Singular-value decomposition of Rietveld least-squares matrix

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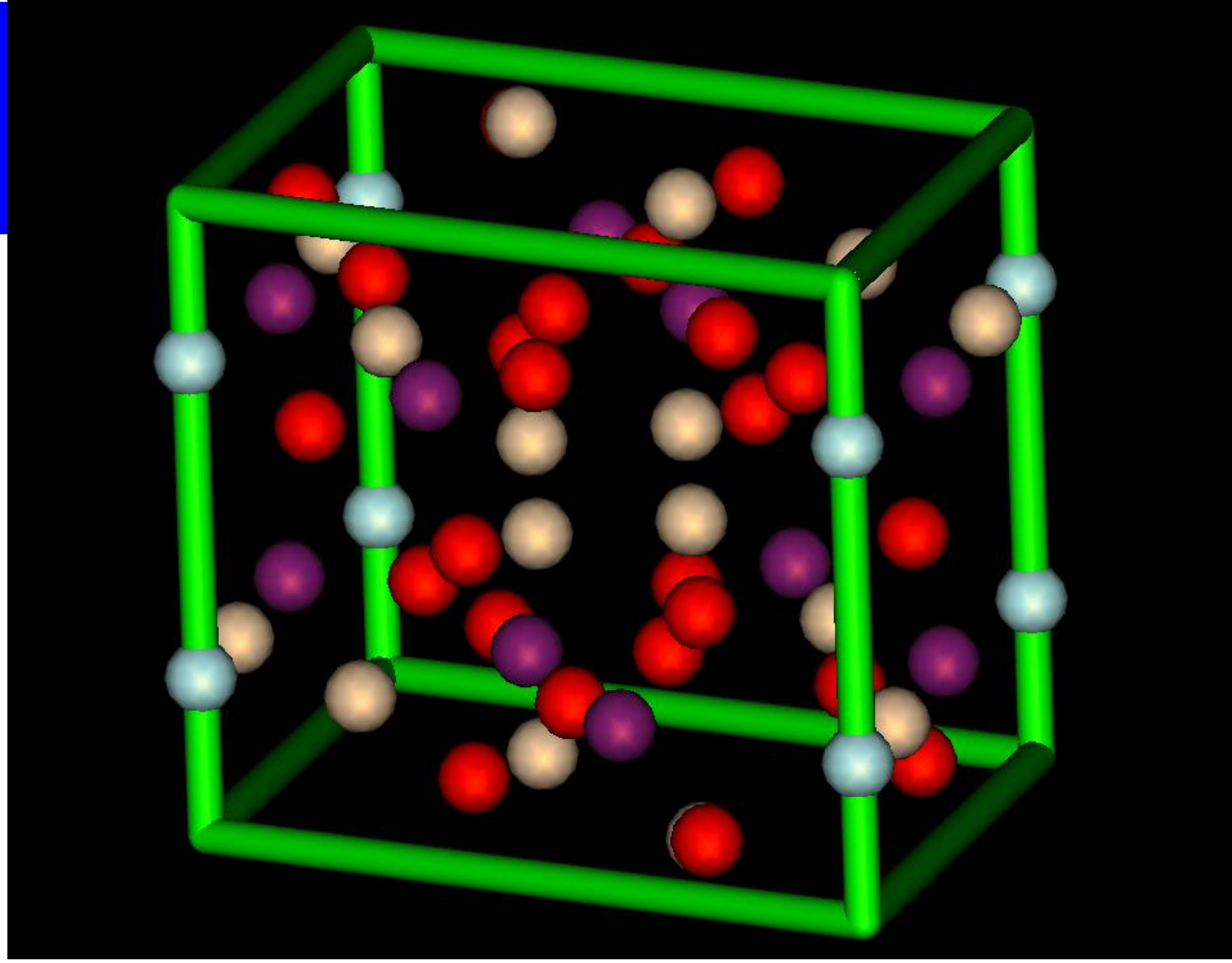
OUTLINE FOR THE TALK

1. Rietveld Method
2. Crystallographic least-squares system of normal equations
3. Diagnosing problematic Rietveld refinements
4. Crystal-chemical Rietveld refinement: A new concept

1. Rietveld Method

Standard Description of a Crystal Structure



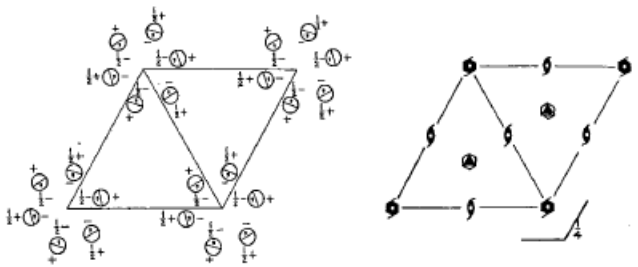
- > space group symmetry
- > cell parameters
- > atom positions

```
SPGNAM= P63/m
CELEDG=      9.367000000     9.367000000     6.884000000
CELANG=     90.000000000    90.000000000   120.000000000
ATOM=     1   Ca    4f   3..          0.333300000     0.666700000     0.001100000
ATOM=     2   Ca    6h   m..          0.241600000     0.007100000     0.250000000
ATOM=     3   P     6h   m..          0.398100000     0.368800000     0.250000000
ATOM=     4   O     6h   m..          0.326200000     0.484300000     0.250000000
ATOM=     5   O     6h   m..          0.588000000     0.466800000     0.250000000
ATOM=     6   O    12i     1          0.341600000     0.256800000     0.070400000
ATOM=     7   F     2a   -6..          0.000000000     0.000000000     0.250000000
```

International Tables for Crystallography…

$P\,6_3/m$ C_{6h}^2 $6/m$ Hexagonal

No. 176 $P\,6_3/m$ Patterson symmetry $P\,6/m$



Origin at centre ($\bar{3}$) on 6_3

Asymmetric unit $0\le x\le\frac{1}{3}$; $0\le y\le\frac{1}{3}$; $0\le z\le\frac{1}{2}$; $x\le(1+y)/2$; $y\le\min(1-x,(1+x)/2)$

Vertices $0,0,0$ $\frac{1}{3},0,0$ $\frac{2}{3},\frac{1}{3},0$ $\frac{1}{3},\frac{2}{3},0$ $0,\frac{1}{3},0$
$0,0,\frac{1}{2}$ $\frac{1}{3},0,\frac{1}{2}$ $\frac{2}{3},\frac{1}{3},\frac{1}{2}$ $\frac{1}{3},\frac{2}{3},\frac{1}{2}$ $0,\frac{1}{3},\frac{1}{2}$

Symmetry operations

(1) 1	(2) 3^+ 0,0,z	(3) 3^- 0,0,z
(4) $2(0,0,\frac{1}{2})$ 0,0,z	(5) $6^-(0,0,\frac{1}{2})$ 0,0,z	(6) $6^+(0,0,\frac{1}{2})$ 0,0,z
(7) $\bar{1}$ 0,0,0	(8) $\bar{3}^+$ 0,0,z; 0,0,0	(9) $\bar{3}^-$ 0,0,z; 0,0,0
(10) m $x,y,\frac{1}{2}$	(11) $\bar{6}^-$ 0,0,z; 0,0,$\frac{1}{2}$	(12) $\bar{6}^+$ 0,0,z; 0,0,$\frac{1}{2}$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (4); (7)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates						Reflection conditions
									General:
12	i	1	(1) x,y,z	(2) $\bar{y},x-y,z$	(3) $\bar{x}+y,\bar{x},z$				$000l$: $l=2n$
			(4) $\bar{x},\bar{y},z+\frac{1}{2}$	(5) $y,\bar{x}+y,z+\frac{1}{2}$	(6) $x-y,x,z+\frac{1}{2}$				
			(7) $\bar{x},\bar{y},\bar{z}$	(8) $y,\bar{x}+y,\bar{z}$	(9) $x-y,x,\bar{z}$				
			(10) $x,y,\bar{z}+\frac{1}{2}$	(11) $\bar{y},x-y,\bar{z}+\frac{1}{2}$	(12) $\bar{x}+y,\bar{x},\bar{z}+\frac{1}{2}$				
									Special: as above, plus
6	h	m . .	$x,y,\frac{1}{4}$	$\bar{y},x-y,\frac{1}{4}$	$\bar{x}+y,\bar{x},\frac{1}{4}$	$\bar{x},\bar{y},\frac{3}{4}$	$y,\bar{x}+y,\frac{3}{4}$	$x-y,x,\frac{3}{4}$	no extra conditions
6	g	$\bar{1}$	$\frac{1}{2},0,0$	$0,\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$hkil$: $l=2n$
4	f	3 . .	$\frac{1}{3},\frac{2}{3},z$	$\frac{2}{3},\frac{1}{3},z+\frac{1}{2}$	$\frac{2}{3},\frac{1}{3},\bar{z}$	$\frac{1}{3},\frac{2}{3},\bar{z}+\frac{1}{2}$			$hkil$: $l=2n$ or $h-k=3n+1$ or $h-k=3n+2$
4	e	3 . .	$0,0,z$	$0,0,z+\frac{1}{2}$	$0,0,\bar{z}$	$0,0,\bar{z}+\frac{1}{2}$			$hkil$: $l=2n$
2	d	$\bar{6}$ . .	$\frac{1}{3},\frac{2}{3},\frac{1}{4}$	$\frac{2}{3},\frac{1}{3},\frac{3}{4}$					$hkil$: $l=2n$ or $h-k=3n+1$ or $h-k=3n+2$
2	c	$\bar{6}$ . .	$\frac{1}{3},\frac{2}{3},\frac{1}{4}$	$\frac{2}{3},\frac{1}{3},\frac{3}{4}$					$hkil$: $l=2n$ or $h-k=3n+1$ or $h-k=3n+2$
2	b	$\bar{3}$ . .	$0,0,0$	$0,0,\frac{1}{2}$					$hkil$: $l=2n$
2	a	$\bar{6}$ . .	$0,0,\frac{1}{4}$	$0,0,\frac{3}{4}$					$hkil$: $l=2n$

Symmetry of special projections

Along [001] $p\,6$ $\boldsymbol{a}'=\boldsymbol{a}$ $\boldsymbol{b}'=\boldsymbol{b}$ Origin at 0,0,z

Along [100] $p\,2g\,m$ $\boldsymbol{a}'=\frac{1}{2}(\boldsymbol{a}+2\boldsymbol{b})$ $\boldsymbol{b}'=\boldsymbol{c}$ Origin at x,0,0

Along [210] $p\,2g\,m$ $\boldsymbol{a}'=\frac{1}{2}\boldsymbol{b}$ $\boldsymbol{b}'=\boldsymbol{c}$ Origin at $x,\frac{1}{2}x$,0

Maximal non-isomorphic subgroups

I [2]$P\,6_3$ 1; 2; 3; 4; 5; 6
[2]$P\,\bar{3}$ 1; 2; 3; 7; 8; 9
[2]$P\,\bar{6}$ 1; 2; 3; 10; 11; 12
[3]$P\,2_1/m$ 1; 4; 7; 10

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

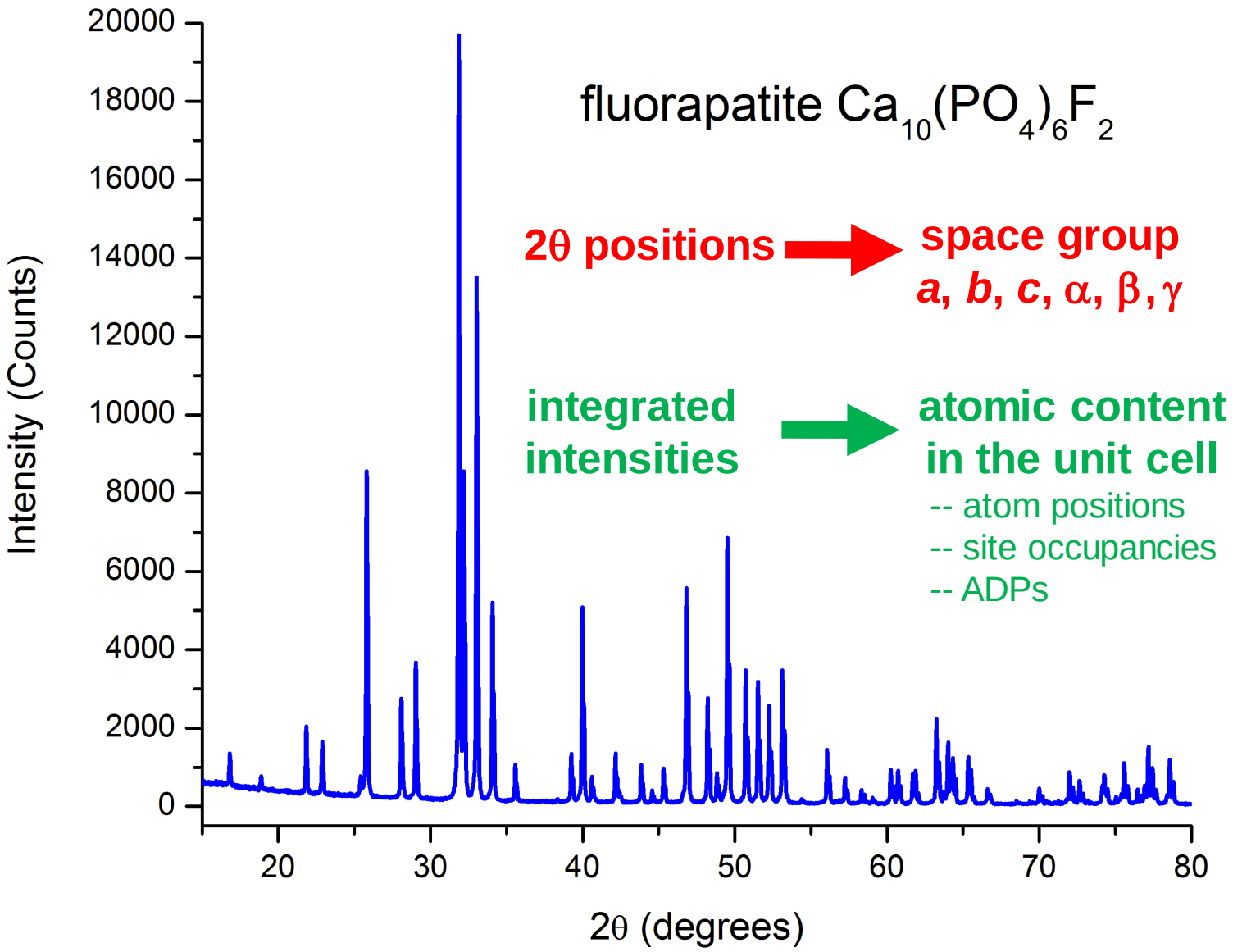
IIc [3]$P\,6_3/m\,(\boldsymbol{c}'=3\boldsymbol{c})$; [3]$H\,6_3/m\,(\boldsymbol{a}'=3\boldsymbol{a},\boldsymbol{b}'=3\boldsymbol{b})$ ($P\,6_3/m$)

Minimal non-isomorphic supergroups

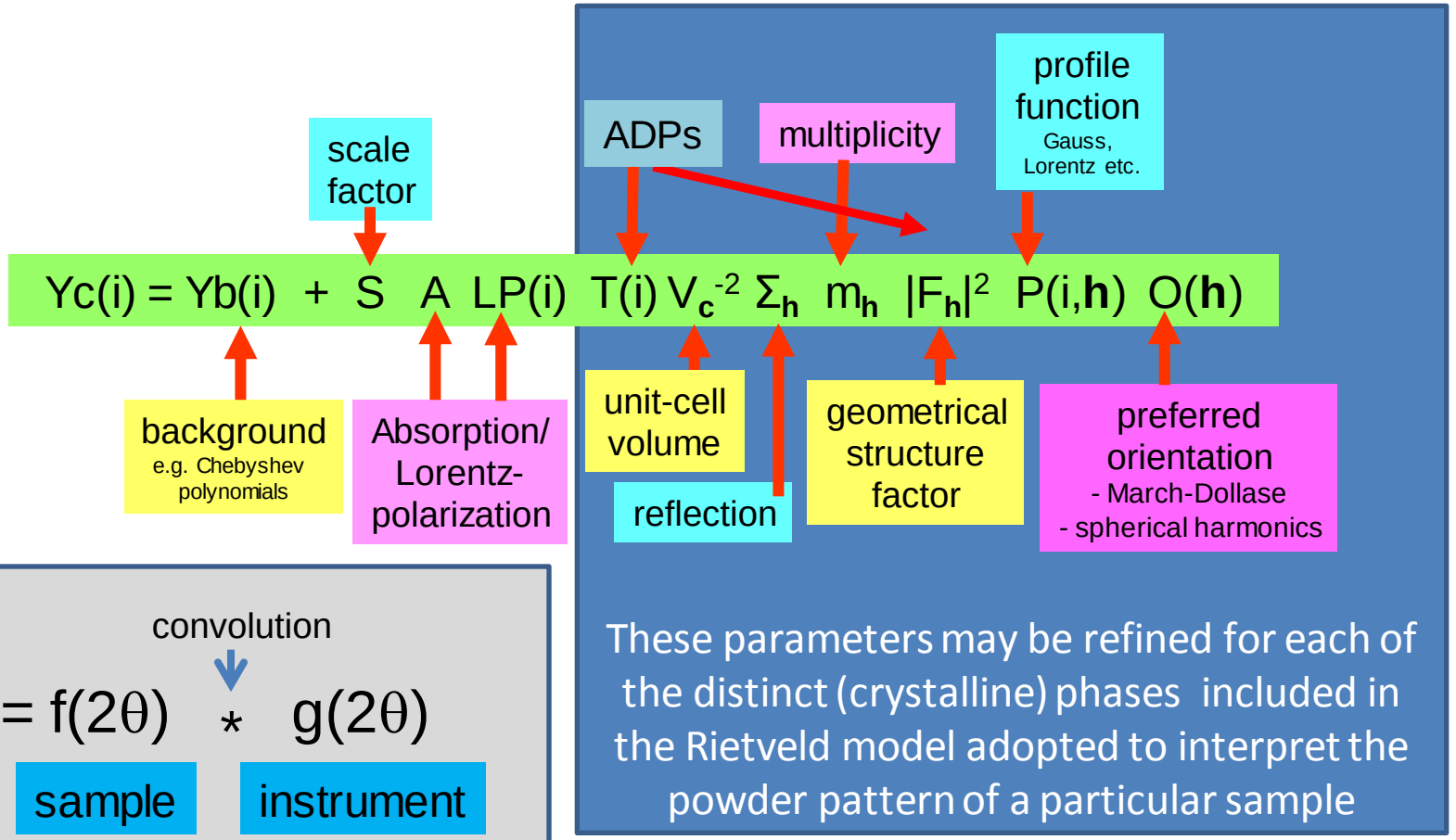
I [2]$P\,6_3/m\,c\,m$; [2]$P\,6_3/m\,m\,c$

II [2]$P\,6/m\,(2\boldsymbol{c}'=\boldsymbol{c})$

X-ray powder pattern of a single-phase crystalline material

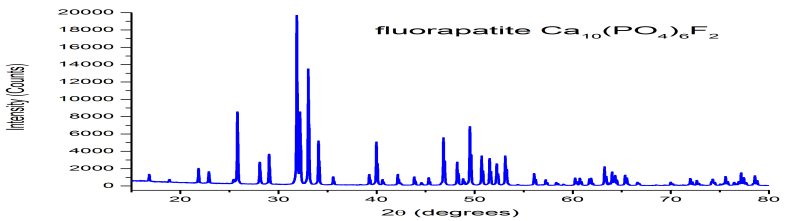


Integrated intensity formula for powder diffraction implemented in Rietveld programs



Calculation and derivatives of Rietveld profiles

Yo(i) =



For each step i, we compare the counts Yo(i) with a calculated diffraction profile Yc(i)

scale factor

thermal factors or ADPs

multiplicity

profile function
Gauss, Lorentz etc.

$$Yc(i) = Yb(i) + S\ A\ LP(i)\ T(i)\ V_c^{-2}\ \Sigma_h\ m_h\ |F_h|^2\ P(i,\mathbf{h})\ O(\mathbf{h})$$

background
Chebyshev polynomials

Absorption/ Lorentz-polarization

unit-cell volume

reflection

geometrical structure factor

preferred orientation
March-Dollase spherical harmonics

P0 is the collection of parameters in all the terms of the expression of Yc(i).
For each parameter p in **P0**, we can write:

$$\partial Yc(i)/\partial p \approx (Yc(i, \mathbf{P0}+\Delta p) - Yc(i,\mathbf{P0})) / \Delta p$$

numerically calculable with small Δp

First two terms of the Taylor series expansion at **P0** of Yc(i,**P**) :

$$Yc(i, \mathbf{P}=\mathbf{P0}+ \Delta\mathbf{p}) \approx Yc(i,\mathbf{P0}) + \Delta\mathbf{p} \bullet \partial Yc(i)/\partial\mathbf{p}$$

easily calculable linear function of Δ**p**

vector

The • indicates a dot product

2. Crystallographic least-squares system of normal equations

Crystallographic Least-squares System of Normal Equations

For each measured intensity i ,
at each step in a powder profile or each reflection for a single crystal,
we have a weighted equation

"weights" — $w(i)\,[Yo(i) - Yc(i,\mathbf{P})] = w(i)\,\Delta(i)$ — "sum of squares"

We look for the model **P** that will minimize $\Sigma_i\, w(i)\,[\Delta(i)]^2$ knowing that

$$Yc(i, \mathbf{P}=\mathbf{P0}+\Delta\mathbf{p}) \approx Yc(i,\mathbf{P0}) + \partial Yc(i)/\partial\mathbf{p} \bullet \Delta\mathbf{p}$$

This gives the linear system of equations:

$$w(i)\,(\partial Yc(i)/\partial\mathbf{p} \bullet \Delta\mathbf{p}) = w(i)\,[Yo(i) - Yc(i,\mathbf{P0})]$$

where the unknowns are the changes $\Delta\mathbf{p}$ to bring to the current model **P0**

that we symbolize as $A \bullet X = B$, with as many equations as there are measured intensities.

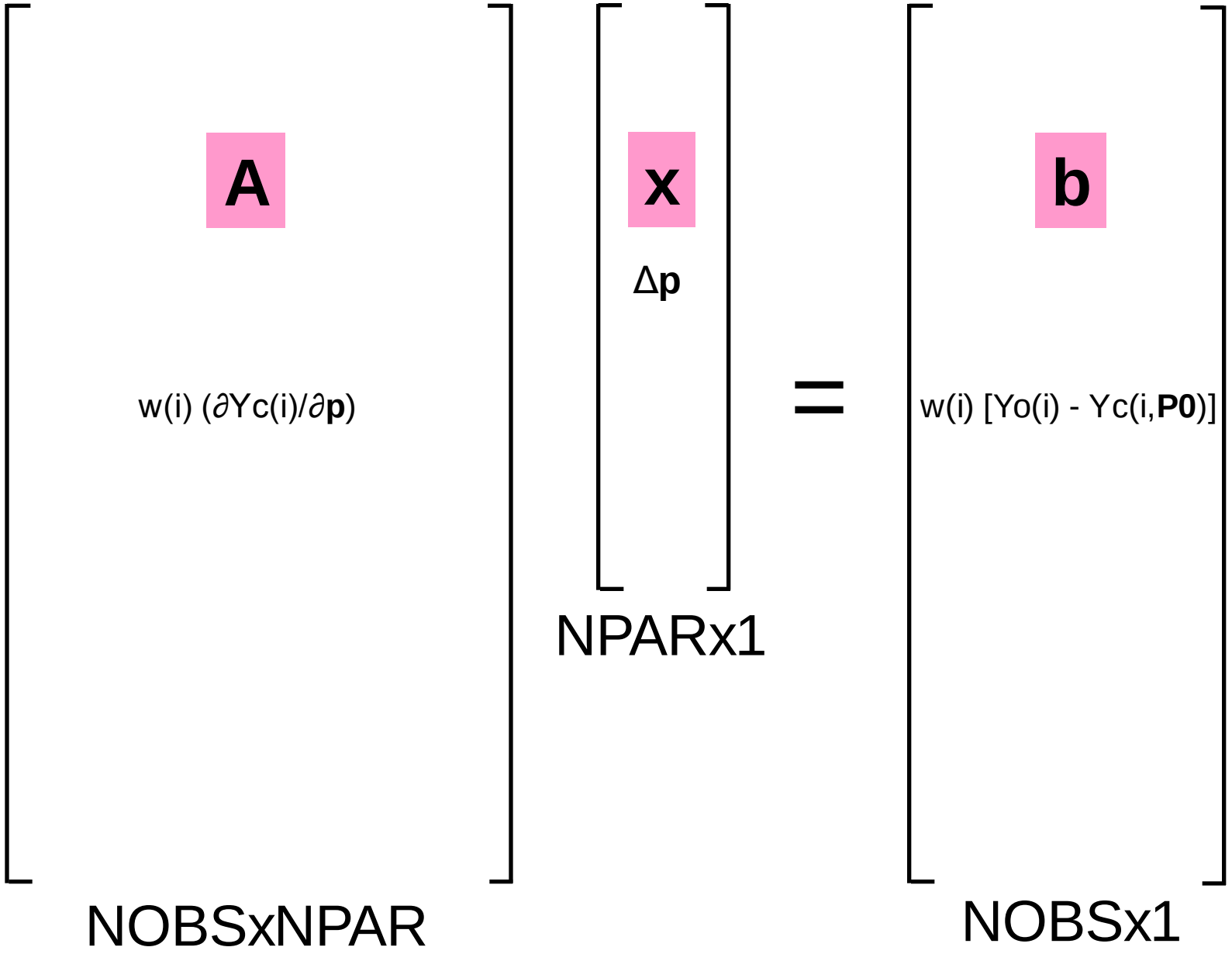
From this, we create the ***normal system of equations***,
with dimension equal in number to the much smaller number of parameters in the model:

"A_matrix" — $\mathbf{A}^T \bullet \mathbf{A} \bullet \mathbf{x} = \mathbf{A}^T \bullet \mathbf{b}$ — "b_vector"

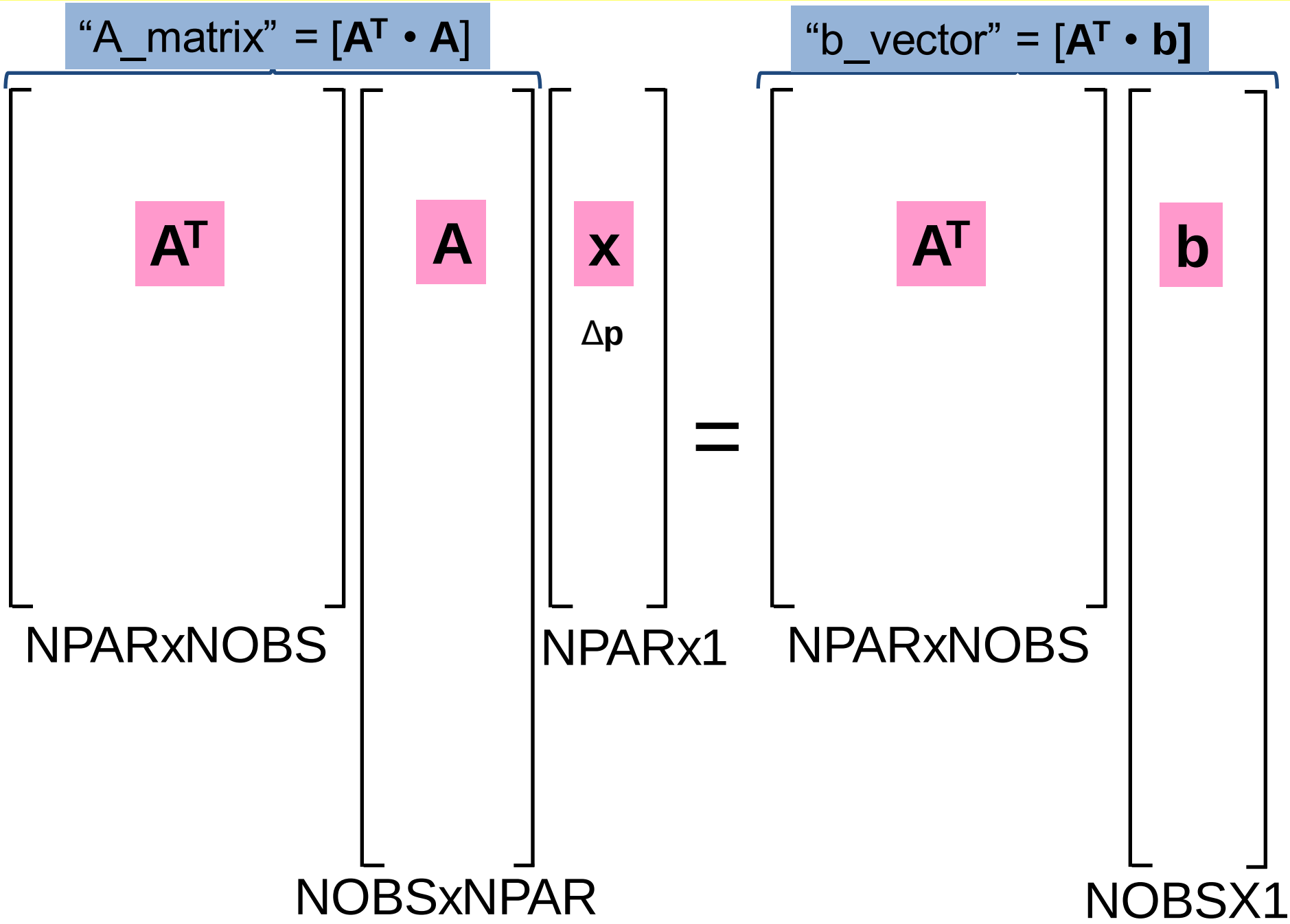
and solve it by *e.g.* matrix inversion as:

$$\mathbf{x} = [\mathbf{A}^T \bullet \mathbf{A}]^{-1} \bullet \mathbf{A}^T \bullet \mathbf{b}$$

This gives the linear system of equations
where the solution **x** the unknowns are the changes **Δp** to bring to the current model **P0**



We then build the “A_matrix” and the “b_vector” as follows



We next solve this
linear "least-squares system of normal equations"
by matrix inversion as:

$$\mathbf{x} = \Delta\mathbf{p} = [\mathbf{A}^T \bullet \mathbf{A}]^{-1} \bullet \mathbf{A}^T \bullet \mathbf{b}$$

matrix inversion of the "A_matrix" is the crucial step

The estimated 1σ standard uncertainty (s.u.) errors (or e.s.d.s) for the refined parameters are obtained as: $\sigma(x_k) = \mathrm{sqrt}([\mathbf{A}^T \bullet \mathbf{A}]^{-1}_{kk})$

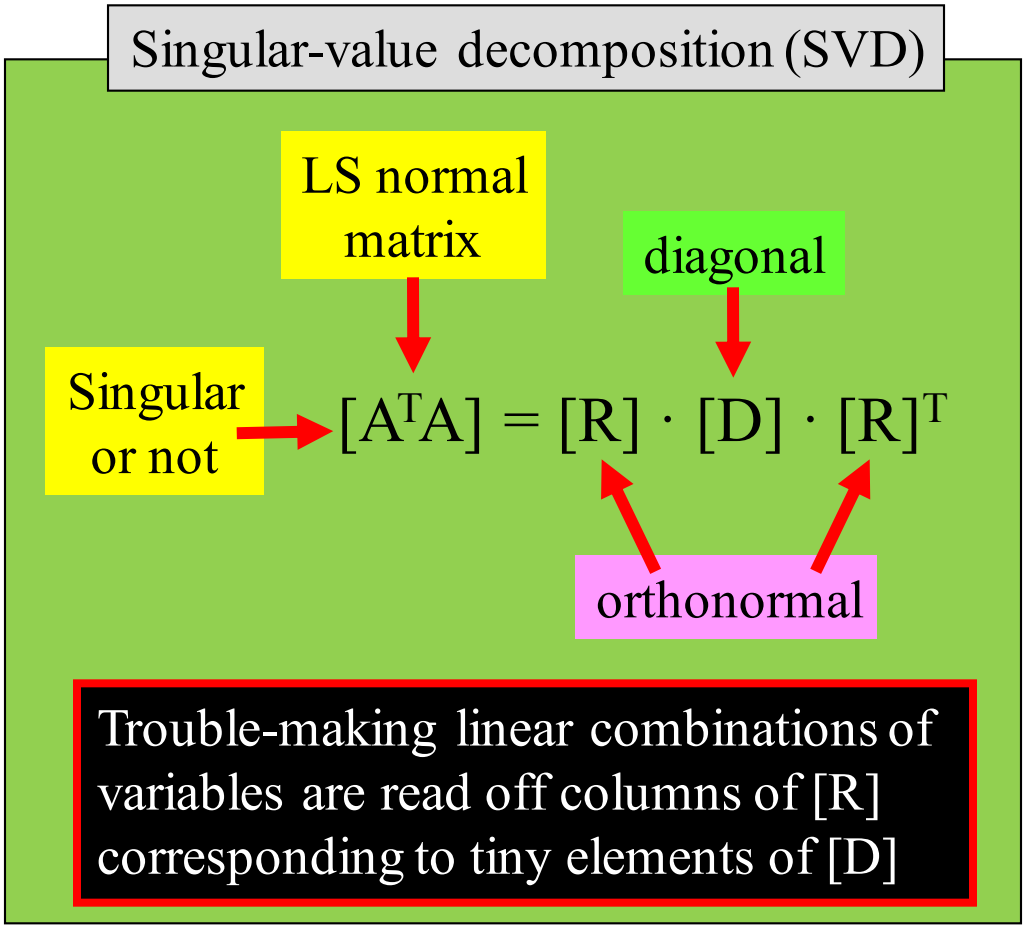
The correlation coefficients C_{jk} for the refined parameters are obtained as: $C_{jk}(x_k) = [\mathbf{A}^T \bullet \mathbf{A}]^{-1}_{jk} / \mathrm{sqrt}\,(M^{-1}_{jj}\, M^{-1}_{kk})$

We repeat iteratively the process until the value
of the "sum of squares" $\Sigma_i\, w(i)\, [\Delta(i)]^2$
does not vary significantly anymore and the differences between each iteration are smaller than a pre-defined threshold

3. Diagnosing problematic Rietveld refinements

Diagnosing problematic Rietveld refinements

Mercier et al. (2006) *J. Appl.* Cryst. **39**: 458-465



SVDdiagnostic ⇒ cure of crystallographic LS model

Software program freely distributed by the author

Diagnosing problematic refinements

Example 1

Comparing least-squares matrices from GSAS and TOPAS Rietveld refinement

Examples of the output of *SVDdiagnostic* for problematic cases of Rietveld refinements of $P6_3/m$ fluorapatite.

(*a*) Standard crystallographic refinement with *TOPAS*; R_{wp} = 8.673%, GOF = 1.550.

```
UNPROCESSED normal matrix
Condition number for matrix of normal equations =  0.785E+13
Error propagation is likely to spoil 13 trailing decimal digits out of probably 14.

Problem is ill-conditioned for double-precision matrix inversion unless error propagation is well taken care of.
Use eigenvectors for small eigenvalues below to diagnose quasi singularity.

Eigenvectors for cr11.out ranked according to eigenvalues are printed as columns below
```

Eigenvector	#:	1..	21	22	23	24	25	26	27	28	29	30	31	32
zero_error	1:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
divslit	2:	0.000..	-0.001	0.001	-0.002	0.000	-0.001	0.001	-0.001	0.001	-0.001	0.000	0.000	-0.002
bkg1040163200	3:	0.000..	0.028	-0.018	0.655	0.152	0.475	0.098	0.374	-0.008	0.334	0.079	0.228	-0.031
bkg1040163201	4:	0.000..	0.010	-0.008	-0.032	0.063	0.054	0.342	0.163	0.483	-0.150	0.618	-0.459	-0.007
bkg1040163202	5:	0.000..	-0.014	0.019	-0.555	-0.167	-0.075	0.093	0.328	0.123	0.526	0.223	0.448	0.021
bkg1040163203	6:	0.000..	-0.012	0.033	0.034	-0.360	0.026	-0.634	0.235	-0.320	0.187	0.313	-0.417	-0.020
bkg1040163204	7:	0.000..	0.001	0.023	0.401	-0.027	-0.487	-0.290	-0.355	0.275	0.053	0.405	0.385	0.016
bkg1040163205	8:	0.000..	0.006	0.000	-0.002	0.598	-0.337	0.151	-0.148	-0.323	0.523	0.067	-0.317	-0.008
bkg1040163206	9:	0.000..	0.004	-0.007	-0.276	0.391	0.482	-0.201	-0.289	-0.285	-0.235	0.455	0.266	0.000
bkg1040163207	10:	0.000..	-0.008	0.008	-0.003	-0.372	0.391	0.135	-0.662	0.150	0.446	-0.032	-0.170	-0.003
bkg1040163208	11:	0.000..	-0.003	0.008	0.148	-0.404	-0.163	0.544	-0.042	-0.604	-0.151	0.298	0.119	0.001
p1SCALE	12:	1.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
CrystalliteSiz	13:	0.000..	0.000	-0.001	-0.026	-0.006	-0.024	0.003	-0.014	0.012	-0.007	-0.002	0.023	-0.999
alat	14:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
clat	15:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
A1z	16:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
beqA1	17:	0.000..	-0.088	0.011	0.007	0.007	0.011	0.005	0.007	0.007	0.002	0.005	0.000	-0.001
A2x	18:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
A2y	19:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
beqA2	20:	0.000..	-0.061	0.005	0.007	0.007	0.009	0.013	0.003	0.006	-0.001	0.003	0.000	0.000
beqB	21:	0.000..	0.061	0.008	0.017	0.007	0.007	0.017	0.007	0.011	0.001	0.001	0.000	-0.001
Bx	22:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
By	23:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
beqO	24:	0.000..	-0.992	0.016	0.024	0.021	0.011	0.010	0.008	0.004	-0.003	0.002	0.001	-0.001
O1x	25:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O1y	26:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O2x	27:	0.000..	-0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O2y	28:	0.000..	-0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O3x	29:	0.000..	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O3y	30:	0.000..	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O3z	31:	0.001..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
beqF	32:	0.000..	0.018	0.999	0.008	0.027	0.022	0.024	0.005	0.007	-0.016	-0.017	0.000	-0.001
Eigenvalues	:	1.78E+12..	1.97E+03	2.68E+02	4.16E+01	3.56E+01	3.01E+01	2.30E+01	2.08E+01	1.44E+01	6.69E+00	5.11E+00	1.15E+00	2.26E-01

Table 2
Examples of ill-conditioned Rietveld refinements.

All background parameters: fixed. Profile parameters: divslit fixed, CrystalliteSize refined.
(*a*) Standard crystallographic refinement with *TOPAS*; R_{wp} = 8.696%, GOF = 1.553.

UNPROCESSED normal matrix

Condition number for matrix of normal equations = 0.342E+13
Error propagation is likely to spoil 13 trailing decimal digits out of probably 14.

Problem is ill-conditioned for double-precision matrix inversion unless error propagation is well taken care of.
Use eigenvectors for small eigenvalues below to diagnose quasi singularity.

Eigenvectors for cr08.out ranked according to eigenvalues are printed as columns below

Eigenvector	#:	1	2	3	4	5 ..	17	18	19	20	21	22
zero_error	1:	0.000	0.159	-0.015	0.004	-0.010 ..	0.000	0.000	0.000	0.000	0.000	0.000
p1SCALE	2:	1.000	0.000	0.000	0.000	0.000 ..	0.000	0.000	0.000	0.000	0.000	0.000
CrystalliteSize	3:	0.000	0.000	0.000	0.000	0.000 ..	0.000	0.000	0.000	0.000	0.001	-1.000
alat	4:	0.000	-0.834	-0.538	-0.001	-0.001 ..	0.000	0.000	0.000	0.000	0.000	0.000
clat	5:	0.000	-0.529	0.843	-0.001	0.000 ..	0.000	0.000	0.000	0.000	0.000	0.000
A1z	6:	0.000	0.000	0.000	-0.008	-0.075 ..	0.000	0.000	-0.001	0.000	0.000	0.000
beqA1	7:	0.000	0.000	0.000	0.000	-0.001 ..	-0.313	0.745	-0.582	0.091	-0.012	0.000
A2x	8:	0.000	0.000	-0.001	0.583	-0.001 ..	0.001	0.001	0.001	0.000	0.000	0.000
A2y	9:	0.000	0.003	-0.001	-0.808	-0.036 ..	0.000	0.000	0.000	0.000	0.000	0.000
beqA2	10:	0.000	0.000	0.000	0.000	0.000 ..	-0.927	-0.369	0.035	0.061	-0.005	0.000
beqB	11:	0.000	0.000	0.000	0.000	0.001 ..	-0.195	0.555	0.806	-0.063	-0.009	0.000
Bx	12:	0.000	0.001	0.004	-0.022	0.693 ..	0.000	0.001	-0.001	0.000	0.000	0.000
By	13:	0.000	-0.001	0.005	0.030	-0.701 ..	0.001	0.000	0.001	0.000	0.000	0.000
beqO	14:	0.000	0.000	0.000	0.000	0.000 ..	0.073	-0.010	0.102	0.992	-0.018	0.000
O1x	15:	0.000	0.000	0.000	0.004	-0.002 ..	0.000	0.001	-0.001	0.000	0.000	0.000
O1y	16:	0.000	0.000	-0.001	0.012	0.049 ..	-0.001	0.000	0.000	0.000	0.000	0.000
O2x	17:	0.000	0.000	0.001	0.020	0.016 ..	-0.001	0.001	-0.002	0.002	0.000	0.000
O2y	18:	0.000	0.000	0.000	-0.070	-0.071 ..	-0.001	0.000	-0.001	0.001	0.000	0.000
O3x	19:	0.000	-0.001	0.001	-0.007	0.068 ..	0.000	0.000	0.000	-0.001	0.000	0.000
O3y	20:	0.000	0.001	-0.001	-0.017	-0.085 ..	0.000	0.000	-0.001	-0.001	0.000	0.000
O3z	21:	0.001	0.000	0.001	-0.005	0.045 ..	0.001	-0.001	0.000	0.000	0.000	0.000
beqF	22:	0.000	0.000	0.000	0.000	0.000 ..	0.009	-0.011	-0.002	-0.019	-1.000	-0.001
Eigenvalues	:	1.80E+12	7.04E+09	2.62E+09	3.69E+08	2.17E+08 ..	9.59E+03	5.13E+03	3.58E+03	2.03E+03	2.73E+02	5.27E-01

Table 3
Final refinements obtained after diagnostic by SVD.

All background and profile parameters needed to be fixed.
(*a*) Standard crystallographic refinement with *TOPAS*; R_{wp} = 8.695 %, GOF = 1.553.

UNPROCESSED normal matrix

Condition number for matrix of normal equations = 0.659E+10
Error propagation is likely to spoil 10 trailing decimal digits out of probably 14.

Problem poorly conditioned for double-precision matrix inversion unless error propagation is well taken care of.
Use eigenvectors for small eigenvalues below to diagnose quasi singularity.

Eigenvectors for cr10.out ranked according to eigenvalues are printed as columns below

Eigenvector	#:	1	2	3	4	5	6 ..	17	18	19	20	21
zero_error	1:	0.000	0.159	-0.015	0.004	-0.010	0.007 ..	0.000	0.000	0.000	0.000	0.000
p1SCALE	2:	1.000	0.000	0.000	0.000	0.000	0.000 ..	0.000	0.000	0.000	0.000	0.000
alat	3:	0.000	-0.834	-0.538	-0.001	-0.001	0.001 ..	0.000	0.000	0.000	0.000	0.000
clat	4:	0.000	-0.529	0.843	-0.001	0.000	0.005 ..	0.000	0.000	0.000	0.000	0.000
A1z	5:	0.000	0.000	0.000	-0.008	-0.075	-0.009 ..	0.000	0.000	-0.001	0.000	0.000
beqA1	6:	0.000	0.000	0.000	0.000	-0.001	0.000 ..	-0.313	0.745	-0.582	-0.091	-0.012
A2x	7:	0.000	0.000	-0.001	0.583	-0.001	0.663 ..	0.001	0.001	0.001	0.000	0.000
A2y	8:	0.000	0.003	-0.001	-0.808	-0.036	0.467 ..	0.000	0.000	0.000	0.000	0.000
beqA2	9:	0.000	0.000	0.000	0.000	0.000	0.001 ..	-0.927	-0.369	0.035	-0.061	-0.005
beqB	10:	0.000	0.000	0.000	0.000	0.001	0.000 ..	-0.195	0.556	0.806	0.064	-0.009
Bx	11:	0.000	0.001	0.004	-0.022	0.693	-0.180 ..	0.000	0.001	-0.001	0.000	0.000
By	12:	0.000	-0.001	0.005	0.030	-0.701	-0.282 ..	0.001	0.000	0.001	0.000	0.000
beq0	13:	0.000	0.000	0.000	0.000	0.000	0.000 ..	0.073	-0.010	0.103	-0.992	-0.018
O1x	14:	0.000	0.000	0.000	0.004	-0.002	0.057 ..	0.000	0.001	-0.001	0.000	0.000
O1y	15:	0.000	0.000	-0.001	0.012	0.049	-0.074 ..	-0.001	0.000	0.000	0.000	0.000
O2x	16:	0.000	0.000	0.001	0.020	0.016	0.018 ..	-0.001	0.001	-0.002	-0.002	0.000
O2y	17:	0.000	0.000	0.000	-0.070	-0.071	0.019 ..	-0.001	0.000	-0.001	-0.001	0.000
O3x	18:	0.000	-0.001	0.001	-0.007	0.068	-0.342 ..	0.000	0.000	0.000	0.001	0.000
O3y	19:	0.000	0.001	-0.001	-0.017	-0.085	0.321 ..	0.000	0.000	-0.001	0.001	0.000
O3z	20:	0.001	0.000	0.001	-0.005	0.045	-0.024 ..	0.001	-0.001	0.000	0.000	0.000
beqF	21:	0.000	0.000	0.000	0.000	0.000	0.000 ..	0.009	-0.011	-0.002	0.019	-1.000
Eigenvalues	:	1.80E+12	7.04E+09	2.62E+09	3.69E+08	2.17E+08	9.32E+07 ..	9.59E+03	5.13E+03	3.58E+03	2.03E+03	2.73E+02

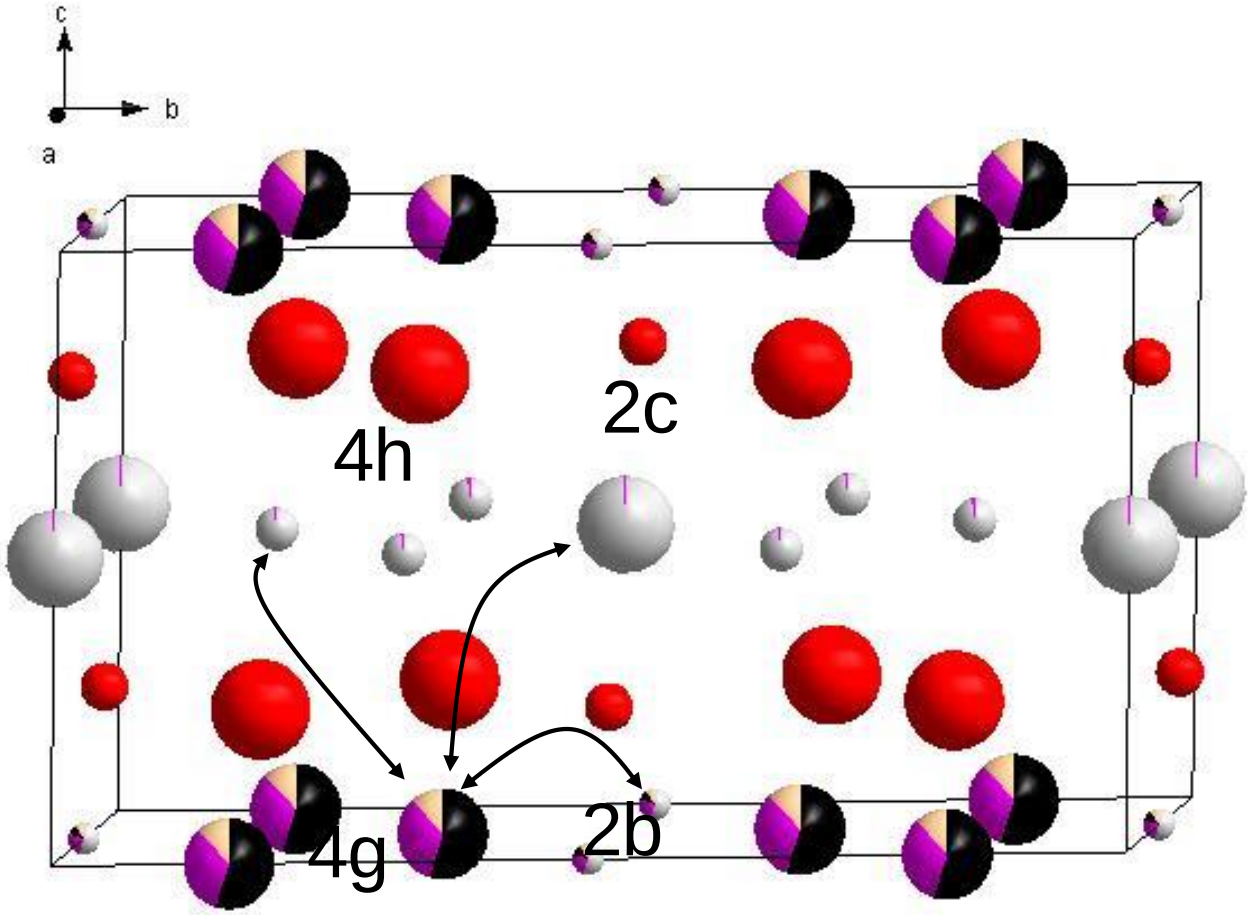
Diagnosing problematic refinements

Example 2

Rietveld refinement of a battery material

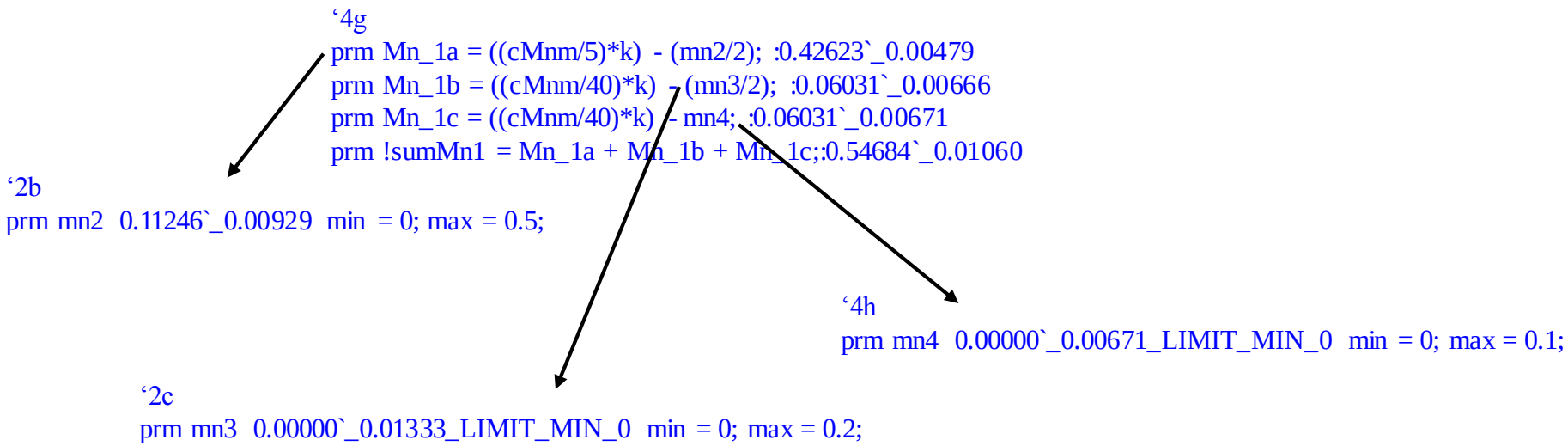
Monoclinic C2/m Li_2MnO_3-type structure

- Just like sharing out a cake – make sure everyone can get a piece!
- 4g to 2b = double occupancy to balance total composition



How to construct the constraints?

- The technique is the same as can be used in GSAS
  - divide each atom occupancy on one site over a number of 'atoms'
  - share each portion with one other site, e.g. for Mn



  - add a scaling factor to change overall Li:TM ratio whilst keeping Mn:Ni:Co ratio constant
  - still makes for quite a lot of additional variables….

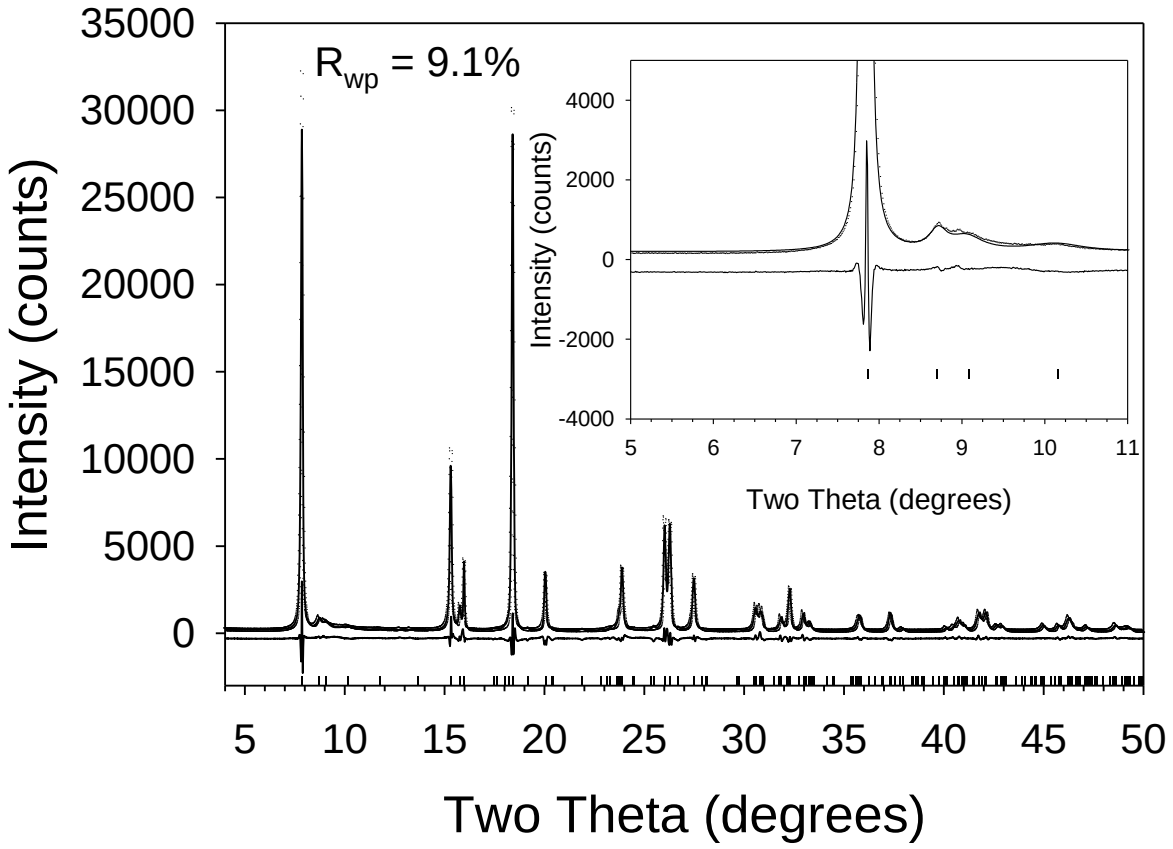
Anisotropic broadening

- Anisotropic broadening can be caused by a variety of reasons
  - Disorder (turbostratic, stacking faults, microstrain)
  - Short range order
  - Crystallite shape
- $Li_{1.2}Mn_{0.4}Ni_{0.3}Co_{0.1}O_2$ has a short range $\sqrt{3}a \times \sqrt{3}a$ ordering with some full pattern anisotropy
- Full pattern: spherical harmonic Lorentzian convolution
- $\sqrt{3}a \times \sqrt{3}a$: individual hkls broadened, e.g.

  lor_fwhm = If(And(H == 0,K == 2,L == 0), a4, 0);
- For structure refinement what causes the broadening and how you model it isn't important – whatever works to correctly evaluate integrated peak areas of the measured intensities!

Fit for the 0.65 Å dataset

- Lack of anisotropic broadening correction affects the distribution of the metals on the 4g and 2b sites



Matrix Conditioning - the starting point

UNPROCESSED normal matrix

Condition number for matrix of normal equations = 0.142E+26

Error propagation is likely to spoil ALL digits in some elements of the normal matrix.
System is singular for double-precision matrix inversion unless error propagation is well taken care of.
Use eigenvectors below to diagnose singularity.
Eigenvectors for combined.out ranked according to eigenvalues are printed as columns below

A bit more than 14!

Eigenvector #:	1 ..	152	153	154	155	156	157	158	159
k	1: -0.001 ..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn2	2: 0.000 ..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
…									
p3	19: -0.003 ..	-0.001	-0.019	-0.001	0.011	-0.039	-0.001	0.000	0.000
p4	20: 0.000 ..	-0.003	-0.022	-0.001	0.012	-0.045	-0.001	0.000	0.000
bkg9920	21: -0.009 ..	0.000	0.000	-0.001	0.001	0.000	0.004	-0.668	0.000
bkg9921	22: -0.003 ..	0.000	0.000	0.004	-0.001	0.000	-0.003	0.401	0.000
bkg9922	23: 0.004 ..	0.000	0.000	0.000	0.001	0.000	0.002	-0.269	0.000
bkg9923	24: 0.001 ..	0.000	0.000	0.000	0.000	0.000	-0.001	0.139	0.000
bkg9924	25: -0.001 ..	0.000	0.000	0.000	0.000	0.000	0.001	-0.077	0.000
bkg9925	26: 0.000 ..	0.001	0.000	0.000	0.000	0.000	0.000	0.044	0.000
……									
Eigenvalues:	0.270E+14 ..	0.912E-05	0.350E-05	0.368E-07	0.875E-09	0.777E-09	0.122E-10	0.877E-11	0.190E-11

PRECONDITIONED normal matrix

Condition number for matrix of normal equations = 0.383E+18

……

Still needs more than double-precision arithmetic

Here the preconditioning doesn't ensure numerical repeatability in inverting the LS matrix for this model and dataset

- There are a lot of variables in this refinement

- *SVDdiagnostic* identified a number of variables that were causing problems, including the background and parameters related to the anisotropic broadening

- After dealing with the problematic variables both the unprocessed and preconditioned matrices have satisfactory conditioning numbers

```
UNPROCESSED normal matrix
Condition number for matrix of normal equations =  0.110E+11
Error propagation is likely to spoil 10 trailing decimal digits out of probably 14.
Problem is ill-conditioned for double-precision matrix inversion unless error propagation is well taken care of.
Use eigenvectors for small eigenvalues below to diagnose quasi singularity.

Eigenvectors for combined_k.out ranked according to eigenvalues are printed as columns below

Eigenvector # :  1 ..          59       60        61         62       63       64        65        66

k       1:      -0.001 ..    -0.008    0.005    -0.002      0.001   -0.003    0.003     0.006    -0.004
mn2     2:       0.000 ..     0.002   -0.032    -0.045      0.000    0.010    0.008    -0.003    -0.010
co2     3:       0.000 ..     0.029    0.023     0.035     -0.004   -0.020    0.006    -0.001    -0.007
ni2     4:       0.000 ..    -0.035    0.009     0.004      0.004    0.009   -0.008     0.010     0.013
……..
Eigenvalues:  0.271E+14..  0.485E+05 0.470E+05 0.351E+05 0.277E+05 0.241E+05 0.762E+04 0.521E+04 0.246E+04


PRECONDITIONED normal matrix
Condition number for matrix of normal equations =  0.883E+04
Error propagation is likely to spoil  4 trailing decimal digits out of probably 14.
Problem well conditioned for double-precision matrix inversion.
……
Eigenvalues:   0.830E+01 ..  0.251E-01 0.201E-01 0.195E-01 0.107E-01  0.625E-02 0.565E-02 0.326E-02 0.940E-03
```

Final refined structure

Space group: C2/m (12)
Overall residuals: R_{wp} = 9.61%, R_p = 7.0%, Durban-Watson = 1.727,
a = 4.98268(23), b = 8.56248(80), c = 5.01340(36) Å, b = 109.2479(95)°
Refined stoichiometry = $Li_{1.165(36)}Mn_{0.402(13)}Ni_{0.323(16)}Co_{0.109(32)}O_2$

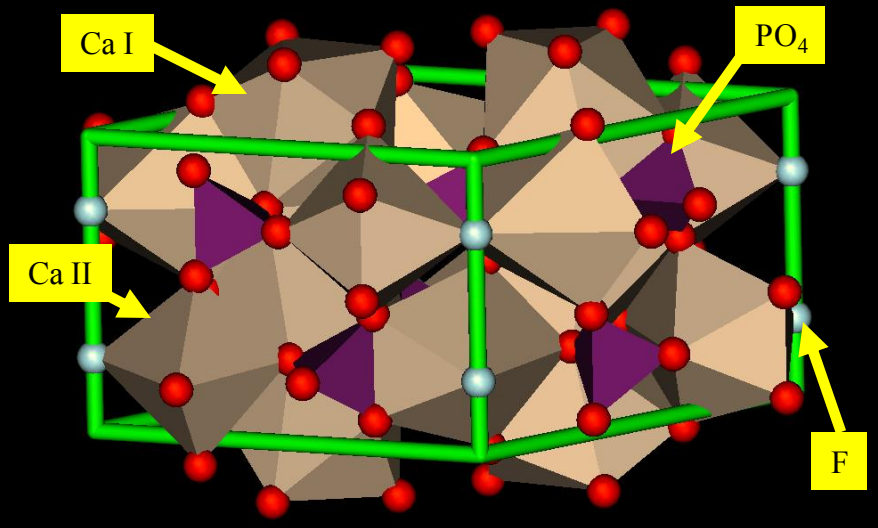
- The final refinement yielded values with reasonable ESDs
- The refined bond lengths agreed closely with those expected from bond valence parameters (low spin Co and Ni values determined from ICSD data)

Site	Atom	x	y	z	Occ	Occ (random)	Biso
4g – M1	Mn	0	0.16597(14)	0	0.5467(105)	0.4793	0.83(2)
	Ni				0.3345(104)	0.3856	
	Co				0.1152(159)	0.1305	
	Li				0.0036(217)	0.0036	
2b – M2	Mn	0	0.5	0	0.1111(93)	0.2152	0.10(6)
	Ni				0.2392(94)	0.1731	
	Co				0.0971(137)	0.0586	
	Li				0.5526(191)	0.5526	
2c – Li1	Li	0	0	0.5	0.9966(274)	0.9966	0.96(33)
	Mn				0.0005(133)	0.0016	
	Ni				0.0022(129)	0.0013	
	Co				0.0008(202)	0.0004	
4h – Li2	Li	0	0.65505(384)	0.5	0.9704(139)	0.9704	0.19(17)
	Mn				0.0000(67)	0.0142	
	Ni				0.0296(66)	0.0115	
	Co				0.0000(102)	0.0039	
4i – O1	O	0.21918(57)	0	0.22220(64)	1	1	0.23(5)
8j – O2	O	0.24292(53)	0.32251(20)	0.22823(39)	1	1	1.00(4)

4. Crystal-chemical Rietveld refinement: A new concept

low solubility

Teeth and bones made of apatite $Ca_5(PO_4)_3(OH,F,Cl)$



dense structure type

Crystal Chemistry of Apatite

$$A^{I}_4 A^{II}_6 (BO_4)_6 X_2$$

A : larger divalent (Ca^{2+}, Sr^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Ba^{2+}, etc.), monovalent (Cs^{+}, Na^{+}, Li^{+}, etc.), and trivalent (La^{3+}, Y^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+}, Dy^{3+}, etc.) cations

B : smaller 3+, 4+, 5+, 6+, and 7+ metals and metalloids (P^{5+}, As^{5+}, V^{5+}, Si^{4+}, S^{6+}, etc.)

X : halides (F^{-}, Cl^{-}, Br^{-}, I^{-}), hydroxyl $(OH)^{-}$, or oxygen ions O^{2-}

Space groups: $P6_3/m$, $P6_3$, $P2_1/m$, $P112_1/b$, etc.

most widespread

distortions in subgroups

MATERIALS APPLICATIONS

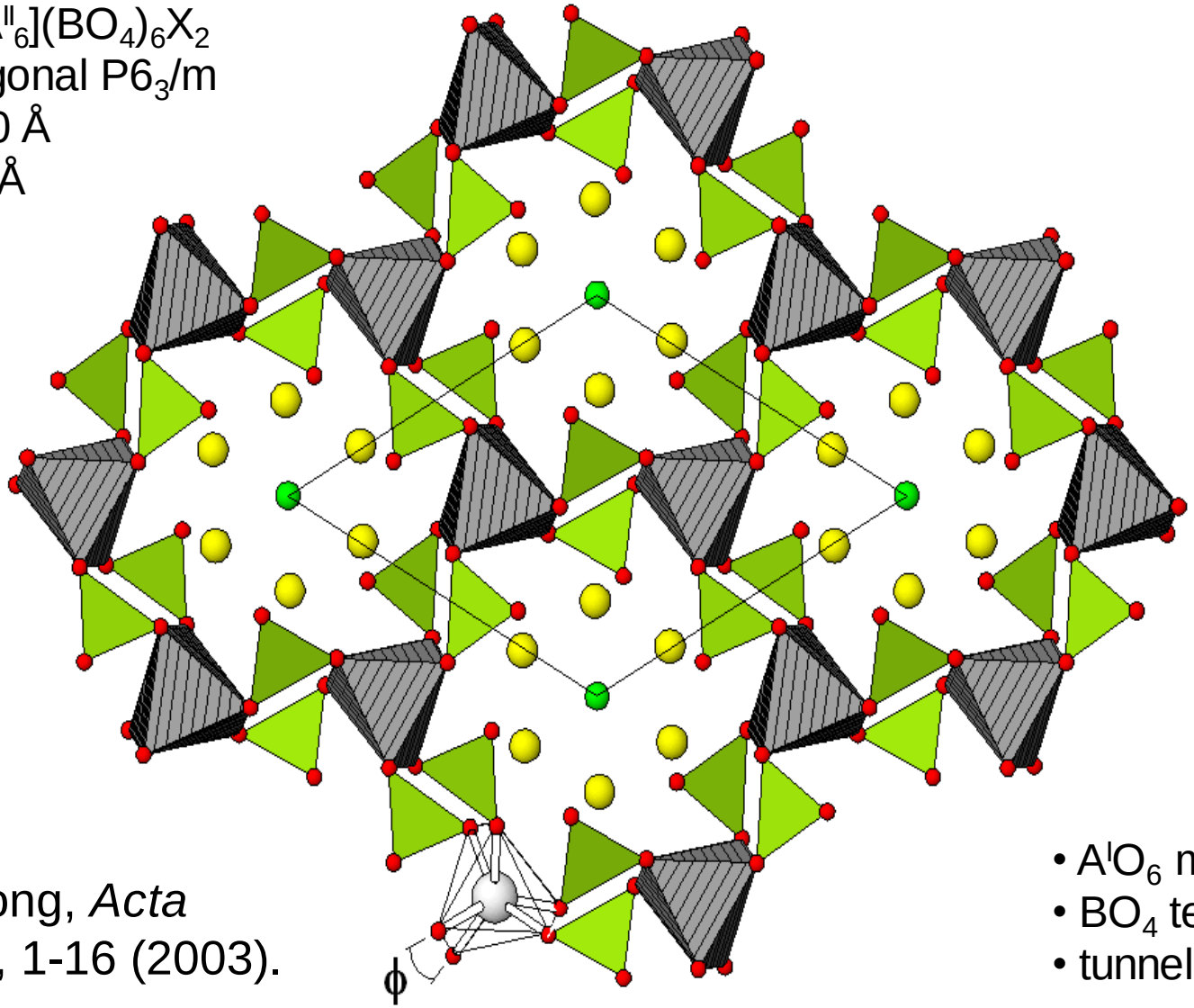
"ECO-APATITES"

toxic metal immobilization from incinerator ash, industrial or mining refuses, high-level radioactive nuclear waste

geochronology
catalysis
environmental remediation
soil treatment
bone replacement
dentistry

Apatite As a Microporous Structure

- $[A^{I}_4][A^{II}_6](BO_4)_6X_2$
- hexagonal $P6_3/m$
- *a* ~ 10 Å
- *c* ~ 7 Å

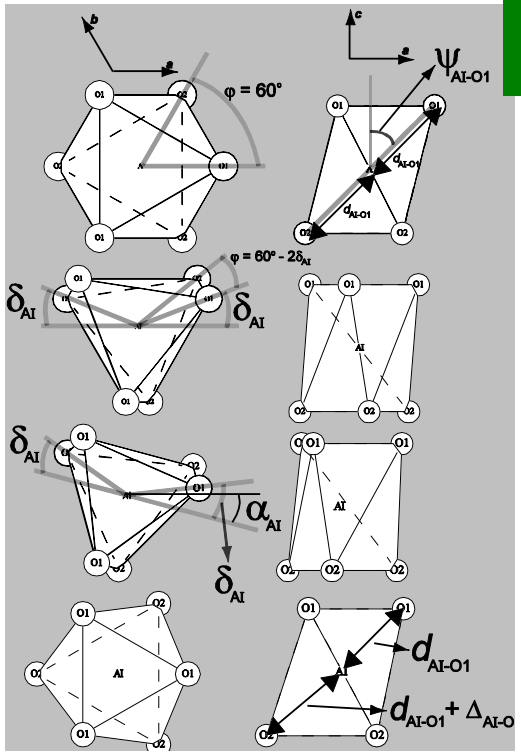


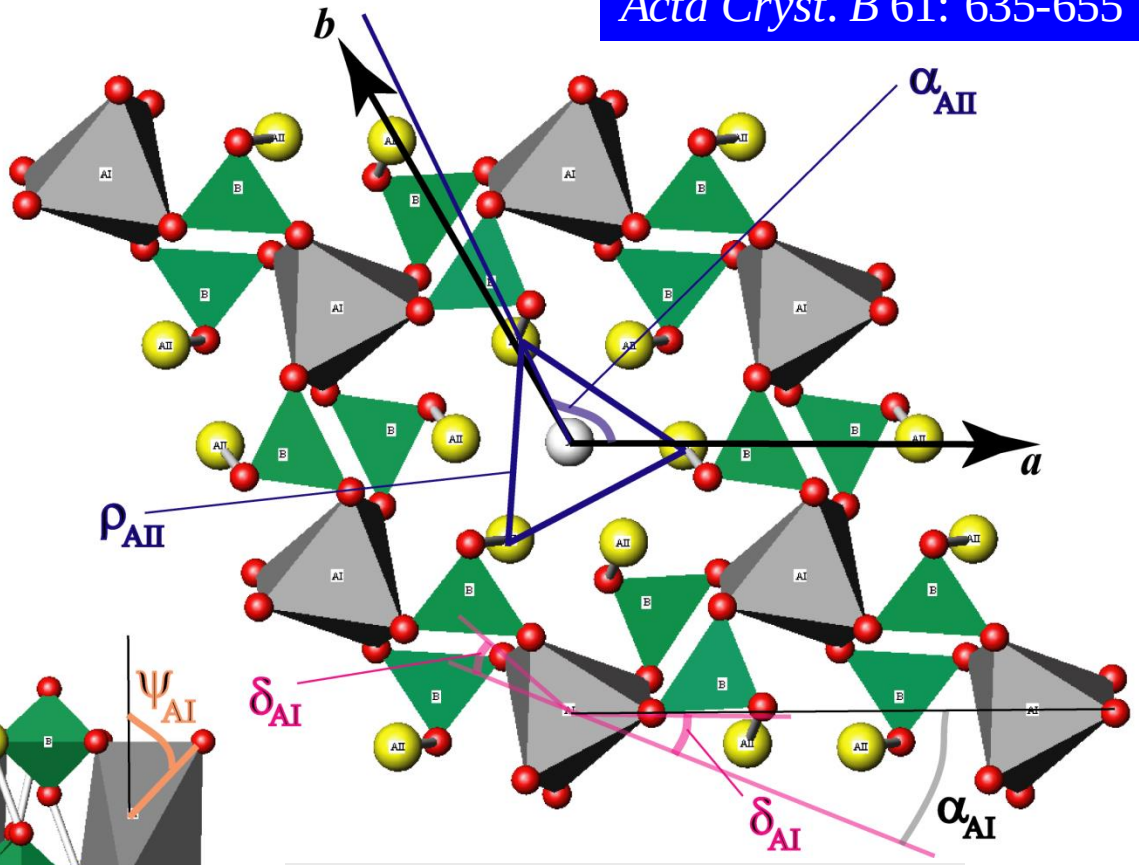
White & Dong, *Acta Cryst*, **B59**, 1-16 (2003).

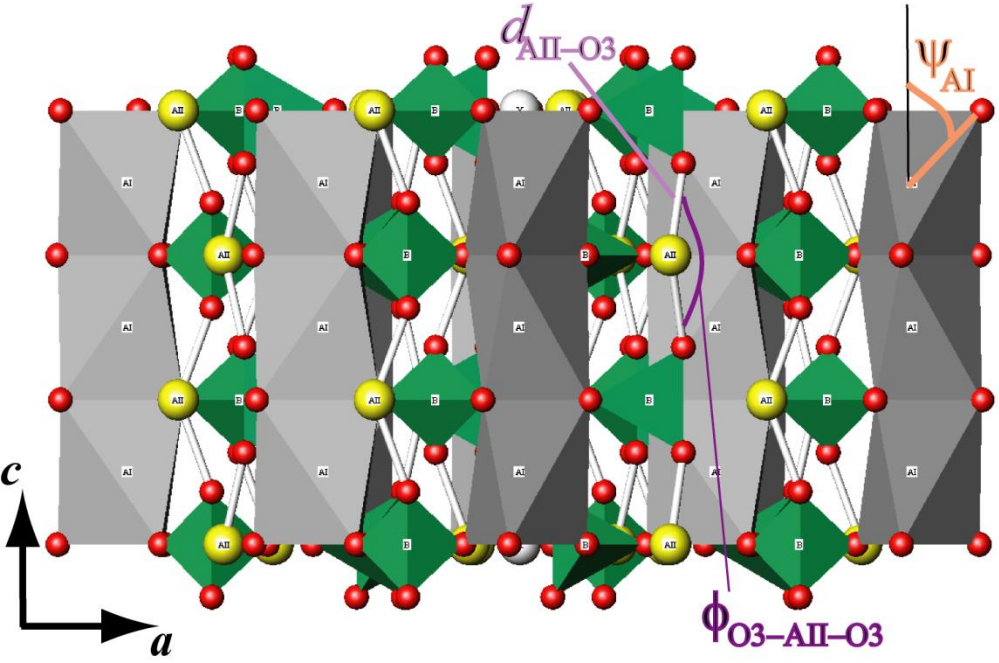
- $A^{I}O_6$ metaprisms
- BO_4 tetrahedra
- tunnel structure

Crystal-chemical parameterization of $P6_3/m$ apatite

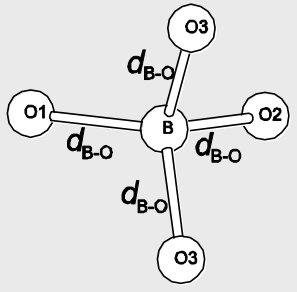
Acta Cryst. B 61: 635-655







τ(O1-B-O2) [x1] = τ(O1-B-O3) [x2] = $\tau_{O\text{-}B\text{-}O}$



τ(O3-B-O3) [x1] = τ(O2-B-O3) [x2] = $\tau'_{O\text{-}B\text{-}O}$

Acta Cryst. B 61: 635-655

Four geometric constraints

$$a = 3^{1/2}\{ d_{AI\text{-}O1}^2 - (1/4)\cdot[d_{B\text{-}O}\sin(\tau'_{O\text{-}B\text{-}O}/2) + d_{AII\text{-}O3}\sin(\phi_{O3\text{-}AII\text{-}O3}/2)]^2 \}^{1/2}\cdot\cos[(\pi/6) - \delta_{AI} - \alpha_{AI}]$$
$$+ 3^{1/2}\cdot\{(d_{AI\text{-}O1}+\Delta_{AI\text{-}O})^2 - (1/4)\cdot[d_{B\text{-}O}\sin(\tau'_{O\text{-}B\text{-}O}/2)+d_{AII\text{-}O3}\sin(\phi_{O3\text{-}AII\text{-}O3}/2)]^2 \}^{1/2}\cdot\cos[(\pi/6)-\delta_{AI}+\alpha_{AI}]$$
$$+ 2\,(3^{1/2})\; d_{B\text{-}O}\sin(\tau_{O\text{-}B\text{-}O}/2)\cos(\theta)$$

where:

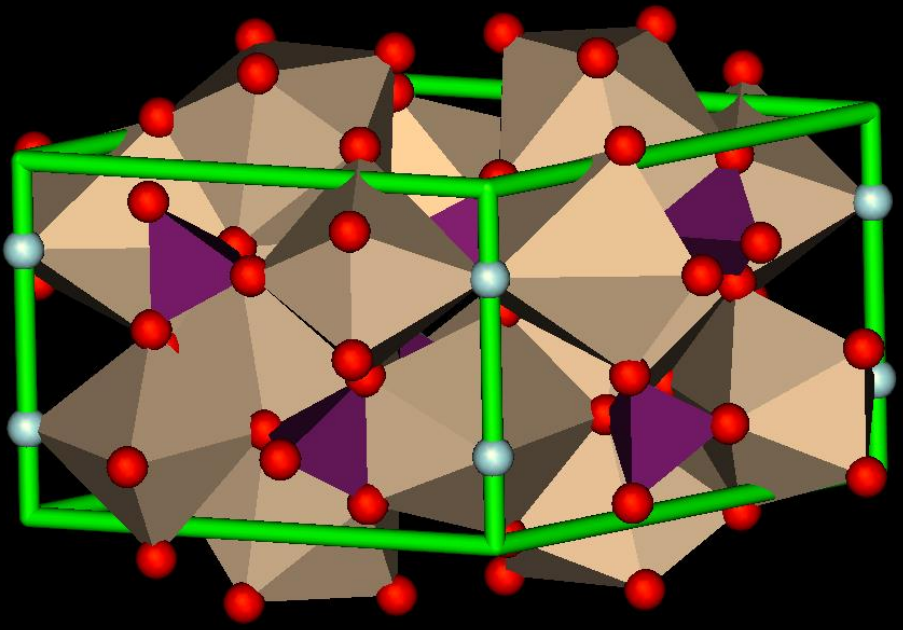
$$\sin(\theta) = \{ \{ d_{AI\text{-}O1}^2 - (1/4)\cdot[d_{B\text{-}O}\sin(\tau'_{O\text{-}B\text{-}O}/2)+d_{AII\text{-}O3}\sin(\phi_{O3\text{-}AII\text{-}O3}/2)]^2 \}^{1/2}\cdot\sin[(\pi/6)-\delta_{AI}-\alpha_{AI}]$$
$$- \{(d_{AI\text{-}O1}+\Delta_{AI\text{-}O})^2-(1/4)\cdot[d_{B\text{-}O}\sin(\tau'_{O\text{-}B\text{-}O}/2)+d_{AII\text{-}O3}\sin(\phi_{O3\text{-}AII\text{-}O3}/2)]^2 \}^{1/2}\cdot\sin[(\pi/6)-\delta_{AI}+\alpha_{AI}] \}$$
$$/\,[2\; d_{B\text{-}O}\sin(\tau_{O\text{-}B\text{-}O}/2)]$$

$$c = 2\cdot[\, d_{B\text{-}O}\sin(\tau'_{O\text{-}B\text{-}O}/2) + d_{AII\text{-}O3}\sin(\phi_{O3\text{-}AII\text{-}O3}/2)]$$

$$\cos(\psi_{AI\text{-}O1}) = [d_{B\text{-}O}\sin(\tau'_{O\text{-}B\text{-}O}/2) + d_{AII\text{-}O3}\sin(\phi_{O3\text{-}AII\text{-}O3}/2)] / [2\cdot d_{AI\text{-}O1}]$$

$z(A^{I}) = 0$ (*i.e.*, cation-centered $A^{I}O6$ polyhedra)

crystal structure of $P6_3/m$ apatite



novel approach

crystal-chemical refinement

standard refinement

Geometrical Parameterization

10 crystal-chemical parameters:
$d_{AI\text{-}O1}$, $\Delta_{AI\text{-}O}$, δ_{AI}, α_{AI}, $d_{B\text{-}O}$, $\tau_{O\text{-}B\text{-}O}$,
ρ_{AII} or $d_{AII\text{-}X}$, $d_{AII\text{-}O3}$, $\phi_{O3\text{-}AII\text{-}O3}$, α_{AII}

4 geometric constraints

initial extraction

Crystallographic Description

14 crystallographic parameters:
a, c, 12 atom coordinates

Numerical equivalence to within 14-digit double-precision accuracy

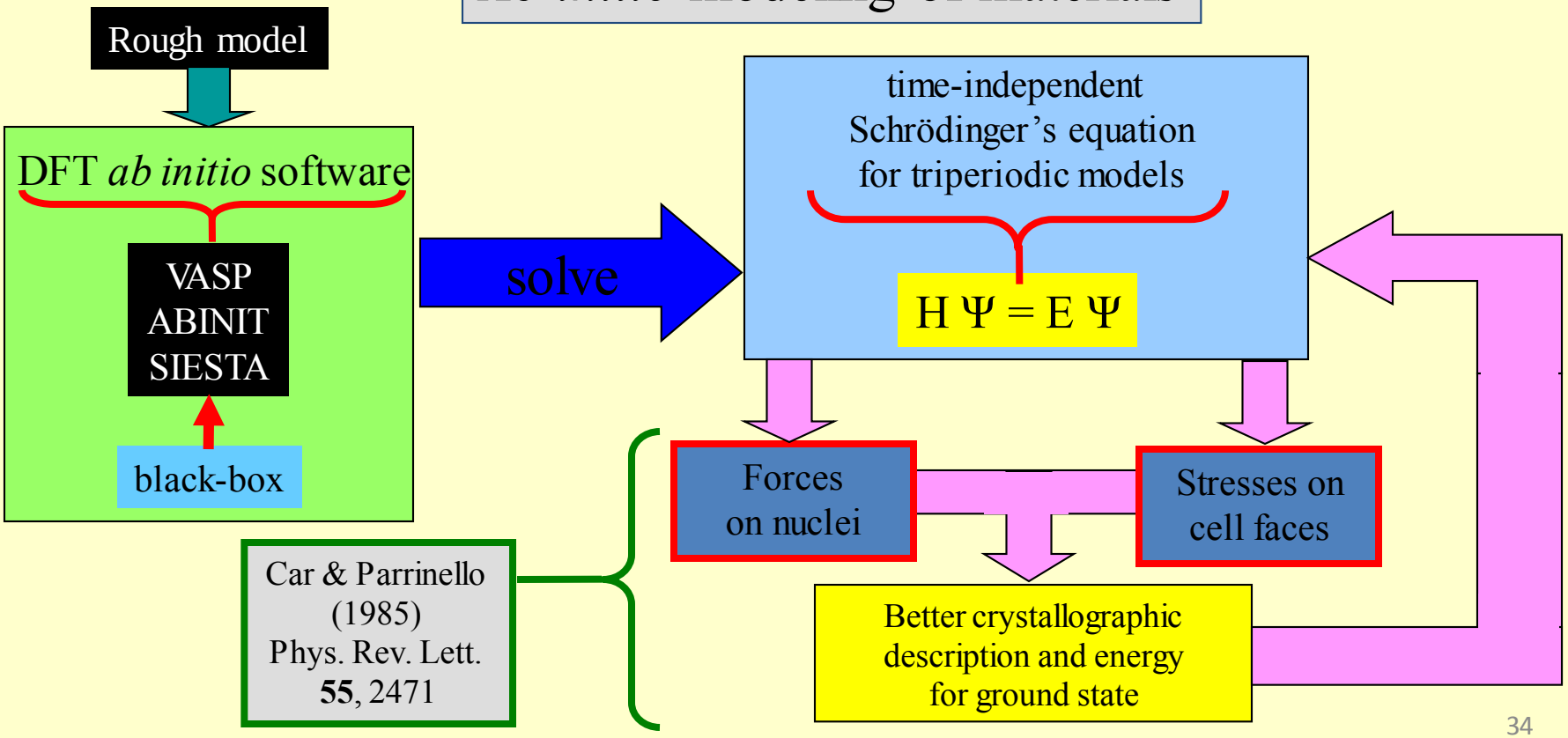
Experimental data used in the study

Acta Cryst. B 61: 635-655

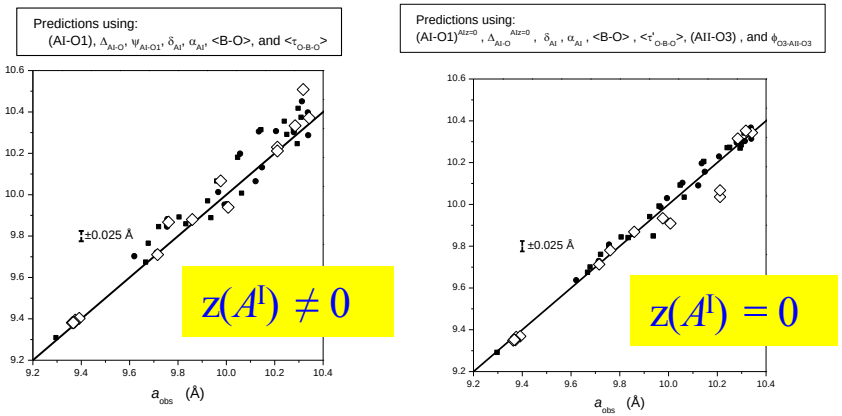
Literature crystallographic results for 18 end-member chemical compositions

- single-crystal refn't with R<4%
- single-crystal refn't with R>4%
- Rietveld refn't of powder data

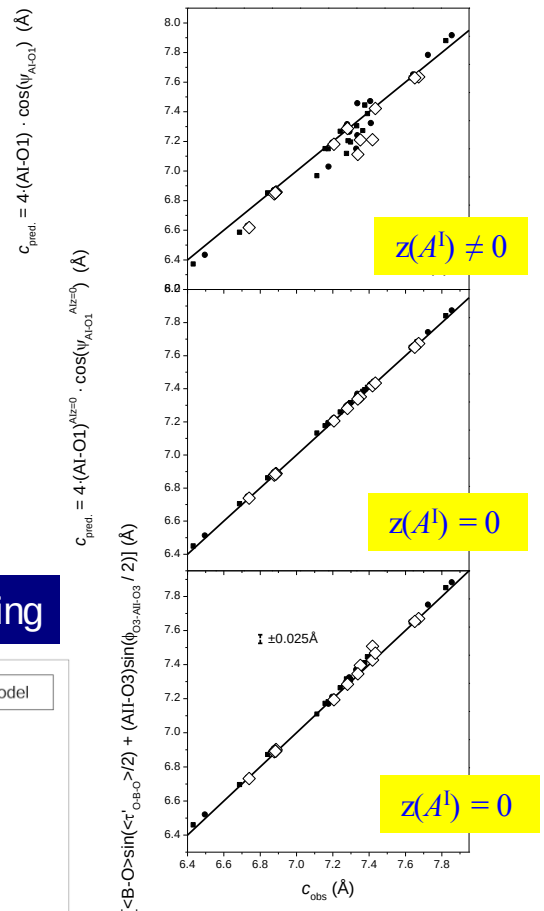
Ab initio modeling of materials



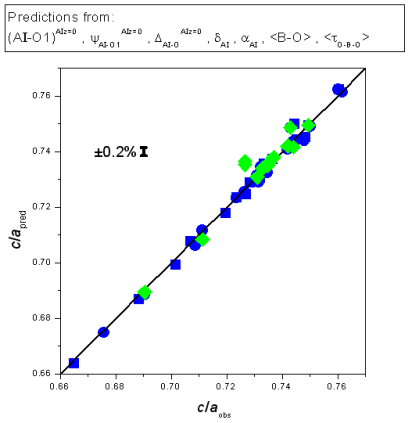
Predictions of *a* from crystal-chemical parameters



Predictions of *c* from crystal-chemical parameters

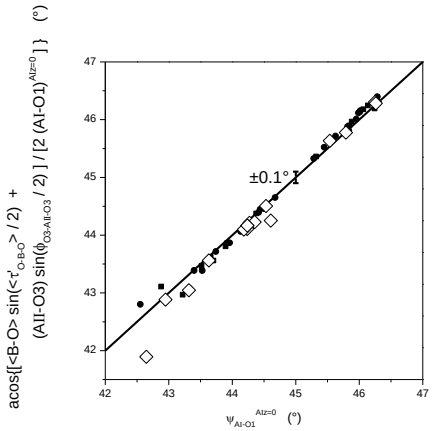


c/a axial ratio

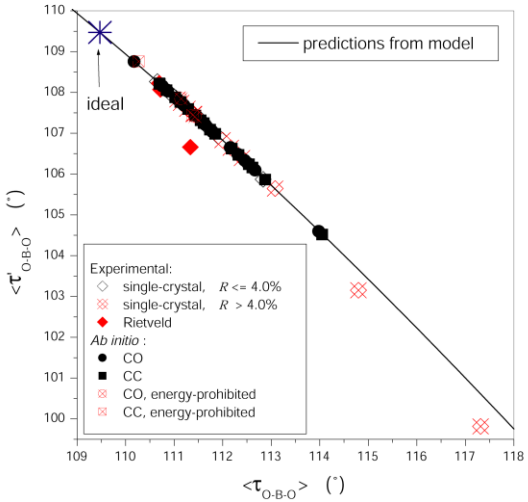


Acta Cryst. B 61: 635-655

AlO_6 bond angle $\psi_{Al\text{-}O1}$



BO_4 bond-angle bending



Analysis shows

Good agreement (within 0.5-2.0%) of *ab initio* results with only the most reliable single-crystal structure refinements

Absence of structural refinement data for "eco-apatite" compounds containing toxic metals (Zn, Hg, V, Cr, Pb, Cd, etc.) that are known to exist or hypothetical

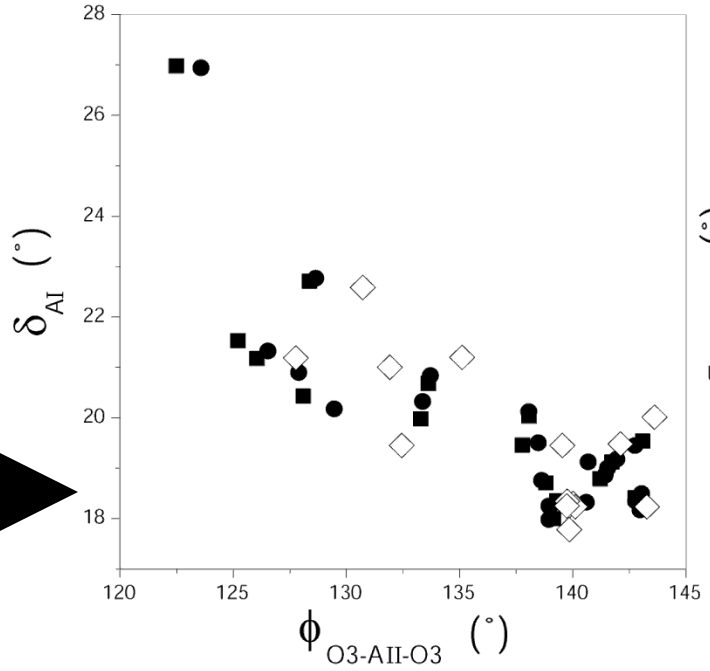
Reliable *ab initio* predictions for crystal structures of 9 eco-apatites

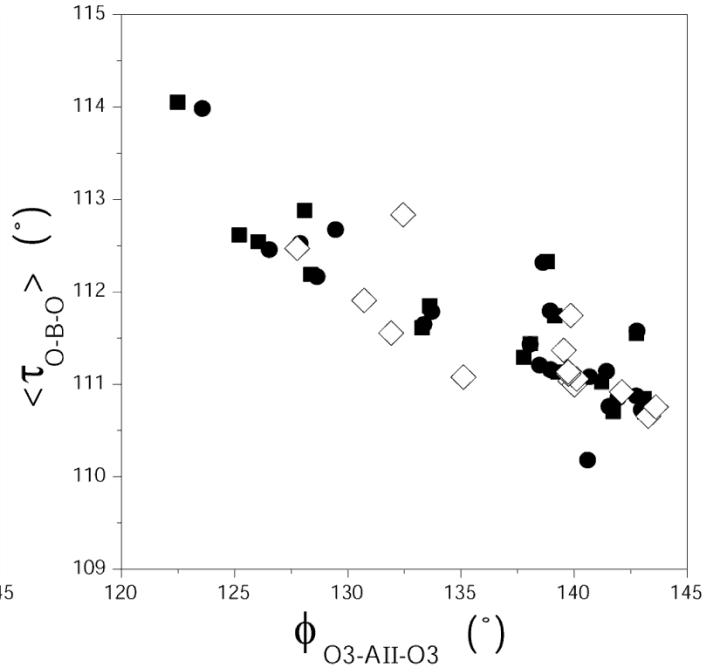
open diamonds = single-crystal, $R \leq 4.0\%$
filled circles = *ab initio* coordinate-only optimization
filled squares = *ab initio* cell-and-coordinate optimization

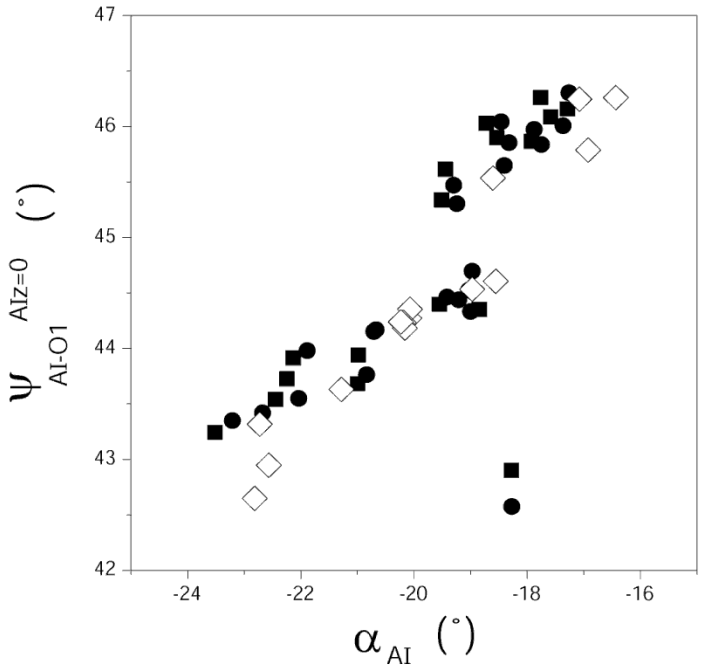
correlations among algebraically independent polyhedral distortion parameters

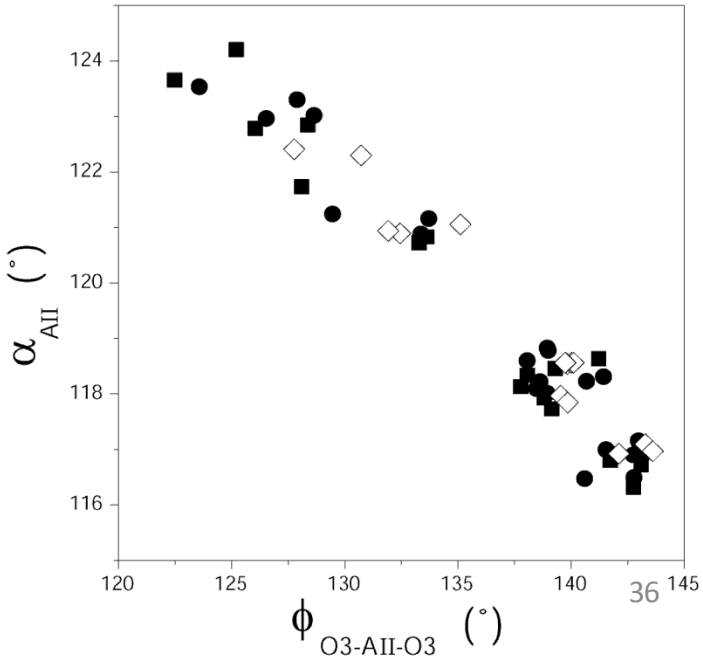
crystal-chemical flexibility of apatite framework

Acta Cryst. B 61: 635-655









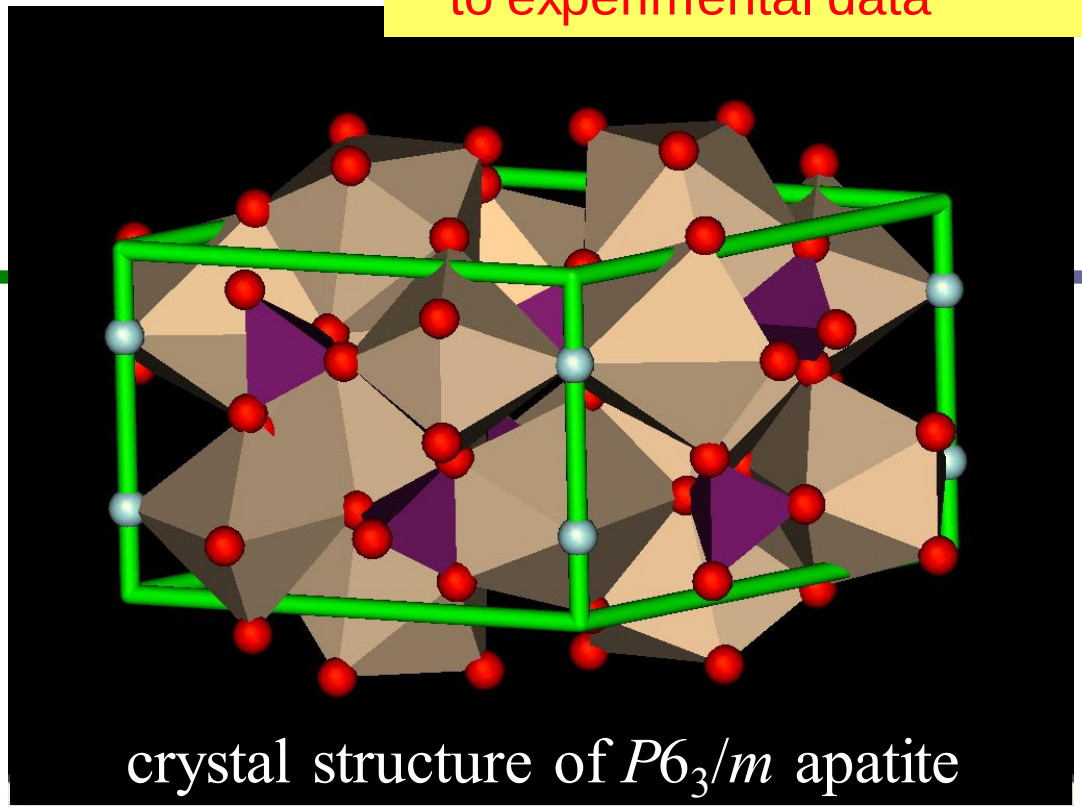
Direct least-squares refinement of crystal-chemical parameters for $P6_3/m$ apatite

J. Appl. Cryst. 39: 369-375

J. Appl. Cryst. 39: 458-465

Creation of a *TOPAS* script for crystal-chemical refinement

Performed both types of refinement on a top-quality XRD powder pattern:
-- numerical stability
-- addition of random noise to experimental data



novel approach

crystal-chemical refinement

Geometrical Parameterization

standard refinement

Crystallographic Description

Crystal-chemical refinement with TOPAS; R_{wp} = 9.231, GOF = 1.650

UNPROCESSED normal matrix

Condition number for matrix of normal equations = 0.790E+13
Error propagation is likely to spoil 13 trailing decimal digits out of probably 14.

CN =0.790E+13

Problem is ill-conditioned for double-precision matrix inversion unless error propagation is well taken care of.
Use eigenvectors for small eigenvalues below to diagnose quasi singularity.

Eigenvectors for ch13.out ranked according to eigenvalues are printed as columns below

Eigenvector #	#:	1 ..	17	18	19	20	21	22	23	24	25	26	27	28
dA1O1	1:	0.000 ..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
DeltaA1O	2:	0.000 ..	-0.001	-0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
deltaA1	3:	0.000 ..	0.027	-0.143	0.000	0.003	-0.006	0.005	0.008	-0.003	-0.004	-0.001	0.000	0.000
alphaA1	4:	0.000 ..	0.009	-0.089	0.001	0.001	-0.001	0.004	0.003	-0.001	0.000	0.000	0.000	0.000
dBO	5:	0.000 ..	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
tauOBO	6:	0.000 ..	-0.005	0.276	-0.001	-0.007	0.006	-0.017	-0.009	0.001	0.003	-0.001	0.001	0.000
rhoA2	7:	0.000 ..	0.001	0.005	0.000	0.000	0.000	-0.001	0.000	0.000	0.000	0.000	0.000	0.000
alphaA2	8:	0.000 ..	-0.007	-0.012	-0.002	-0.008	-0.001	-0.001	0.002	0.000	0.002	0.000	0.000	0.000
dA2O3	9:	0.000 ..	0.000	-0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
phiO3A2O3	10:	0.000 ..	-0.018	0.945	-0.012	0.001	0.005	-0.022	-0.017	0.009	0.000	-0.003	0.001	-0.002
zero_error	11:	0.000 ..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
divslit	12:	0.000 ..	0.001	0.000	-0.002	0.000	0.001	-0.001	0.001	0.001	0.001	0.000	0.000	-0.002
bkg805787520	13:	0.000 ..	-0.017	0.002	0.650	0.170	-0.488	-0.123	-0.344	-0.011	-0.339	0.082	0.228	-0.032
bkg805787521	14:	0.000 ..	-0.006	-0.014	-0.033	0.063	-0.058	-0.347	-0.143	0.481	0.151	0.619	-0.460	-0.006
bkg805787522	15:	0.000 ..	0.020	-0.016	-0.544	-0.186	0.076	-0.108	-0.328	0.125	-0.526	0.225	0.448	0.020
bkg805787523	16:	0.000 ..	0.030	0.017	0.059	-0.363	-0.018	0.617	-0.265	-0.321	-0.194	0.311	-0.417	-0.019
bkg805787524	17:	0.000 ..	0.020	0.015	0.401	0.000	0.495	0.305	0.335	0.276	-0.049	0.401	0.385	0.017
bkg805787525	18:	0.000 ..	0.003	0.002	-0.032	0.607	0.328	-0.140	0.155	-0.319	-0.522	0.064	-0.317	-0.009
bkg805787526	19:	0.000 ..	-0.006	0.015	-0.297	0.367	-0.481	0.226	0.281	-0.286	0.237	0.455	0.265	0.000
bkg805787527	20:	0.000 ..	0.006	0.013	-0.002	-0.377	-0.371	-0.095	0.679	0.158	-0.442	-0.034	-0.169	-0.003
bkg805787528	21:	0.000 ..	0.007	-0.006	0.159	-0.392	0.171	-0.545	0.080	-0.603	0.146	0.298	0.117	0.001
pISCALE	22:	1.000 ..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
pICS	23:	0.000 ..	-0.001	-0.002	-0.025	-0.007	0.024	-0.002	0.013	0.013	0.008	-0.002	0.022	-0.999
beqA1	24:	0.000 ..	0.014	-0.015	0.009	0.006	-0.011	-0.005	-0.007	0.008	-0.002	0.005	-0.001	-0.001
beqA2	25:	0.000 ..	0.003	0.002	0.007	0.006	-0.009	-0.013	-0.002	0.006	0.001	0.003	0.000	0.000
beqO	26:	0.000 ..	0.006	-0.004	0.022	0.020	-0.013	-0.009	-0.005	0.004	0.003	0.002	0.001	-0.001
beqB	27:	0.000 ..	0.004	0.010	0.016	0.008	-0.007	-0.017	-0.004	0.011	0.000	0.001	0.000	-0.001
beqX	28:	0.000 ..	0.998	0.022	0.009	0.023	-0.022	-0.021	-0.003	0.008	0.017	-0.016	0.000	-0.002
Eigenvalues	:	1.84E+12 ..	2.86E+02	1.26E+02	4.22E+01	3.58E+01	3.02E+01	2.33E+01	2.12E+01	1.45E+01	6.76E+00	5.15E+00	1.16E+00	2.33E-01

Standard crystallographic refinement with TOPAS; R_{wp} = 8.673, GOF = 1.550

UNPROCESSED normal matrix

Condition number for matrix of normal equations = 0.785E+13

CN =0.785E+13

Error propagation is likely to spoil 13 trailing decimal digits out of probably 14.

Problem is ill-conditioned for double-precision matrix inversion unless error propagation is well taken care of.

Use eigenvectors for small eigenvalues below to diagnose quasi singularity.

Eigenvectors for cr11.out ranked according to eigenvalues are printed as columns below

Eigenvector	#:	1..	21	22	23	24	25	26	27	28	29	30	31	32
zero_error	1:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
divslit	2:	0.000..	-0.001	0.001	-0.002	0.000	-0.001	0.001	-0.001	0.001	-0.001	0.000	0.000	-0.002
bkg1040163200	3:	0.000..	0.028	-0.018	0.655	0.152	0.475	0.098	0.374	-0.008	0.334	0.079	0.228	-0.031
bkg1040163201	4:	0.000..	0.010	-0.008	-0.032	0.063	0.054	0.342	0.163	0.483	-0.150	0.618	-0.459	-0.007
bkg1040163202	5:	0.000..	-0.014	0.019	-0.555	-0.167	-0.075	0.093	0.328	0.123	0.526	0.223	0.448	0.021
bkg1040163203	6:	0.000..	-0.012	0.033	0.034	-0.360	0.026	-0.634	0.235	-0.320	0.187	0.313	-0.417	-0.020
bkg1040163204	7:	0.000..	0.001	0.023	0.401	-0.027	-0.487	-0.290	-0.355	0.275	0.053	0.405	0.385	0.016
bkg1040163205	8:	0.000..	0.006	0.000	-0.002	0.598	-0.337	0.151	-0.148	-0.323	0.523	0.067	-0.317	-0.008
bkg1040163206	9:	0.000..	0.004	-0.007	-0.276	0.391	0.482	-0.201	-0.289	-0.285	-0.235	0.455	0.266	0.000
bkg1040163207	10:	0.000..	-0.008	0.008	-0.003	-0.372	0.391	0.135	-0.662	0.150	0.446	-0.032	-0.170	-0.003
bkg1040163208	11:	0.000..	-0.003	0.008	0.148	-0.404	-0.163	0.544	-0.042	-0.604	-0.151	0.298	0.119	0.001
p1SCALE	12:	1.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
CrystalliteSiz	13:	0.000..	0.000	-0.001	-0.026	-0.006	-0.024	0.003	-0.014	0.012	-0.007	-0.002	0.023	-0.999
alat	14:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
clat	15:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
A1z	16:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
beqA1	17:	0.000..	-0.088	0.011	0.007	0.007	0.011	0.005	0.007	0.007	0.002	0.005	0.000	-0.001
A2x	18:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
A2y	19:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
beqA2	20:	0.000..	-0.061	0.005	0.007	0.007	0.009	0.013	0.003	0.006	-0.001	0.003	0.000	0.000
beqB	21:	0.000..	0.061	0.008	0.017	0.007	0.007	0.017	0.007	0.011	0.001	0.001	0.000	-0.001
Bx	22:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
By	23:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
beqO	24:	0.000..	-0.992	0.016	0.024	0.021	0.011	0.010	0.008	0.004	-0.003	0.002	0.001	-0.001
O1x	25:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O1y	26:	0.000..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O2x	27:	0.000..	-0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O2y	28:	0.000..	-0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O3x	29:	0.000..	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O3y	30:	0.000..	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O3z	31:	0.001..	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
beqF	32:	0.000..	0.018	0.999	0.008	0.027	0.022	0.024	0.005	0.007	-0.016	-0.017	0.000	-0.001
Eigenvalues	:	1.78E+12..	1.97E+03	2.68E+02	4.16E+01	3.56E+01	3.01E+01	2.30E+01	2.08E+01	1.44E+01	6.69E+00	5.11E+00	1.15E+00	2.26E-01

Standard crystallographic refinement with TOPAS; R_{wp} = 8.695, GOF = 1.553

UNPROCESSED normal matrix

Condition number for matrix of normal equations = 0.659E+10
Error propagation is likely to spoil 10 trailing decimal digits out of probably 14.

CN =0.659E+10

Problem poorly conditioned for double-precision matrix inversion unless error propagation is well taken care of.
Use eigenvectors for small eigenvalues below to diagnose quasi singularity.

Eigenvectors for cr10.out ranked according to eigenvalues are printed as columns below

Eigenvector	#:	1	2	3	4	5	6 ..	17	18	19	20	21
zero_error	1:	0.000	0.159	-0.015	0.004	-0.010	0.007 ..	0.000	0.000	0.000	0.000	0.000
plSCALE	2:	1.000	0.000	0.000	0.000	0.000	0.000 ..	0.000	0.000	0.000	0.000	0.000
alat	3:	0.000	-0.834	-0.538	-0.001	-0.001	0.001 ..	0.000	0.000	0.000	0.000	0.000
clat	4:	0.000	-0.529	0.843	-0.001	0.000	0.005 ..	0.000	0.000	0.000	0.000	0.000
A1z	5:	0.000	0.000	0.000	-0.008	-0.075	-0.009 ..	0.000	0.000	-0.001	0.000	0.000
beqA1	6:	0.000	0.000	0.000	0.000	-0.001	0.000 ..	-0.313	0.745	-0.582	-0.091	-0.012
A2x	7:	0.000	0.000	-0.001	0.583	-0.001	0.663 ..	0.001	0.001	0.001	0.000	0.000
A2y	8:	0.000	0.003	-0.001	-0.808	-0.036	0.467 ..	0.000	0.000	0.000	0.000	0.000
beqA2	9:	0.000	0.000	0.000	0.000	0.000	0.001 ..	-0.927	-0.369	0.035	-0.061	-0.005
beqB	10:	0.000	0.000	0.000	0.000	0.001	0.000 ..	-0.195	0.556	0.806	0.064	-0.009
Bx	11:	0.000	0.001	0.004	-0.022	0.693	-0.180 ..	0.000	0.001	-0.001	0.000	0.000
By	12:	0.000	-0.001	0.005	0.030	-0.701	-0.282 ..	0.001	0.000	0.001	0.000	0.000
beqO	13:	0.000	0.000	0.000	0.000	0.000	0.000 ..	0.073	-0.010	0.103	-0.992	-0.018
O1x	14:	0.000	0.000	0.000	0.004	-0.002	0.057 ..	0.000	0.001	-0.001	0.000	0.000
O1y	15:	0.000	0.000	-0.001	0.012	0.049	-0.074 ..	-0.001	0.000	0.000	0.000	0.000
O2x	16:	0.000	0.000	0.001	0.020	0.016	0.018 ..	-0.001	0.001	-0.002	-0.002	0.000
O2y	17:	0.000	0.000	0.000	-0.070	-0.071	0.019 ..	-0.001	0.000	-0.001	-0.001	0.000
O3x	18:	0.000	-0.001	0.001	-0.007	0.068	-0.342 ..	0.000	0.000	0.000	0.001	0.000
O3y	19:	0.000	0.001	-0.001	-0.017	-0.085	0.321 ..	0.000	0.000	-0.001	0.001	0.000
O3z	20:	0.001	0.000	0.001	-0.005	0.045	-0.024 ..	0.001	-0.001	0.000	0.000	0.000
beqF	21:	0.000	0.000	0.000	0.000	0.000	0.000 ..	0.009	-0.011	-0.002	0.019	-1.000
Eigenvalues	:	1.80E+12	7.04E+09	2.62E+09	3.69E+08	2.17E+08	9.32E+07 ..	9.59E+03	5.13E+03	3.58E+03	2.03E+03	2.73E+02

Crystal-chemical refinement with TOPAS; R_{wp} = 9.231, GOF = 1.648

UNPROCESSED normal matrix

Condition number for matrix of normal equations = 0.221E+11

CN =0.221E+11

Error propagation is likely to spoil 10 trailing decimal digits out of probably 14.

Problem is ill-conditioned for double-precision matrix inversion unless error propagation is well taken care of.
Use eigenvectors for small eigenvalues below to diagnose quasi singularity.

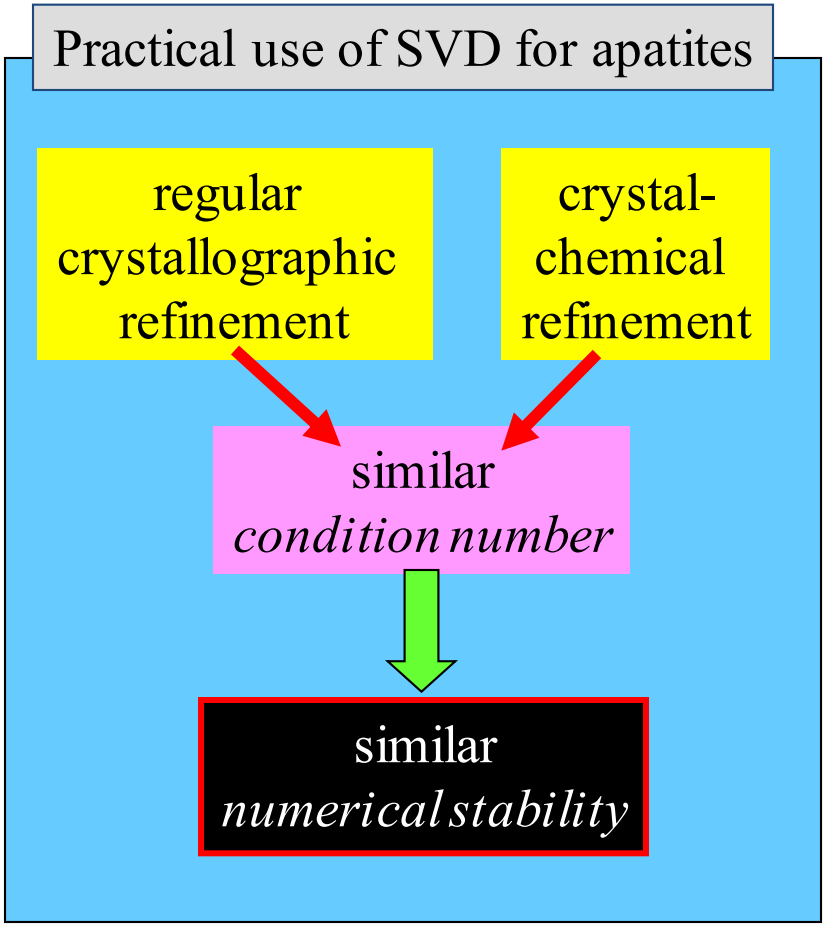
Eigenvectors for ch12.out ranked according to eigenvalues are printed as columns below

Eigenvector	#:	1	2	3	4	5	6 ..	13	14	15	16	17
dA1O1	1:	0.000	0.718	-0.213	0.009	-0.610	0.255 ..	-0.001	0.000	0.000	0.000	0.000
DeltaA1O	2:	0.000	0.433	-0.129	0.014	0.221	-0.840 ..	0.002	0.001	0.000	-0.001	0.002
deltaA1	3:	0.000	0.003	-0.001	0.000	0.008	-0.005 ..	-0.161	-0.074	0.500	0.028	0.086
alphaA1	4:	0.000	0.016	-0.005	0.001	0.024	0.004 ..	0.007	0.017	0.195	0.000	0.051
dBO	5:	0.000	0.537	0.521	0.037	0.557	0.295 ..	0.001	-0.001	0.000	0.000	-0.001
tauOBO	6:	0.000	0.006	-0.009	0.000	0.016	0.001 ..	-0.051	0.003	-0.811	-0.020	-0.185
rhoA2	7:	0.000	0.000	0.000	0.000	-0.194	-0.279 ..	-0.001	-0.003	-0.003	0.001	-0.004
alphaA2	8:	0.000	0.000	0.000	0.000	0.000	-0.001 ..	0.814	0.472	0.046	-0.006	0.010
dA2O3	9:	0.000	-0.088	0.816	0.018	-0.480	-0.255 ..	-0.001	0.001	-0.009	0.000	0.007
phiO3A2O3	10:	0.000	-0.001	0.006	0.000	-0.004	-0.003 ..	0.008	-0.003	0.211	-0.017	-0.977
zero_error	11:	0.000	-0.031	-0.030	0.999	-0.010	0.003 ..	0.000	0.000	0.000	0.000	0.000
p1SCALE	12:	1.000	0.000	0.000	0.000	0.000	0.000 ..	0.000	0.000	0.000	0.000	0.000
beqA1	13:	0.000	0.000	0.000	0.000	0.001	0.005 ..	0.021	-0.075	0.066	0.016	0.015
beqA2	14:	0.000	0.000	0.000	0.000	0.000	0.002 ..	0.150	-0.003	-0.008	0.005	-0.002
beqO	15:	0.000	0.000	0.000	0.000	-0.001	-0.001 ..	0.451	-0.875	-0.023	0.009	0.001
beqB	16:	0.000	0.000	0.000	0.000	0.000	-0.003 ..	-0.287	-0.001	-0.032	0.002	-0.013
beqX	17:	0.000	0.000	0.000	0.000	0.000	-0.001 ..	0.004	0.014	-0.027	0.999	-0.023
Eigenvalues	:	1.87E+12	1.57E+11	1.95E+10	6.59E+07	8.98E+06	3.09E+06 ..	2.66E+03	2.12E+03	5.97E+02	2.91E+02	8.47E+01

Numerical stability of Rietveld refinements

J. Appl. Cryst. 39: 458-465

In both cases, profile-shape and background parameters needed to be fixed at some arbitrary values



SVDdiagnostic → cure of Rietveld LS model

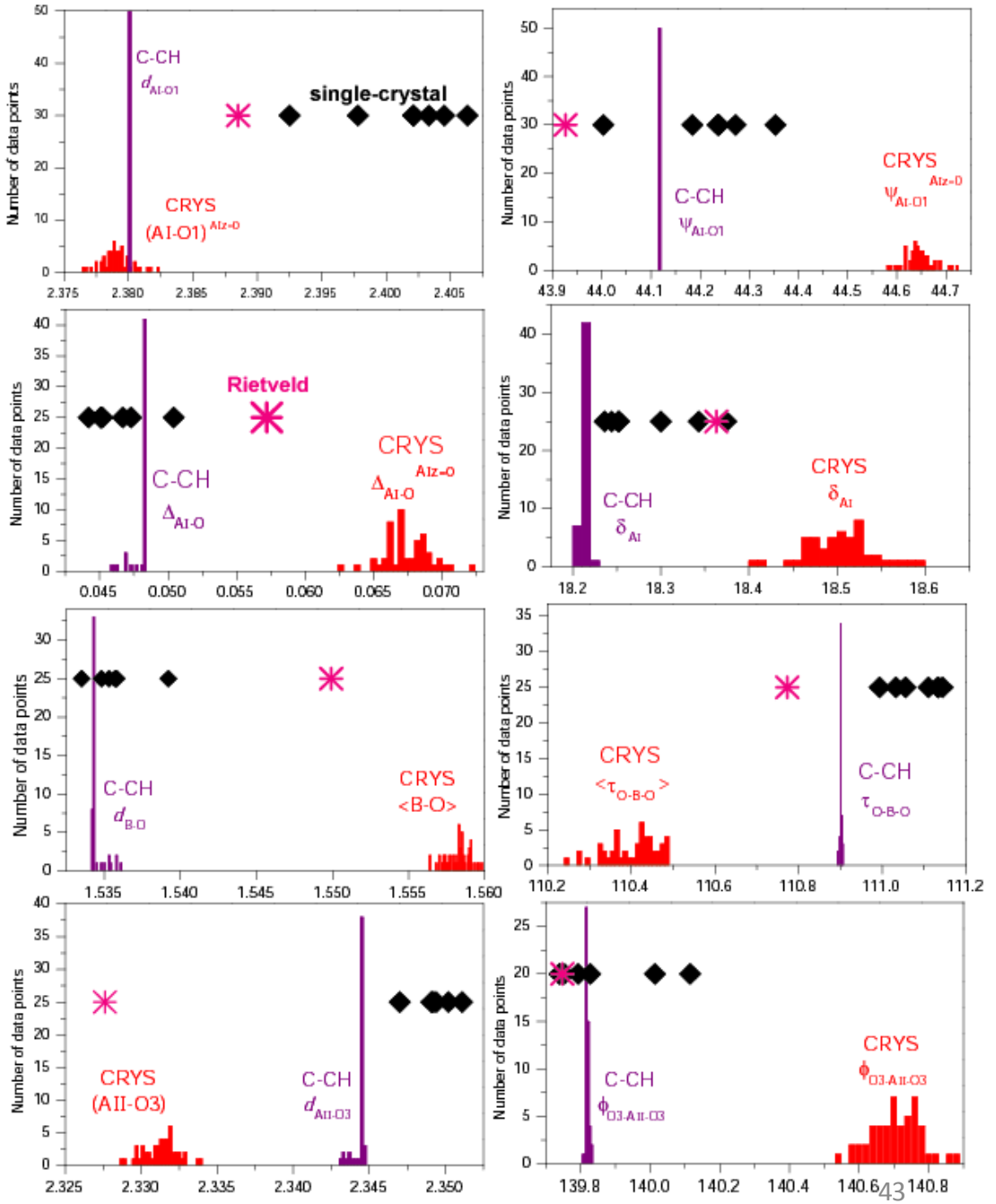
Software program freely distributed by the author

J. Appl. Cryst. 39: 369-375

Experimental proof of the greater precision and accuracy of crystal-chemical refinement

CORROBORATION

Observed a precision increase by nearly an order of magnitude in the least-squares E.S.D.s.



Observed a precision increase by nearly an order of magnitude in the least-squares E.S.D.s.

C-CH

Ca1:0	O1:4	2.39802	(42)													
	O1:0	2.39802	(42)	74.151	(16)											
	O1:3	2.39802	(42)	74.151	(16)	74.151	(16)									
	O2:1	2.44645	(63)	154.7555	(48)	123.939	(10)	93.026	(18)							
	O2:2	2.44645	(63)	75.948	(23)	93.026	(18)	154.7555	(48)	123.94	(10)					
	O2:5	2.44645	(63)	75.948	(23)	75.948	(23)	123.939	(10)	93.026	(18)	154.7555	(48)			

CRYS

Ca1:0	O1:4	2.3711	(24)													
	O1:0	2.3711	(24)	73.65	(10)											
	O1:3	2.3711	(24)	73.65	(10)	73.65	(10)									
	O2:1	2.4541	(29)	154.291	(92)	124.684	(84)	93.322	(96)							
	O2:2	2.4541	(29)	75.71	(10)	93.322	(96)	154.291	(92)	124.68	(84)					
	O2:5	2.4541	(29)	75.71	(10)	75.71	(10)	124.684	(84)	93.322	(96)	154.291	(92)			

C-CH

Ca2:0	O3:3	2.33557	(57)	102.584												
	O3:2	2.33557	(57)	141.067	(65)	102.584										
	O2:4	2.3874	(13)	85.67	(47)	85.670	(47)	152.267								
	O3:7	2.5069	(13)	74.889	(36)	77.442	(20)	135.735	(52)	81.085						
	O3:6	2.5069	(13)	59.349	(37)	74.889	(36)	135.735	(52)	77.442	(20)	81.085				
	O1:0	2.6868	(13)	149.635	(21)	149.635	(21)	100.708	(56)	72.247	(32)	72.247	(32)			

CRYS

Ca2:0	O3:2	2.3314	(20)													
	O3:3	2.3314	(20)	140.70	(13)											
	O2:4	2.3442	(29)	85.758	(61)	85.758	(61)									
	O3:7	2.5115	(25)	74.145	(81)	135.87	(11)	77.419	(53)							
	O3:6	2.5115	(25)	59.568	(93)	74.145	(81)	77.419	(53)	135.87	(11)					
	O1:0	2.6691	(25)	149.313	(55)	149.313	(55)	100.595	(94)	72.013	(74)	72.013	(74)			

J. Appl. Cryst. (2005) 39: 369-375

C-CH

P:0	O1:0	1.53407	(50)													
	O3:1	1.53407	(37)	110.9056	(44)											
	O3:0	1.53407	(37)	108.0000	(16)	110.9056	(44)									
	O2:0	1.53407	(50)	107.9996	(39)	107.9996	(39)	110.9056	(14)							
	Ca2:4	3.0708	(14)	114.887	(33)	54.2946	(69)	54.2946	(69)	134.21	(33)					
	O2:3	3.16969	(95)	44.951	(28)	69.936	(34)	68.676	(14)	68.676	(14)	179.159	(34)			

CRYS

P:0	O3:1	1.5364	(20)													
	O3:0	1.5364	(20)	108.58	(17)											
	O1:0	1.5792	(39)	110.27	(12)	110.27	(12)									
	O2:0	1.5807	(29)	110.62	(16)	108.52	(11)	108.52	(11)							
	Ca2:4	3.0673	(11)	116.03	(14)	133.350	(86)	54.590	(86)	54.590	(86)					
	O2:3	3.115	(32)	44.558	(71)	71.47	(20)	177.908	(98)	68.69	(12)	68.69	(12)			

Application of *SVDdiagnostic* to $Ca_{10}(V_xP_{1-x}O_4)_6F_2$ eco-apatites

UNPROCESSED normal matrix

Condition number for matrix of normal equations = 0.279E+11
Error propagation is likely to spoil 10 trailing decimal digits out of probably 14.

Problem is ill-conditioned for double-precision matrix inversion unless error propagation is well taken care of.
Use eigenvectors for small eigenvalues below to diagnose quasi singularity.

Eigenvectors for final_fit.out ranked according to eigenvalues are printed as columns below

Eigenvector # :	1	2	3	..	13	14	15	16	17	18
dA101 1:	0.000	0.715	-0.208	..	-0.025	0.004	-0.006	0.005	0.001	0.000
DeltaA10 2:	0.000	0.435	-0.126	..	0.017	-0.003	0.005	0.001	-0.002	0.000
deltaA1 3:	0.000	0.003	-0.001	..	-0.267	-0.281	-0.022	0.498	0.028	-0.012
alphaA1 4:	0.000	0.016	-0.005	..	0.803	-0.422	0.332	0.139	-0.017	-0.002
dBO 5:	0.000	0.537	0.523	..	-0.002	0.011	-0.006	-0.005	0.001	0.000
tauOBO 6:	0.000	0.007	-0.009	..	-0.014	-0.152	0.058	-0.848	0.015	0.014
rhoA2 7:	0.000	0.000	-0.001	..	0.031	0.002	0.003	-0.020	0.002	0.001
alphaA2 8:	0.000	0.000	0.000	..	0.294	0.739	0.317	0.058	0.001	0.002
dA2O3 9:	0.000	-0.096	0.816	..	0.002	-0.011	0.005	-0.004	-0.001	-0.008
phiO3A2O3 10:	0.000	-0.001	0.006	..	-0.002	-0.004	-0.002	0.018	0.012	1.000
zero_error 11:	0.000	-0.038	-0.036	..	0.000	0.000	0.000	0.000	0.000	0.000
p1SCALE 12:	1.000	0.000	0.000	..	0.000	0.000	0.000	0.000	0.000	0.000
p1MS 13:	-0.001	0.000	0.000	..	-0.001	0.000	0.000	0.000	0.000	0.000
beqA1 14:	0.000	0.000	0.000	..	-0.076	0.203	-0.126	0.080	-0.001	-0.001
beqA2 15:	0.000	0.000	0.000	..	0.052	0.127	-0.030	-0.014	0.008	-0.001
beqO 16:	0.000	0.000	0.000	..	0.409	0.016	-0.865	-0.013	0.004	-0.002
beqB 17:	0.000	0.000	0.000	..	-0.137	-0.340	0.142	-0.039	0.011	-0.002
beqX 18:	0.000	0.000	0.000	..	0.021	0.005	0.007	0.001	0.999	-0.012
Eigenvalues :	0.871E+12	0.448E+11	0.609E+10	..	0.342E+04	0.306E+04	0.218E+04	0.560E+03	0.275E+03	0.312E+02

bond-angle variables

$\phi_{O3\text{-}AII\text{-}O3}$ and $\tau_{O\text{-}B\text{-}O}$

are poorly determined

Acta Cryst. B 63: 37-48

stability of crystal-chemical least-squares extraction increased by by fixing those variables

UNPROCESSED normal matrix

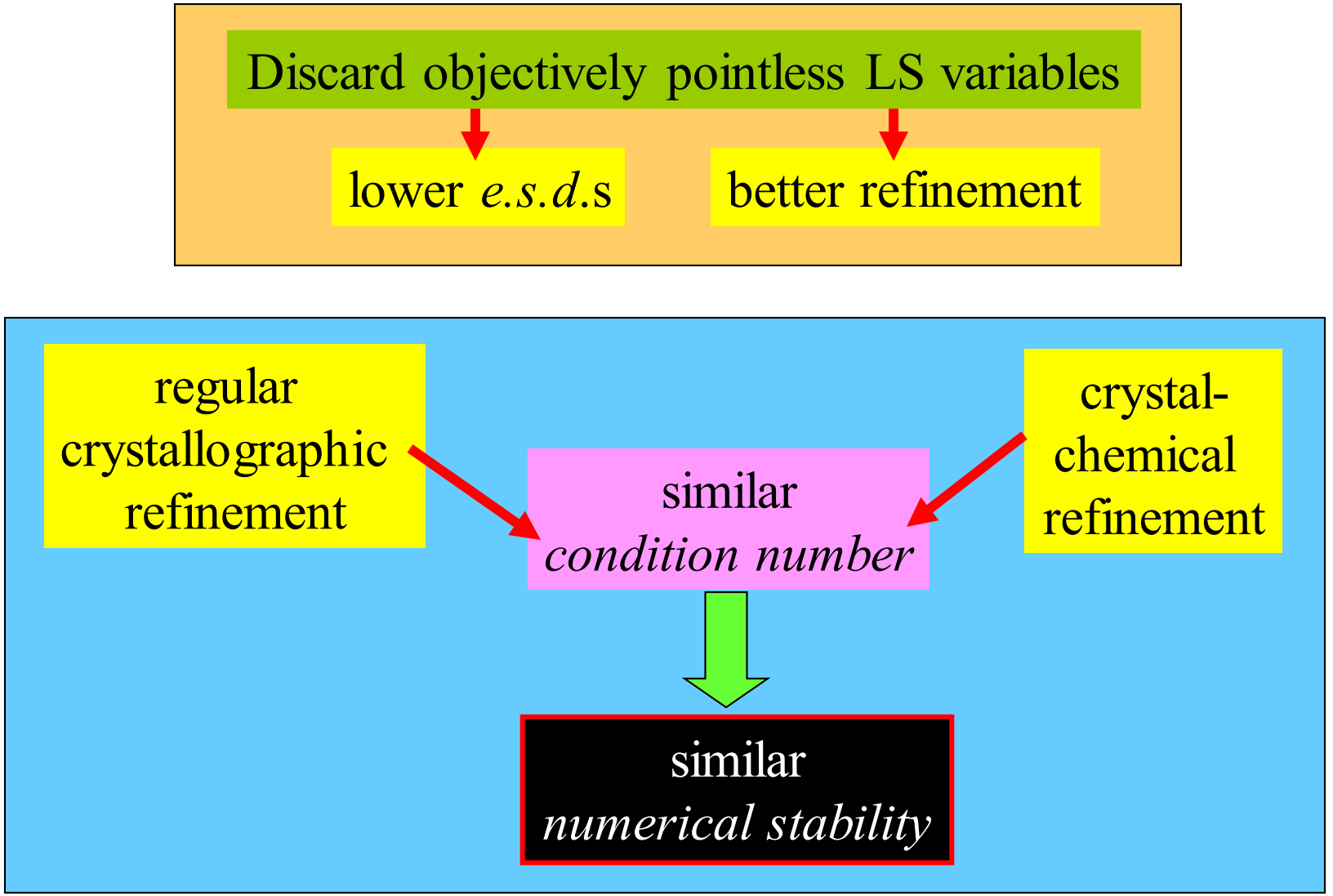
Condition number for matrix of normal equations = 0.319E+10
Error propagation is likely to spoil 10 trailing decimal digits out of probably 14.

Problem poorly conditioned for double-precision matrix inversion unless error propagation is well taken care of.
Use eigenvectors for small eigenvalues below to diagnose quasi singularity.

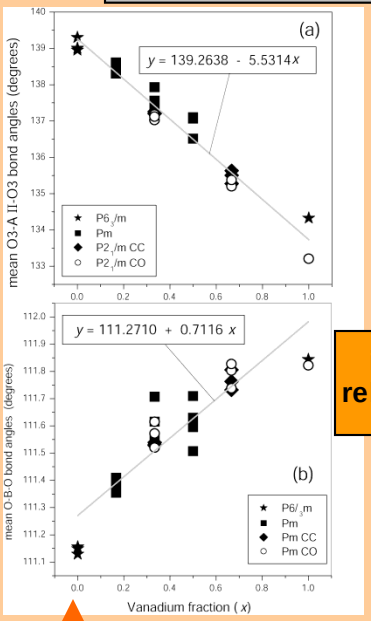
Eigenvectors for final_fit.out ranked according to eigenvalues are printed as columns below

Eigenvector # :	1	2	3	4	5	..	13	14	15	16
dA101 1:	0.000	0.716	-0.208	0.023	-0.416	..	0.026	0.001	0.004	0.000
DeltaA10 2:	0.000	0.434	-0.126	0.003	-0.147	..	-0.018	0.001	-0.004	0.002
deltaA1 3:	0.000	0.003	-0.001	0.000	0.008	..	0.383	0.642	-0.063	-0.034
alphaA1 4:	0.000	0.016	-0.005	0.001	0.014	..	-0.819	0.379	-0.314	0.015
dBO 5:	0.000	0.536	0.524	0.042	0.584	..	0.002	-0.014	0.007	-0.001
rhoA2 6:	0.000	0.000	-0.001	-0.002	-0.458	..	-0.030	-0.012	0.000	-0.002
alphaA2 7:	0.000	0.000	0.000	0.000	-0.001	..	-0.142	-0.619	-0.310	-0.002
dA2O3 8:	0.000	-0.096	0.816	0.024	-0.504	..	-0.001	0.012	-0.006	0.001
zero_error 9:	0.000	-0.038	-0.036	0.999	-0.003	..	0.000	0.000	0.000	0.000
p1SCALE 10:	1.000	0.000	0.000	0.000	0.000	..	0.000	0.000	0.000	0.000
p1MS 11:	-0.001	0.000	0.000	0.010	0.014	..	0.001	0.000	0.000	0.000
beqA1 12:	0.000	0.000	0.000	0.000	0.001	..	0.197	-0.097	0.118	-0.001
beqA2 13:	0.000	0.000	0.000	0.000	0.003	..	-0.034	-0.111	0.031	-0.008
beqO 14:	0.000	0.000	0.000	0.000	-0.002	..	-0.345	0.011	0.876	-0.004
beqB 15:	0.000	0.000	0.000	0.000	-0.002	..	-0.025	0.196	-0.135	-0.010
beqX 16:	0.000	0.000	0.000	0.000	0.000	..	-0.023	-0.016	-0.004	-0.999
Eigenvalues :	0.871E+12	0.448E+11	0.611E+10	0.241E+08	0.546E+07	..	0.348E+04	0.292E+04	0.221E+04	0.273E+03

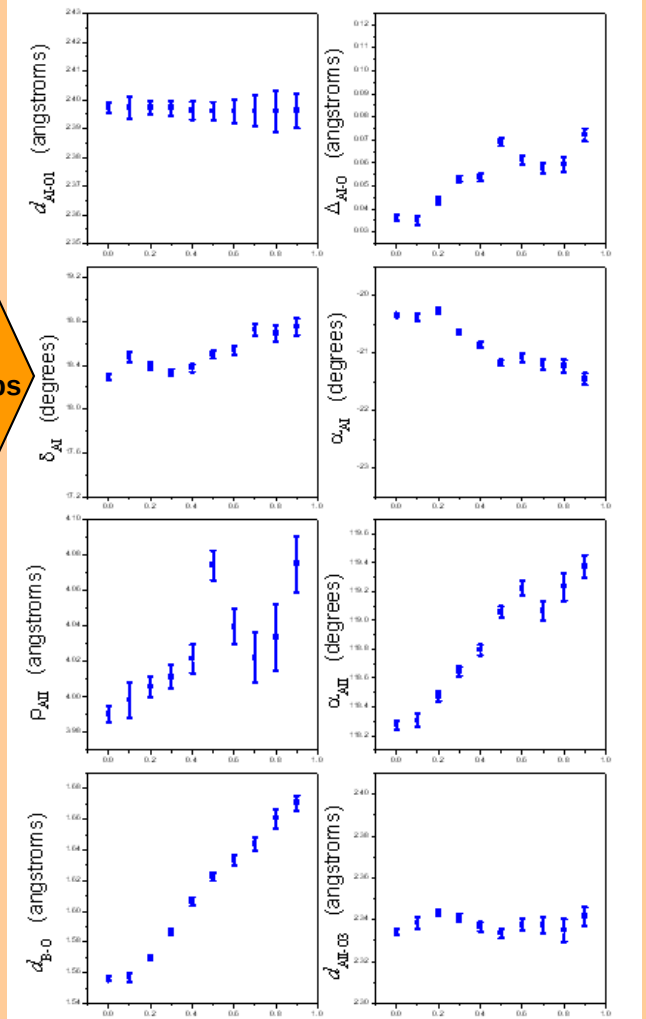
Practical use of SVD for diagnosing Rietveld refinement



ab-initio-constrained crystal-chemical Rietveld refinement



imposed relationships

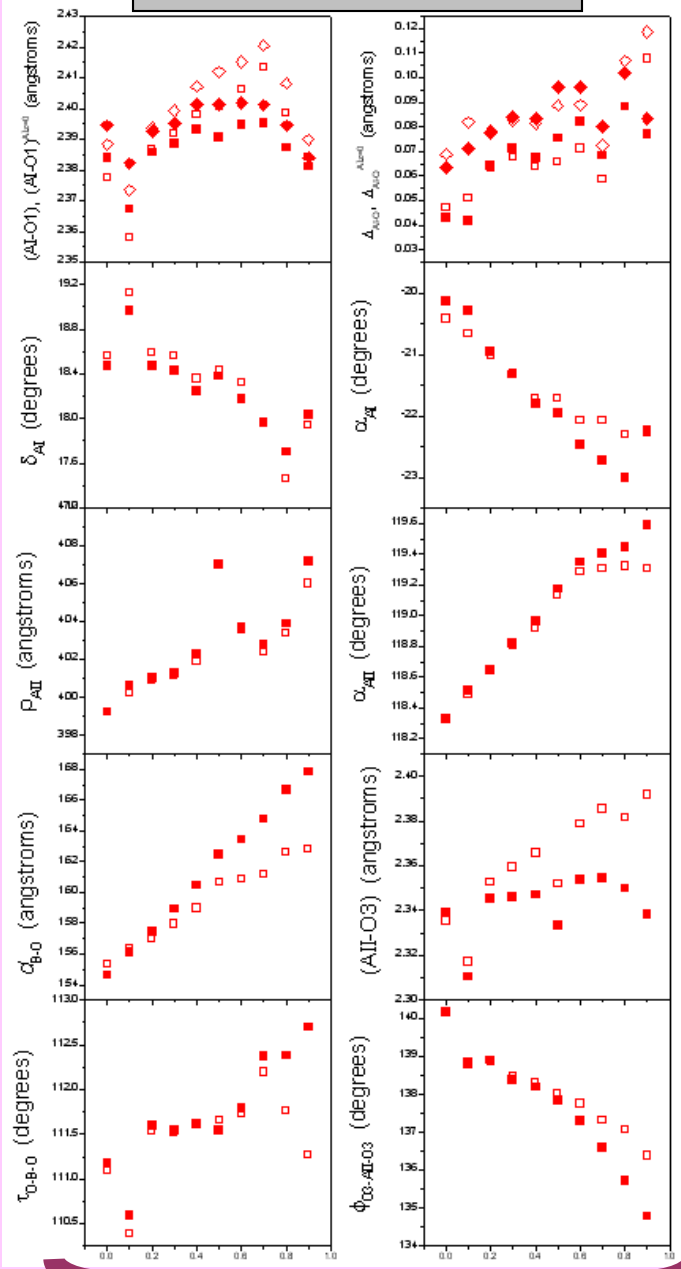


ab initio optimized values for bond-angle variables poorly determined by least-squares processing of experimental data sets

precise extraction of crystal chemistry for $Ca_{10}(V_xP_{1-x}O_4)_6F_2$ solid solutions

Acta Cryst. B (2007) 63: 37-48

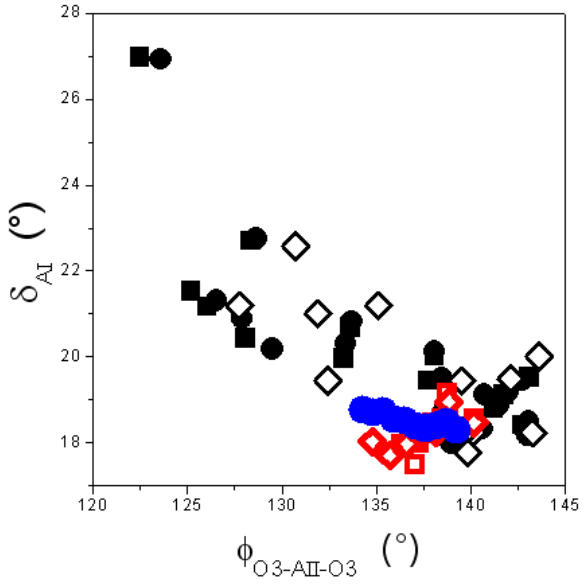
standard Rietveld refinement

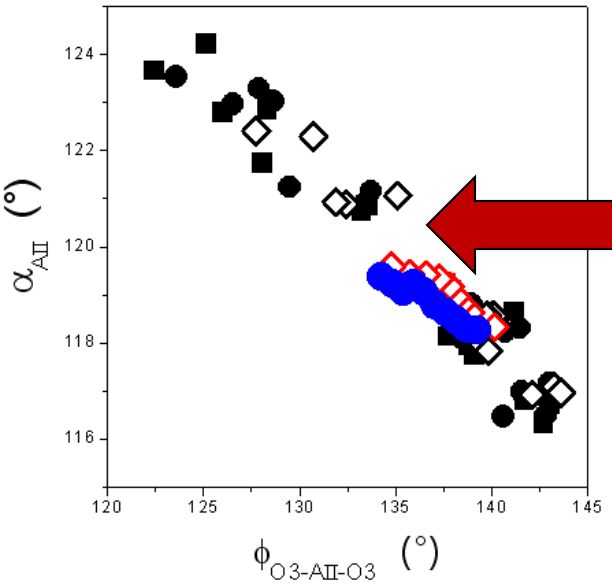


inconclusive results

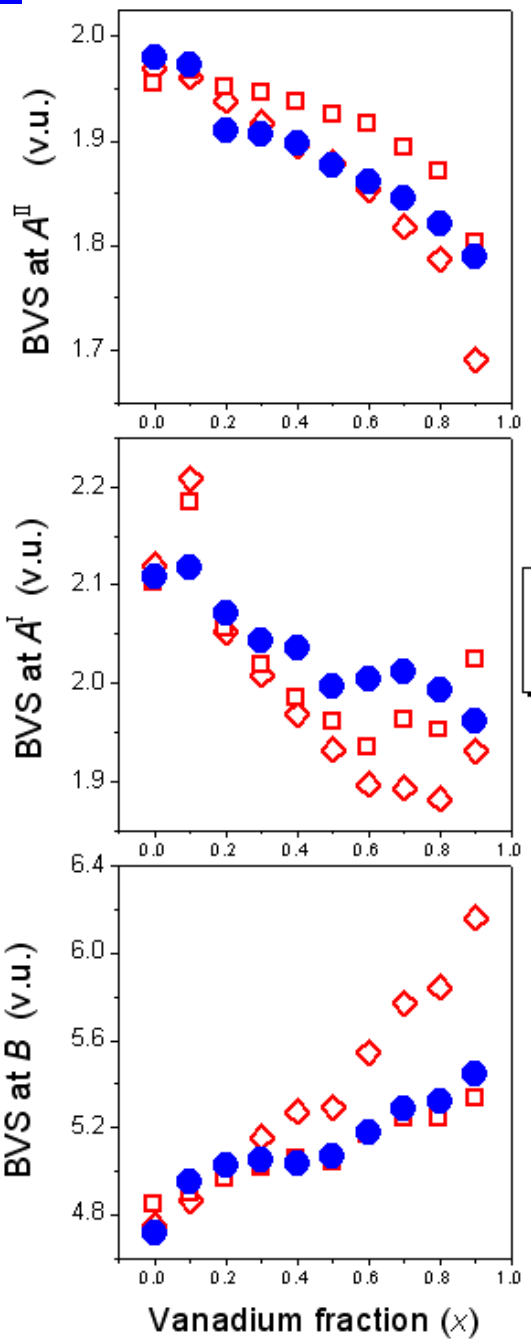
Acta Cryst. B (2007) 63: 37-48

bond valence sums



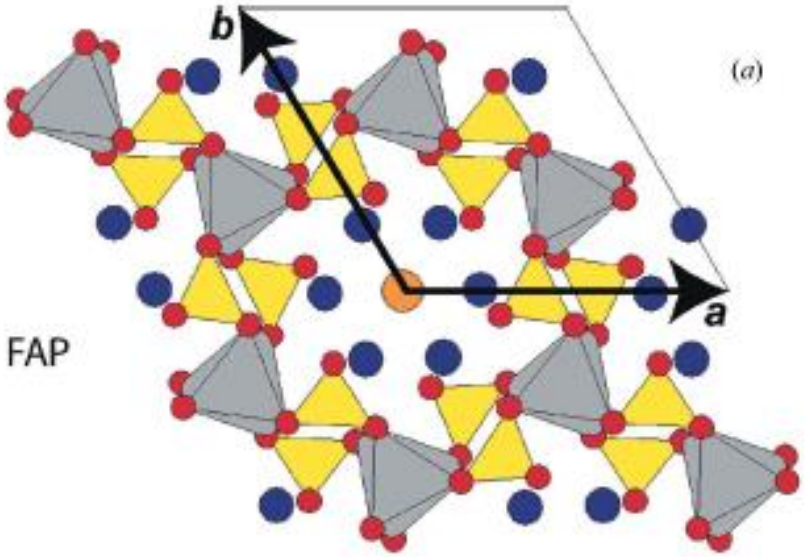


triclinic apatites



Discovery of triclinic apatites structure type

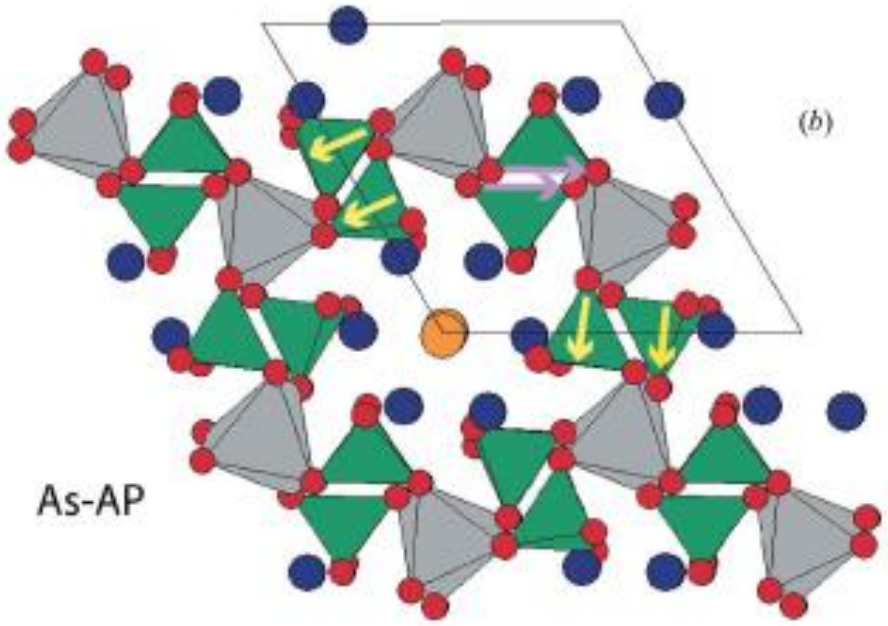
Acta Cryst. B (2007) 63: 251-256

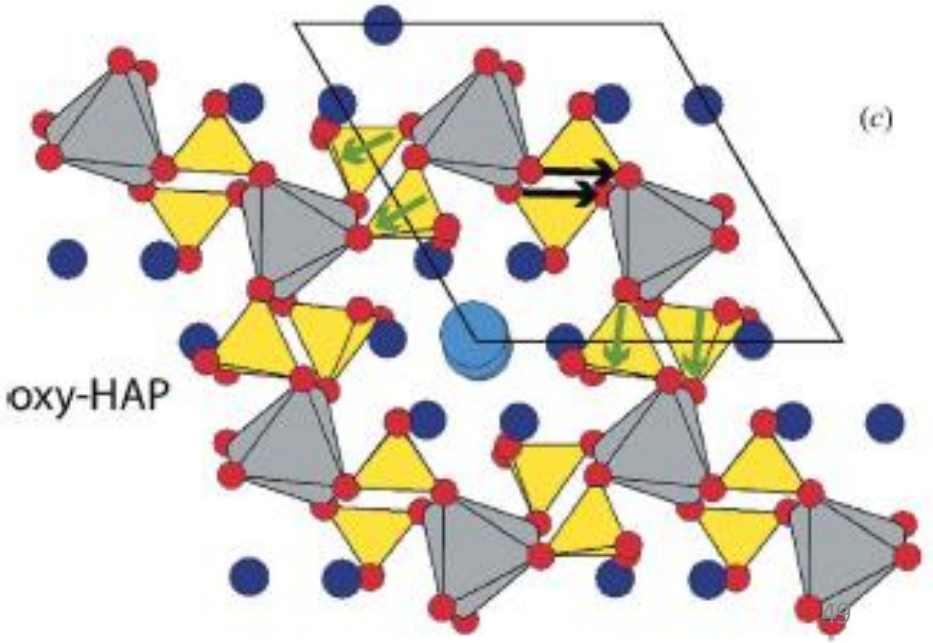


Tetrahedra	Along *a* (°)	Along *b* (°)	Along [110] (°)
As-AP	12	11	5
V-AP	8.5	9.5	3
Oxy-HAP[(a)]	14	6	1
$La_{10-x}(GeO_4)_6O_{3-1.5x}$[(b)]	18.5	13.5	3

References: (*a*) Alberius-Henning *et al.*, 2001); (*b*) León-Reina *et al.* (2003).

$Ca_{10}(PO_4)_6F_2$ and $Ca_{10}(PO_4)_6F_2$ predicted to be isostructural





References Summary and Conclusions

-- We developed and explained an SVD approach to objective assessment of numerical stability for Rietveld refinements.

Mercier *et al*. (2006), *J. Appl. Cryst.*, 39: 458-465

-- A crystal-chemically parameterized model of *P*6$_3$*lm* apatite was developed. Equivalence to standard crystallographic description has been shown.

Mercier *et al*. (2005), *Acta Cryst. B,* 61: 635-655

-- A *TOPAS* script was developed allowing direct least-squares extraction of crystal-chemical parameters for *P*6$_3$*lm* apatites.

Mercier *et al*. (2006), *J. Appl. Cryst.*, 39: 369-375

-- By imposing *ab initio* results in a crystal-chemical Rietveld refinement, a precise description of $Ca_{10}(V_xP_{1-x}O_4)_6F_2$ eco-apatites has been obtained.

Mercier *et al*. (2007), *Acta Cryst. B*, 63: 37-48

-- Triclinic apatites were demonstrated to correspond to a new structure type, by both neutron and X-ray diffraction as well as *ab initio* calculations.

Baikie *et al*. (2007), *Acta Cryst. B,* 61: 251-256

Inorganic Chemistry

Article

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The Crystal Chemistry of $Ca_{10-y}(SiO_4)_3(SO_4)_3Cl_{2-x-2y}F_x$ Ellestadite

Yanan Fang,*[,†] Clemens Ritter,[‡] and Tim White[†,§]

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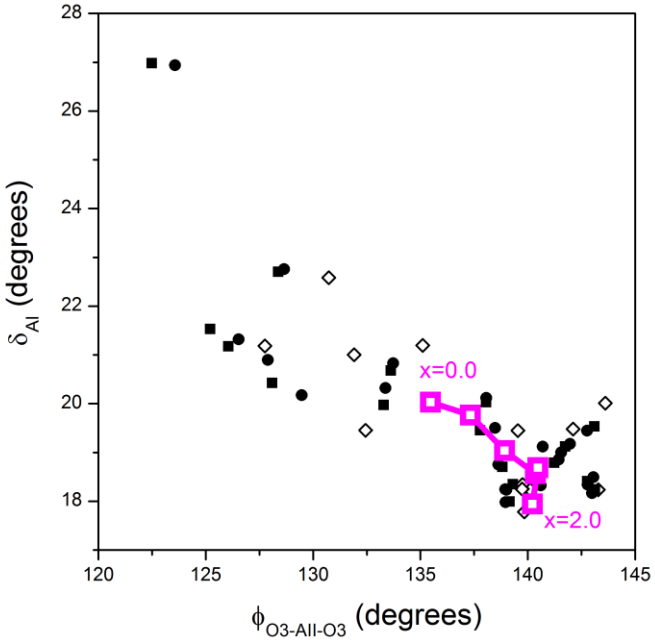
[‡]Institute Laue-Langevin, 6 rue Jules Horowitz, 38042 Grenoble Cedex 9, France

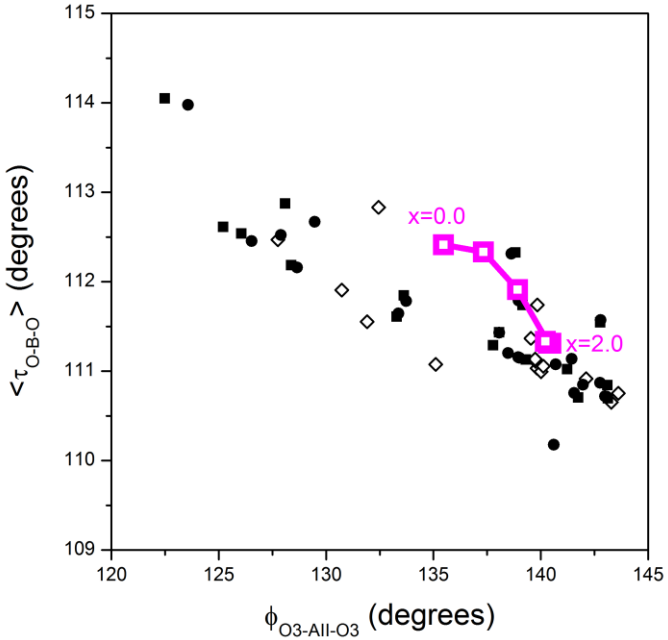
[§]Centre for Advanced Microscopy, Sullivan's Creek Road, Australian National University, Canberra ACT 0200 Australia

Supporting Information

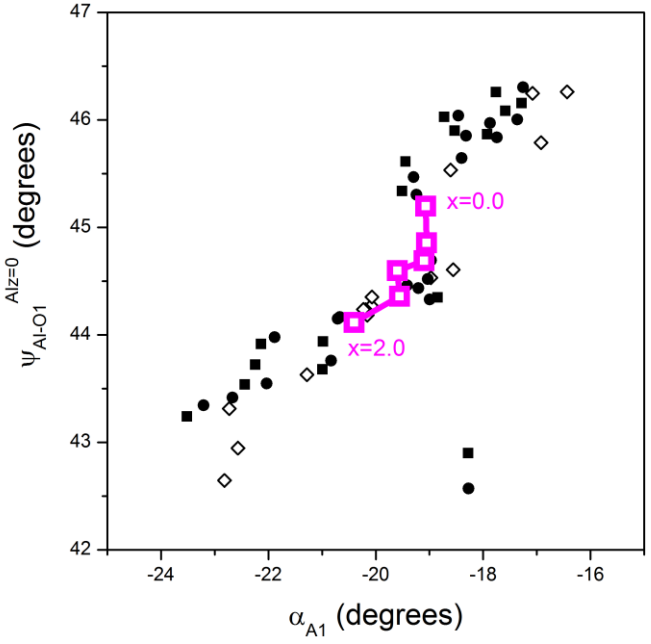
ABSTRACT: Fluor-chlorellestadite solid solutions $Ca_{10}(SiO_4)_3(SO_4)_3Cl_{2-x}F_x$, serving as prototype crystalline matrices for the fixation of hazardous fly ash, were synthesized and characterized by powder X-ray and neutron diffraction (PXRD and PND), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR). The lattice parameters of the ellestadites vary linearly with composition and show the expected shrinkage of unit cell volume as fluorine (IR = 1.33 Å) displaces chlorine (IR = 1.81 Å). FTIR spectra indicate little or no OH^- in the solid solutions. All compositions conform to $P6_3/m$ symmetry where F^- is located at the 2*a* (0, 0, $^1/_4$) position, while Cl^- is displaced out of the 6*h* Ca(2) triangle plane and occupies 4*e* (0, 0, *z*) split positions with *z* ranging from 0.336(3) to 0.4315(3). Si/S randomly occupy the 6*h* tetrahedral site. Ellestadites rich in Cl ($x \leq 1.2$) show an overall deficiency in halogens (<2 atom per formula unit), particularly Cl as a result of $CaCl_2$ volatilization, with charge balance achieved by the creation of Ca vacancies ($Ca^{2+} + 2Cl^- \rightarrow \square_{Ca} + 2\square_{Cl}$) leading to the formula $Ca_{10-y}(SiO_4)_3(SO_4)_3Cl_{2-x-2y}F_x$. For F-rich compositions the vacancies are found at Ca(2), while for Cl-rich ellestadites, vacancies are at Ca(1). It is likely the loss of $CaCl_2$ which leads tunnel anion vacancies promotes intertunnel positional disorder, preventing the formation of a $P2_1/b$ monoclinic dimorph, analogous to that reported for $Ca_{10}(PO_4)_6Cl_2$. Trends in structure with composition were analyzed using crystal-chemical parameters, whose systematic variations served to validate the quality of the Rietveld refinements.

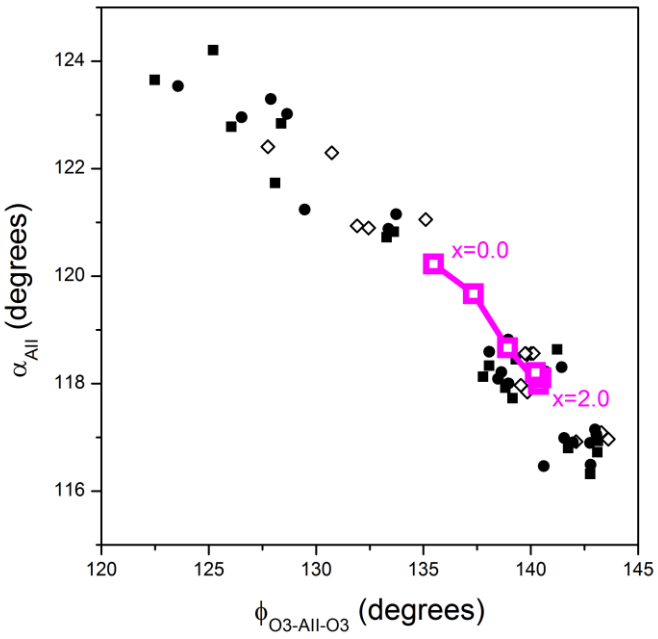
dx.doi.org/10.1021/ic201673r | Inorg. Chem. 2011, 50, 12641–12650





$Ca_{10-y}(SiO_4)_3(SO_4)_3Cl_{2-x-2y}F_x$





Inorganic Chemistry

The Crystal Chemistry of $Ca_{10-y}(SiO_4)_3(SO_4)_3Cl_{2-x-2y}F_x$ Ellestadite

Yanan Fang,*[†] Clemens Ritter,[‡] and Tim White[†,§]

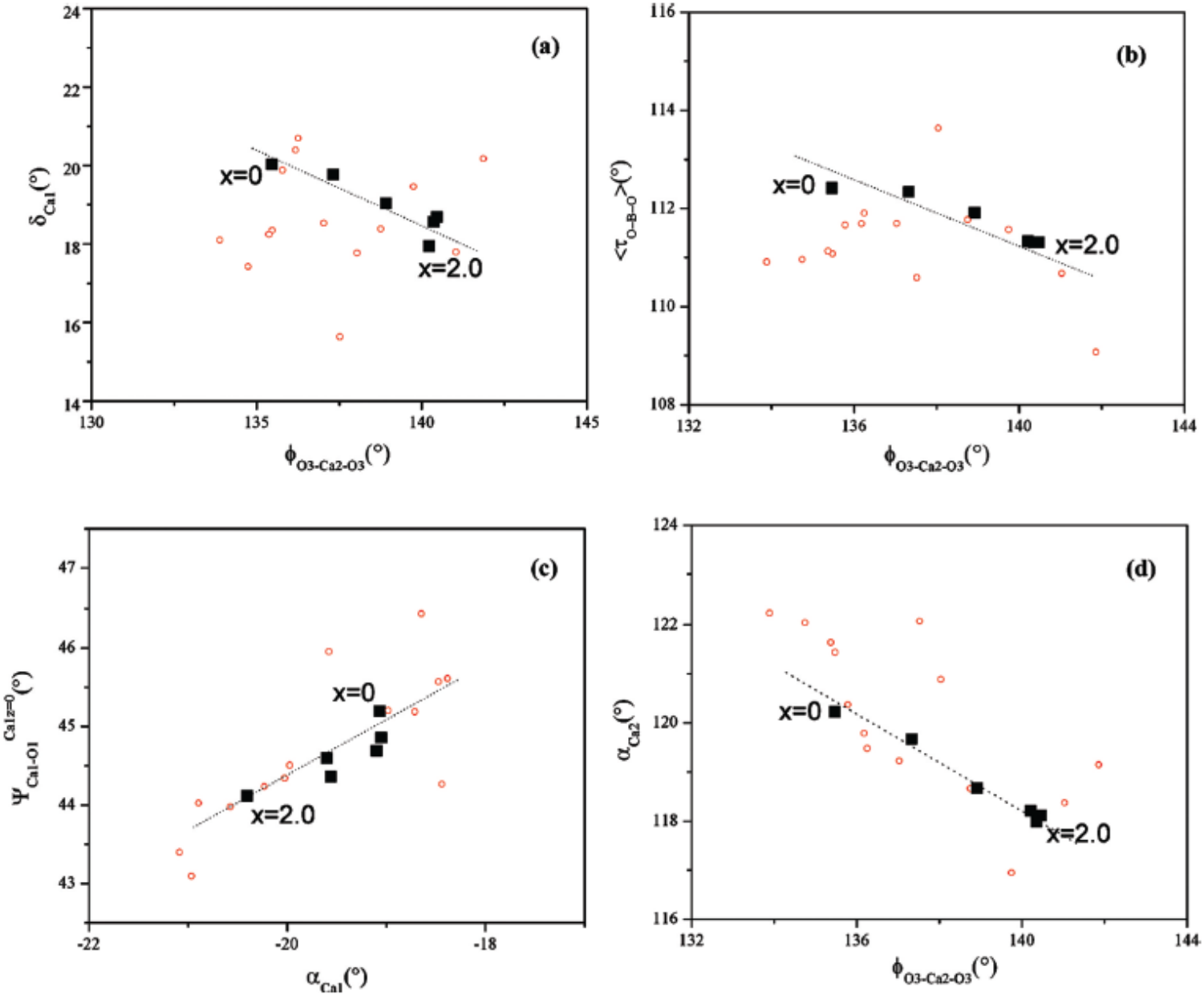


Figure 9. Correlations observed between polyhedral distortion parameters: (a) δ_{Ca1} versus $\phi_{O3-Ca2-O3}$, (b) $<\tau_{O-B-O}>$ versus $\phi_{O3-Ca2-O3}$, (c) $\Psi_{Ca1-O1}^{Ca1\ z=0}$ versus α_{Ca1}, and (d) α_{Ca2} versus $\phi_{O3-Ca2-O3}$. These figures should be compared with Figure.8 in Mercier et al.[33] Circles: published data; large filled squares: this study. (δ_{Ca1}:counter-rotation angle of CaO_6 polyhedra; $\phi_{O3-Ca2-O3}$: O3−Ca2−O3 bond angle; $<\tau_{O-B-O}>$: O−B−O bond-bending angle; $\Psi_{Ca1-O1}^{Ca1\ z=0}$: angle that an $Ca1_{z=0}$−O1 bond makes with respect to *c*; α_{Ca1}: orientation of CaO_6 polyhedra with respect to *a*; α_{Ca2}: orientation of Ca2 triangles with respect to *a*.).