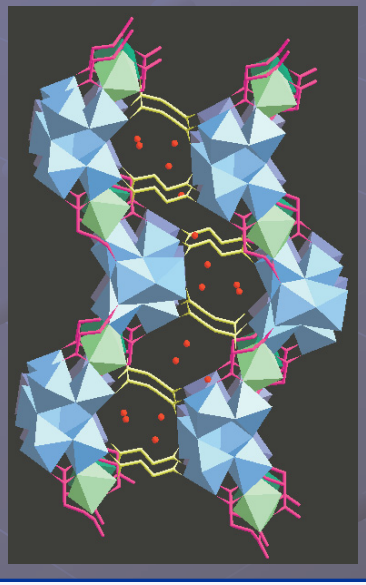
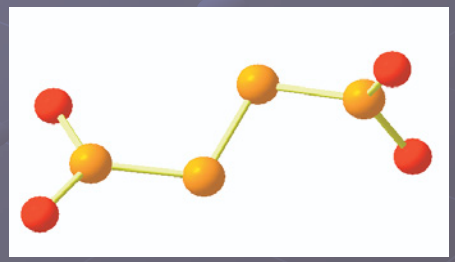
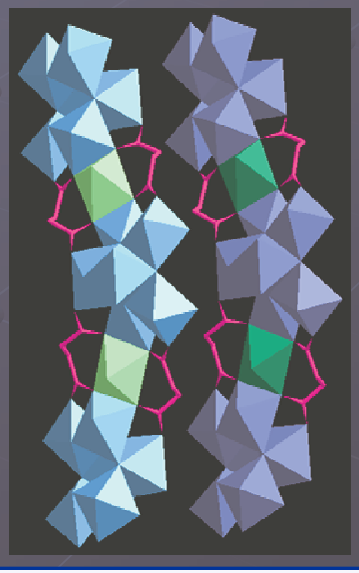








$Ni_7(OH)_2(C_4H_4O_4)_6(H_2O)_2\ 1.6H_2O$

High-resolution synchrotron data collection on the Swiss-Norwegian Beamline at the ESRF (λ = 0.7999 Å)

Indexing – (DICVOL91)

monoclinic solution P2/c
M_{20} =40 and F_{20} = 156 (0.0018,72)

Rhombohedral solution R-3c
a =21.0372(1) Å c = 45.7975(4) Å
V = 17552.9(3) Å^3

Checking for a higher symmetry (Le Page)

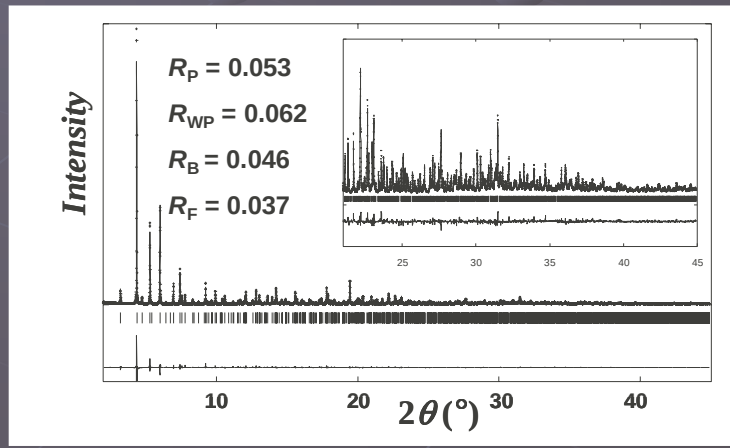
Structural determination : SHELXTL
1253 reflections extracted (FullProf)
Direct methods calculations (SHELXS)

location of:
- the 4 independent Ni atoms
- 13 surrounding oxygens

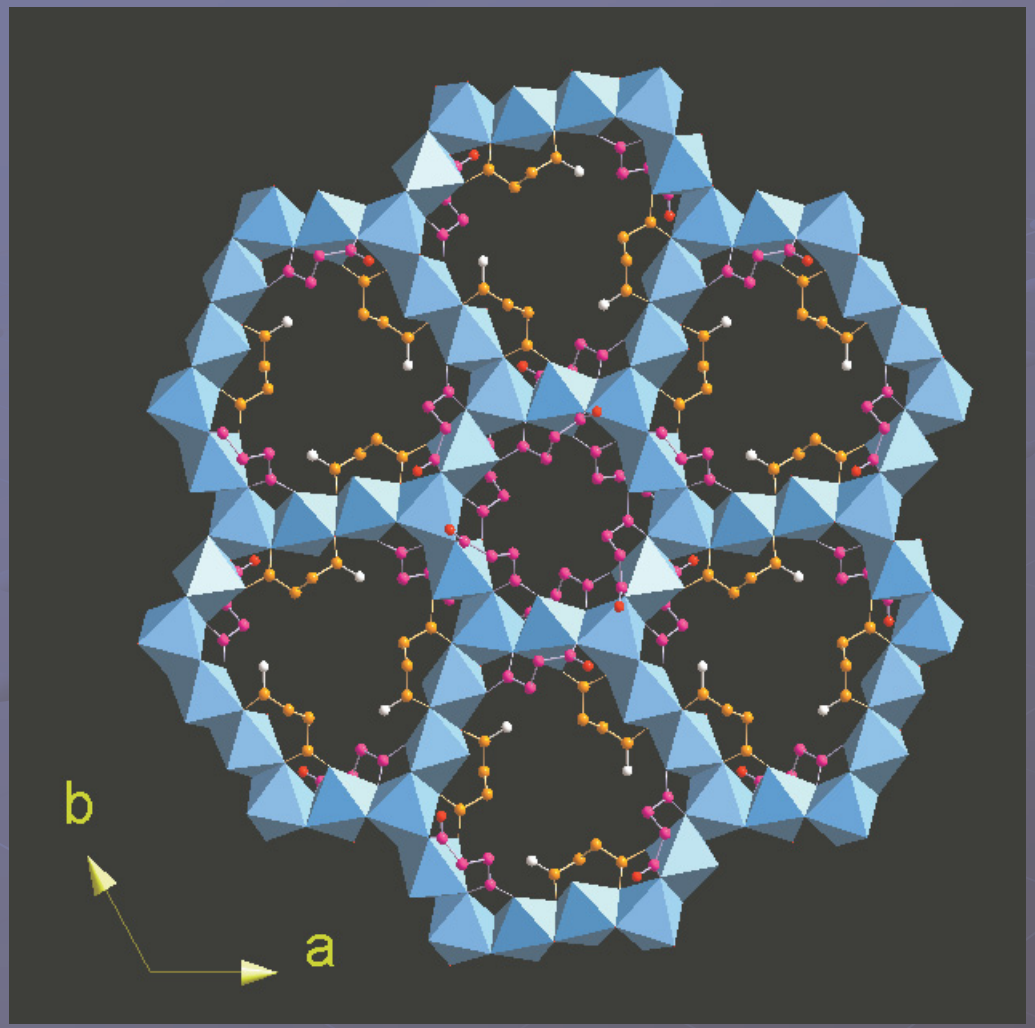
Rietveld refinement (FullProf - WinPLOTR)
R_B = 0.28 R_F = 0.17

Difference Fourier calculation (SHELXL)

Rietveld refinement



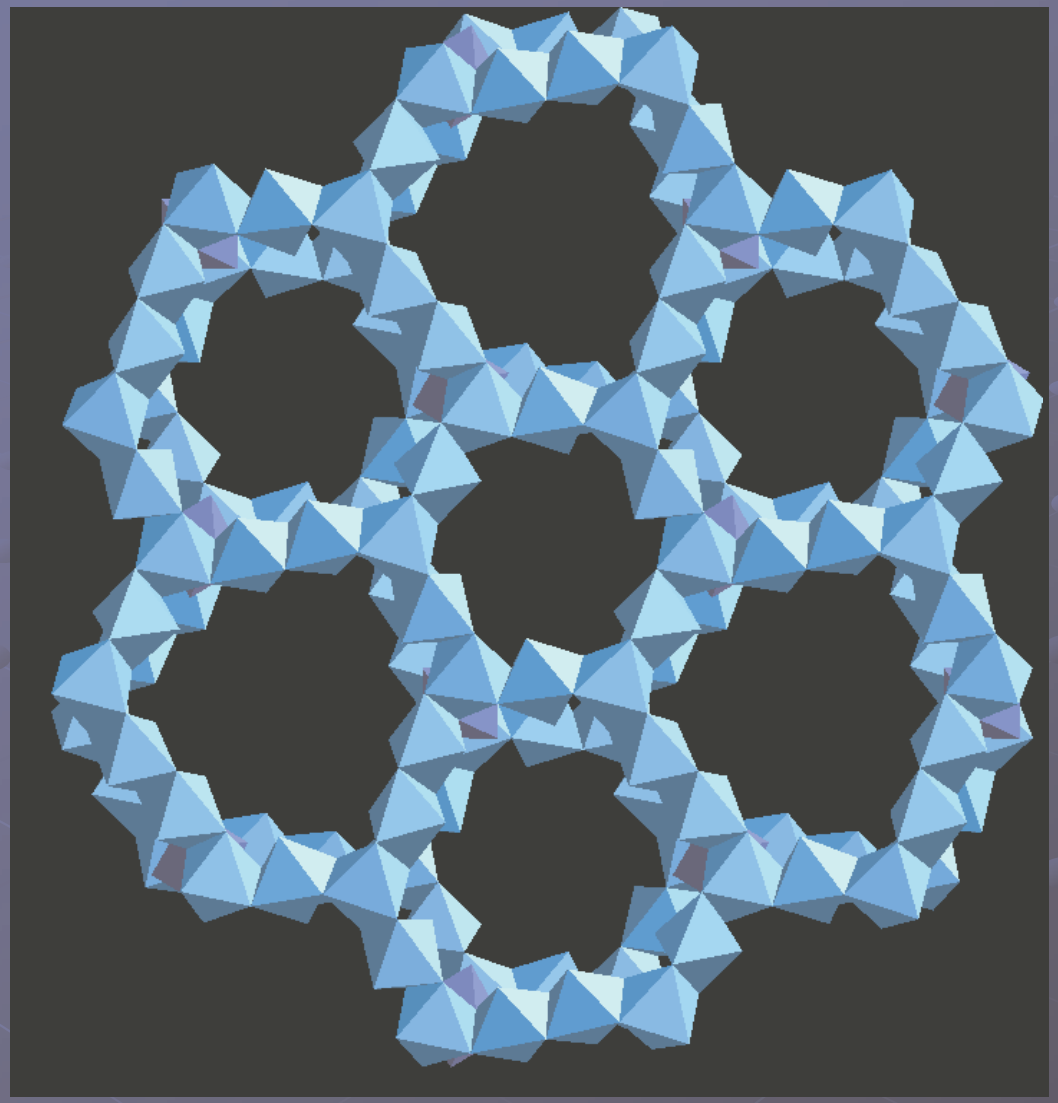
$Ni_7(OH)_2(C_4H_4O_4)_6(H_2O)_2.1.6\ H2O$

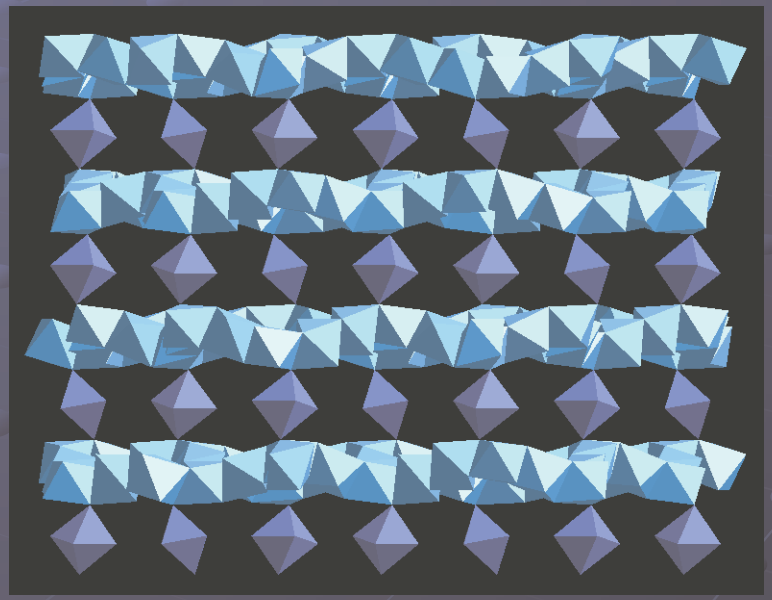


- First 3D M – O – M dicarboxylate
- 15- and 12- membered rings of edge-sharing NiO_6 octahedra

P. M. Forster, A.K. Cheetham, *Angew. Chem. Int. Ed.*, **41**, 457 (2002)

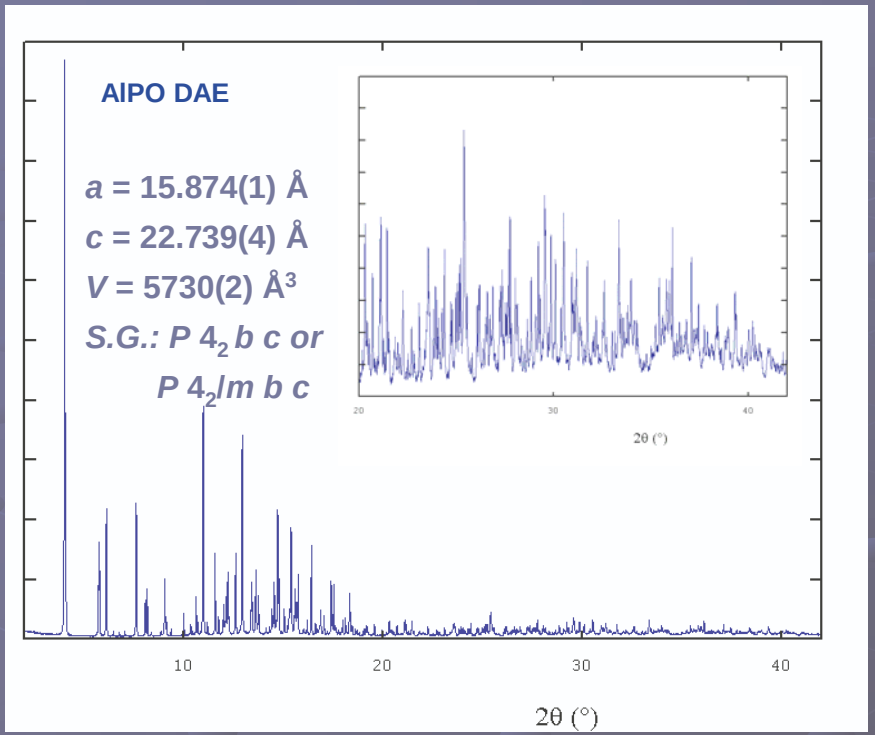
$Ni_7(OH)_2(C_4H_4O_4)_6(H_2O)_2.1.6\ H_2O$

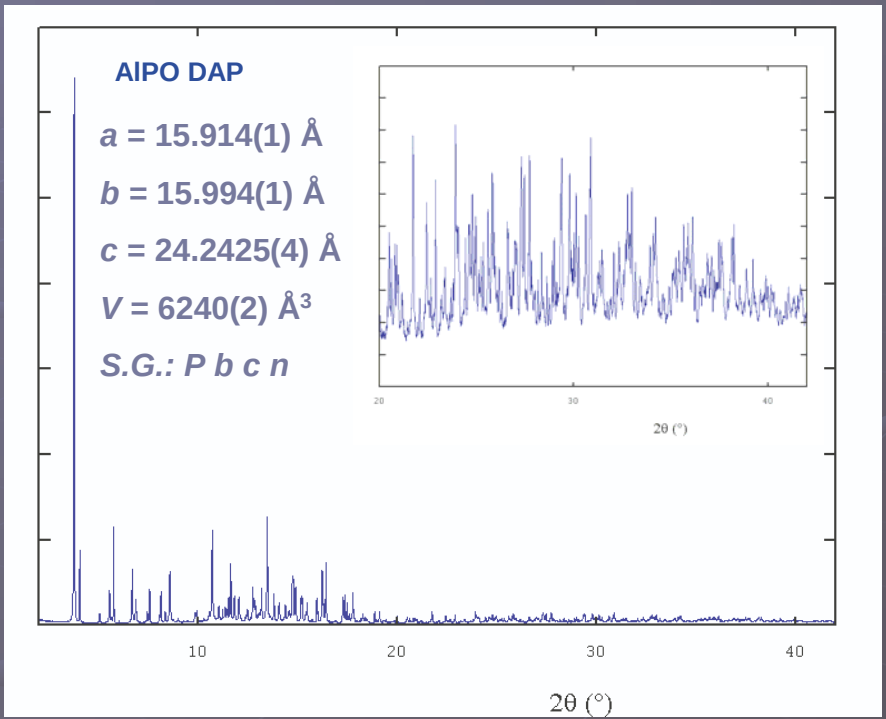




What to do now with complex inorganic polycrystalline materials without any atomic contrast?

Synchrotron data (ESRF, SNBL) (λ = 0.79986)





Simulation ← **A multi-step approach ?** → NMR

↓

Diffraction

Can we apply this method to our complex AlPos ?
First case: AlPO-dae

NMR → Hydrogen interations disturb chemical shifts
difficult interpretation

→ Probably 7 P for 5 Al (chemical analysis = 1.43)

→ Independent Al: 2 AlO_4, 1 AlO_5 and 2 AlO_6 with the same multiplicity
Most in agreement with *P* 4_2 *b c*

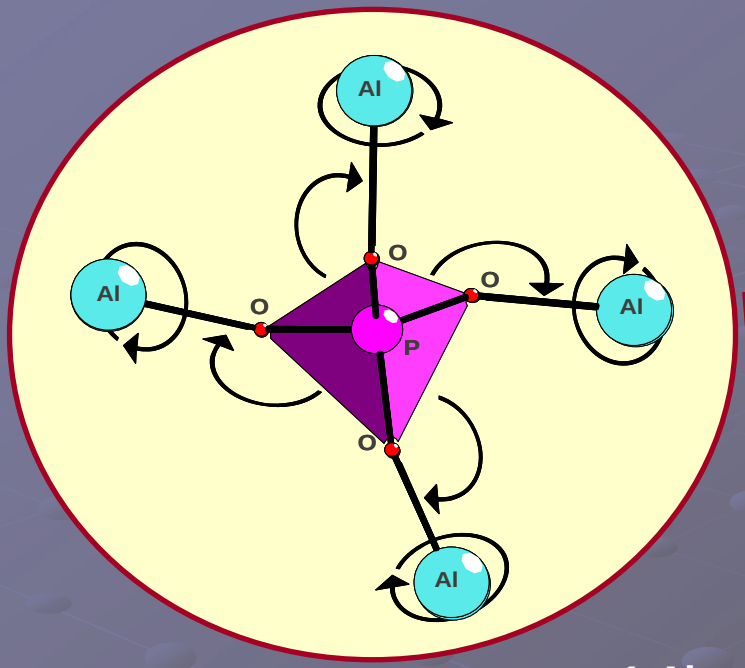
Simulation → AASBU : impossible (no integrant unit from NMR)

Diffraction → Direct methods (EXPO and shelxs) : unclear
impossible to find all Al and P atoms
$|E^2-1| = 0.732$ => Spacegroup : *P*4_2 *b c*

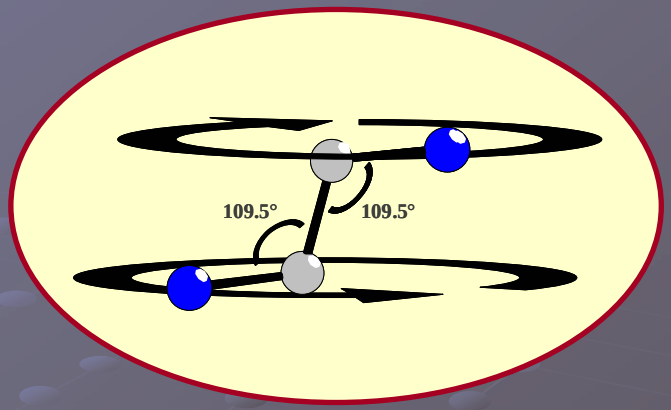
71 parameters ← Simulated annealing (FOX) with 7 PO_4, 5
Al and 2 organic moieties : no
convergence

How to solve the problem ?

1 flexible unit PO_4Al_4

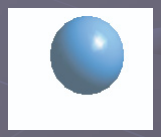


2 amines

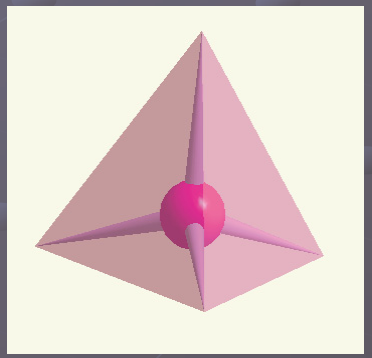


Fox

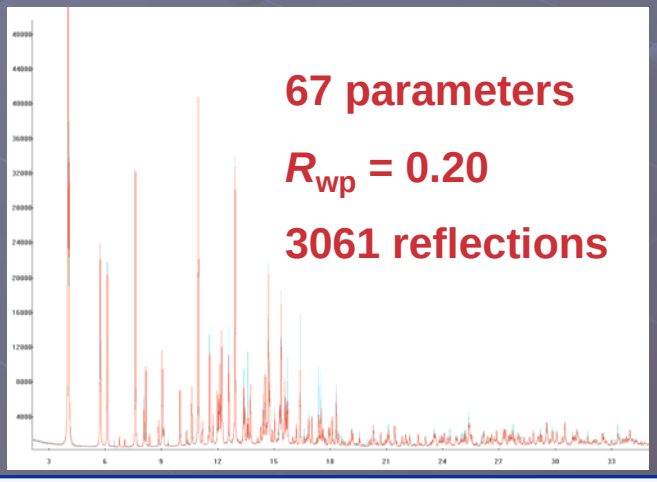
1 Al



6 PO_4



Randomized positions

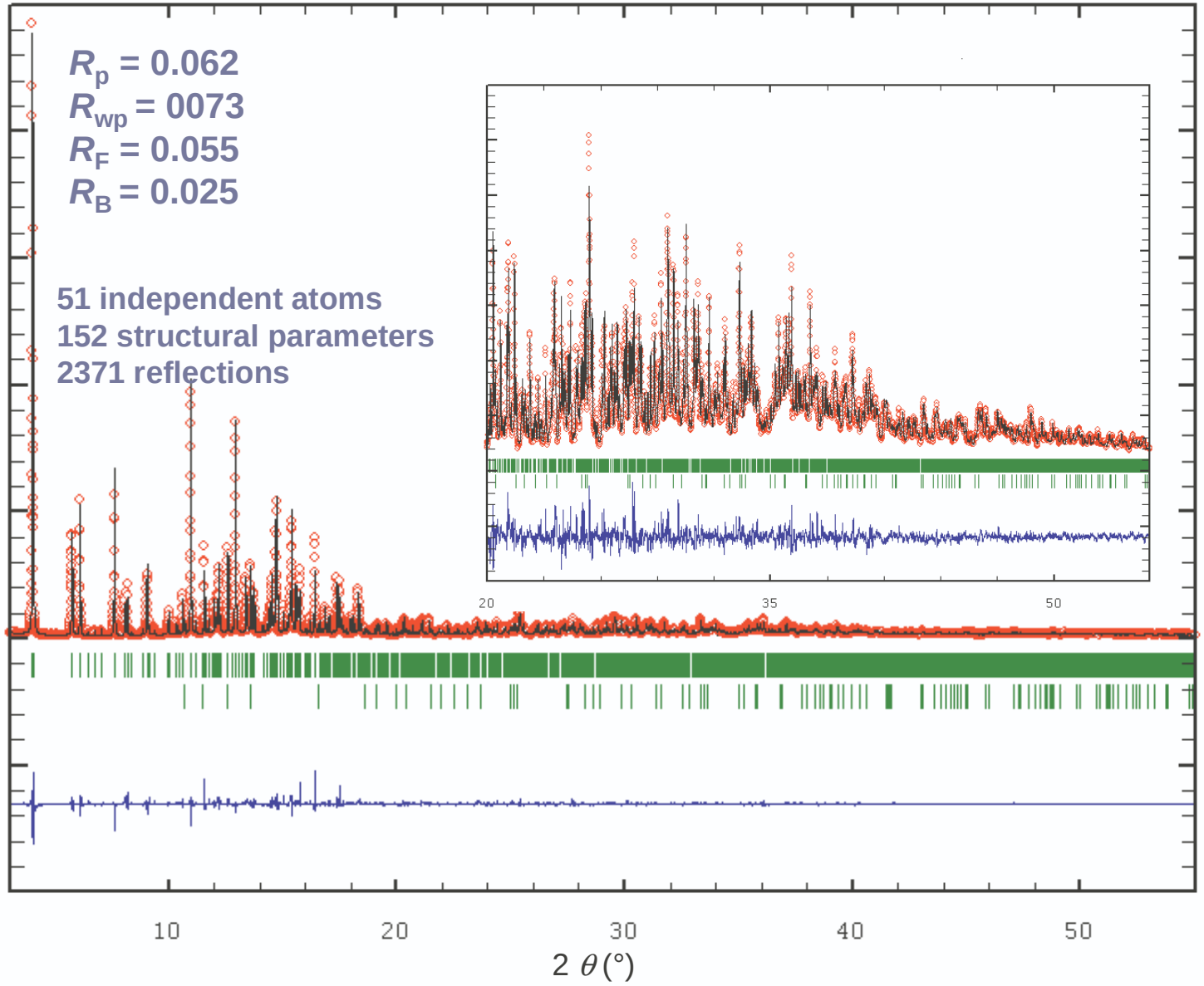


67 parameters

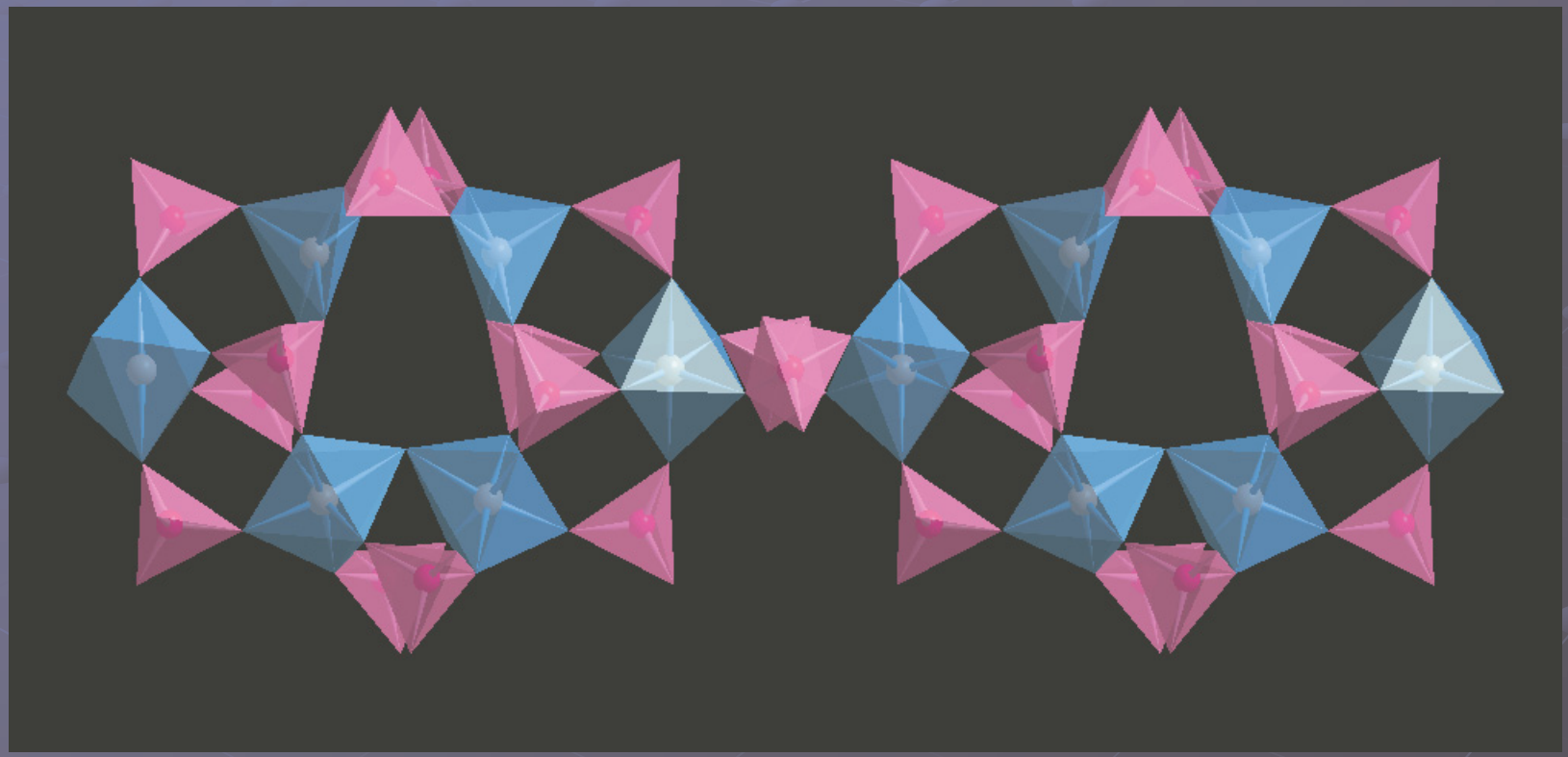
R_{wp} = 0.20

3061 reflections

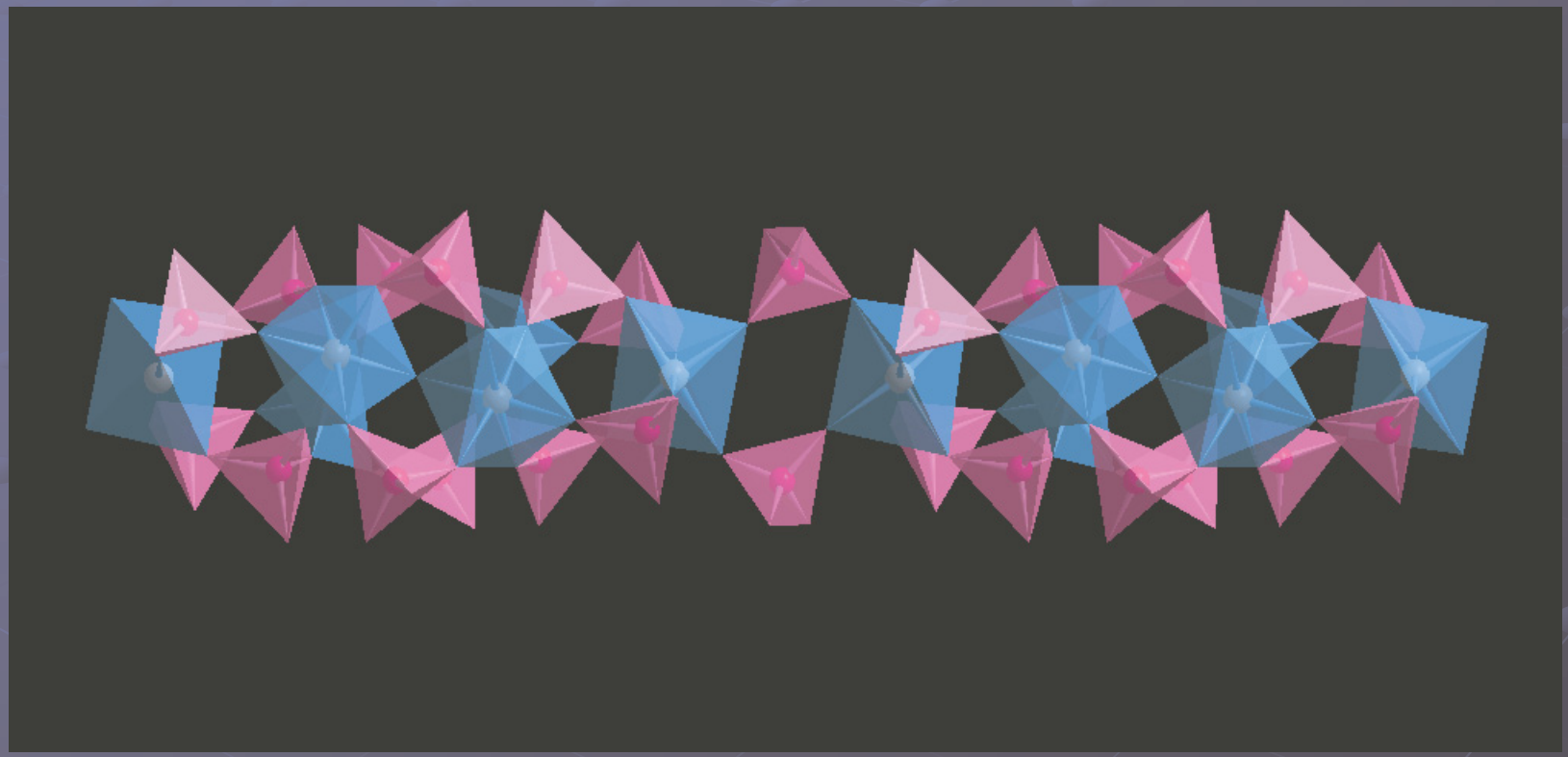
$Al_{10}(PO_4)_9(HPO_4)_5(OH)$ $(H_3N\text{-}CH_2\text{-}CH_2\text{-}NH_3)_4$ 4 H_2O



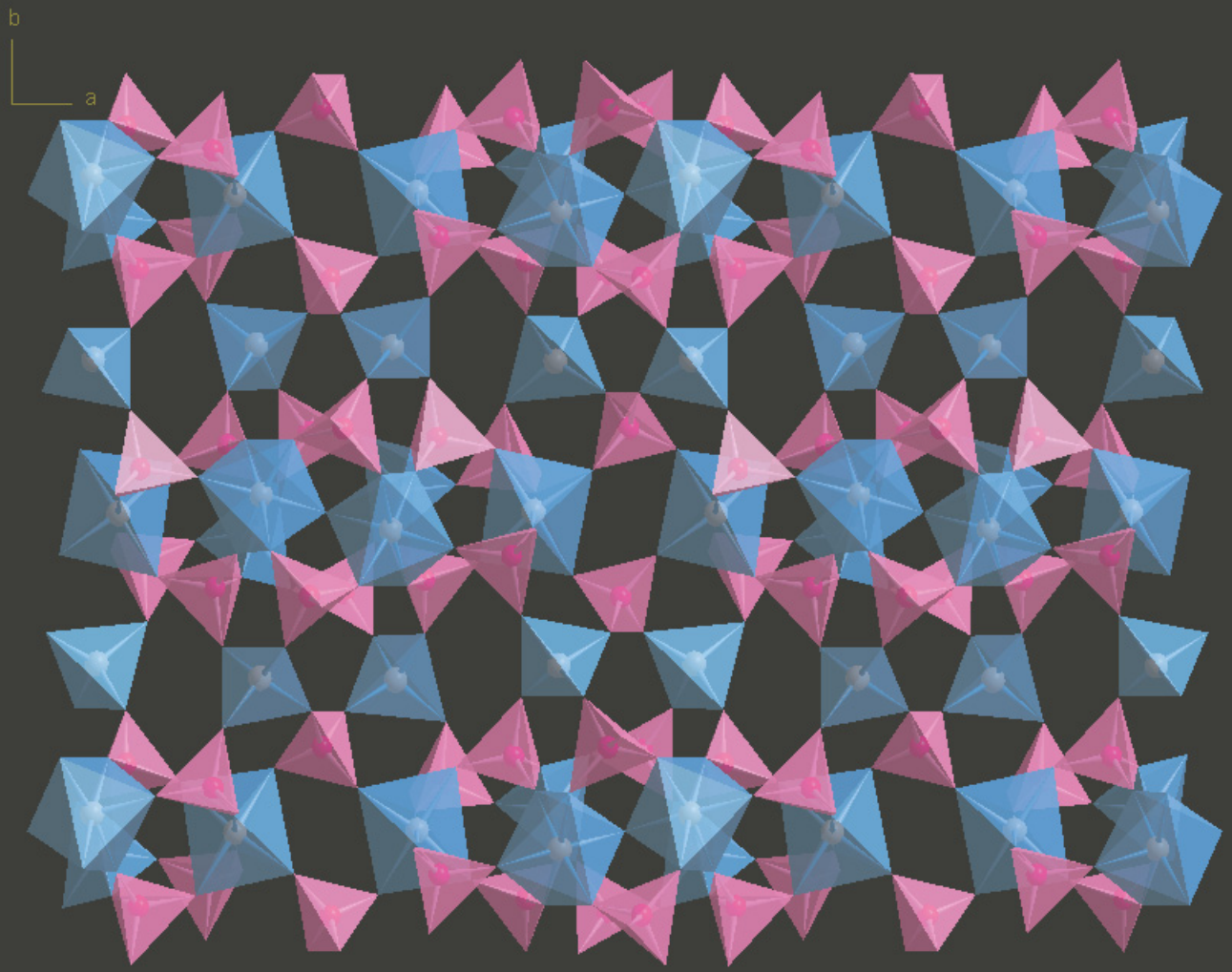
AlPO-dae - $Al_{10}(PO_4)_9(HPO_4)_5(OH)$ $(H_3N\text{-}CH_2\text{-}CH_2\text{-}NH_3)_4$ 4 H_2O



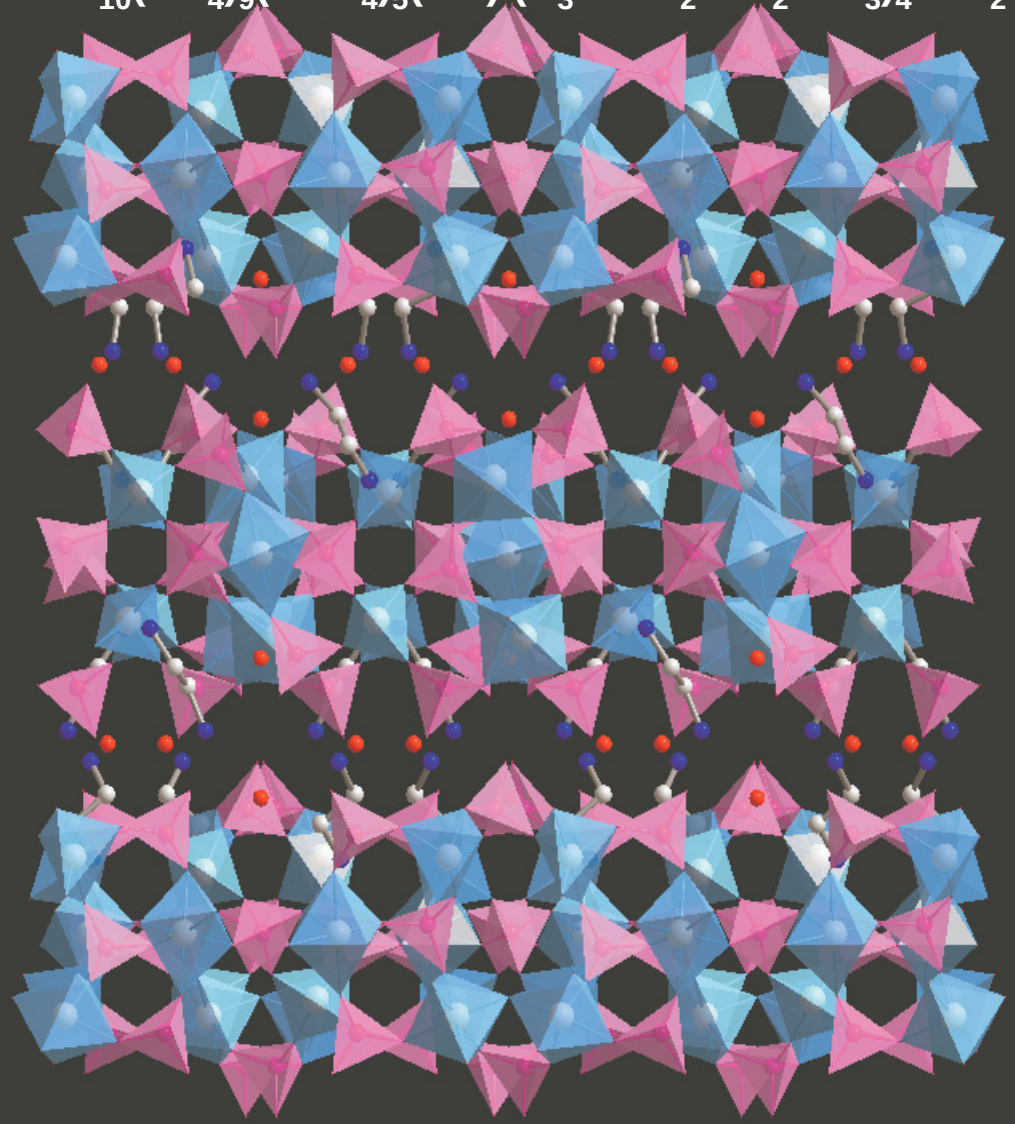
AlPO-dae - $Al_{10}(PO_4)_9(HPO_4)_5(OH)\ (H_3N\text{-}CH_2\text{-}CH_2\text{-}NH_3)_4\ 4\ H_2O$



AlPO-dae - $Al_{10}(PO_4)_9(HPO_4)_5(OH)$ $(H_3N\text{-}CH_2\text{-}CH_2\text{-}NH_3)_4$ 4 H_2O



AlPO-dae - $Al_{10}(PO_4)_9(HPO_4)_5(OH)$ $(H_3N\text{-}CH_2\text{-}CH_2\text{-}NH_3)_4$ 4 H_2O



AlPO-dap

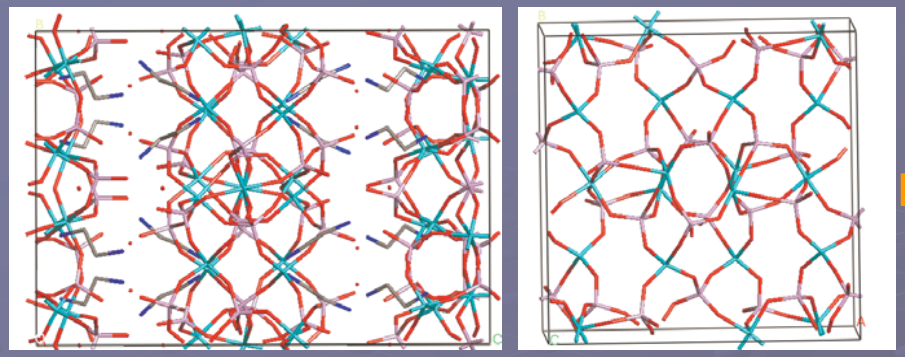
NMR → Probably 7 P for 5 Al (chemical analysis = 1.47)

→ 6 independent Al: 2 AlO_4 (2) , 2 AlO_5 (2) and 2 AlO_6 (1)
7 independent P
In agreement with *P b c n*

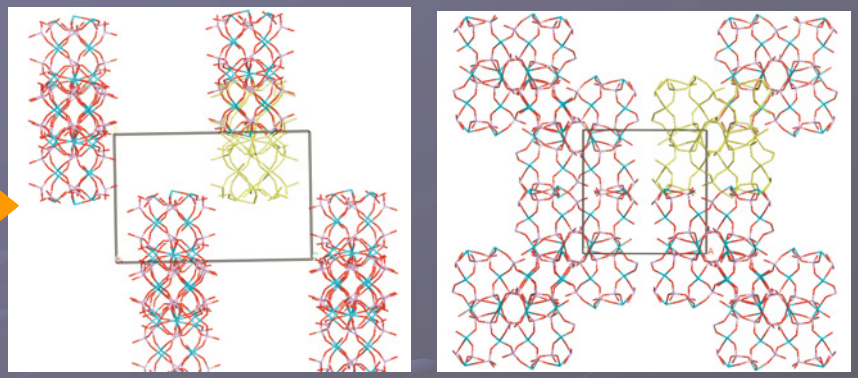
Simulation → AASBU : impossible (no integrant unit from NMR)

Diffraction → Simulated annealing (FOX) with 1 PO_4Al_4, 6 PO_4, 2 Al and 2 organic moieties
Starting positions of inorganic objects deduced from AlPO-dae structure (Materials Studio)

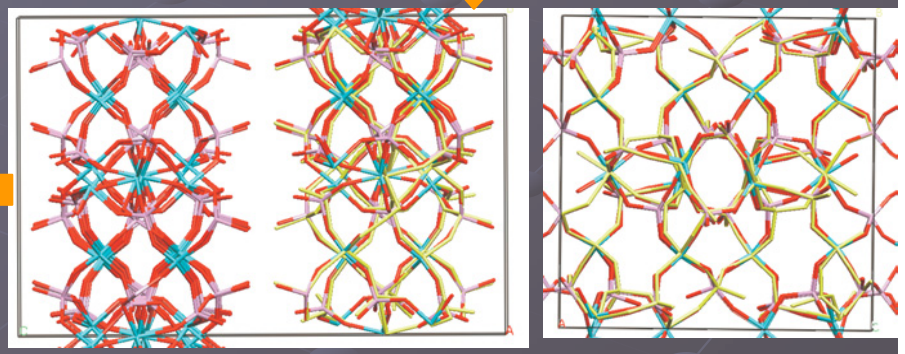
AlPO-dap



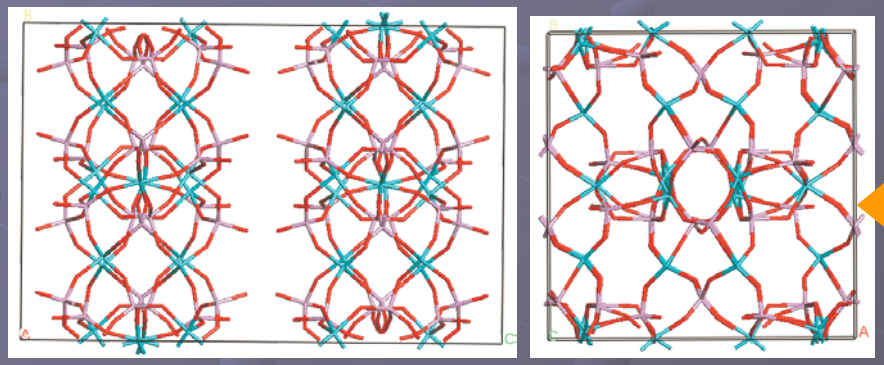
Calculation of all atomic coordinates of an isolated layer



Introduction of this layer in the orthorhombic unit cell – s.g *P b c n*



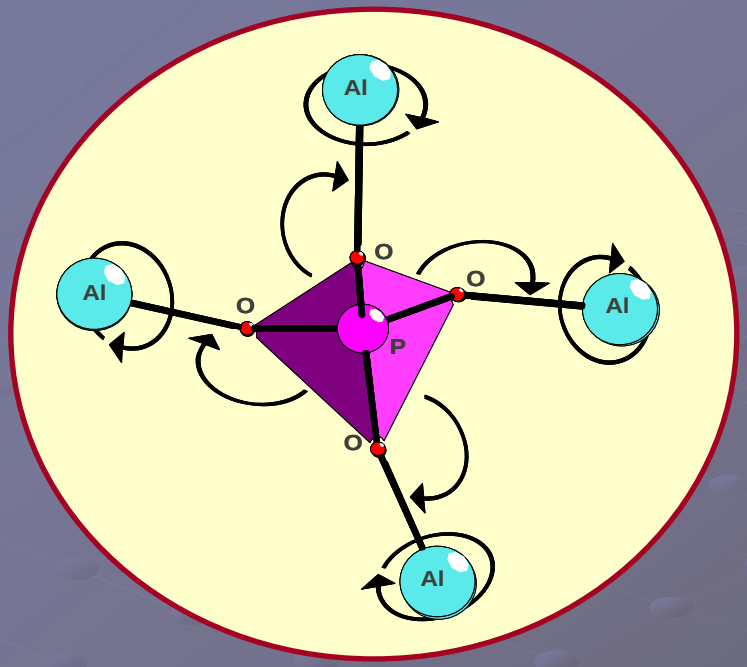
Series of translations and rotations of the layer until exact overlapping of atoms



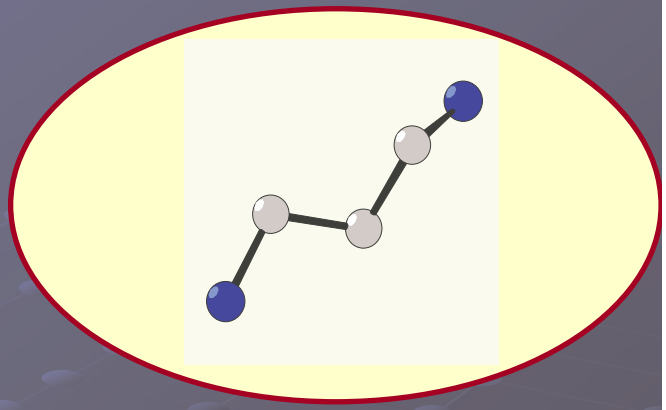
Removal of all redundant atoms

AlPO-dap

1 flexible unit PO_4Al_4

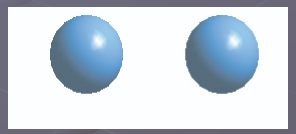


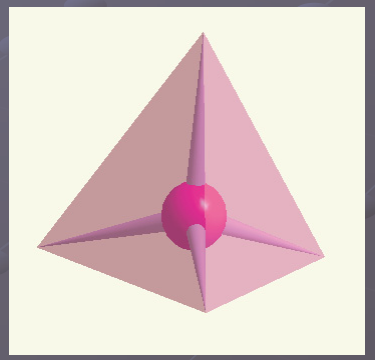
2 amines



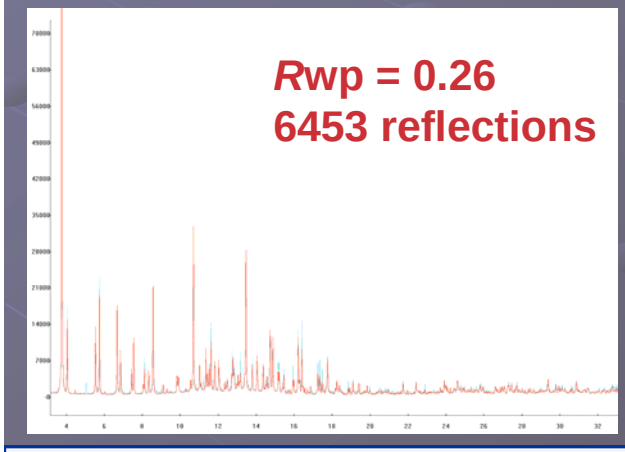
Fox

2 Al



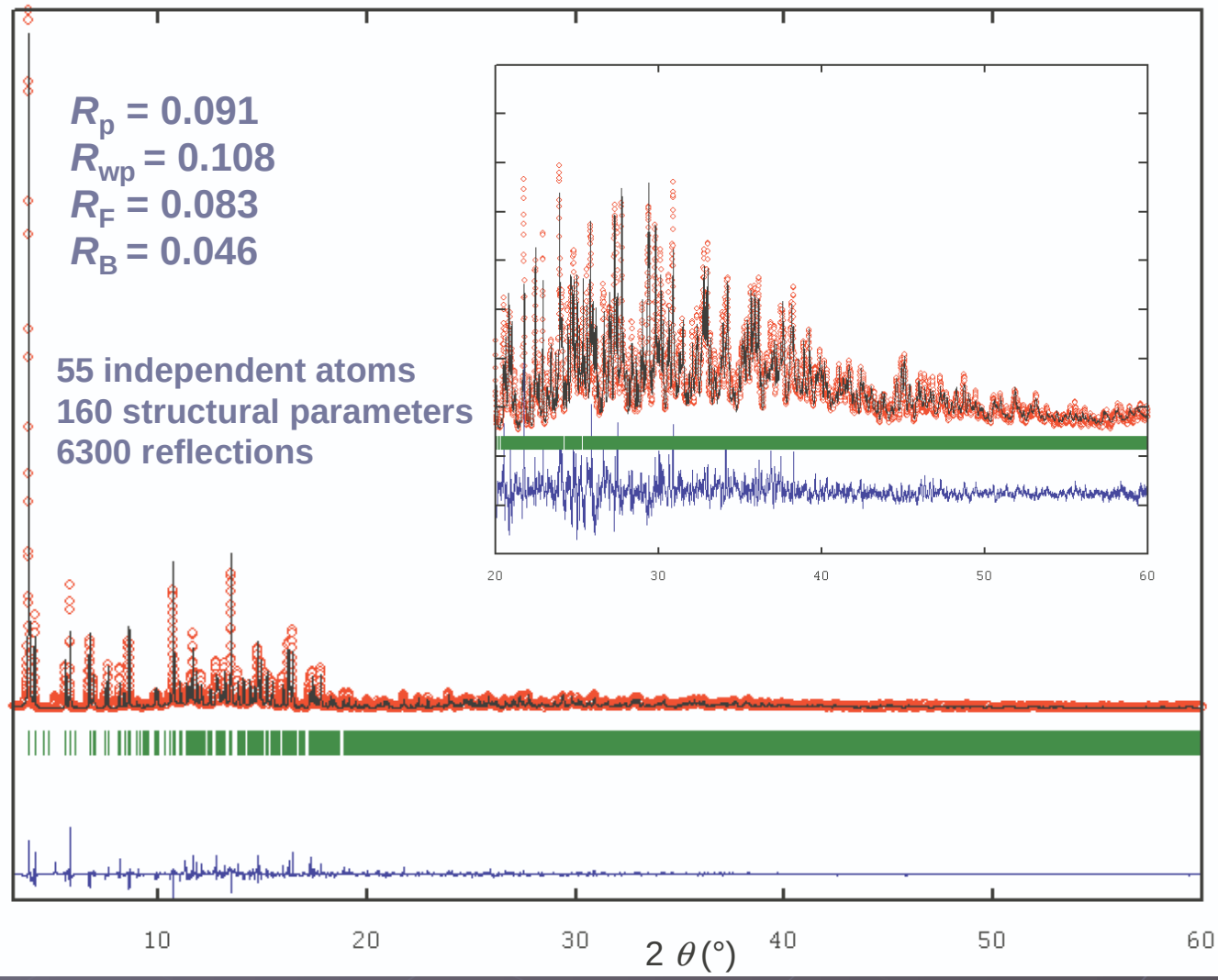


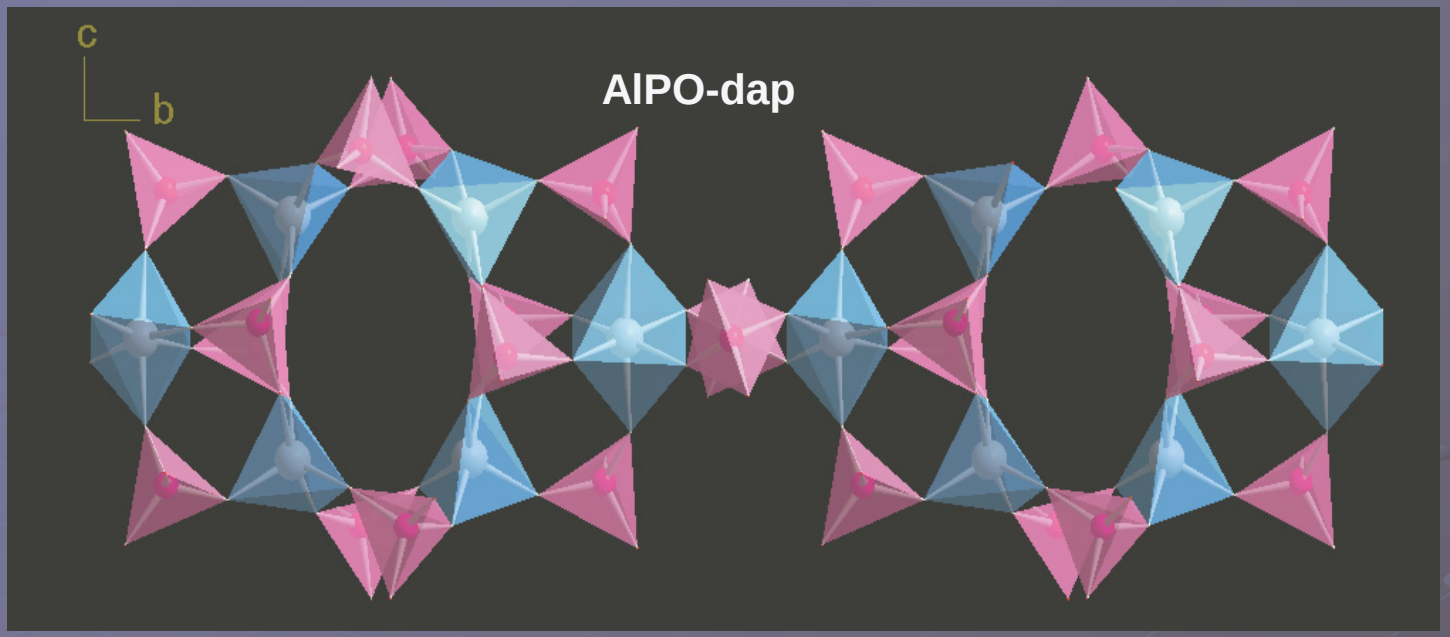
6 PO_4

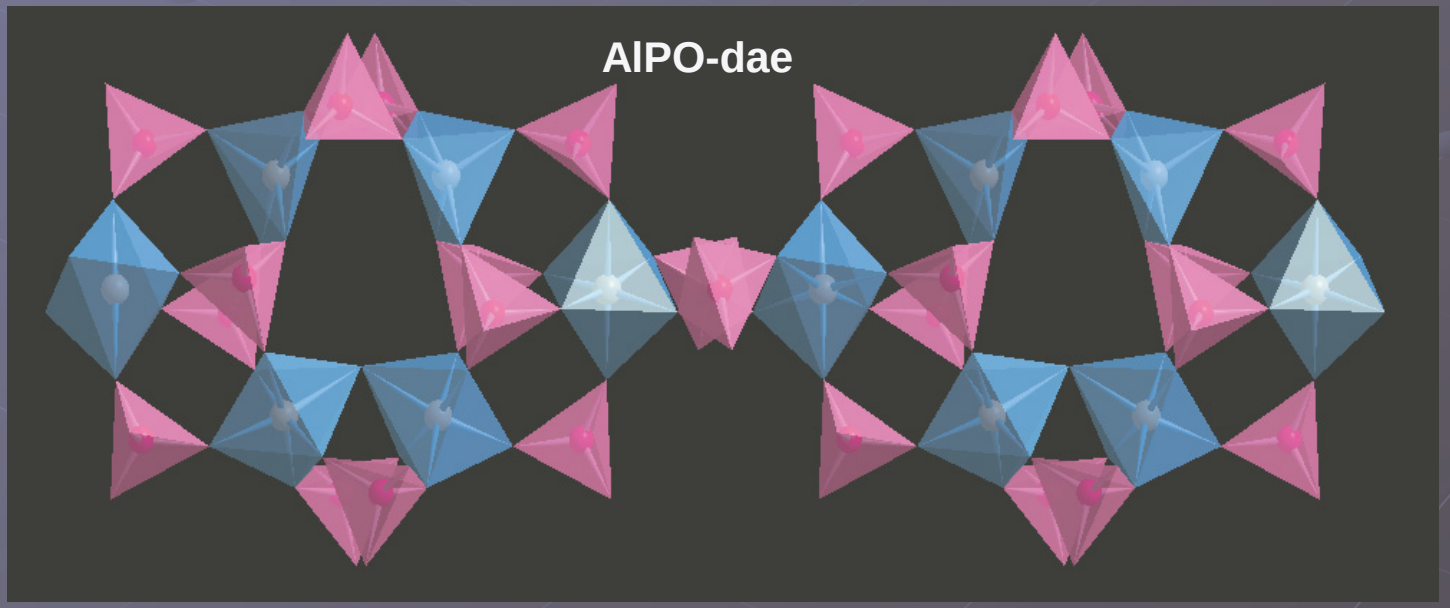


Initial positions of the inorganic layer deduced from the AlPO-dae structure

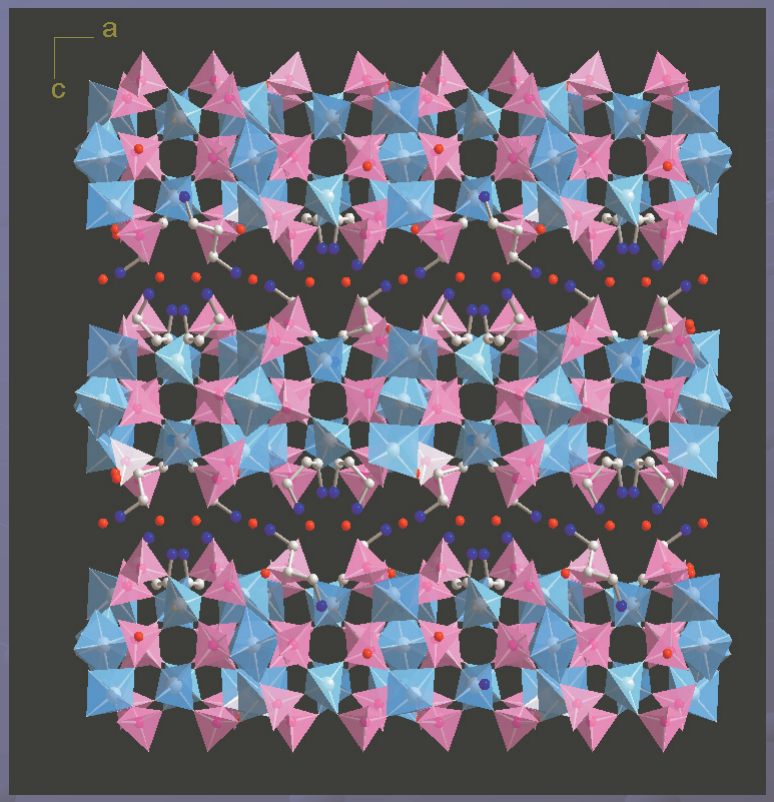
$Al_{10}(PO_4)_{10}(HPO_4)_4(H_3N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_3)_4\ 5.5\ H_2O$



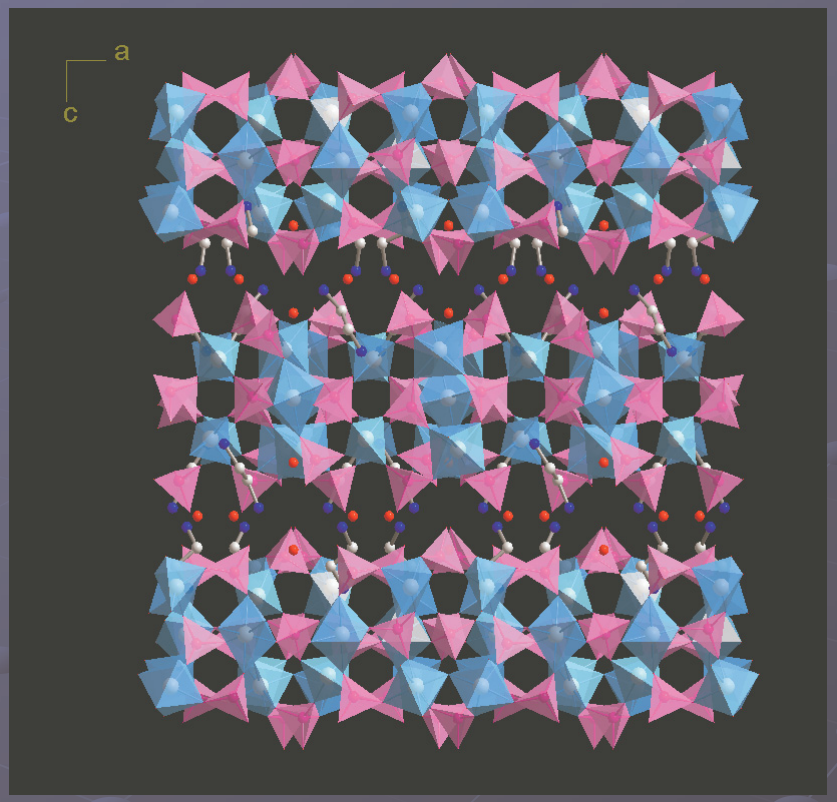

c
b
AlPO-dap


AlPO-dae

AlPO-dap



AlPO-dae



Acknowledgments

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- Julien Dutour, Dr. Caroline Mellot-Draznieks and Dr. Francis Taulelle

- Wouter Van Beek (SNBL, ESRF)

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