Crystal structures from powder diffraction, principles, difficulties and progress

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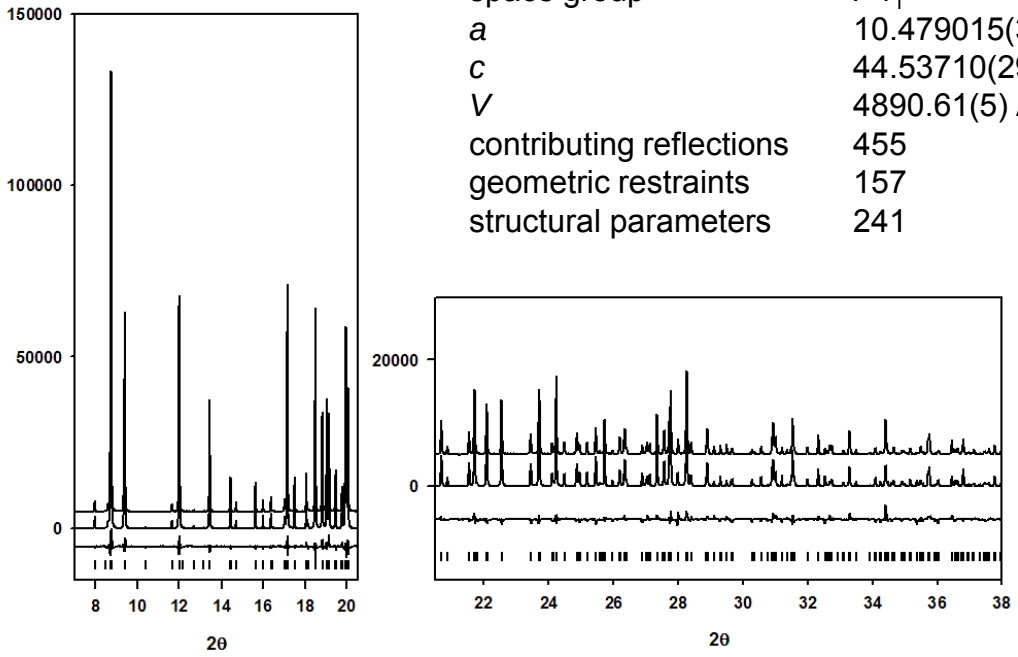
Crystal structures from powders, where we are?

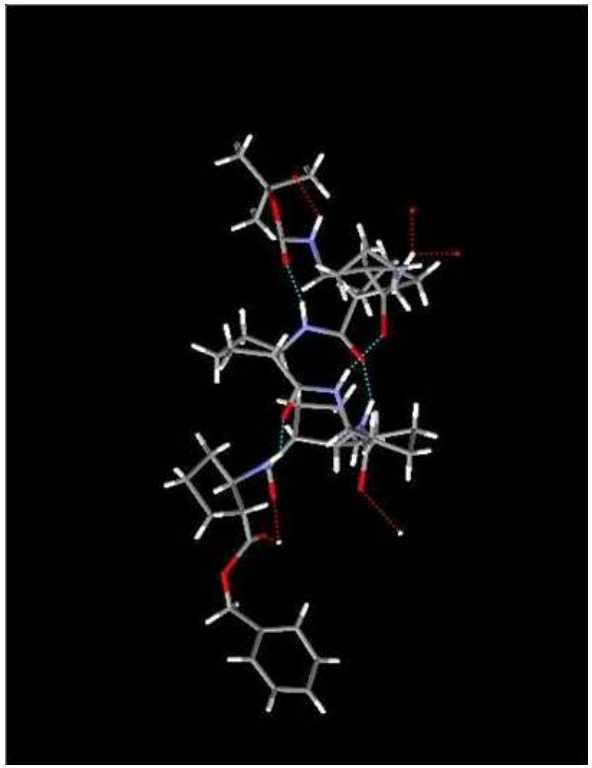
63 organic atoms from powders ab initio

(= chemical composition including molecular fragments+diffraction)

ACPC6

unit cell	$C_{48}\ N_6\ O_9$ (Z=4)
space group	$P4_1$
a	10.479015(35) Å
c	44.53710(29) Å
V	4890.61(5) Å^3
contributing reflections	455
geometric restraints	157
structural parameters	241





RMC in parallel tempering mode,
2 Å resolution, > $2 \cdot 10^6$ trials

J. Am. Chem. Soc. **2011**, 133, 17618–17621

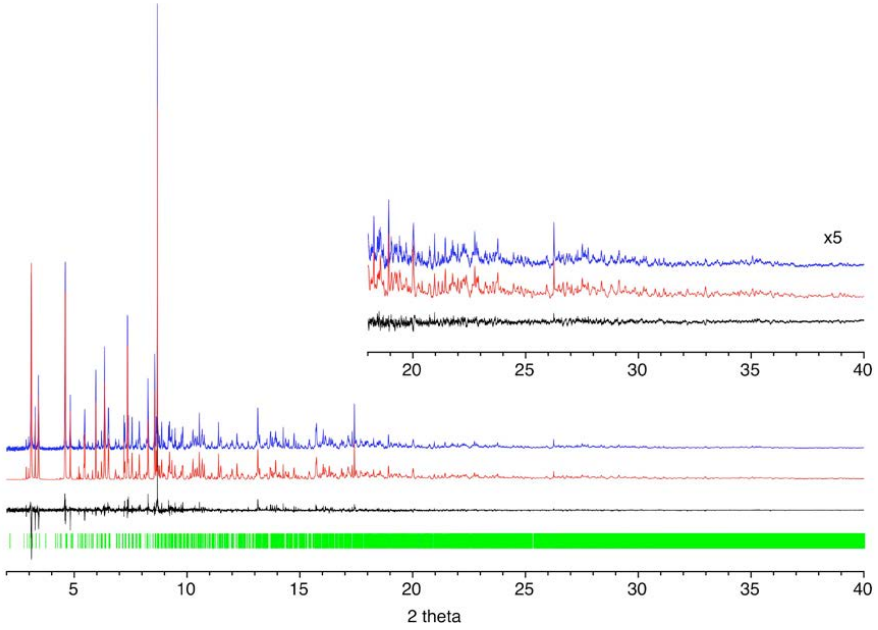
77 inorganic atoms from powders ab initio

Angew. Chem. Int. Ed. 2011, **50**, 8139 –8142

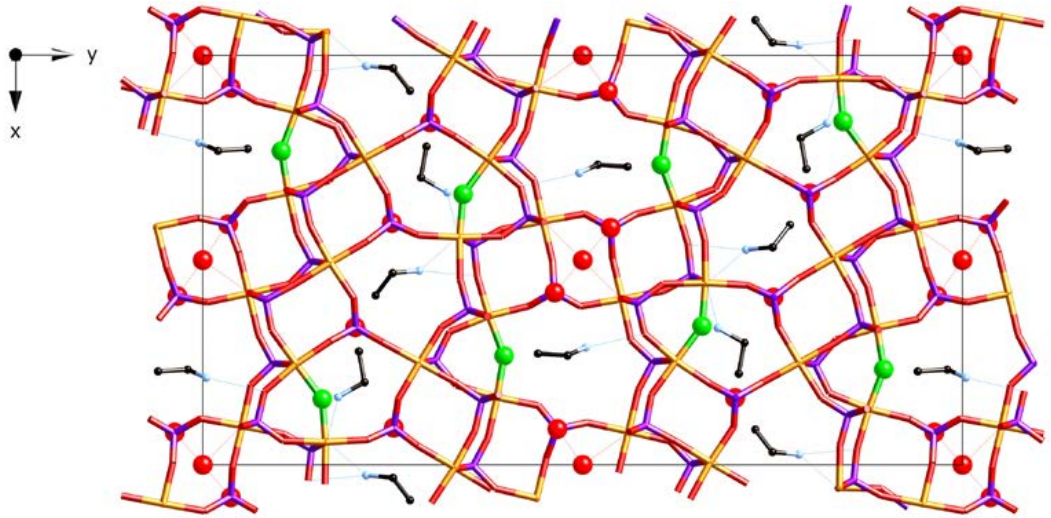
ZrPOF-EA

unit cell
$[(C_2H_7NH)_2(H_2O)][Zr_8P_{12}O_{44}F_2(OH)_4]$ (Z=4)

space group	*Pbam*
a	19.9565(2) Å
b	37.0665(5) Å
c	6.6168(1) Å
V	4894.56 Å^3
contributing reflections	6681
geometric restraints	271
structural parameters	161



Charge-flipping, 0.73 Å resolution



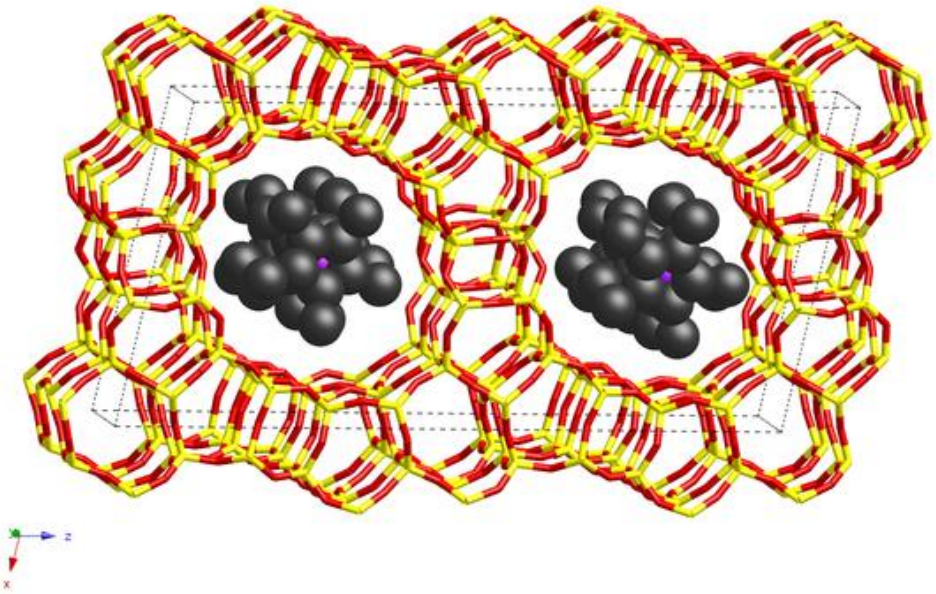
Structure of ZrPOF-EA showing the locations of the ethylammonium cations and the water molecules within the zirconium phosphate framework.

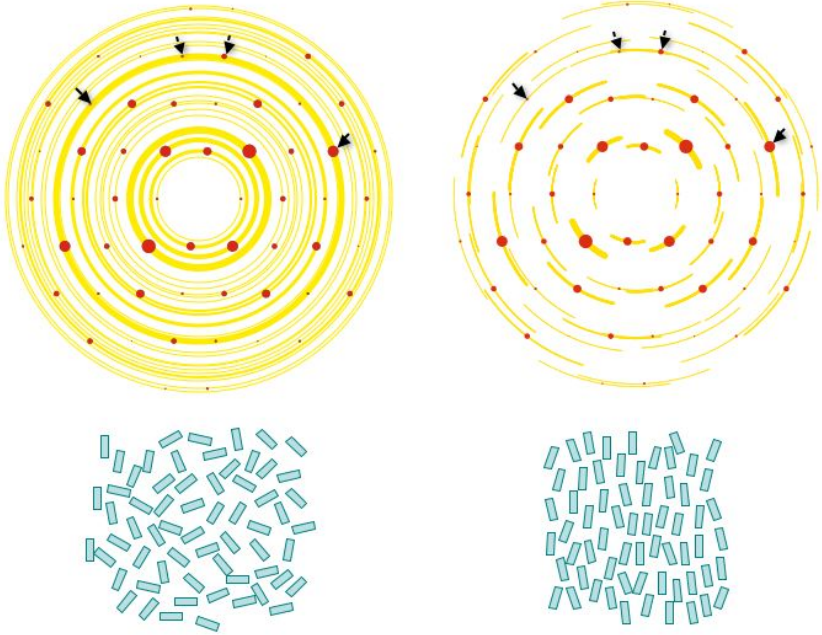
117 inorganic atoms from textured powders

J. Am. Chem. Soc. (1999), **121**, 6242-6247

UTD-1

unit cell	$(Si_{32}O_{64})$. (Cp*)2-$CoF_{0.75}OH_{0.25}$ (Z=2)
space group	*Pc*
a	14.9701(1) Å
b	8.4761(1) Å
c	30.0278(2) Å
β	102.65(1)°
contributing reflections	3519
geometric restraints	464
structural parameters	349

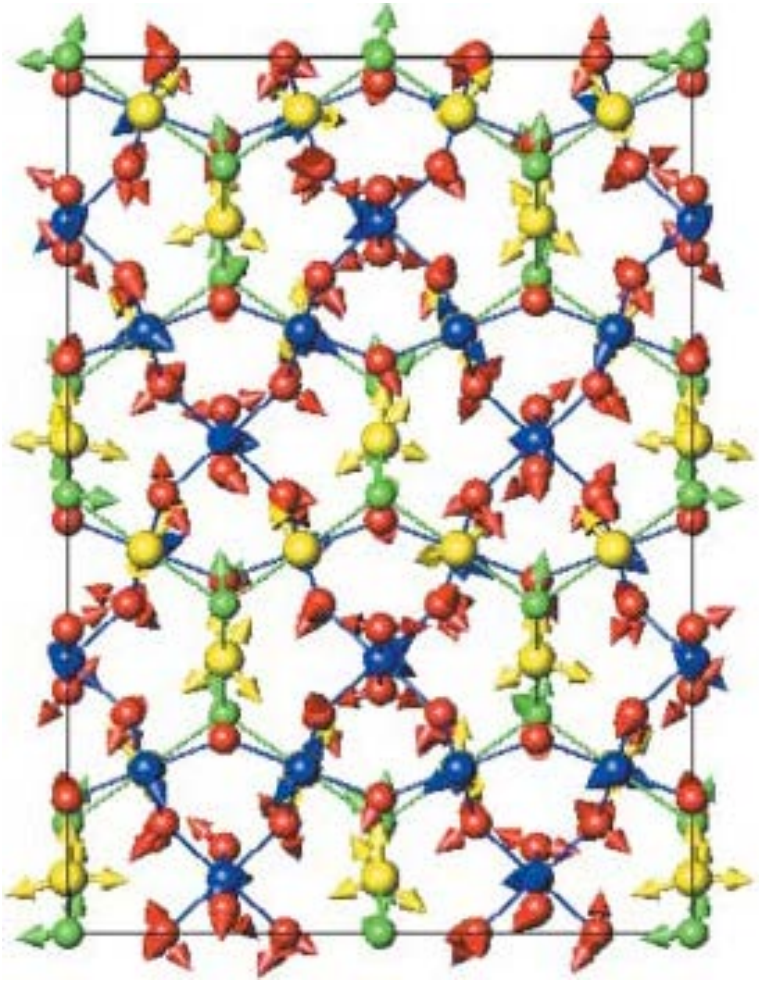




Texture assisted direct methods, 1.1 Å resolution

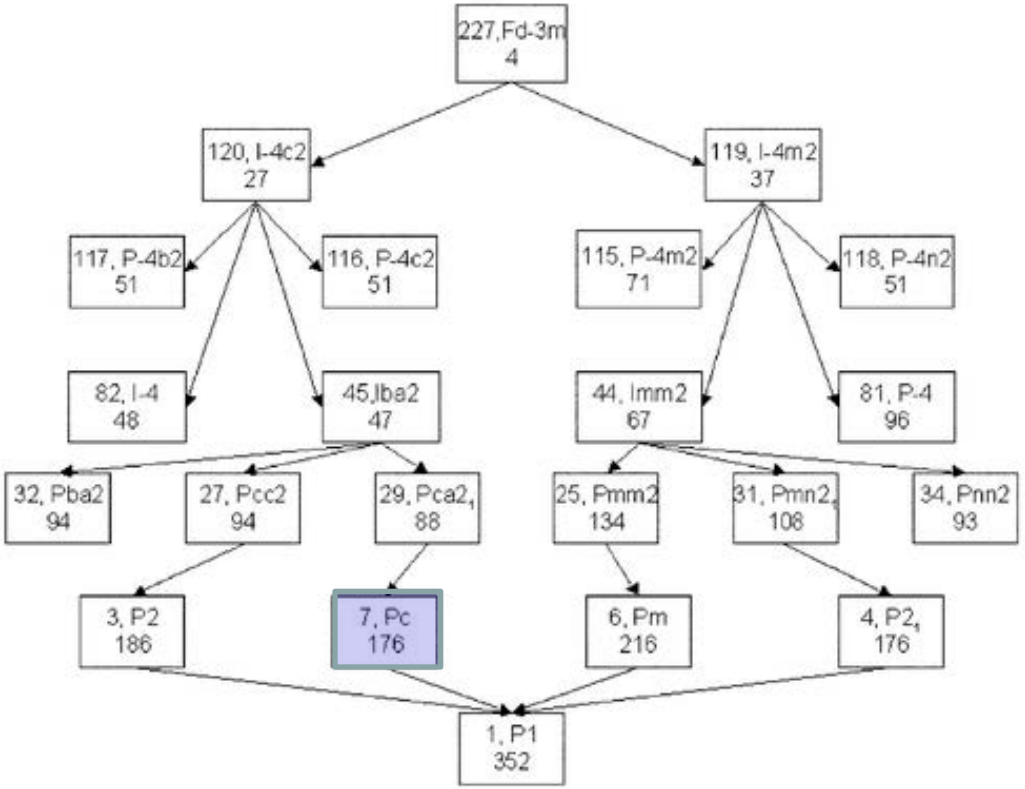
176 inorganic atoms from powders by symmetry guided solution

J. *Mater. Chem.*, **2003**, 13, 2098-2103



A view of the unit cell of α-$Bi_2Sn_2O_7$. Bi atoms and their displacements from the ideal pyrochlore structure shown as yellow vectors,
Sn as blue, O as red and O' as green.

Structure of α-$Bi_2Sn_2O_7$ by search in subgroups of the pyrochlore space group *Fd*-3*m*.



Crystal chemistry assisted RMC in simulated annealing mode,
X-ray data with 0.6 Å resolution,
neutron data with 1 Å resolution

Indexing – still a bottleneck

Only length of vectors $\boldsymbol{r}^*_{hkl,}$ solving the quadratic form:

$$Q_{hkl} = 1/d^2_{hkl} = h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2hka^*b^*\cos\gamma^* + 2klb^*c^*\cos\alpha^* + 2hla^*c^*\cos\beta^*$$

Observed : ~ 20 $d_{hkl}(\sigma_{hkl})$

Variables : $a^*, b^*, c^*, \alpha^*, \beta^*, \gamma^*$

Constrains : *h k l* are integers

R. Shirley: "*Powder indexing works beautifully on good data, but with poor data it will usually not work at all*. "

Success of the indexing increases proportionally with the number of different applied indexing programs. *Z. Kristallographie* **2004**, *219*, 783

Observing crystallographic extinctions increases figure-of-merit of the cell.

Don't be afraid of big cells!

Indexing – algorithms

Active use of zones (Runge, Ito, de Wolf)

ITO - Visser J.W. J. *Appl. Cryst.* (1969) **2**, 89

Exhaustive

Taupin - Taupin D. J. *Appl. Cryst.* (1973) **6**, 380-385

semi-Exhaustive

Treor - Werner P.E., Eriksson L., Westdahl M. *J. Appl. Cryst*. (1985) **18**, 367-370

N-Treor - Altomare A. et al. J. *Appl. Cryst.* (2000) **33**, 1180

dichotomy

Dicvol - Louër D., Louër M. J. *Appl. Cryst.* (1972) **5**, 271

Dicvol04 - Boultif A., Louër D. J. *Appl. Cryst.* (1991) **24**, 987

Fox - Cerny R. et al. *CPD Newsletter no. **35*** (2007) 16-19

X-Cell - *www.accelrys.com*

Singular Value Decomposition

SVD-Index - Topas (*Coelho A.A. J. Appl. Cryst.* 2003, **36**, 86–95*)*

Global optimization

GA - Kariuki B.M. et al. *J. Synchrotron Rad*. 1999, **6**, 87

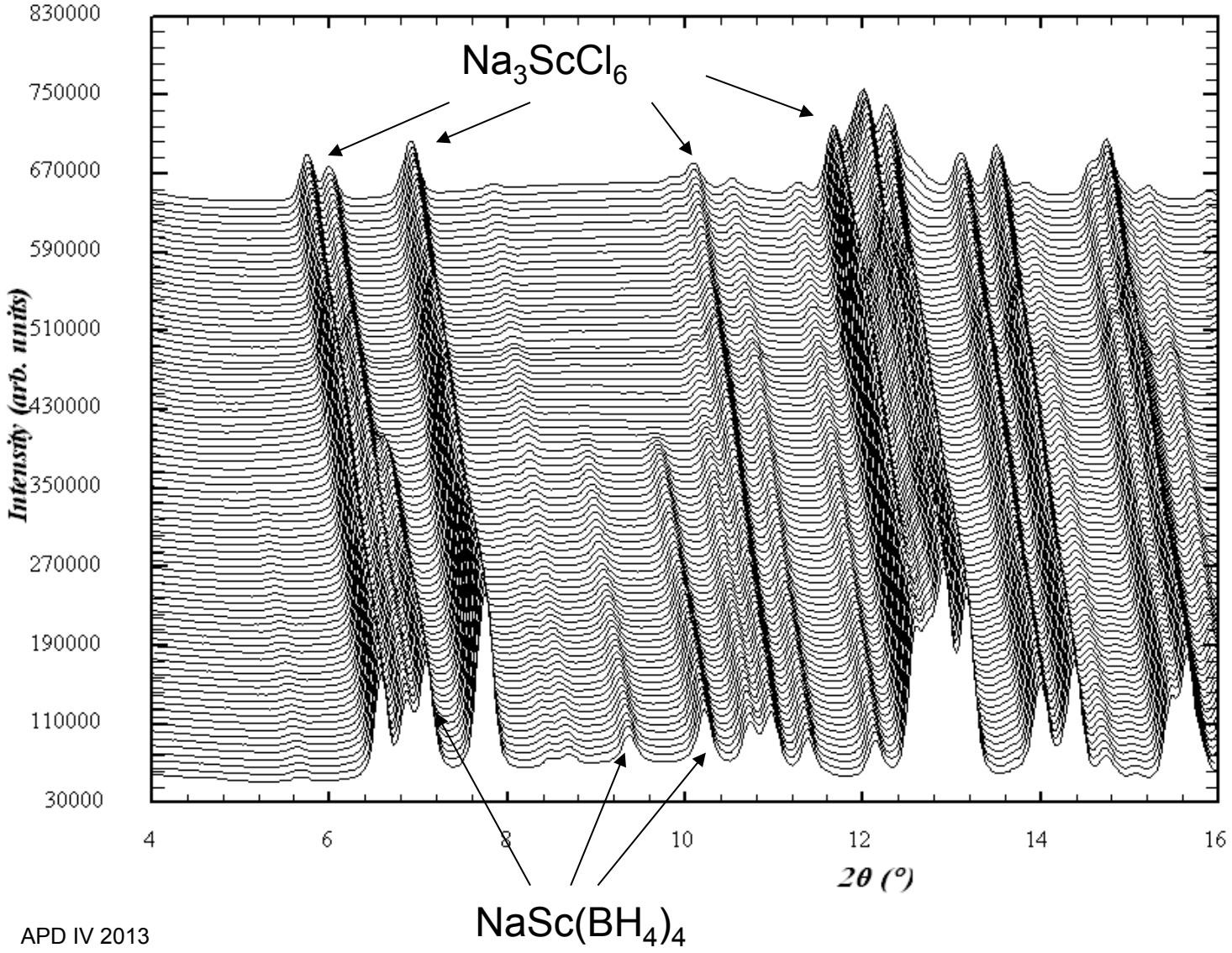
McMaille - Le Bail A., *Powder Diffraction* **19** (2004) 249-254

Topas - lpSearch

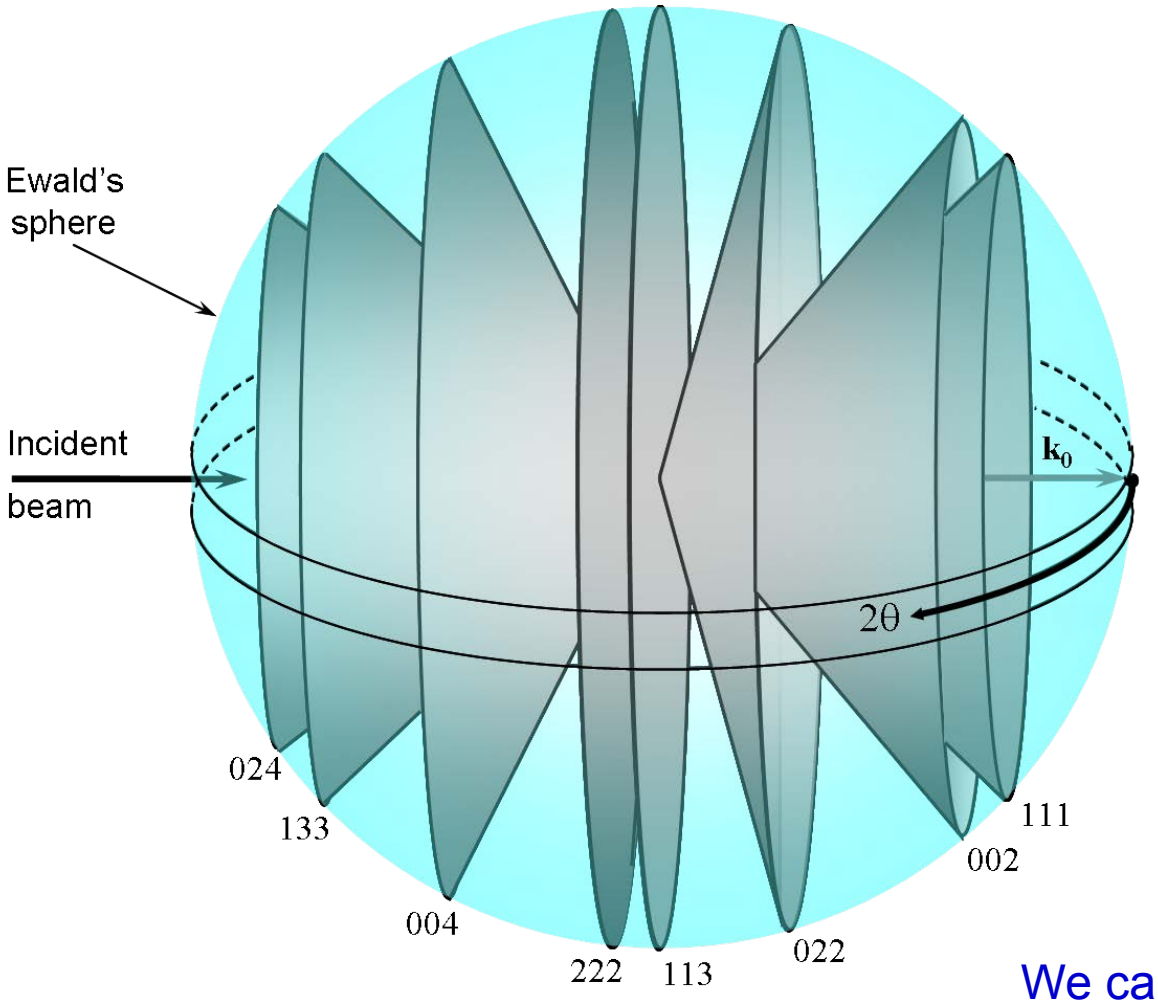
Temperature assisted indexing

$$4NaBH_4 + 2ScCl_3 \rightarrow NaSc(BH_4)_4 + Na_3ScCl_6$$

Z. Kristallographie **2011**, *226*, 882-891



Fast and/or low noise data - 2D-detectors

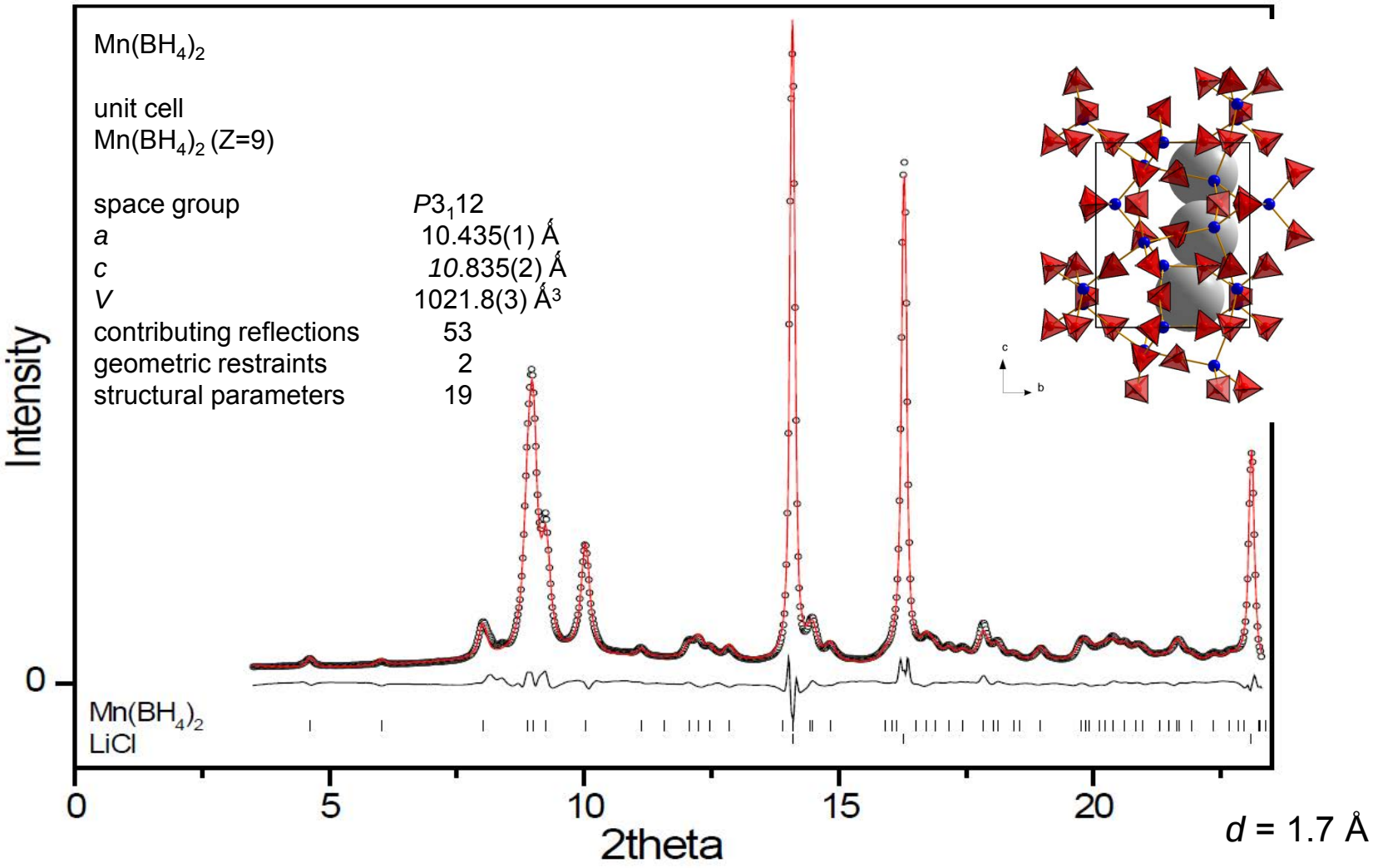


We can solve from fast or bad data

- intermediate and metastable phases
- structural parameters as function of time or external stimuli

7 inorganic atoms from low resolution low noise data

SNBL, image plate, λ = 0.72846 Å, R_{wp} = 0.05, χ^2 = 130, R_{Bragg} = 0.02



Rietveld plot of $Mn(BH_4)_2$ showing good modeling of weak Bragg peaks with synchrotron data from 2D-detector with high counting statistics.

Which method for structure solution?

Ideal sample

- enough time to crystallize
- equilibrium
- careful sample preparation
- representative?
    - chemistry of the compound
    - physics of the compound

Real sample

- real conditions of crystallization
- in-situ
- sample as grown
- representative!
    - reactions
    - applications

Reciprocal space methods
(intensity extraction based)

Direct space methods
(pattern modeling based)

Which method for structure solution?

Ideal sample

Real sample

Reciprocal space methods
(intensity extraction based)
- need intensity extraction
- high resolution data (< 1 Å)

- direct methods
- Patterson
- charge flipping (dual space)
- combined methods (diffraction+microscopy)

Direct space methods
(pattern modeling based)
- no intensity extraction, need for additional info
- any resolution (2 Å)

- global optimization
  - Reverse Monte Carlo
    (simulated annealing, parallel temp.)
  - evolution algorithms

Topology or symmetry guided algorithms
- framework building (zeolites, MOFs) – FOCUS
- crystal chemistry analysis (from the average structure to a superstructure, chemical analogy)

www.ccp14.ac.uk
www.iucr.org/resources/other-directories/software

Intensity extraction based

Reciprocal space:

Direct methods

EXPO - *J. Appl. Cryst.*, **37** (2004) 1025-1028

DOREES-POWSIM - *J. Appl. Cryst.* **25** (1992) 237-243

squared structure

XLENS - *Acta Cryst.* (2011). A**67**, 63-67

Maximum entropy

MICE - *Trans. Amer. Cryst. Association.* (1994), **30**, 15-27

Dual space:

Charge flipping

Superflip - *J. Appl. Cryst.* **40**, 786-790

Topas - *www.topas-academic.net, www.bruker.com*

Topology guided

FOCUS (framework building, structural envelopes)

- *J. Appl. Cryst.* (1999) **32**, 536-542

- *J. Appl. Cryst.* (1997) **30**, 1167-1172

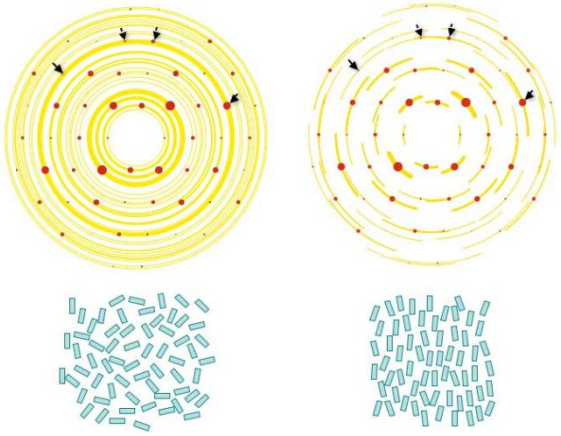
Symmetry guided (from the average structure to a superstructure, chemical analogy)

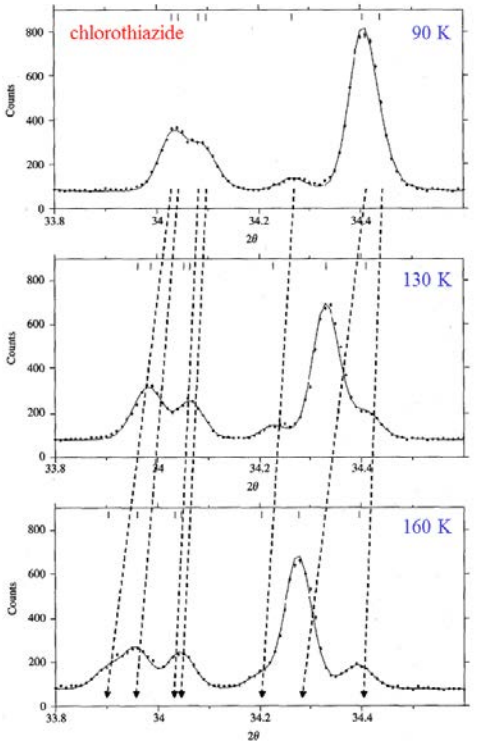
any Rietveld

Intensity extraction assistance

Multipattern:

Texture — ETHZ – MAUD - *J. Appl. Cryst*. (**2013**) 46, 173-180





Temperature (anisotropy of dilatation)

J. Mater. Chem. **7**(3) (1997) 569-572
Angew. Chem. Int. Ed. **42** (2003) 2029-2032

Single pattern:

Patterson — Patterson Squaring or Max. Entropy - *J. Appl. Cryst.* (1987) **20**, 316-319
J. Appl. Cryst. (1993) **26**, 396-404

DOREES-POWSIM, EXPO

Triplet relation — DOREES-POWSIM, EXPO

Pattern modeling based

Reciprocal space (powder pattern modelling):

RMC

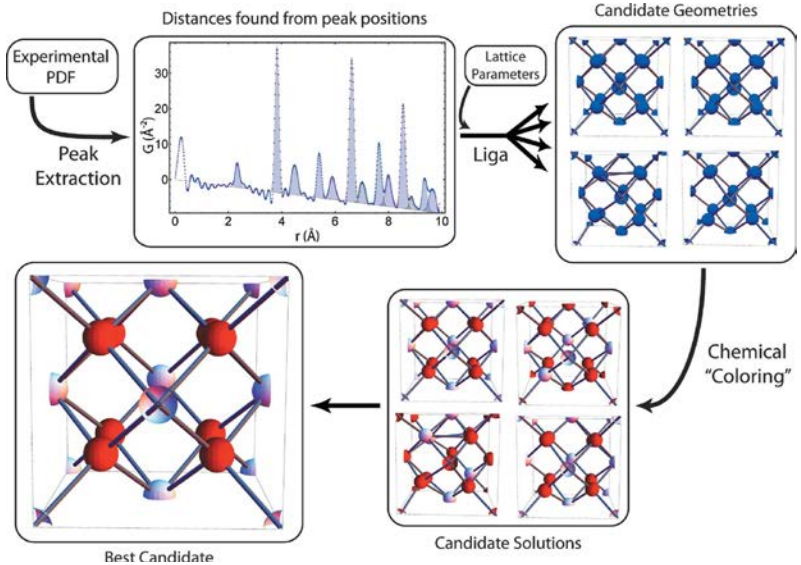
Simulated annealing	DASH (organics) - *J. Appl. Cryst.* **39** (2006) 920-915
Parallel tempering	Fox (inorganics) - *J. Appl. Cryst.* **35** (2002) 734-743

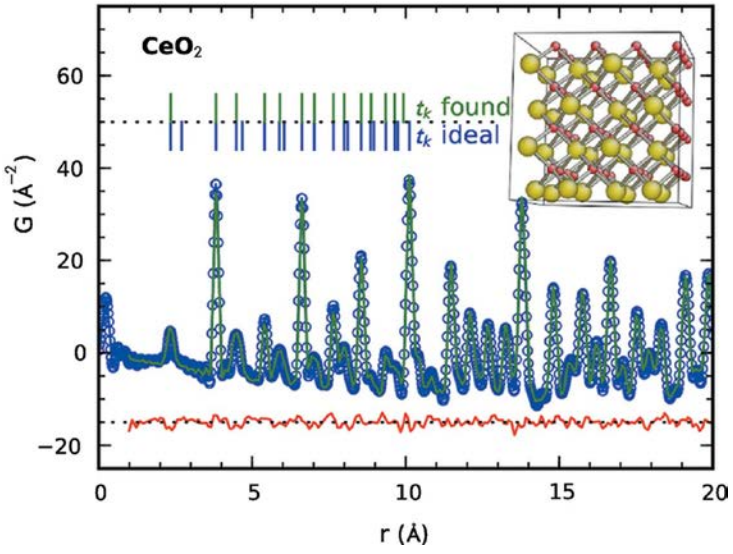
Evolutionary algorithms (rather organics)

Differential evolution	POSSUM - *Chem. Comm.* **2002**, 880
Genetic	EAGER - *Chem. Phys. Lett.* **280** (1997) 189
	GAP - *Z. Kristallogr.* **212** (1997) 550-552

Direct space (PDF modelling):

RMC	RMCprofile - *J. Appl. Cryst.* **34** (2001) 630-8
Liga algorithm	Juhas - J. Appl. Cryst. (2010). 43, 623–629





Pattern modeling based computer programs

Program	Access	GO	CF	Reference	Web
DASH	C	SA	P,I	*Chem. Commun.* 93 (1998)	www.ccdc.cam.ac.uk
EAGER	A	GA	WP	*Acta Cryst.* A, 54, 632 (1998)	www.cardiff.ac.uk/chemy/staff/harris.html
(former GAPSS)				*Chem. Phys. Lett.* 280, 189 (1997)	
ENDEAVOUR	C	SA	I+E	*J.Appl.Cryst.* 32, 864 (1999)	www.crystalimpact.com
ESPOIR	O	MC	L	*Mat. Sci. Forum* 378-381, 65 (2001)	www.cristal.org
FOCUS	O	-	I+TS	*J. Appl. Cryst.* 30, 985 (1997)	www.crystal.mat.ethz.ch
FOX	O	SA(PT)	WP,I,AC	*J.Appl.Cryst.* 35, 734 (2002)	objcryst.sf.net
FULLPROF	O	SA	I	*Physica* B192, 55 (1993)	www.ill.fr/pages/science/IGroups/diff/Soft/fp/index.ht
GAP	A	GA	P,I	*Z. Kristallogr.* 212 (1997) 550-552	
GEST	O	GA	I	*J. Appl. Cryst.*(2007)	crystallography.zhenjie.googlepages.com/GEST.html
MAUD	O	SA,GA	I,E	*Newsl. CPD* 21, 14 (1999)	www.ing.unitn.it/~maud/
MRIA	A	GS, SA	I	*J.Appl.Cryst.* 22, 447 (1992)	
OCTOPUS	A	MC	WP	*Angew. Chem. Int. Ed.* 36, 770 (1997)	www.cardiff.ac.uk/chemy/staff/harris.ht
ORGANA	A	MC(E)	I+E	*J. Appl. Cryst.* 38, 688-693 (2005)	
POSSUM	A	DE	WP	*Chem. Commun.* 880 (2002)	www.chem.bham.ac.uk/staff/tremayne.shtml
POWDERSOLVE	C	MC	WP	*J. Appl.Cryst.* 32, 1169 (1999)	www.accelrys.com
PSSP	O	SA	L		powder.physics.sunysb.edu/programPSSP/pssp.html
SAFE	A	SA	WP+SE	*J.Appl.Cryst.* 35, 243 (2002)	www.crystal.mat.ethz.ch
SA	A	SA	WP	*J. Appl. Cryst.* 30, 294 (1997)	ch-www.st-andrews.ac.uk/staff/pgb/group
TOPAS	C	SA	I,WP,E	*J. Appl. Cryst.* 33, 899 (2000)	members.optusnet.com.au/~alancoelho
ZEFSAII	O	MC(B)	I+AC	*J. Chem. Phys.* 110, 1754 (1999)	www.mwdeem.rice.edu/zefsaII

Access : C = Commercial with academic prices, O = Open access, A = contact the authors

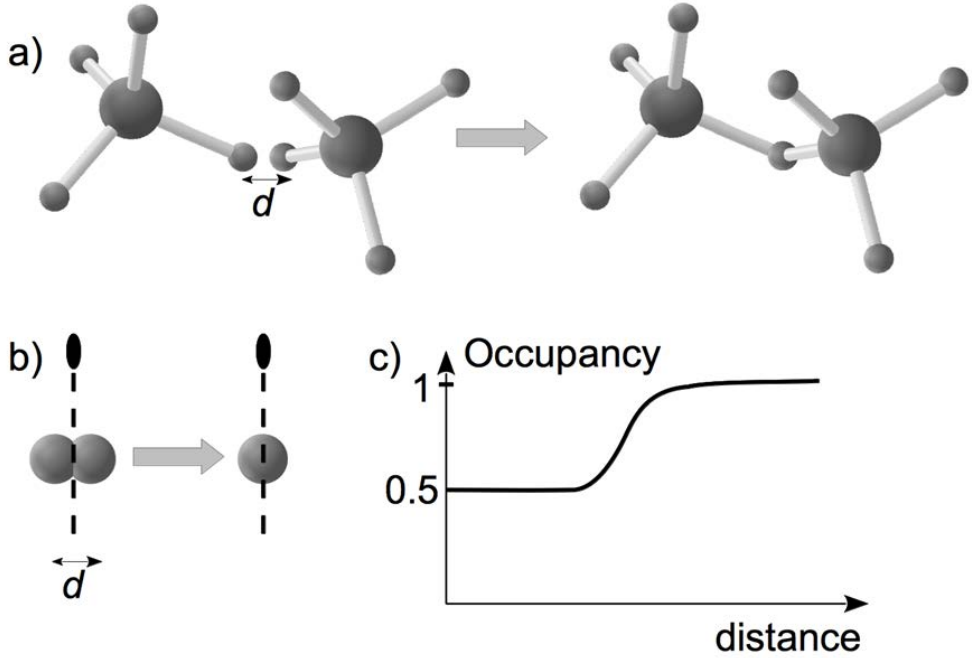
GO = Global Optimization : MC = Monte Carlo, MC(B) = biased Monte Carlo, GS = grid search,
SA = MC+Simulated Annealing, PT = MC+Parallel Tempering,
GA = Genetic Algorithm, DE = Differential Evolution

CF = CostFunction : P = Pawley, L = Le Bail, I = Integrated intensities, WP = Whole Pattern,
E = potential energy, SE = structure envelopes, AC = Atomic Coordination,
TS = Topology Search

Pattern modeling assistance

Chemistry of the unit cell:

Dynamical Occupancy Correction Fox



Symmetry analysis EPCryst - J. Appl. Cryst. (2011) **44**, 230–237

Bonding constraints all

Crystal energy:

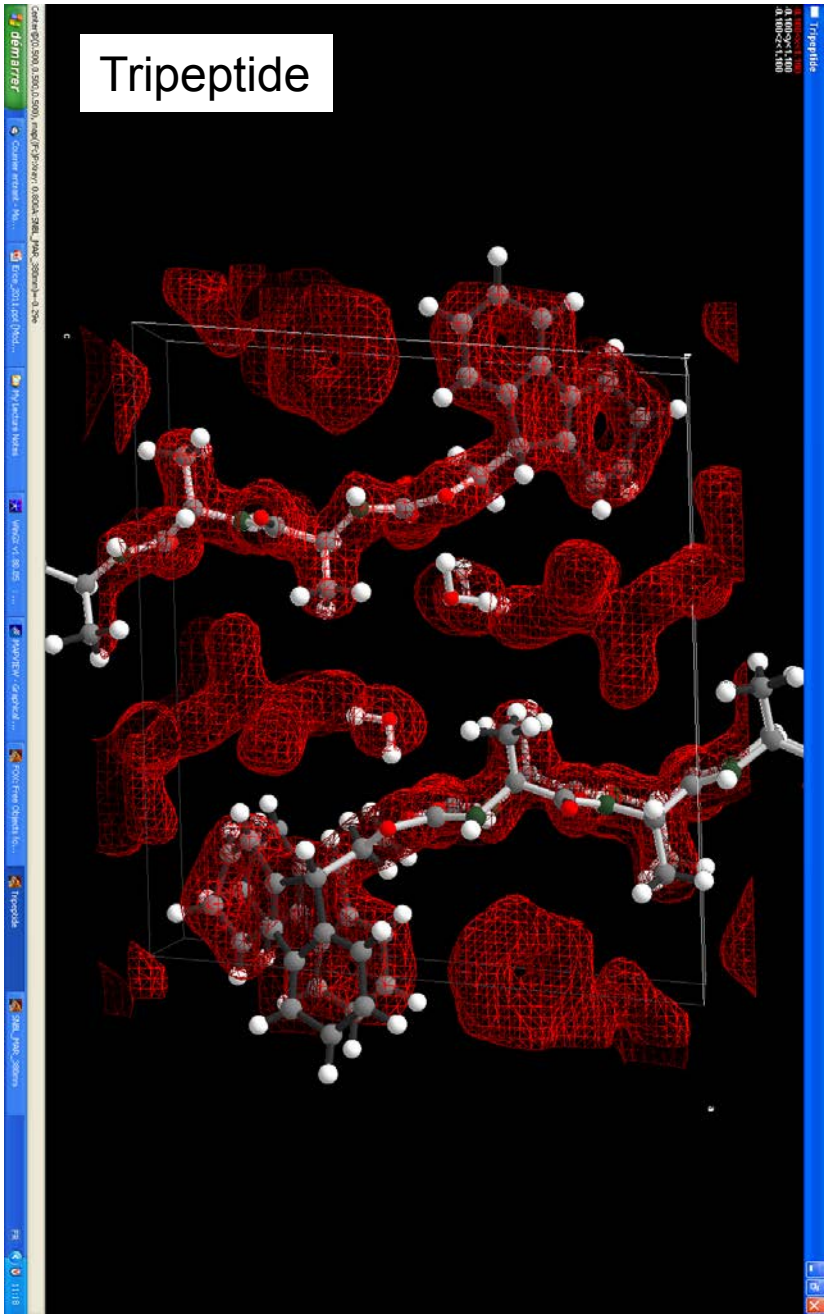
Electrostatic potentials Topas

Endeavour - *www.crystalimpact.com*

Crystal chemistry:

Structural systematic and analogy helps! Use the databases!

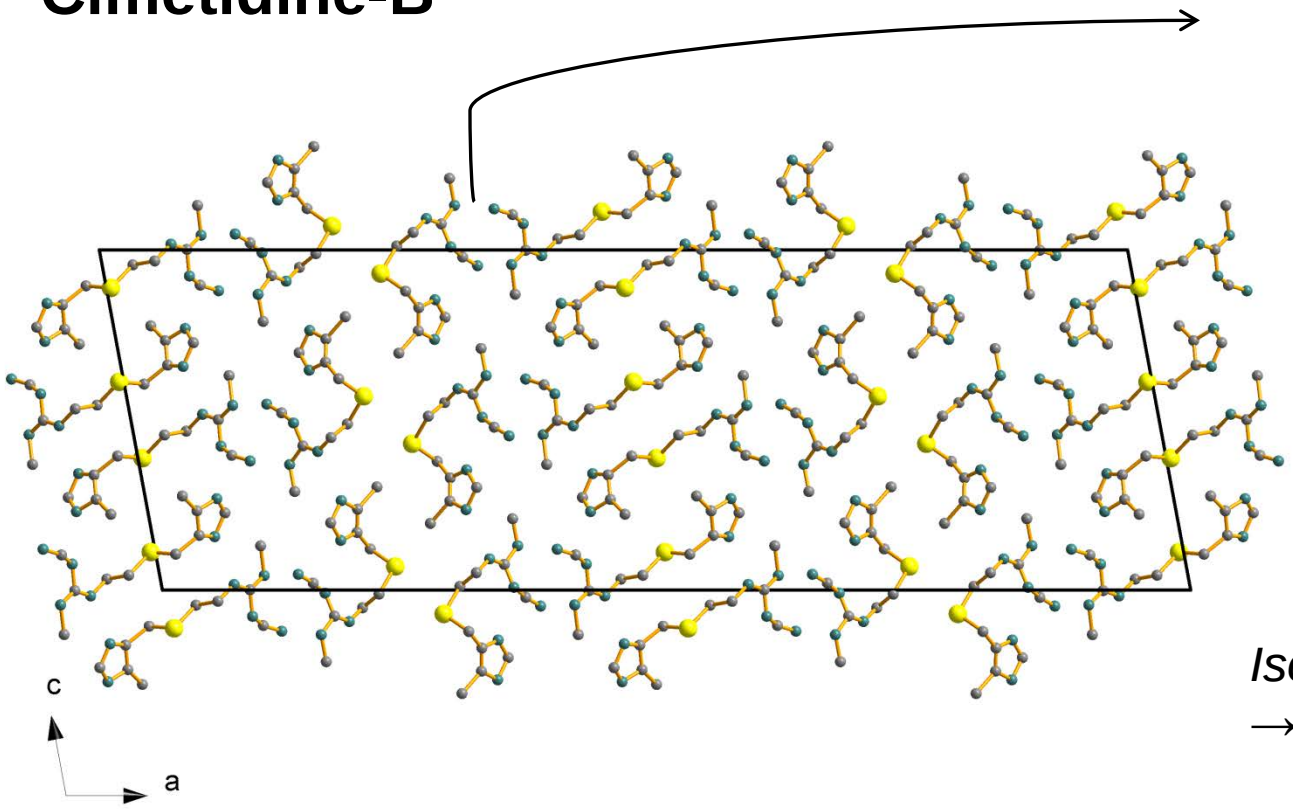
E-maps, nonmolecular vs. molecular

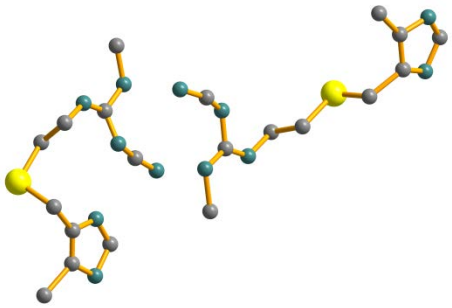


Molecular Compounds

Bonds that extend within a molecule "*intramolecular*" – strong, covalent bond.
Molecules create the crystal by "*intermolecular*" bonds – weaker, van der Waals, hydrogen, halogen bond.

Cimetidine-B





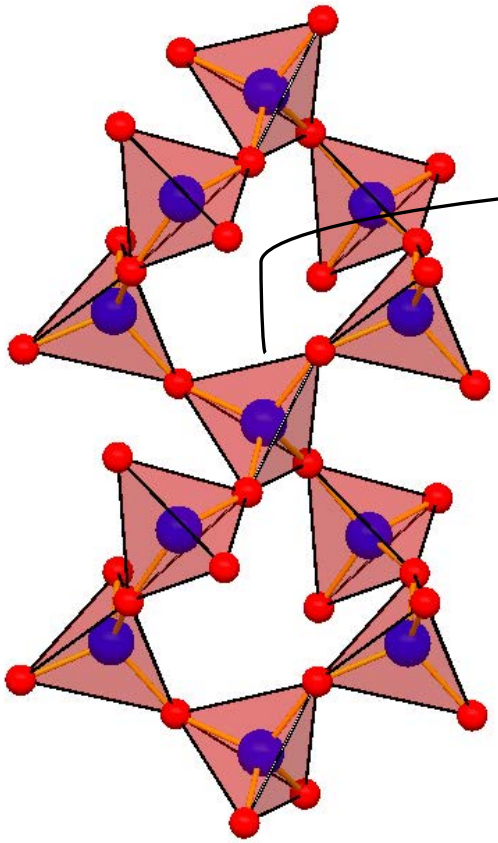
Cimetidine-A Cimetidine-C

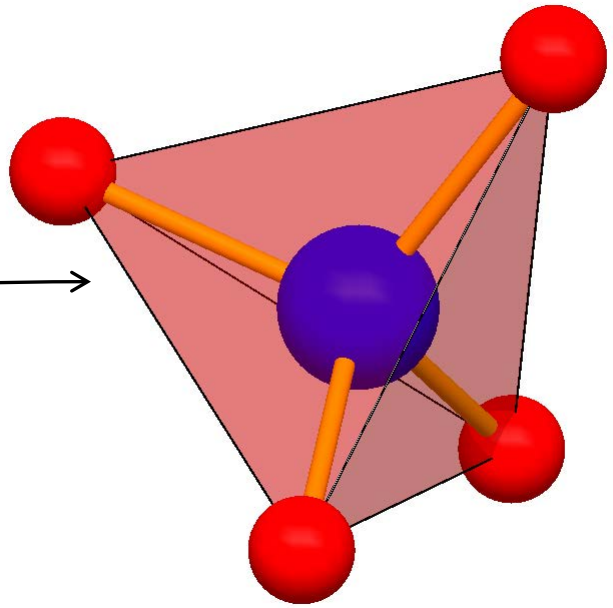
Isolable neutral molecules
→ good **building units**

Nonmolecular Compounds - Extended Solids

Bonds that extend "*infinitely*" in three dimensions through a crystal.
No *isolable neutral molecular units*, just local *bonding geometries* and *formula units*.

SiO_2



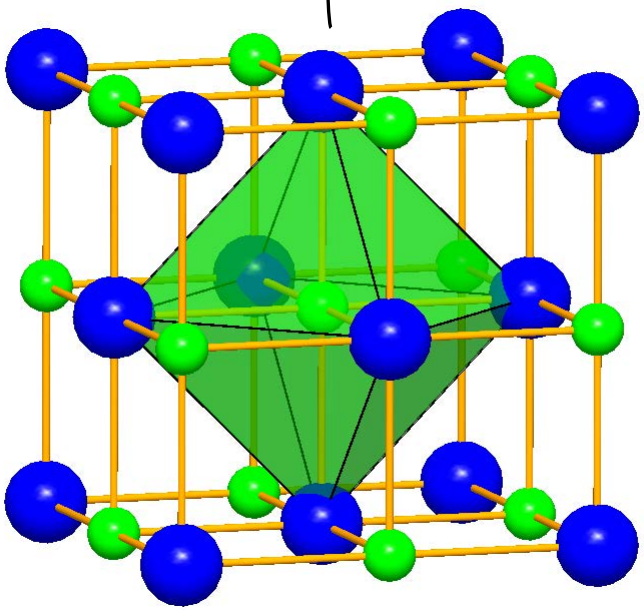


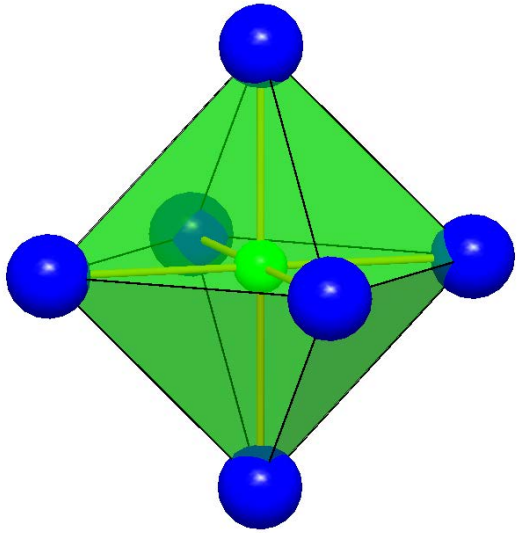
Molecule ? Complex anion $[SiO_4]^{4-}$
covalent bonds
accounts for
all bonds around Si
→ good **building unit**

Nonmolecular Compounds - Extended Solids

Bonds that extend "*infinitely*" in three dimensions through a crystal.
No *isolable neutral molecular units*, just local *bonding geometries* and *formula units*.

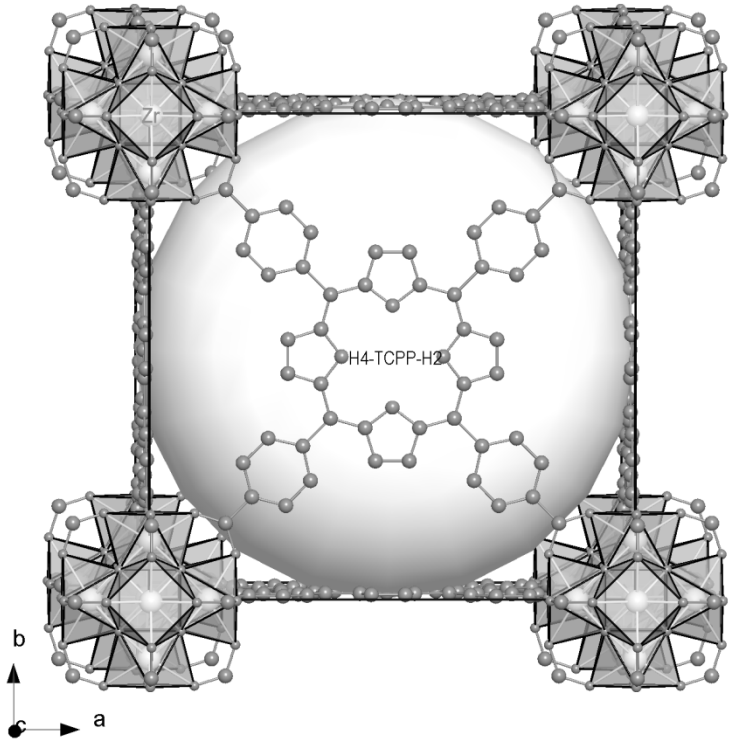
NaCl

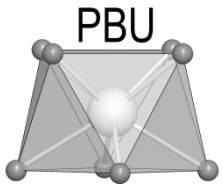


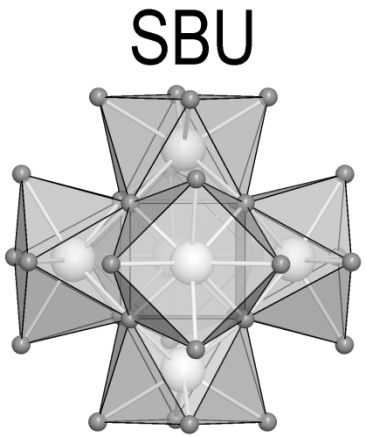


Molecule ?
formula – $[NaCl_6]^{5-}$
no *covalent bond*
not *isolable*, not neutral
but accounts for
all bonds around Cl
→ good **building unit**

Primary and secondary building units, active use of topology







MOF-525

The SBU is built from six square-antiprismatic PBU ZrO_8.

Cuboctahedral SBU $Zr_6O_4(OH)_4$ connected by tetracarboxyphenylporphyrin (H_4-TCPP-H_2) linkers.

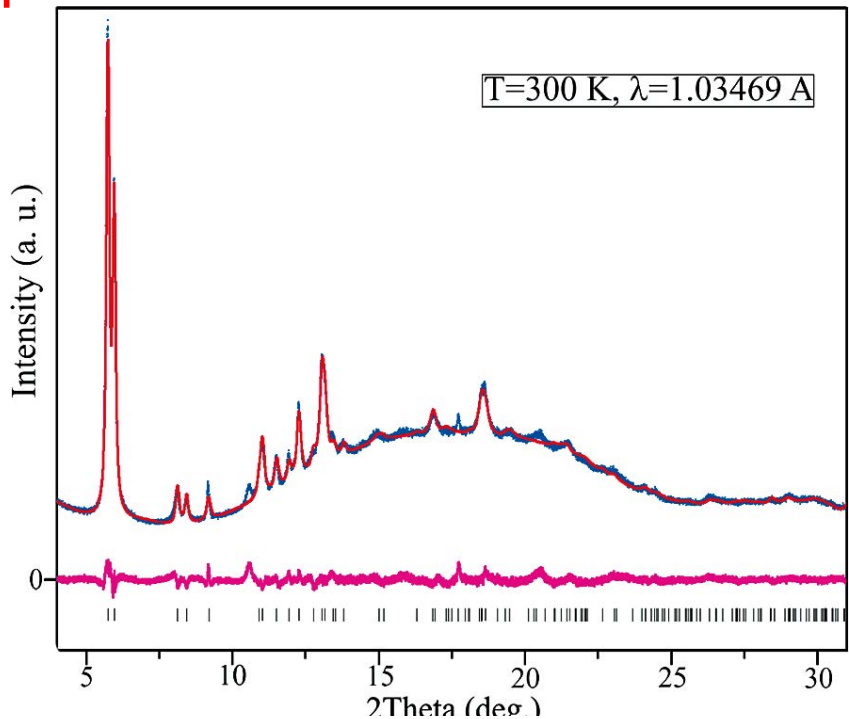
Morris et al. *Inorg. Chem*. (2012).

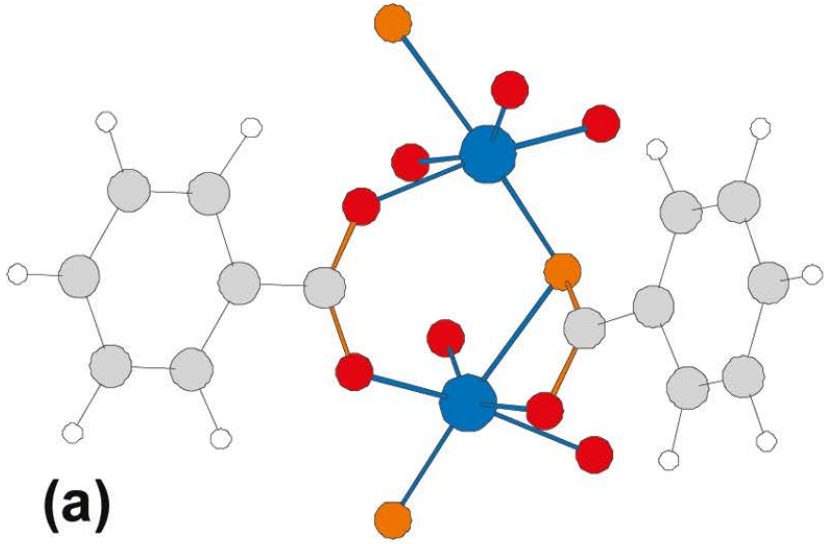
Structure validation – help of theoreticians

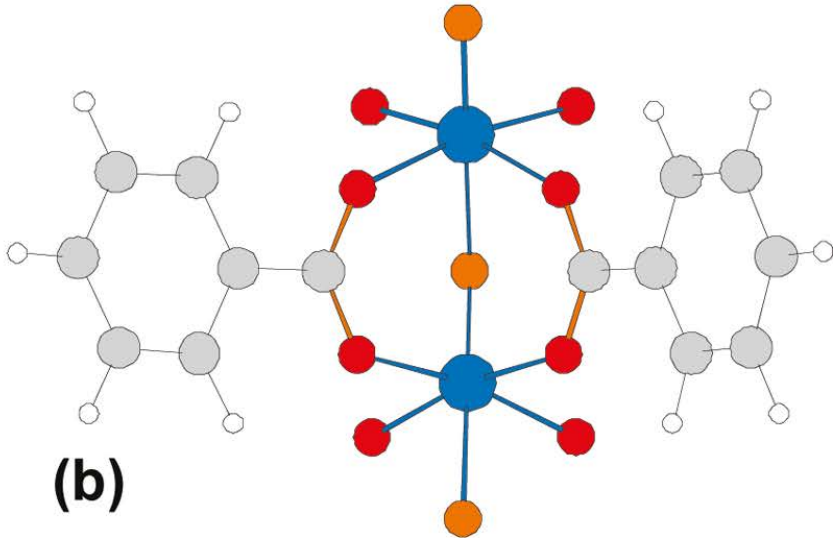
Nanocrystalline inorganic-organic hybrid vanadium oxobenzoate, $VO(C_6H_5COO)_2$

Chem. Mater. 2009, **21**, 3356–3369

Even if the XRD pattern exhibits the features typical of a low crystalline product and the initial structure of the DFT geometry optimization was far from the final solution, both techniques converged toward the same architecture.



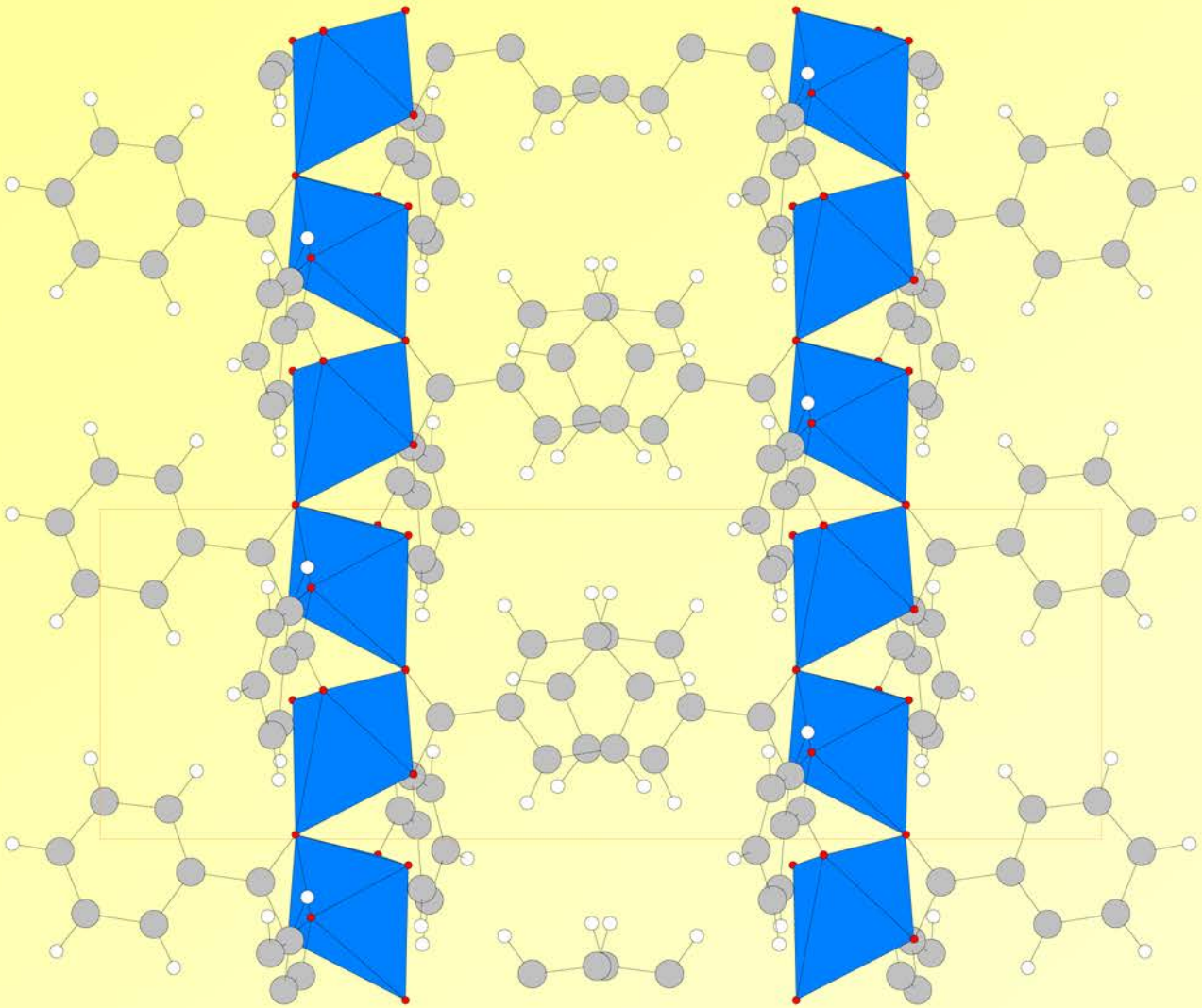




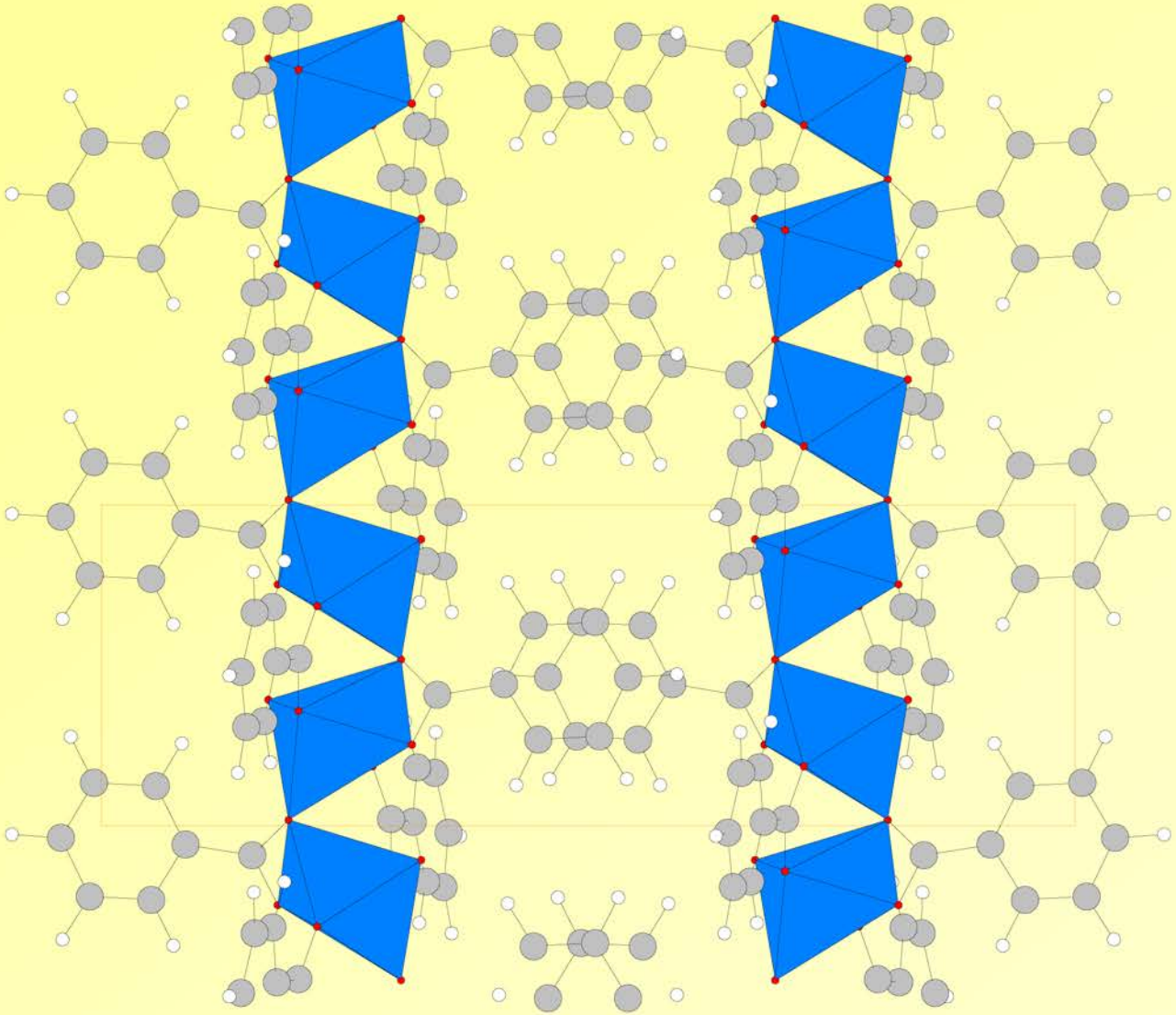
as solved from PD

corrected by DFT

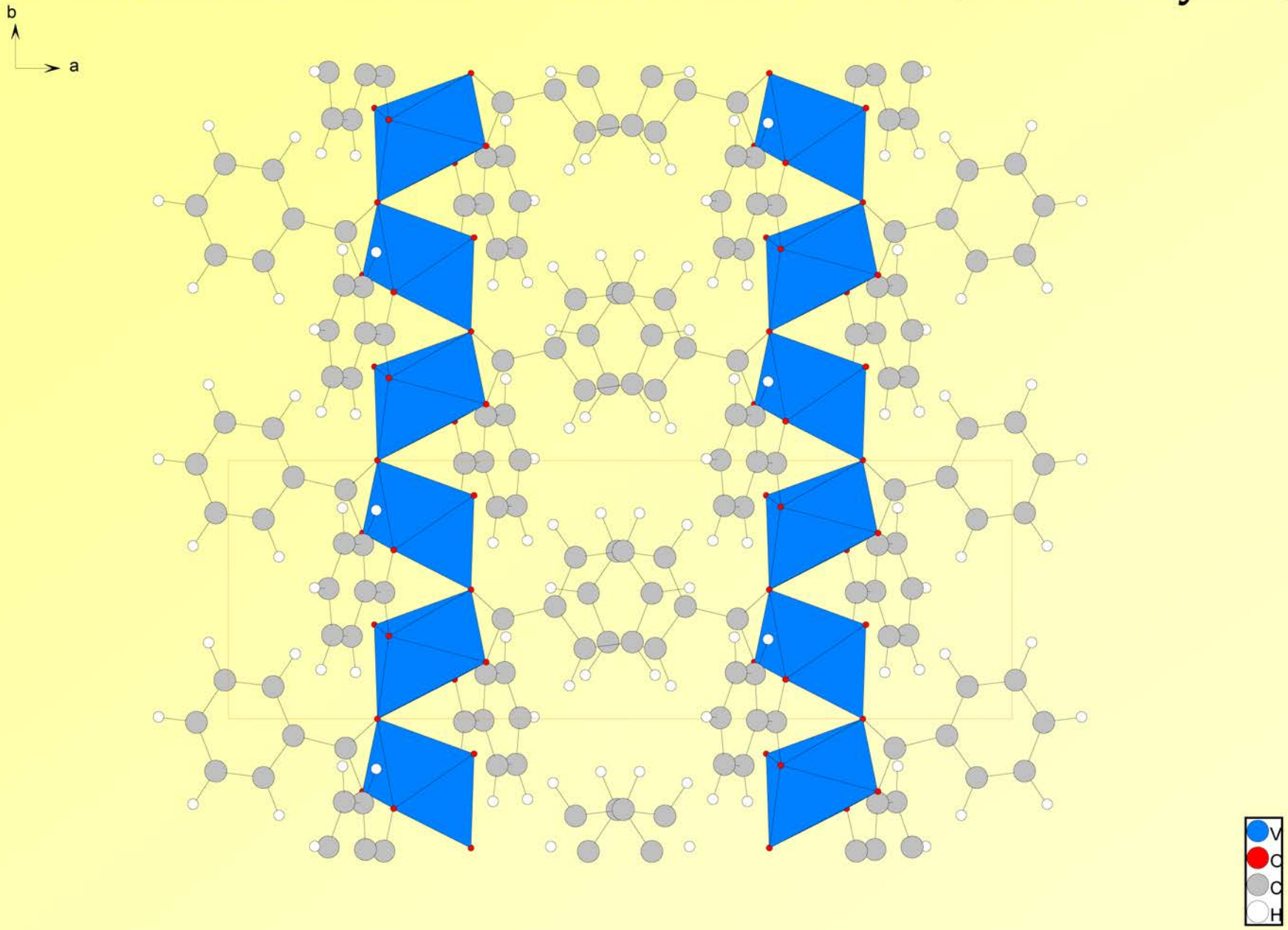
VOB – MODEL 1 – INITIAL STRUCTURE



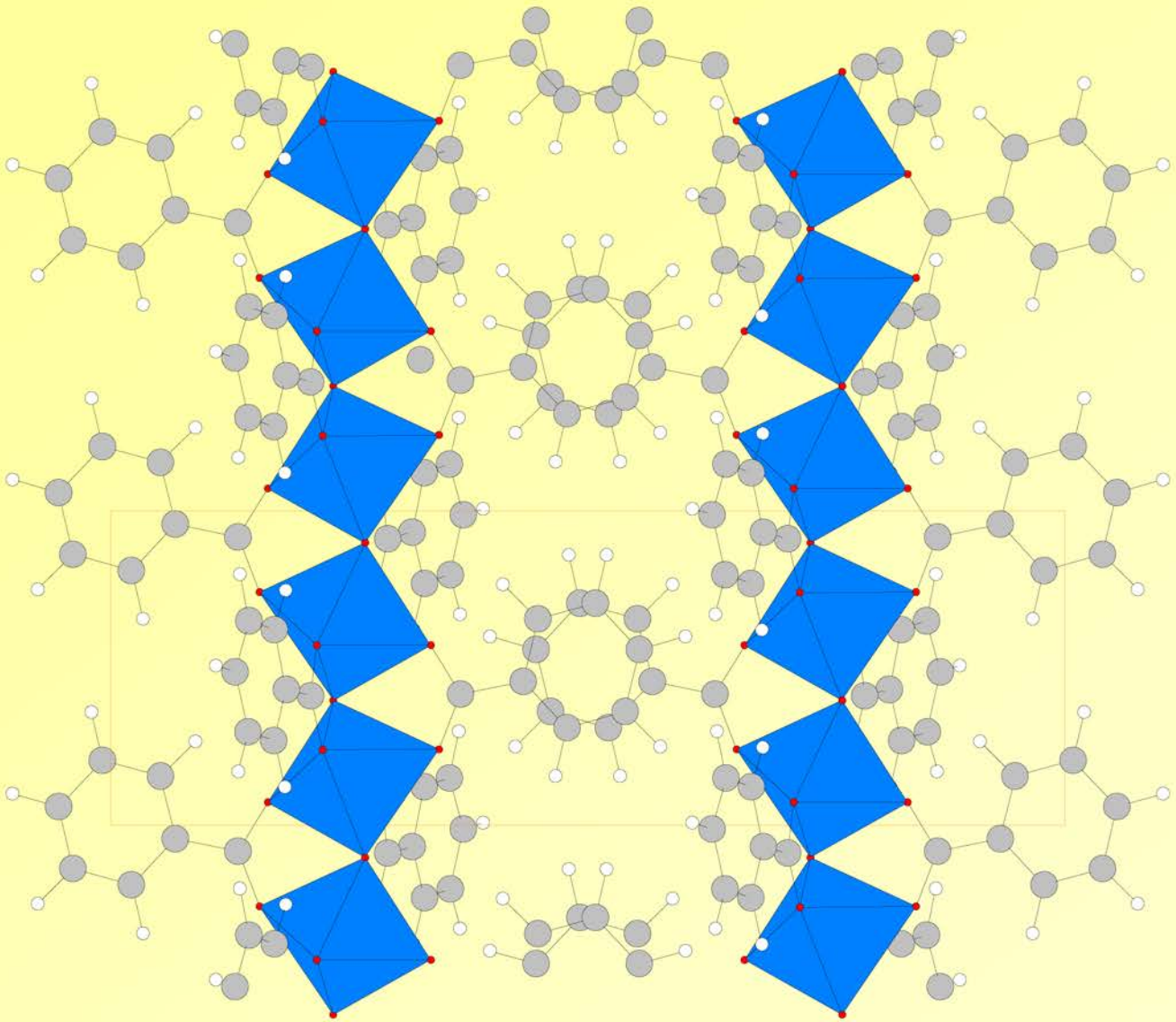
VOB – MODEL 1 – OPTIMIZED STRUCTURE (after 60 cycles)



VOB – MODEL 1 – OPTIMIZED STRUCTURE (after 120 cycles)



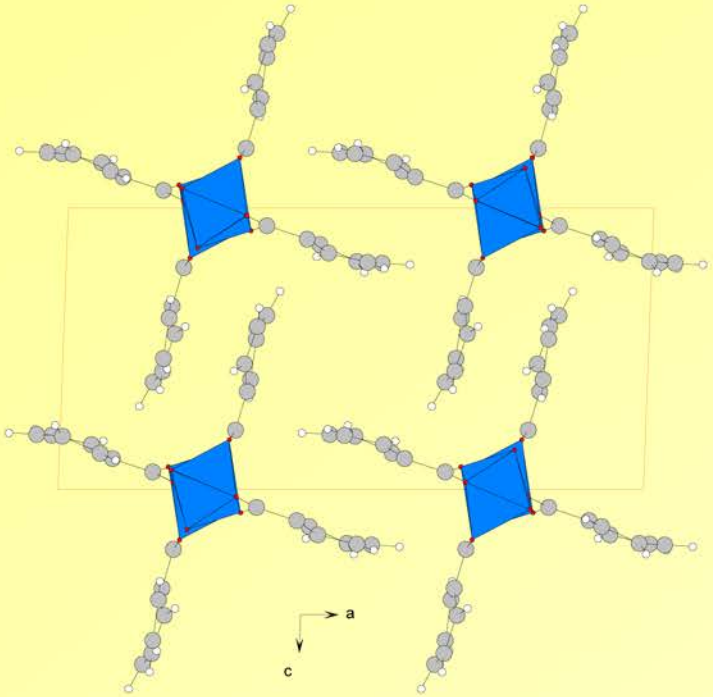
VOB – MODEL 1 – OPTIMIZED STRUCTURE (after 240 cycles)



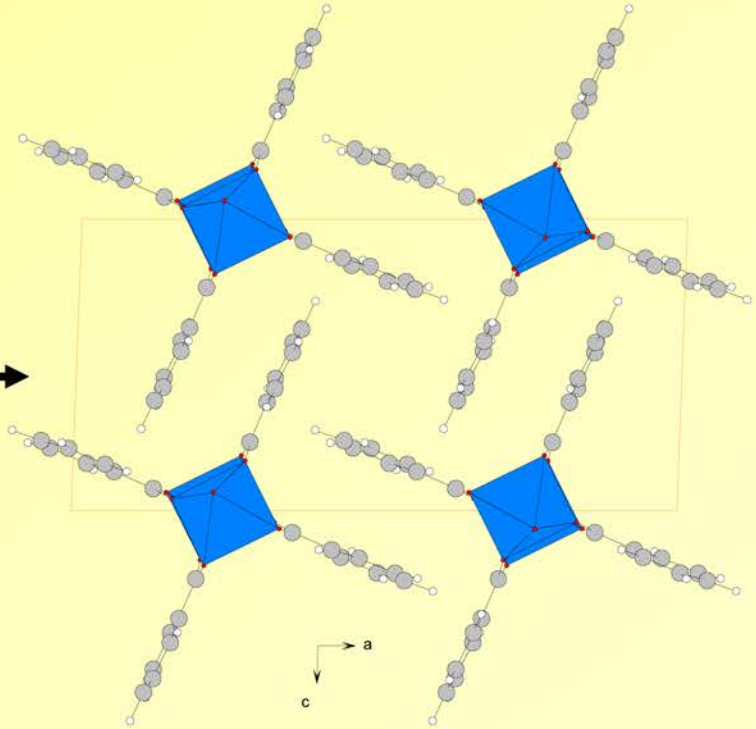
IMPORTANT CHANGE

VOB – MODEL 1

BEFORE
GEOM. OPT.

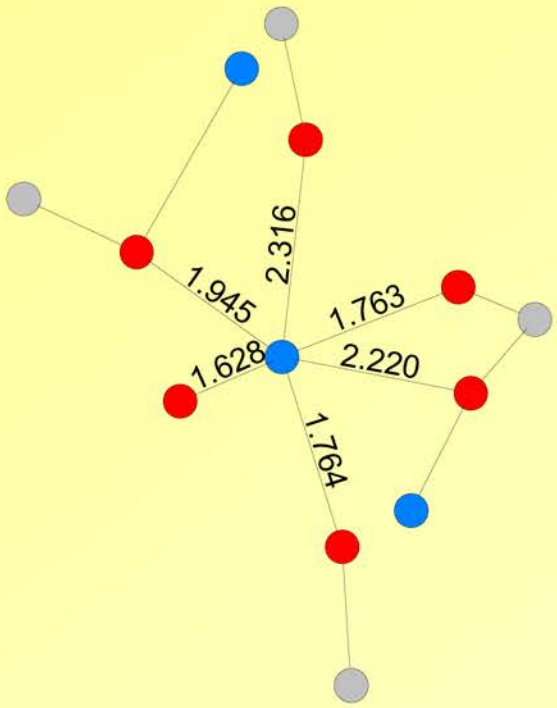


AFTER
GEOM. OPT. (not converged)



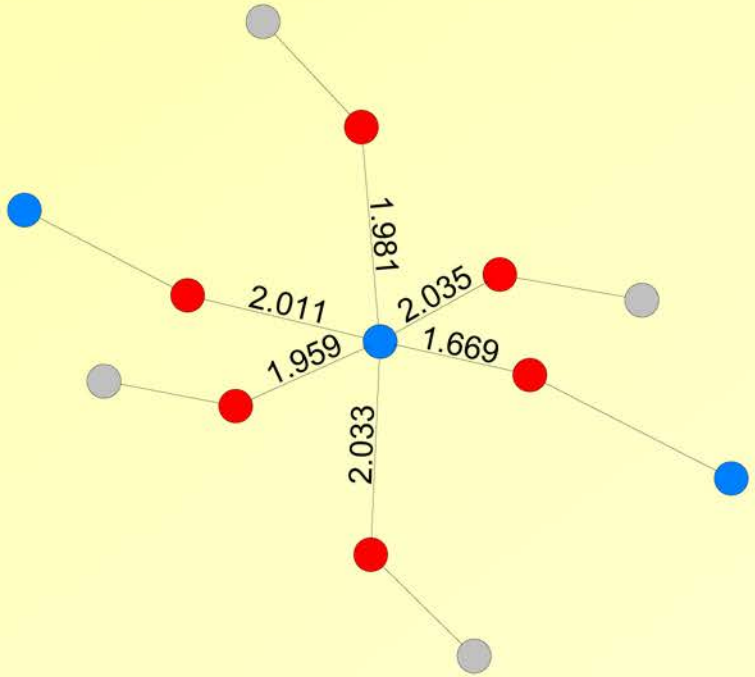
VOB – MODEL 1

BEFORE
GEOM. OPT.



BVS = 4.8

AFTER
GEOM. OPT. (not converged)

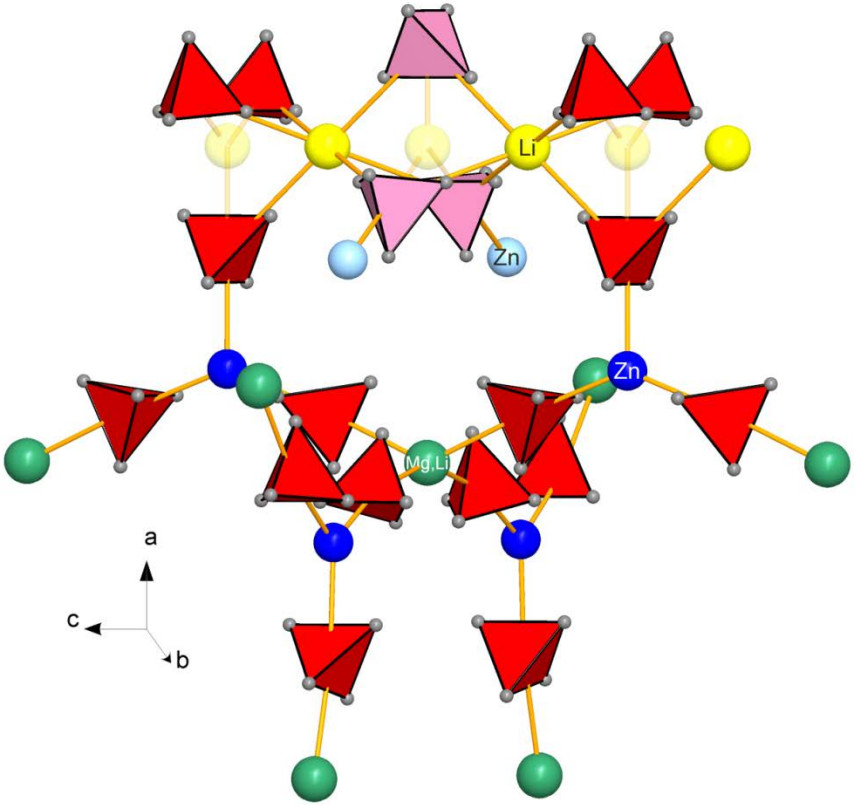


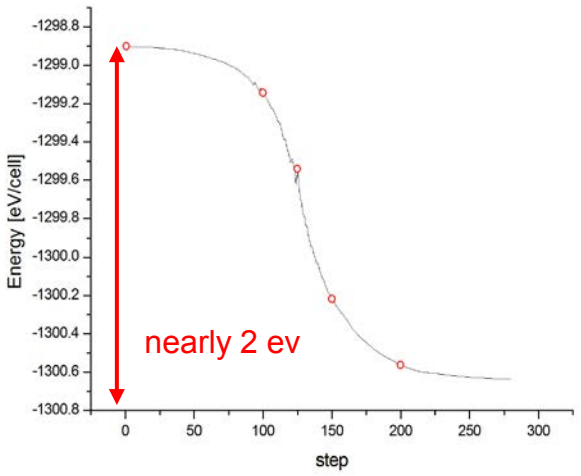
BVS = 4.1

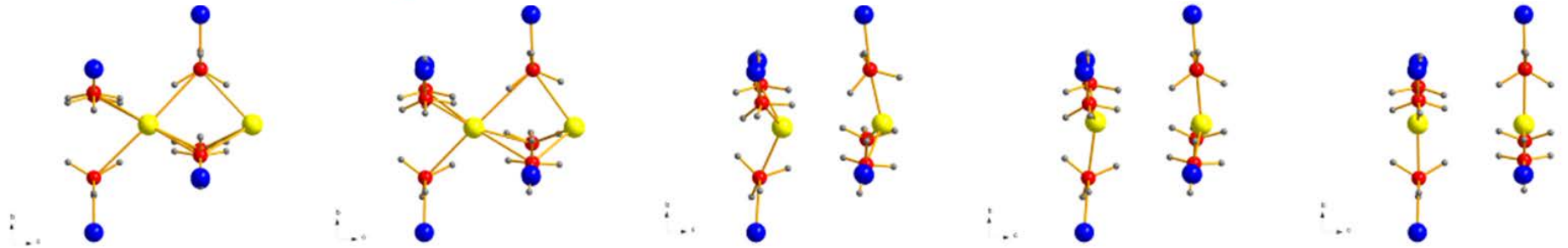
Structure validation – help of theoreticians

$Li_3MZn_5(BH_4)_{15}$

Li goes triangular! Independant on functional and correction







Perspectives for intensity extraction based methods: Single crystal methods with nano-crystals

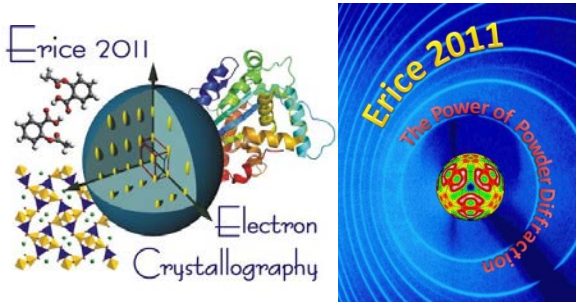
Electron crystallography

Strong interaction probe (electron) – sample (electron) → Dynamic scattering

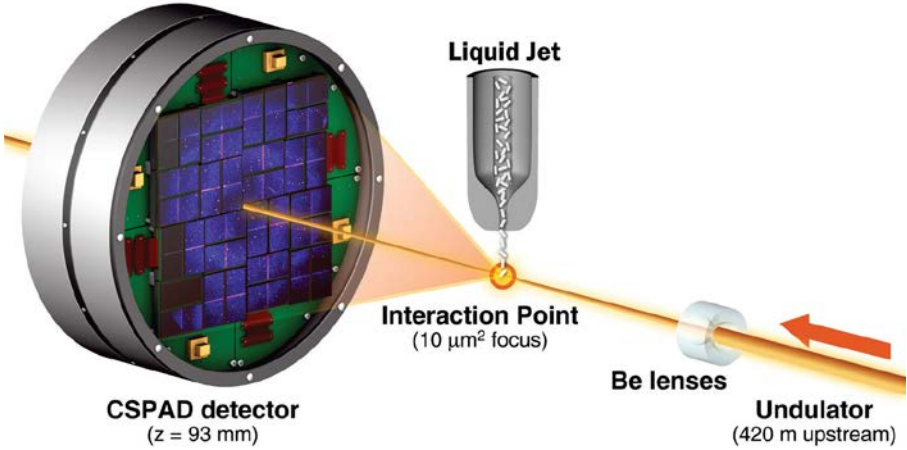
Precession electron diffraction (PED) → Kinematical scattering

Convergent beam electron diffraction (CBED) → Symmetry analysis, structure

Combining HRTEM with X-ray diffraction – dual method → phases from HRTEM images, intensities from XPD



www.crystalerice.org/



Serial femtosecond X-crystallography (SFX)

Nature 470 (**2011**) 73–77; *Science* 337 (**2012**) 362-364

Laue microdiffraction - SFX with white beam

Perspectives for pattern modeling based methods

Distributed computing – available for DASH, Fox

Learn from structure prediction (review *in Nature Materials* **7**, 2008, 937-946):

- Started with close packed comps. - Pannetier et al., *Nature* **346** (1990)343-345
- Biggest progress in molecular comps.

  - Neumann et al., *Angew. Chem. Int. Ed*. **47** (2008) 2427-2430
- Greatest success in framework comps.

  AASBU - Mellot-Draznieks et al., *Angew. Chem. Int. Ed*. **39** (2000)2270-2275
  topology modeling - *Nature Materials* **3**, 2004, 234-238

  GRINSP - *J. Appl. Cryst*. **38**, 2005, 389-395

DFT global optimizers:

- DFT + evolutionary algorithm (USPEX) - *J. Chem. Phys*. **124**, 2006, 244704
- DFT + simulated annealing - *Phys. Chem. Chem. Phys*., 2006, **8**, 1778–1784
- DFT + minima hopping (molecular dynamics) - *J. Chem. Phys*. **120**, 9911 (2004)

Joint use of diffraction and *ab-initio* calculations

Need to accelerate the DFT calculations.

DFT guided diffraction or diffraction guided DFT?

Prediction guided solution or solution guided prediction?

Peter Debye and Paul Scherrer, 1916

LiF and Si structures from PD

(P. Debye, P. Scherrer, "Interferenzen an regellos orientierten Teilchen im Röntgenlicht," *Phys. Z.* 17 (**1916**) 277-282.)

Li-Atome sowie die *F*-Atome eines solchen Gitters gehen nämlich je aus der Parallelverschiebung eines Würfels mit besetzten Mitten der Seitenflächen hervor. Von den *Li*-Atomen sind also als Grundstock im Elementarwürfel 4 Exemplare anzunehmen, für welche das Schema gilt

$$\begin{array}{lll} p_1 = 0, & q_1 = 0, & r_1 = 0, \\ p_2 = 0, & q_2 = 1/2, & r_2 = 1/2, \\ p_3 = 1/2, & q_3 = 0, & r_3 = 1/2, \\ p_4 = 1/2, & q_4 = 1/2, & r_4 = 0. \end{array}$$

Tabelle I (*LiF*, Kupferstrahlung).

Schwärzung	ϑ in Grad	$\sin\frac{\vartheta}{2}$	h_1,h_2,h_3	$\frac{\sin\vartheta/2}{\sqrt{h_1^2+h_2^2+h_3^2}}$	Zahl der Ebenen	Intensität
s. s.	30,0	0,259	1, 1, 1.	0,150	8	—
s.	33,8	0,290	1, 1, 1.	0,168	8	—
st.	37,8	0,323	1, 1, 1.	0,187	8	3,85
st.	44,2	0,377	2, 0, 0.	0,189	6	10,2
s.	56,2	0,472	2, 2, 0.	0,167	12	—
st.	63,8	0,528	2, 2, 0.	0,187	12	10,2
s. s.	67,4	0,554	3, 1, 1.	0,167	24	—
s. s.	71,4	0,583	2, 2, 2.	0,168	8	—
m.	76,6	0,620	3, 1, 1.	0,187	24	3,15
m.	80,8	0,647	2, 2, 2.	0,187	8	4,51
m.	97,8	0,753	4, 0, 0.	0,188	6	1,86
s.	111,0	0,824	3, 3, 1.	0,189	24	1,82
st.	116,0	0,848	4, 2, 0.	0,190	24	8,10
st.	137,6	0,932	4, 2, 2.	0,190	24	6,75
s. s.	153,2	0,973	4, 4, 0.	0,172	12	—
st.	166,6	0,993	{3,3,3. / 5,1,1.}	0,191	{8 / 24}	1,71

Entsprechend gilt für die *F*-Atome

$$\begin{array}{lll} p_1 = 1/2, & q_1 = 1/2, & r_1 = 1/2, \\ p_2 = 1/2, & q_2 = 1, & r_2 = 1, \\ p_3 = 1, & q_3 = 1/2, & r_3 = 1, \\ p_4 = 1, & q_4 = 1, & r_4 = 1/2. \end{array}$$

Bildet man nun mit Hilfe dieser Angaben den Strukturfaktor S, dann findet man

$$S = (A_{Li} + e^{i\pi(h_1+h_2+h_3)} A_F) \qquad (3)$$

$$\left\{1 + e^{i\pi(h_2+h_3)} + e^{i\pi(h_3+h_1)} + e^{i\pi(h_1+h_2)}\right\}$$

Ordnet man nun die Indizestriplets nach steigenden Quadratsummen und läßt mit Rücksicht auf α) die gemischten Indizes fort, dann bekommt man die in Tabelle I in der vierten Spalte groß gedruckten Zusammenstellungen. Ist das Modell richtig, dann muß jede beobachtete Linie denselben Wert von

$$\frac{\sin\vartheta/2}{\sqrt{h_1^2+h_2^2+h_3^2}}$$

liefern. Daß dem tatsächlich so ist, zeigen die großgedruckten Zahlen der fünften Spalte. Der kleine Gang der Zahlen von 0,187 bis 0,191, der übrigens nur etwa 2 Proz. ausmacht, ist außerdem leicht erklärlich durch den Umstand, daß das Stäbchen in der Kamera nicht genau im Mittelpunkt gestanden hat.

Eine Kontrolle liefert die Ausführung derselben Rechnung an den in kleinem Druck angegebenen auf die β-Linie bezüglichen Zahlen der Tabelle. Auch sie liefern eine gute Konstanz des oben genannten Verhältnisses und bestätigen damit das Modell von neuem. Die zu alleroberst in der Tabelle I aufgeführte, sehr schwache Linie bildet die einzige Ausnahme. Sie ist nicht mit Sicherheit reell. Wir führen sie trotzdem mit auf, weil die Tabelle dem tatsächlichen Gang der Beobachtungen entsprechen soll, bei welcher zuerst der Film ausgemessen wurde, ohne eine Tabelle der erwarteten Gesetzmäßigkeit zur Hand zu haben, während nachher die Gesetzmäßigkeiten an Hand der Zahlen festgestellt wurden, ohne die Aufnahme weiter zu berücksichtigen.

Tabelle I wird vervollständigt durch eine 6. Spalte, in der für jede Linie die Zahl der mitwirkenden Netzebenen angegeben ist. In der 7. Spalte stehen die mit Hilfe dieser Zahl und mit Rücksicht auf das im vorigen Paragraphen hervorgehobene Resultat über die Abhängigkeit der Intensität von $h_1^2+h_2^2+h_3^2$ für dieselbe ausgerechneten Werte. Da es sich nur um

werden. Sie ist ebenso angeordnet wie Tabelle I.

Tabelle III (*Si*, Kupferstrahlung).

Schwärzung	in ϑ Grad	$\sin\frac{\vartheta}{2}$	h_1,h_2,h_3	$\frac{\sin\vartheta/2}{\sqrt{h_1^2+h_2^2+h_3^2}}$	Zahl der Ebenen	Intensität
s. s.	26,0	0,225	1, 1, 1.	0,130	8	—
st.	28,8	0,248	1, 1, 1.	0,143	8	1,33
s. s.	43,2	0,369	2, 2, 0.	0,130	12	—
st.	47,8	0,405	2, 2, 0.	0,143	12	1,50
s.	51,8	0,437	3, 1, 1.	0,132	24	—
m–st	56,2	0,471	3, 1, 1.	0,142	24	1,09
s. s.	63,0	0,522	4, 0, 0.	0,131	6	—
m.	68,6	0,563	4, 0, 0.	1,141	6	0,275
m.	76,6	0,620	3, 3, 1.	0,142	24	0,630
s. s. s.	81,2	0,651	4, 2, 2.	0,133	24	—
m–st	87,4	0,691	4, 2, 2.	0,141	24	1,00
m.	94,8	0,736	{3,3,3 / 5,1,1}	0,142	{8 / 24}	0,595
s. s. s.	99,0	0,760	4, 4, 0.	0,134	12	—
s.–m.	107,2	0,805	4, 4, 0.	0,142	12	0,375
m–st	114,0	0,839	5, 3, 1.	0,142	48	0,690
m–st	127,4	0,896	6, 2, 0.	0,142	24	0,600
s. s. s.	132,4	0,915	4, 4, 4.	0,132	8	—
m.	136,0	0,927	5, 3, 3.	0,141	24	0,278
s.	146,2	0,957	7, 1, 4.	0,134	48	—
m.	158,8	0,983	4, 4, 4.	0,142	8	0,167

Der einzige Unterschied besteht darin, daß nun nicht dasselbe Modell wie bei *LiF* zur Erklärung paßte. Es fehlen jetzt nämlich nicht allein die gemischten Indizes bei den nach steigender Quadratsumme geordneten Triplets der Spalte 5, sondern außerdem noch die geraden Indizes, deren Summe $(h_1+h_2+h_3)$ kein Vielfaches von 4 ist. Das Fehlen dieser Indizes bei der Reflexion im monochromatischen Licht ist aber für das charakteristisch. mentarwürfel s Gitter aufgeba relativen Koordi

$$\begin{array}{lll} p_4 = 1/2, & q_4 = 1/2, & r_4 = 0, \\ p_5 = 1/4, & q_5 = 1/4, & r_5 = 1/4, \\ p_6 = 1/4, & q_6 = 3/4, & r_6 = 3/4, \\ p_7 = 3/4, & q_7 = 1/4, & r_7 = 3/4, \\ p_8 = 3/4, & q_8 = 3/4, & r_8 = 1/4. \end{array}$$

$$\begin{array}{lll} p_1 = 0, & q_1 = 0, & r_1 = 0, \\ p_2 = 0, & q_2 = 1/2, & r_2 = 1/2, \\ p_3 = 1/2, & q_3 = 0, & r_3 = 1/2, \end{array}$$

The pionneers

Peter Debye and Paul Scherrer

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