Exploiting the precision and accuracy of powder diffraction profiles with appropriately parameterized Rietveld refinement models

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NRC·CNRC

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Exploiting the Precision and Accuracy of Powder Diffraction Profiles with Appropriately Parameterized Rietveld Refinement Models

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Topics for the talk

Part 1

Background notions
- Rietveld least-squares refinement
- Singular value decomposition of the least-squares matrix

Part 2

Rietveld refinement of apatite-type structures
- Crystal-chemical parameterization
- Numerical stability of Rietveld least-squares refinement
- Complementarity of ab initio modeling with Rietveld crystal-chemical structure determination

Part 3

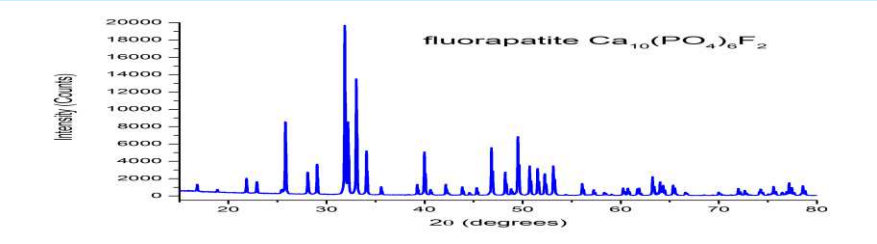
Rietveld refinement of battery materials
- Transition-metal site occupancies and anisotropic broadening in a refinement with a large number of fitted parameters

Part 4

Concluding remarks
- Troubleshooting ill-conditioned refinements with *SVDdiagnostics*
- Increased precision and accuracy with appropriately parameterized Rietveld models

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 correction

multiplicity

profile function
Gauss, Lorentz etc.

$$Yc(i) = Yb(i) + S\ AL(i)\ T(i)\ \Sigma_{\mathbf{h}}\ m_{\mathbf{h}}\ |F_{\mathbf{h}}|^2\ P(i,\mathbf{h})\ O(\mathbf{h})$$

background
Chebyshev polynomials

Absorption/ Lorentz-polarization

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 Δp

vector

The • indicates a dot product

Least-squares Rietveld refinement

For each step i in the Rietveld profile, we have a weighted equation

$$w(i)\,[Yo(i) - Yc(i,\mathbf{P})] = w(i)\,\Delta(i)$$

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

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

This gives the linear system of equations:

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

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 steps in the profile.

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

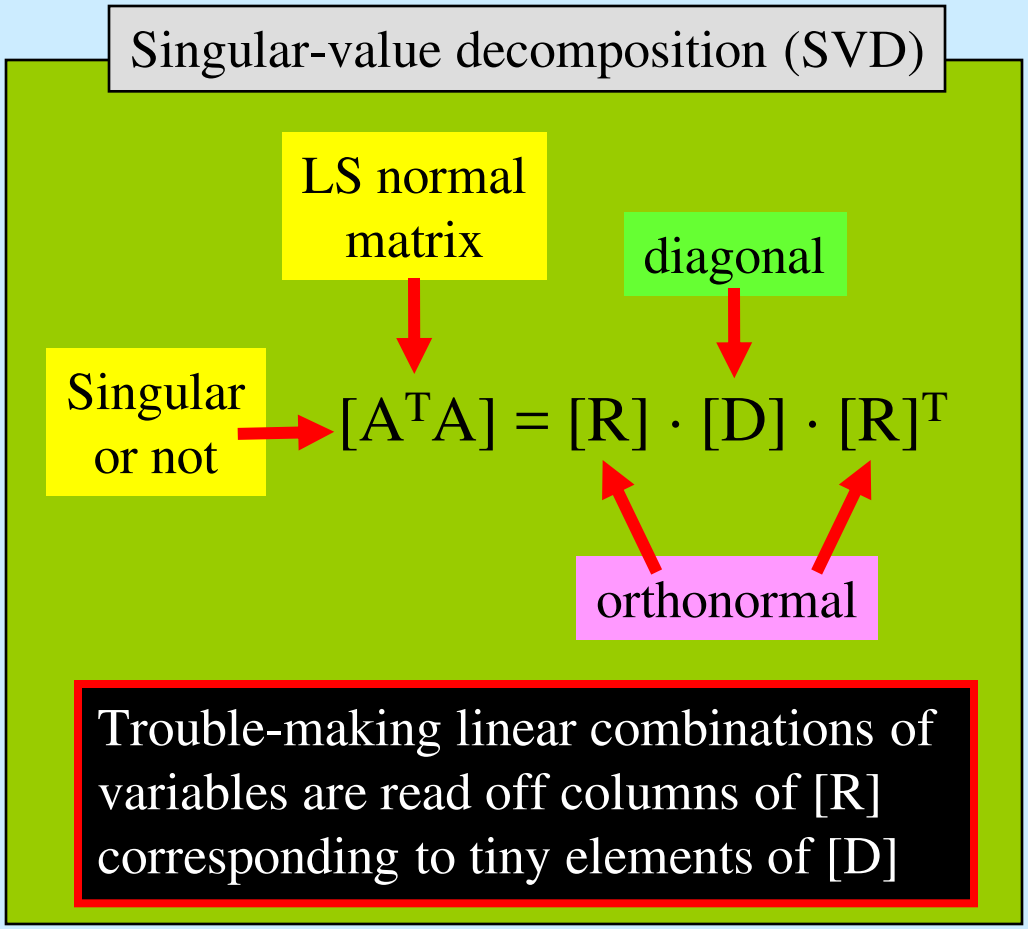
$$A^T \bullet A \bullet X = A^T \bullet B$$

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

$$X = [A^T \bullet A]^{-1} \bullet A^T \bullet B$$

Numerical stability of Rietveld refinements

J. Appl. Cryst. 39: 458-465



SVDdiagnostic → cure of Rietveld LS model

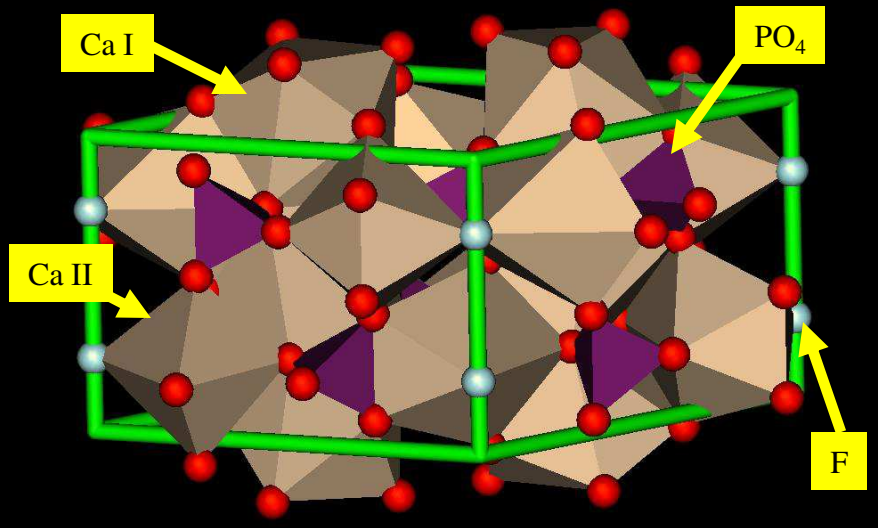
Software program freely distributed at www.tothcanada.com

Part 2

Rietveld refinement of apatite-type structures

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

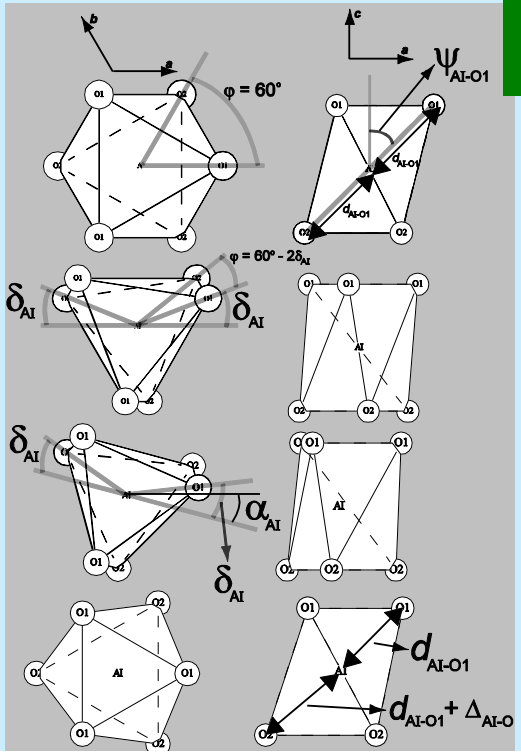
"ECO-APATITES"

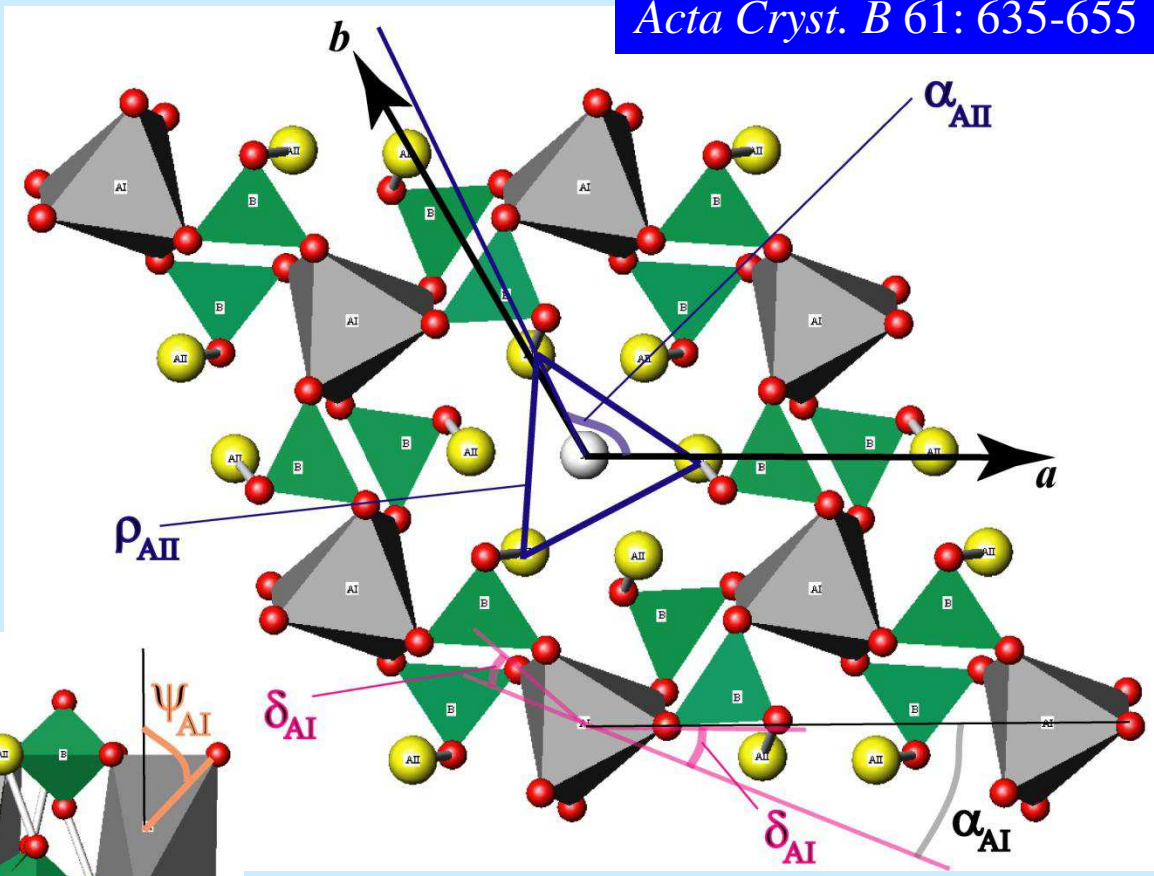
toxic metal immobilization from incinerator ash, industrial or mining refuses, high-level radioactive nuclear waste

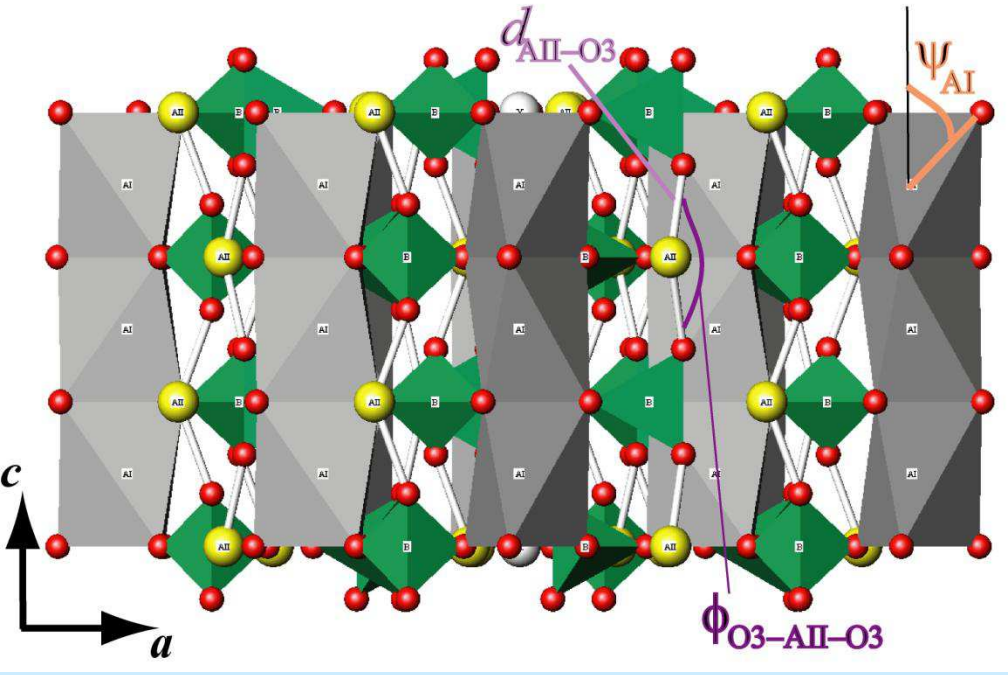
geochronology
catalysis
environmental remediation
soil treatment
bone replacement
dentistry

Crystal-chemical parameterization of $P6_3/m$ apatite

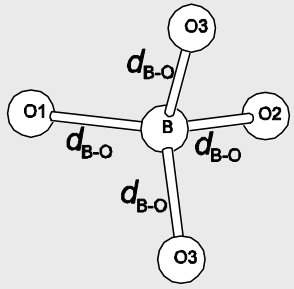
Acta Cryst. B 61: 635-655







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] = $\tau'_{O\text{-}B\text{-}O}$

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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:

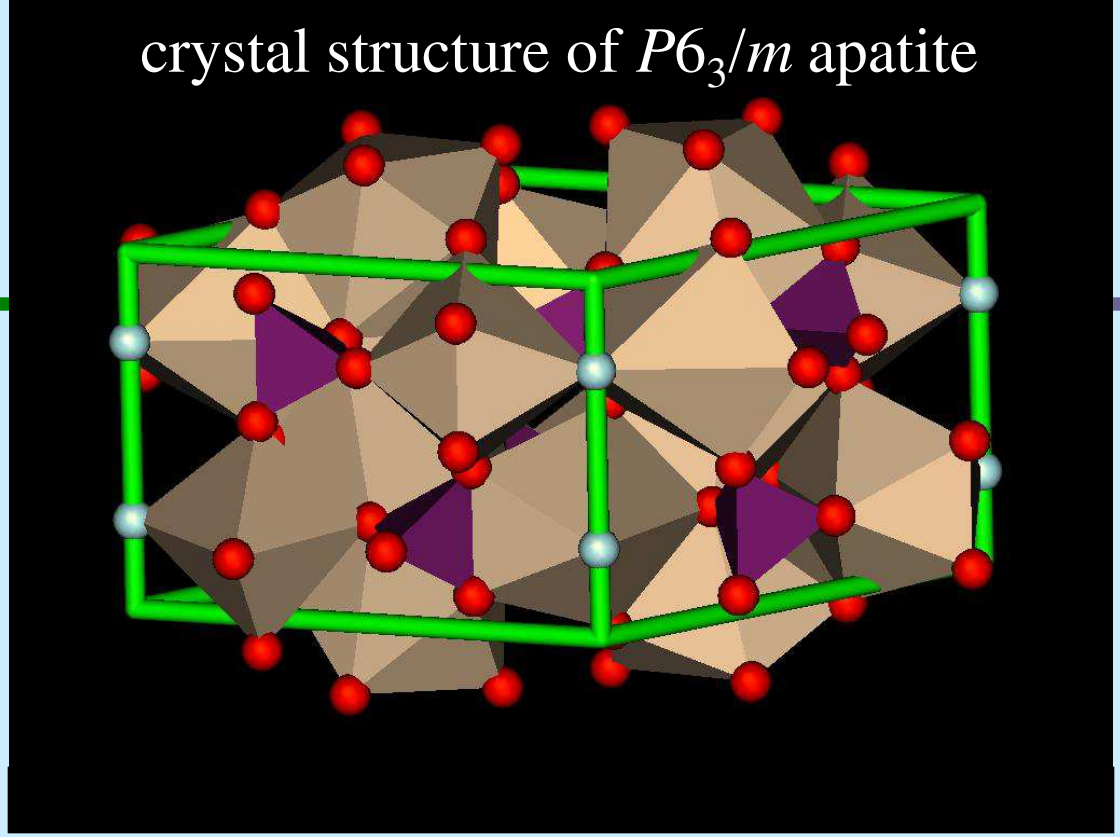
$$\sin(\theta) = \{\{ d_{AI\text{-}O1}^2 - (1/4)\cdot[d_{B\text{-}O}\sin(\tau'_{O\text{-}B\text{-}O}/2)+d_{AII\text{-}O3}\sin(\phi_{O3\text{-}AII\text{-}O3}/2)]^2 \}^{1/2}\cdot\sin[(\pi/6)-\delta_{AI}-\alpha_{AI}]$$
$$- \{(d_{AI\text{-}O1}+\Delta_{AI\text{-}O})^2-(1/4)\cdot[d_{B\text{-}O}\sin(\tau'_{O\text{-}B\text{-}O}/2)+d_{AII\text{-}O3}\sin(\phi_{O3\text{-}A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

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

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

$z(A^{I}) = 0$ (*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

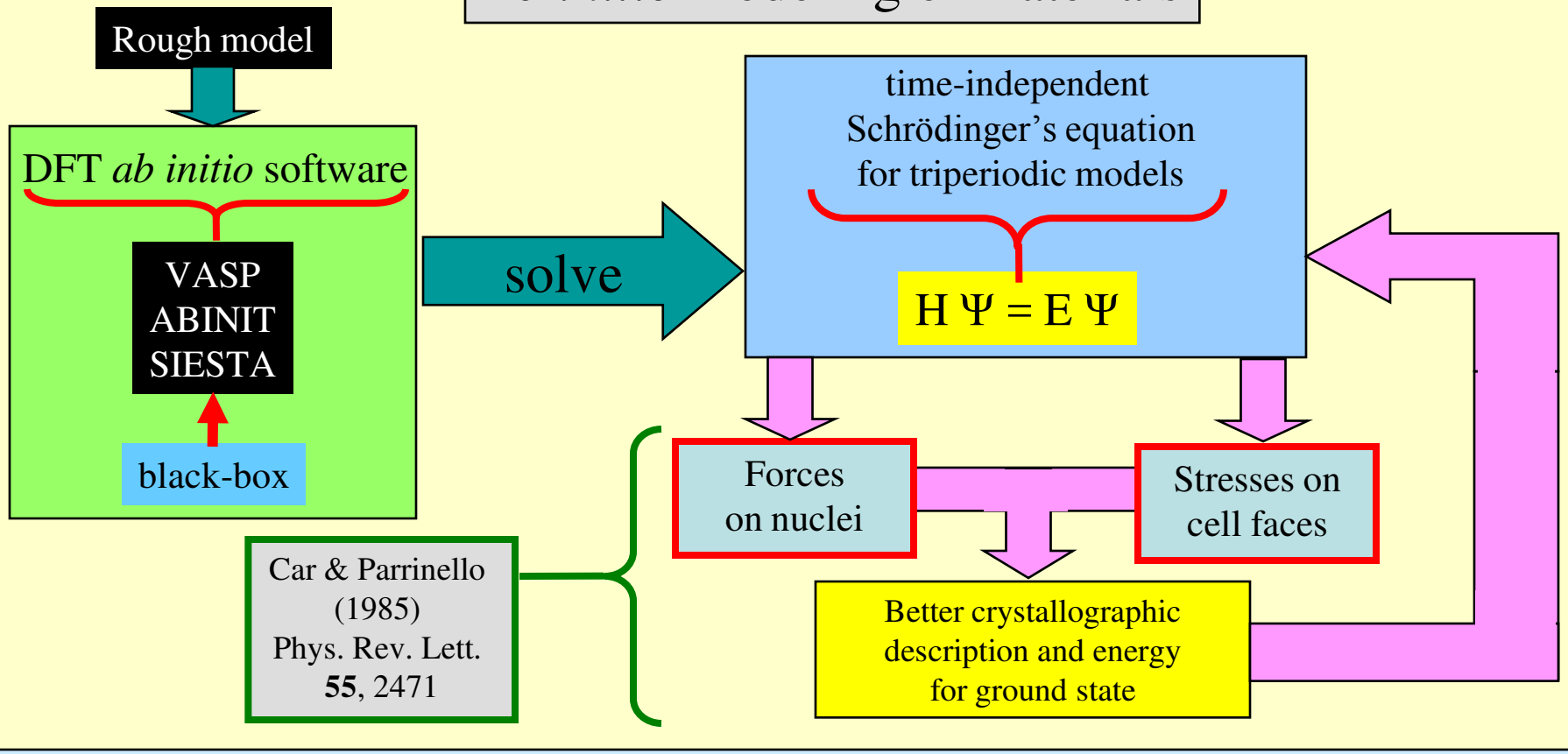
Experimental data used in the study

Acta Cryst. B 61: 635-655

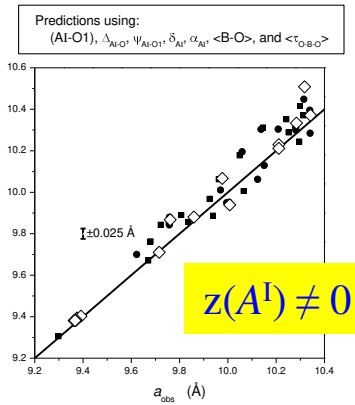
Literature crystallographic results for 18 end-member chemical compositions

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

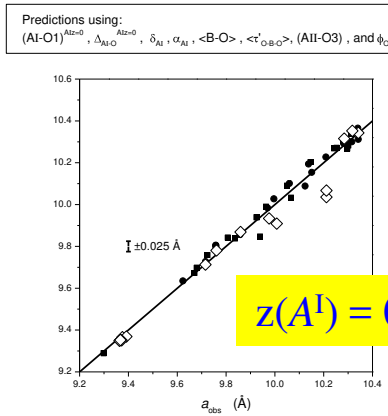
Ab initio modeling of materials



Predictions of *a* from crystal-chemical parameters

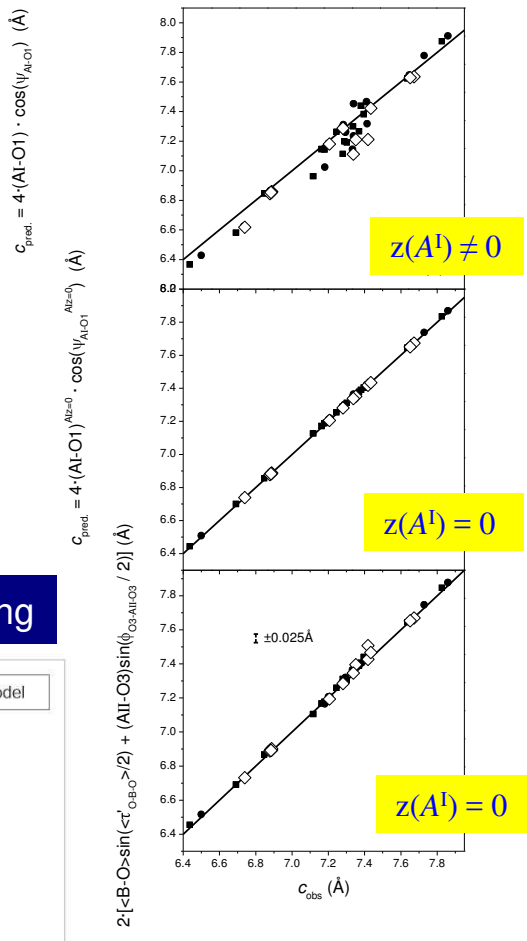


$z(A^I) \neq 0$

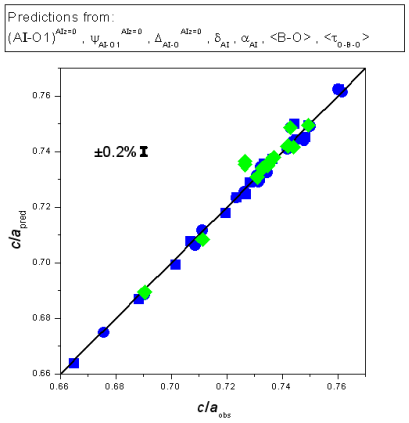


$z(A^I) = 0$

Predictions of *c* from crystal-chemical parameters



c/*a* axial ratio



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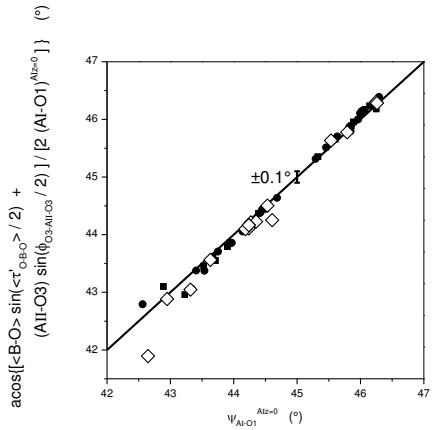
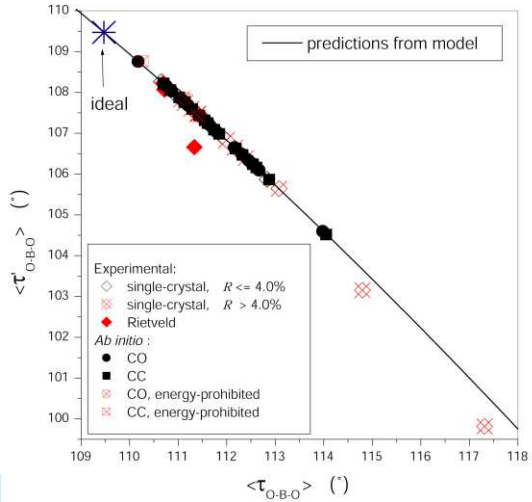
AlO_6 bond angle $\psi_{Al\text{-}O1}$



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

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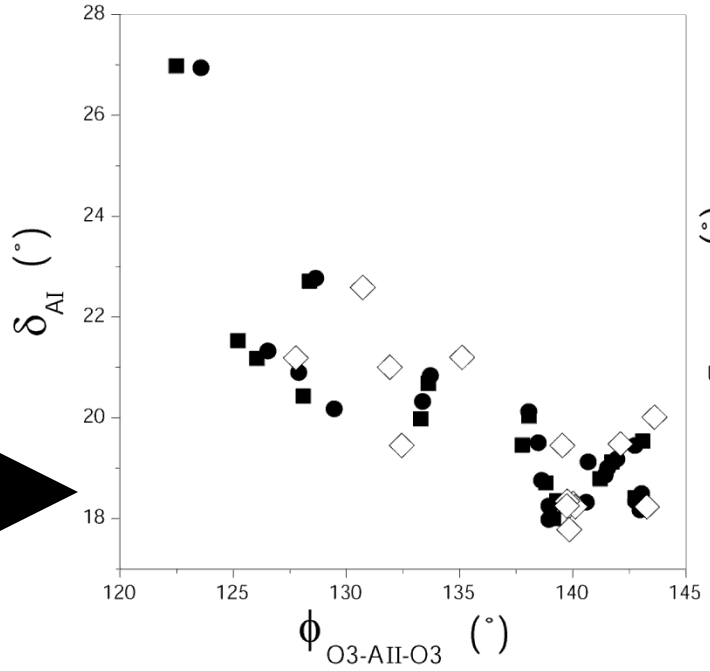
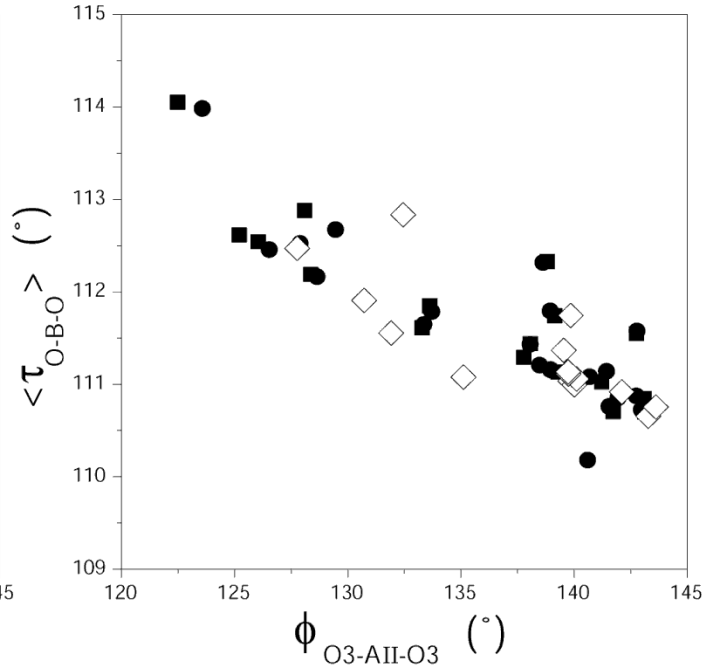
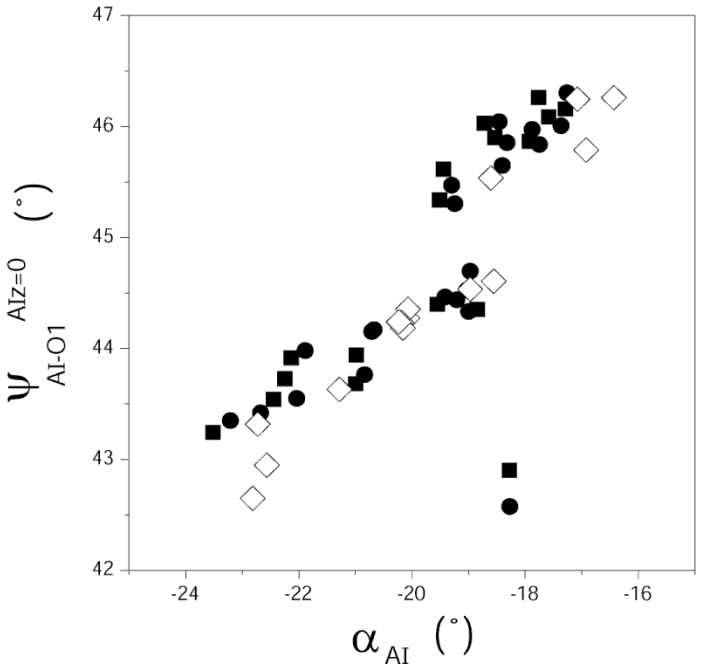
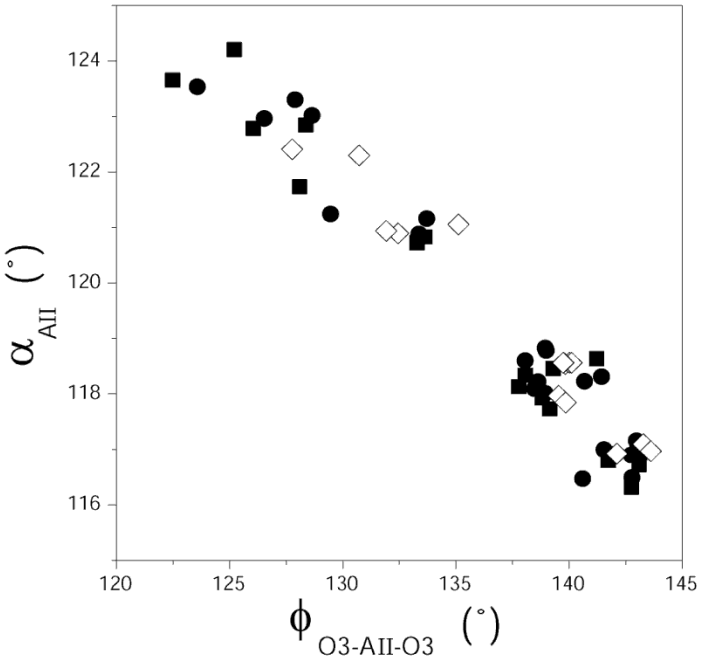








Direct least-squares refinement of crystal-chemical parameters for $P6_3/m$ apatite

J. Appl. Cryst. 39: 369-375

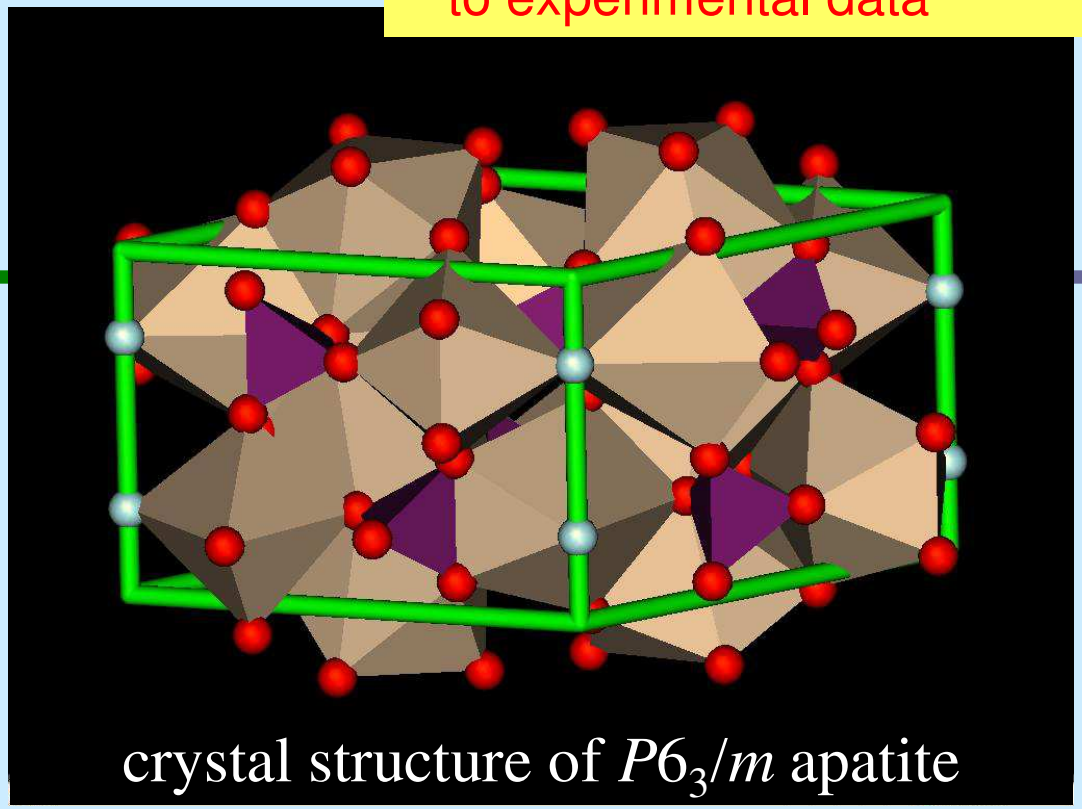
J. Appl. Cryst. 39: 458-465

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



standard refinement

Geometrical Parameterization

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
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CN =0.785E+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 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

CN =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
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.

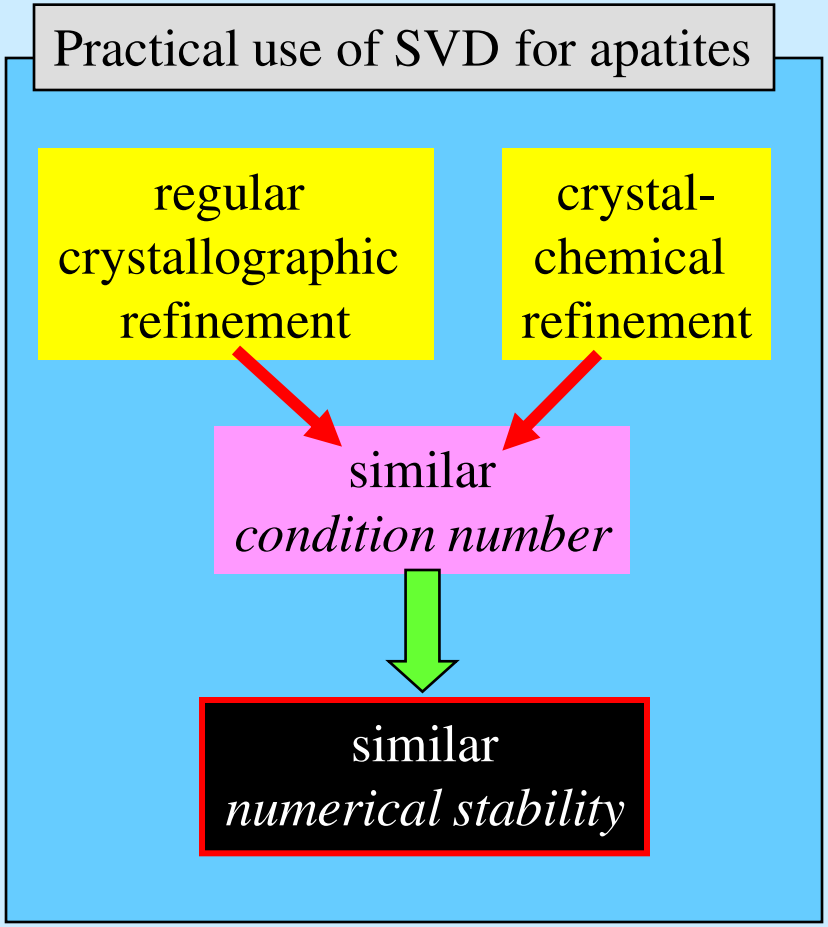
Eigenvectors for ch12.out ranked according to eigenvalues are printed as columns below

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

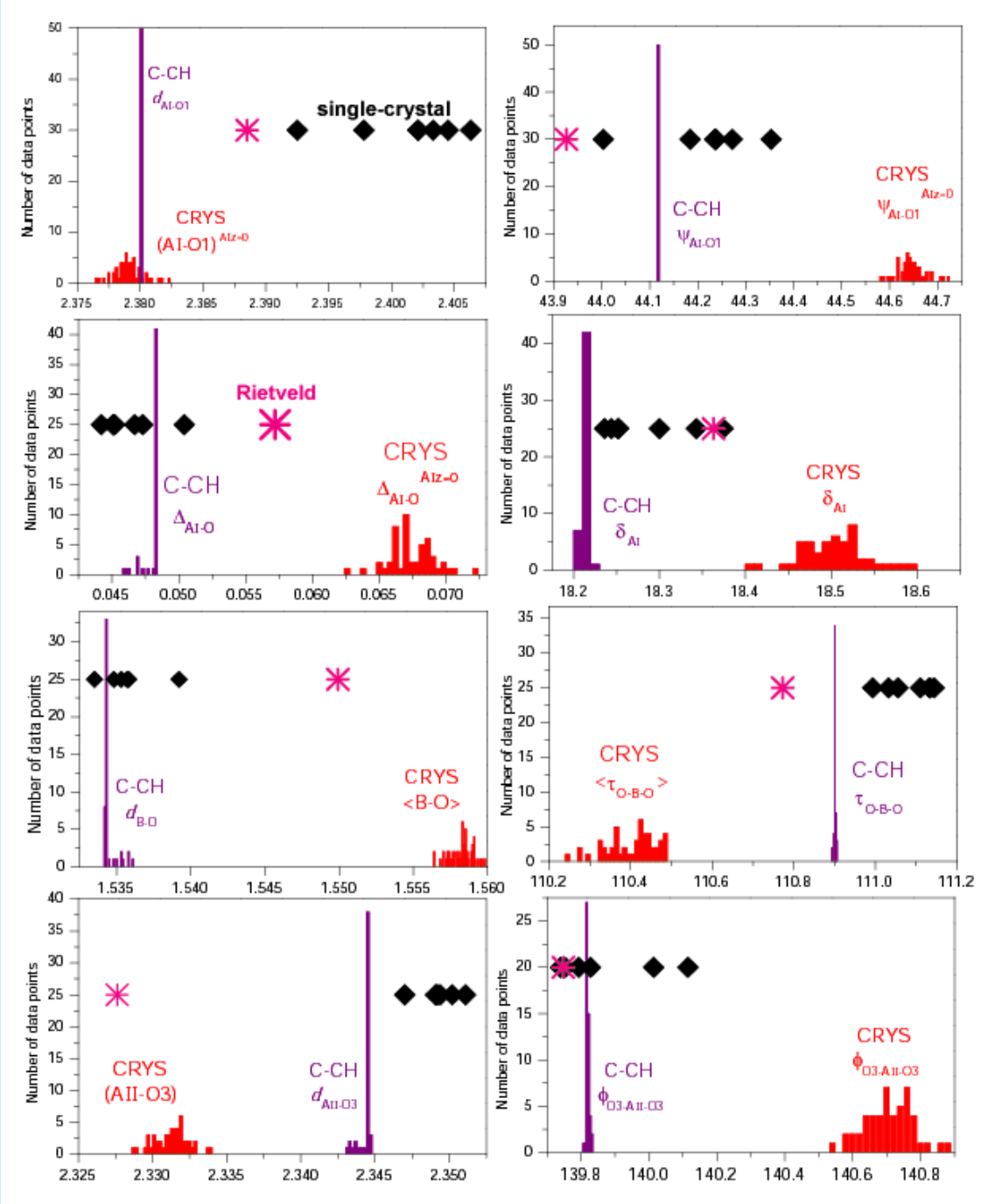
Software program freely distributed at www.tothcanada.com

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)			

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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)			

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	0.514
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

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

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

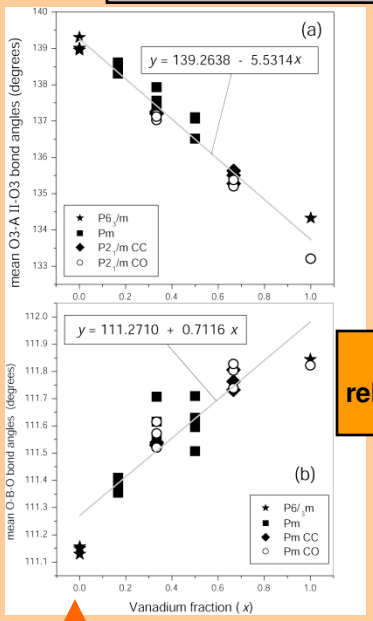
Condition number for matrix of normal equations = 0.319E+10
Error propagation is likely to spoil 10 trailing decimal digits out of probably 14.

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.

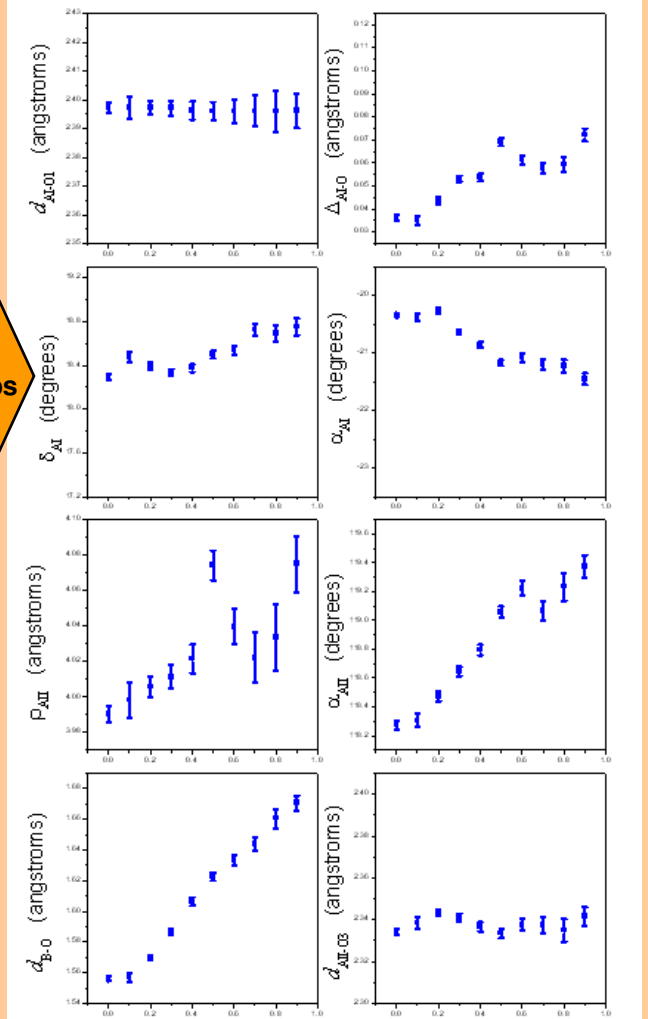
Eigenvectors for final_fit.out ranked according to eigenvalues are printed as columns below

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

ab-initio-constrained crystal-chemical Rietveld refinement



imposed relationships

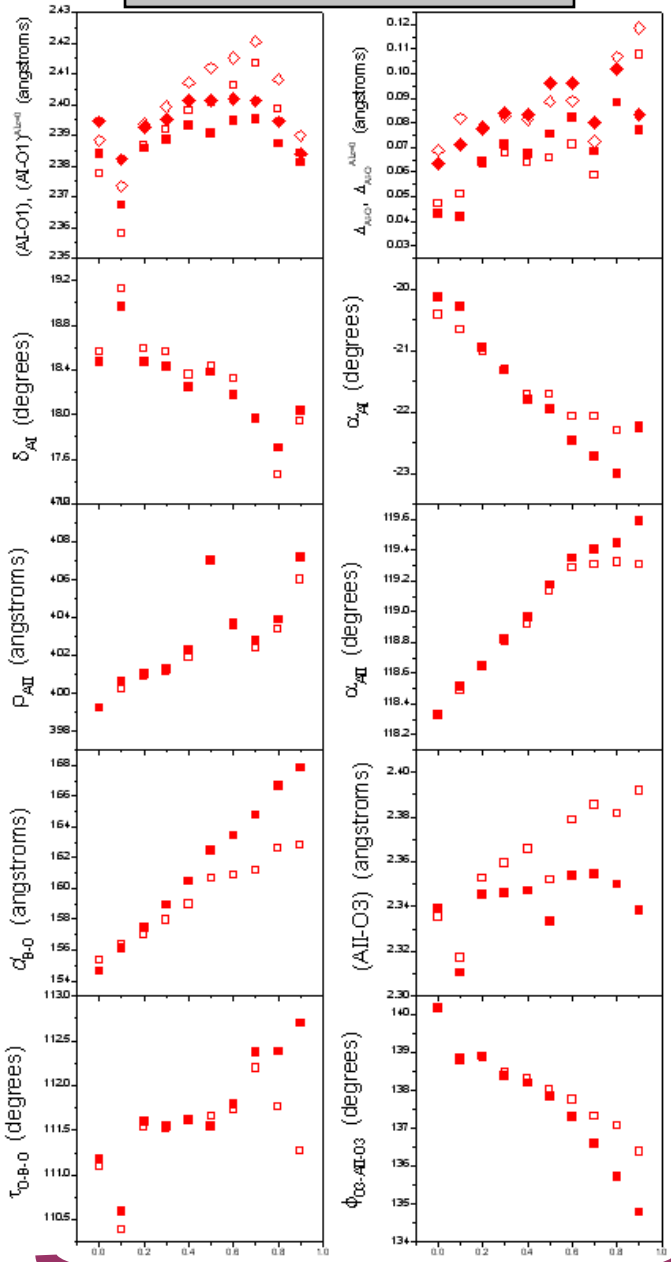


ab initio optimized values for bond-angle variables poorly determined by least-squares processing of experimental data sets

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

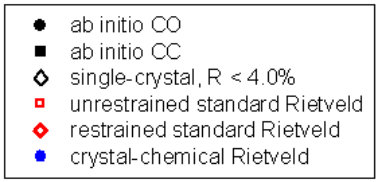
standard Rietveld refinement

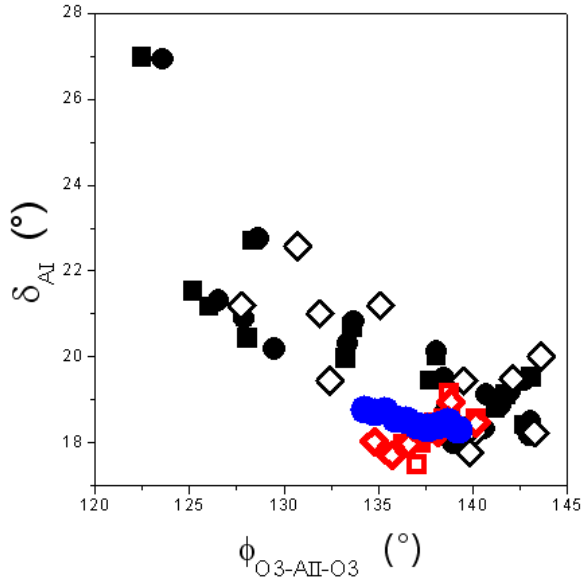


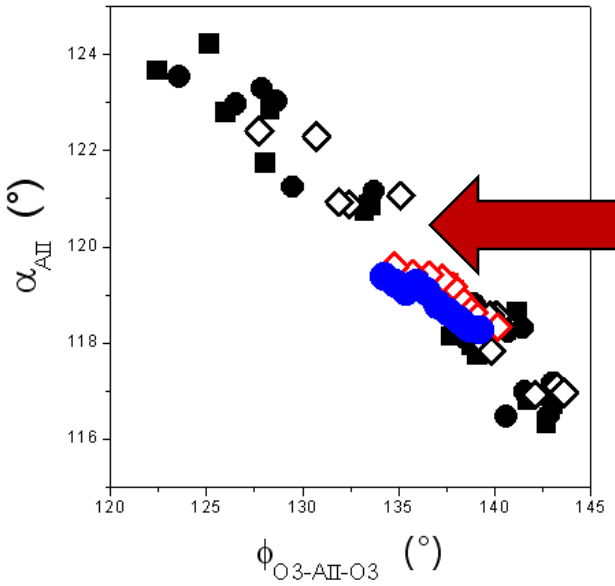
inconclusive results

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

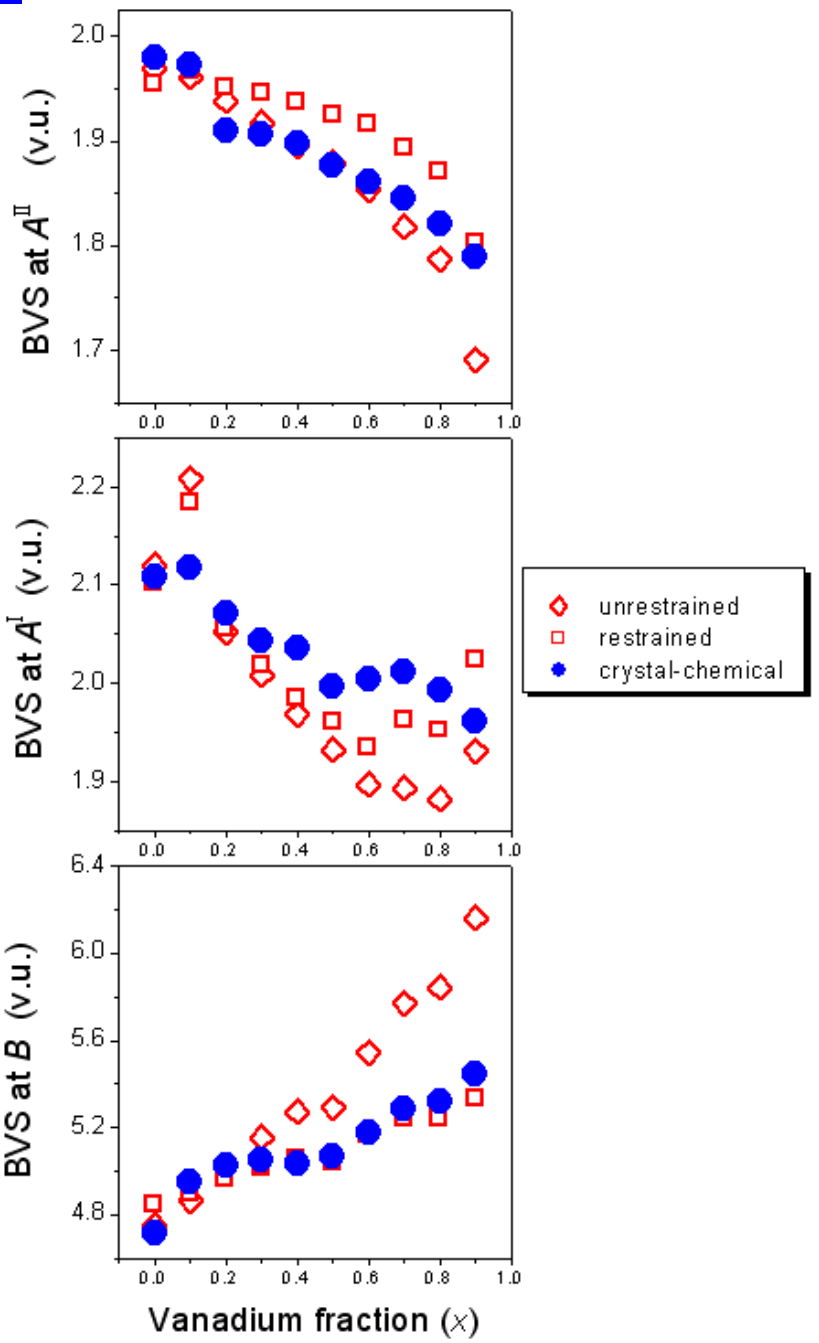
bond valence sums





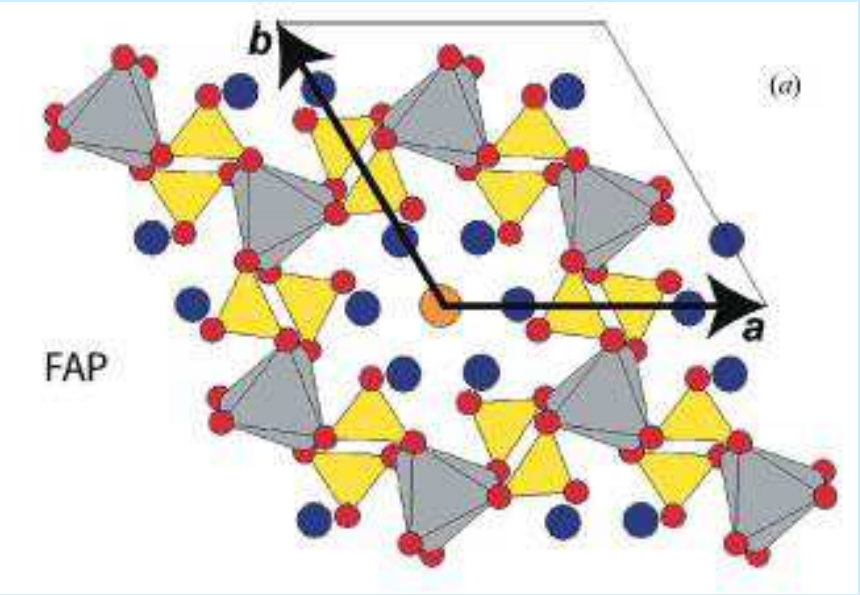


triclinic apatites



Discovery of triclinic apatites structure type

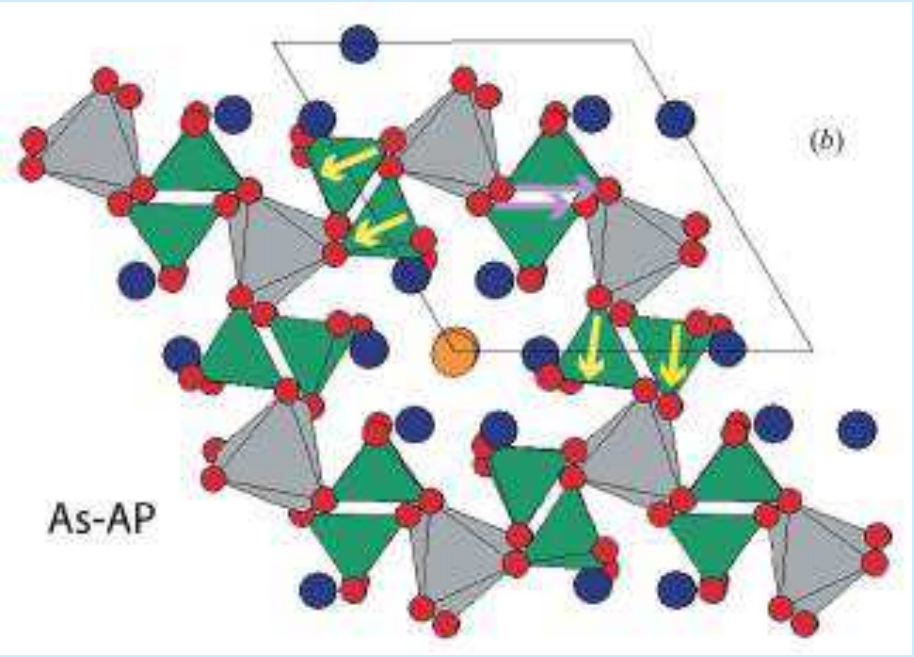
Acta Cryst. B (2007) 63: 251-256

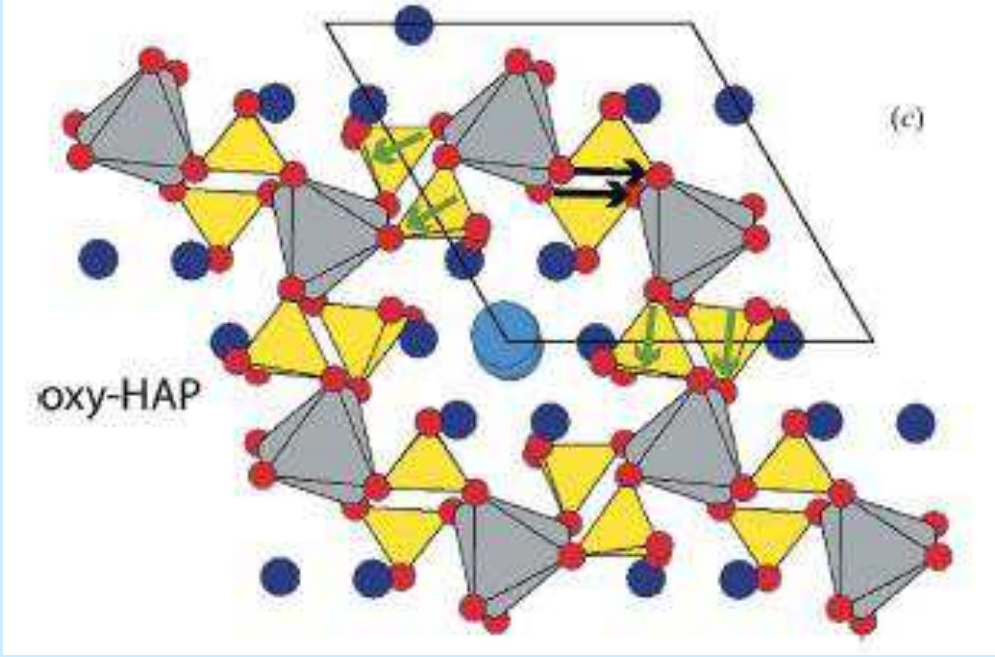


Tetrahedra	Along *a* (°)	Along *b* (°)	Along [110] (°)
As-AP	12	11	5
V-AP	8.5	9.5	3
Oxy-HAP[(a)]	14	6	1
$La_{10-x}(GeO_4)_6O_{3-1.5x}$[(b)]	18.5	13.5	3

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





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Part 3

Rietveld refinement of battery materials

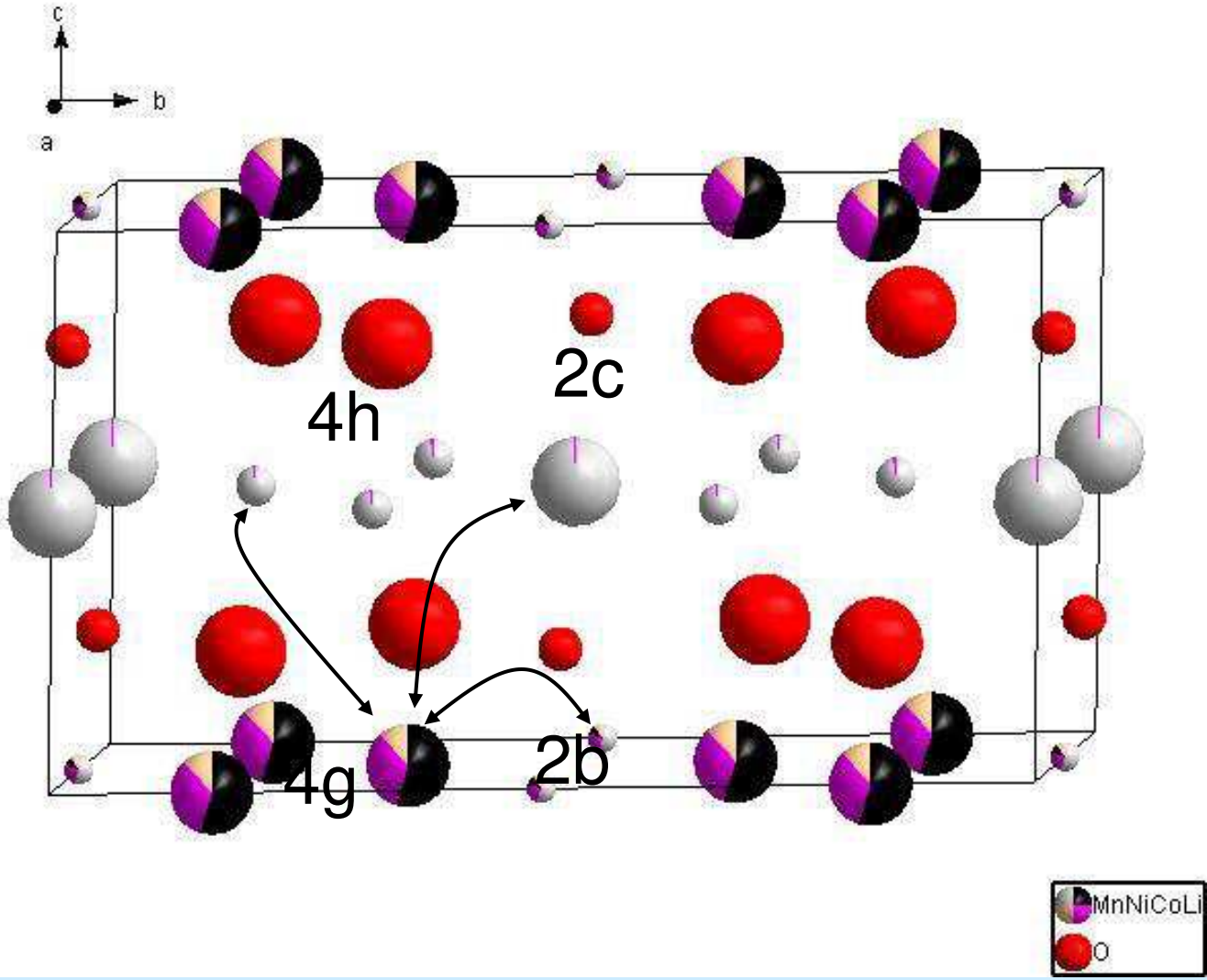
Monoclinic C2/m Li_2MnO_3-type structure

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

Li layer

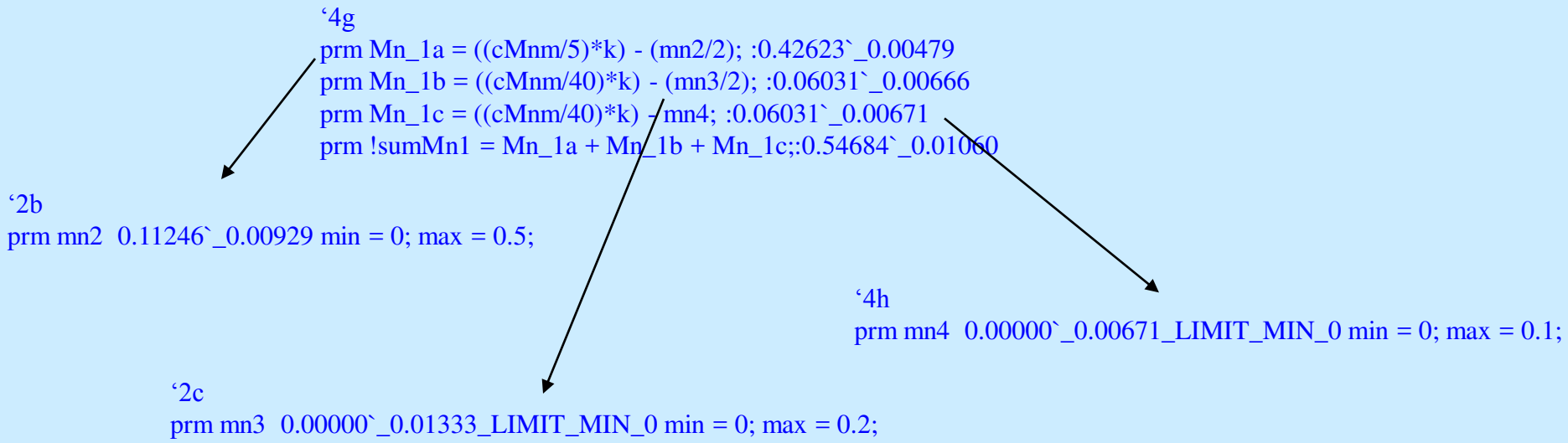
O layer

TM layer



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….

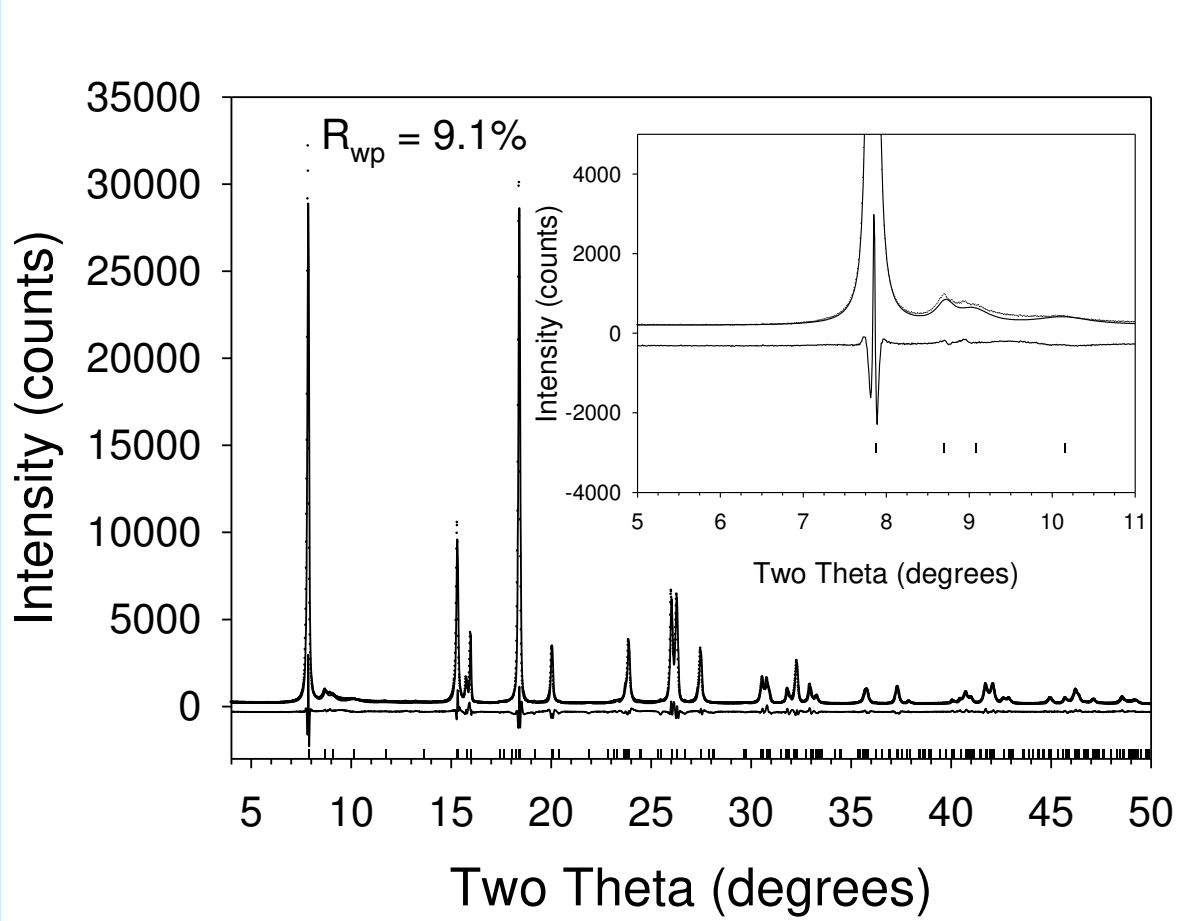
Anisotropic broadening

- 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 $\sqrt{3}a \quad \sqrt{3}a$ ordering with some full pattern anisotropy
- Full pattern: spherical harmonic Lorentzian convolution
- $\sqrt{3}a \quad \sqrt{3}a$: 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)º
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)

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Part 4: Conclusions

SVD of Rietveld least-squares matrix provides a straightforward, objective means of assessing the numerical stability and trouble-shooting ill-conditioned Rietveld refinements.

For a high-quality fluorapatite powder pattern:
-- Crystal-chemical refinement, a new concept, was shown more precise and more accurate than standard crystallographic refinement, while being as numerically stable and much less sensitive to noise in experimental data.

For limited-quality powder data on the $Ca_{10}(V_xP_{1-x}O_4)_6F_2$ apatite system:
-- *Ab initio* constrained crystal-chemical refinment was necessary to obtain a precise and accurate crystallographic description of this system.
-- For the same experimental data ,standard refinements were of questionable accuracy leading to inconclusive results.

For the standard Rietveld refinement of a battery material, which involved many refinement parameters, *SVDdiagnostics* was proven invaluable to sort out which parameters needed to be fixed in order obtain a reliable and plausible crystallographic description of this material.