Alternative Ways of Describing Structures: Symmetry-Mode Refinements

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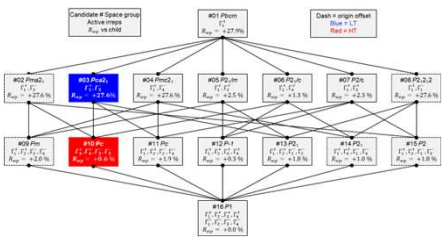
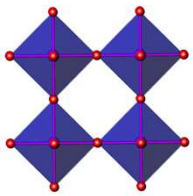
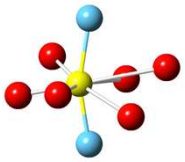
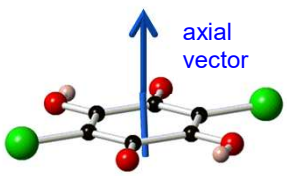
Motivation

- Phase transitions are important in many areas of chemistry, physics and materials science
- Understanding phase transitions can be complicated, especially with just powder diffraction data
- Distortion-mode or symmetry-mode refinements can help (especially for non-reconstructive transitions)









Outline of session

- What are symmetry modes?
- ISODISTORT tool
- Symmetry mode Rietveld refinement
- Tricks (we'll skip most but they're in the notes)
  - efficient parameters
  - refining the space group (?)
  - exhaustive searches
  - Genetic Algorithms
- Other applications of symmetry modes

- Hands-on symmetry mode refinements (>45 minutes)

Dictionary/syntax/background – see the notes

parent structure *n*. the reference structure to which the structure under consideration is referred.

parent space group *n*. the mathematical group describing the space group symmetry of the parent structure; a supergroup of the symmetry group of the structure under consideration.

child structure *n*. the structure under consideration which is derived from the parent structure.

isotropy subgroup *n*. a subgroup accessible by considering the possible distortions of the parent structure.

irreducible representation *n*. representations that are expressed in block diagonal form blah blah blah blah blah blah blah blah blah blah blah.

Order parameter *n*. blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah.

Order parameter direction *n*. blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah blah

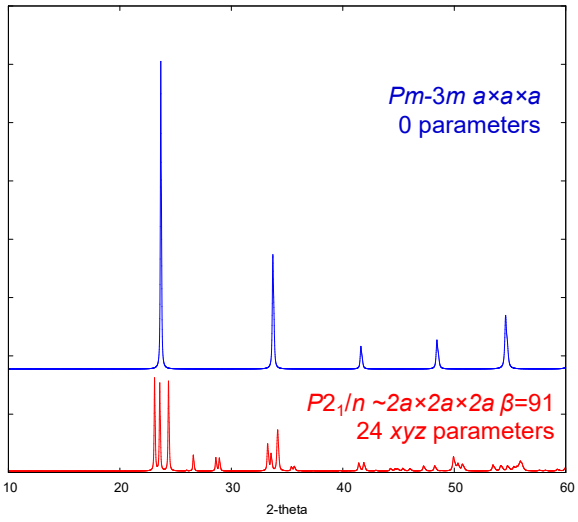
See notes online

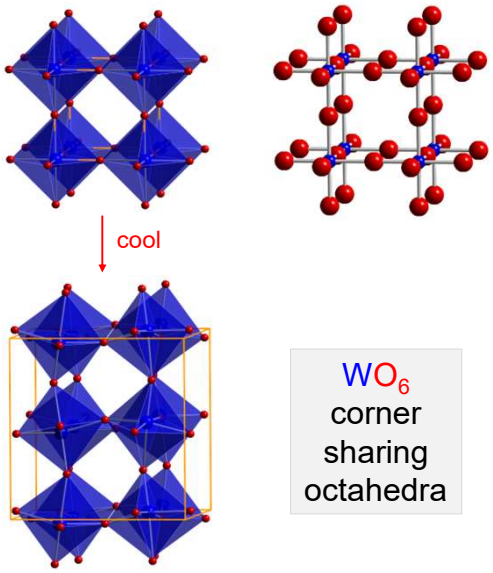
See ISODISTORT help pages at https://stokes.byu.edu/iso/isodistorthelp.php

See Mark Senn's dictionary notes at https://pcgschool2018.wordpress.com/

Stuttgart page

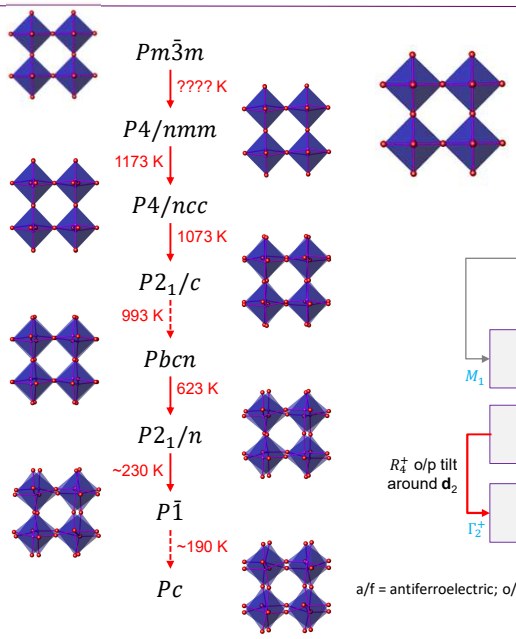
WO_3 phase transitions and powder diffraction

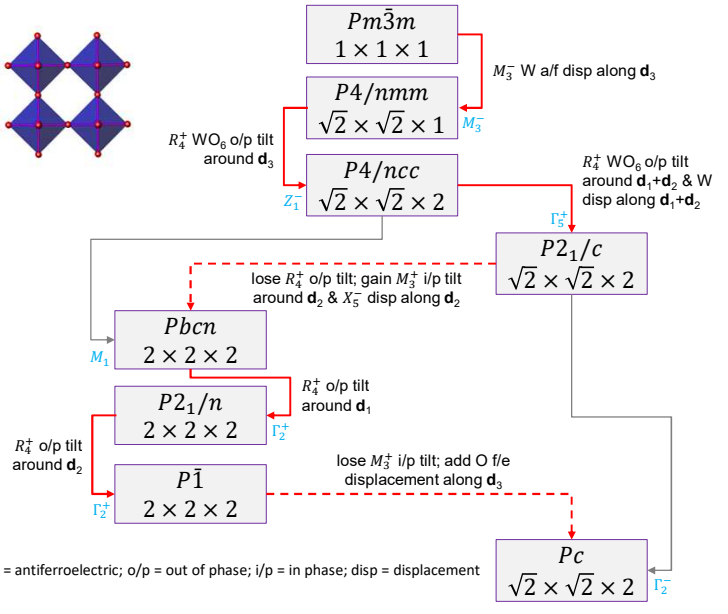




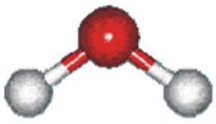
WO_6 corner sharing octahedra

Example system: WO_3 – group subgroup tree

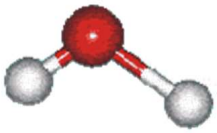




Analogy: distorted H_2O molecule and normal modes



\+ distortion =

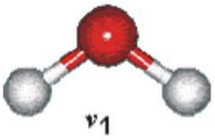


"parent + distortion = child"

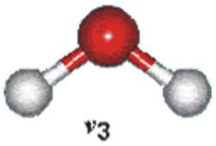
high symmetry
C_{2v} or *mm*
parent

lower symmetry
C_s or *m*
child

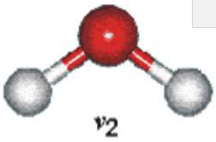
normal modes orthogonal



symmetric stretch
irrep a_1



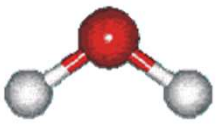
asymmetric stretch
irrep b_2



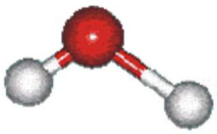
bend
irrep a_1

http://www.lsbu.ac.uk/water/vibrat.html

Analogy: distorted H_2O molecule and normal modes



\+ b_2 irrep distortion =



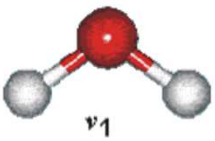
"parent + distortion = child"

irrep = recipe for breaking symmetry

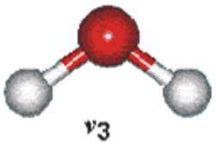
high symmetry
C_{2v} or *mm*

lower symmetry
C_s or *m*

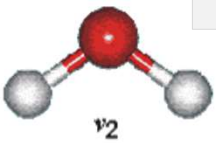
normal modes orthogonal



symmetric stretch
irrep a_1



asymmetric stretch
irrep b_2



bend
irrep a_1

http://www.lsbu.ac.uk/water/vibrat.html

ım.ac.uk/john.evans Stuttgart 2025

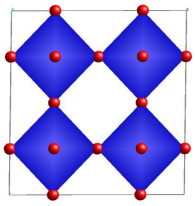
Symmetry-adapted distortion modes

Parent high symmetry structure and space group

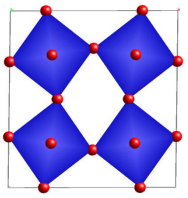
atomic displacements transform as an irrep of parent structure

distortion

Distorted child = parent + mode amplitudes isotropy subgroup



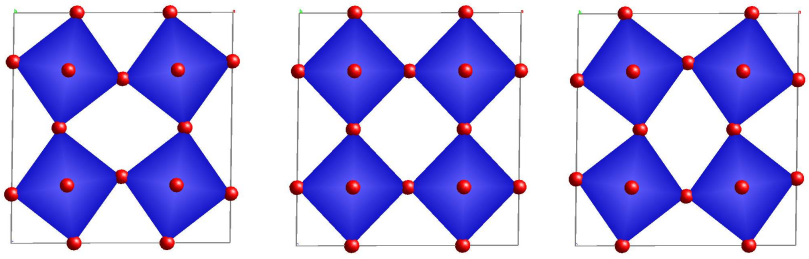
$Pm\bar{3}m\left[\frac{1}{2},\frac{1}{2},0\right]M_3^+(0,0,a)[O:d]Eu(a)$



B. J. Campbell, H. T. Stokes, D. E. Tanner, and D. M. Hatch, "ISODISPLACE: a web-based tool for exploring structural distortions", *J. Appl. Cryst.* **39**, 607-614 (2006).

Rotational O symmetry mode

$$Pm\bar{3}m\left[\frac{1}{2},\frac{1}{2},0\right]M_3^+(0;a;0)[O:d]E_u(a)$$

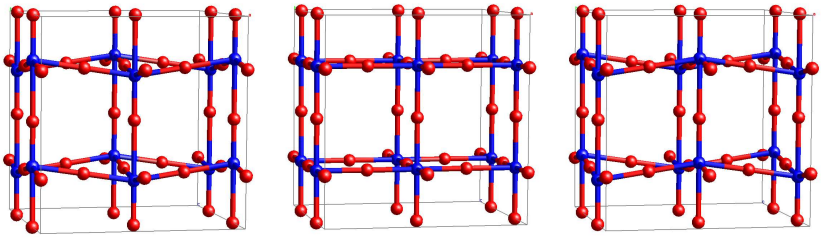


a = -0.30 *a* = 0 *a* = +0.30

Child = Parent + Distortion Mode Amplitude

Antiferroelectric W symmetry mode

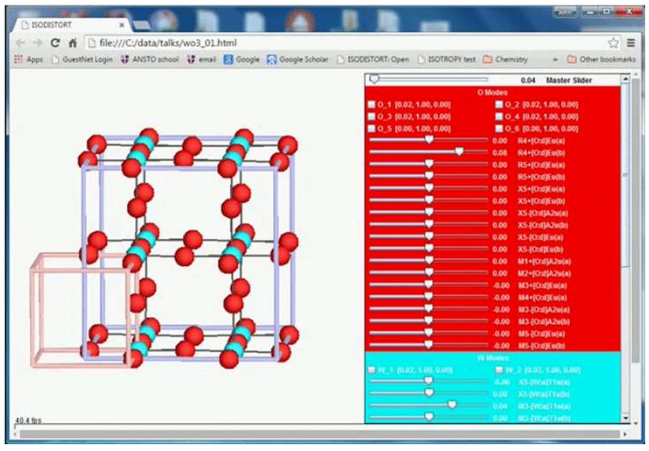
$$Pm\bar{3}m\left[\frac{1}{2},\frac{1}{2},0\right]M_3^-(a;b;0)[W:a]T_{1u}(a)$$



a = -0.30 *a* = 0 *a* = +0.30

Child = Parent + Distortion Mode Amplitude

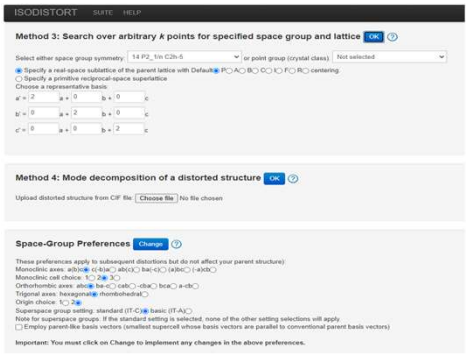
ISODISTORT web interface to explore symmetry

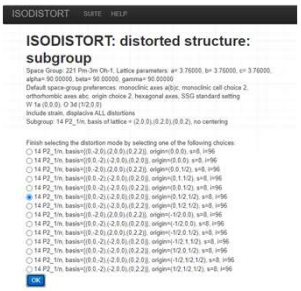


http://stokes.byu.edu/isodistort.html
Harold Stokes and Branton Campbell

ISODISTORT demo? (https://stokes.byu.edu/iso/isodistort.php)

1. Upload parent CIF & transform to $P2_1/n$ → 2. Choose cell and origin → 3. Save for Rietveld



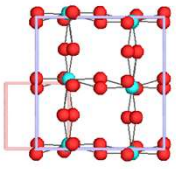


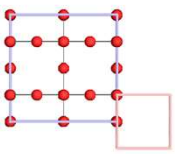
www tutorial example

ISOVIZ demo?

Parent to $P2_1/n$ known structure method 4 (wo3_pm3m_p21un_woodward_method4.isoviz)

Parent to $P2_1/n$ (wo3_pm3m_p21un_woodward.isoviz)





Symmetry mode Rietveld instruction file

Conventional Rietveld

```
'structure description in Rietveld file (TOPAS syntax)

space_group P21/n

site W1 x @ 0.2481 y @ 0.0342 z @ 0.7815
site W2 x @ 0.2513 y @ 0.0277 z @ 0.2865
...
site O6 x @ 0.2849 y @ 0.4850 z @ 0.9922
etc
```

← refine coords

Replace usual *xyz* coordinates with symmetry-allowed distortions

B.J. Campbell, J.S.O Evans, F. Perselli and H. T. Stokes, *IUCr Computational Newsletter*, **8**, November 2007

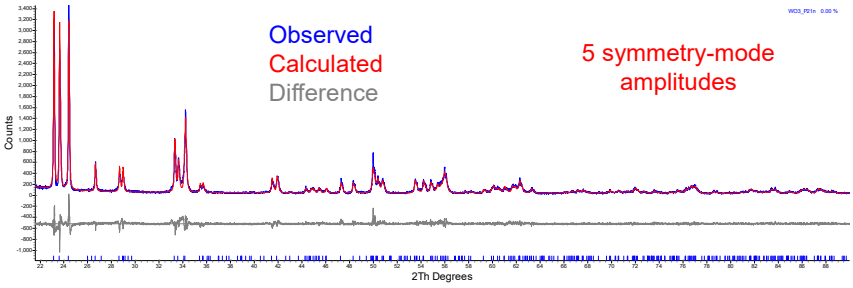
Symmetry-mode Rietveld

```
'structure description in Rietveld file (TOPAS syntax)

space_group P21/n 'optional?

'symmetry mode amplitudes
prm a1_X5- 0.0
prm a2_X5- 0.0
prm a3_M3- 0.0
prm a4_M3- 0.0
prm a5_M5- 0.0
prm a6_M5- 0.0
...
prm a24_M5- 0.0

site W1 x = 1/4+c(-a3-a6) y = 0+c(+a1+a2) z = 3/4+c(+a4+a5)
site W2 x = 1/4+c(+a3-a6) y = 0+c(-a2+a2) z = 1/4+c(+a4-a5)
...
etc
```

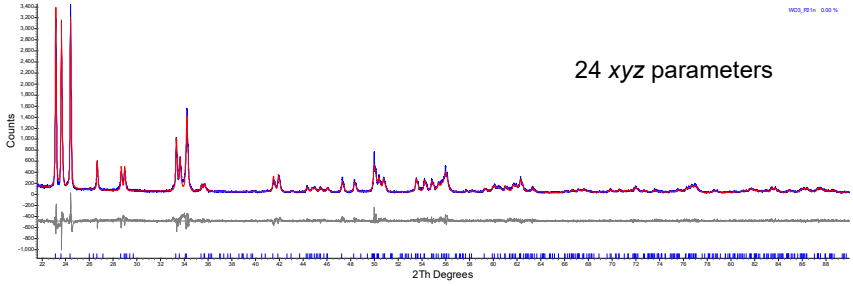
← refine amplitudes

[c = constant = 0.04702 in this specific case comes from ISODISTORT]

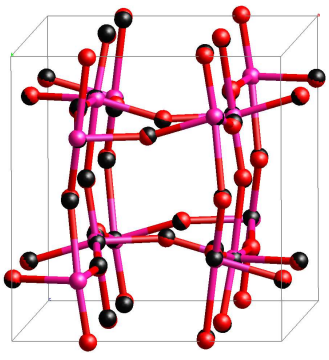
Symmetry-Mode Rietveld refinement



5 symmetry-mode amplitudes



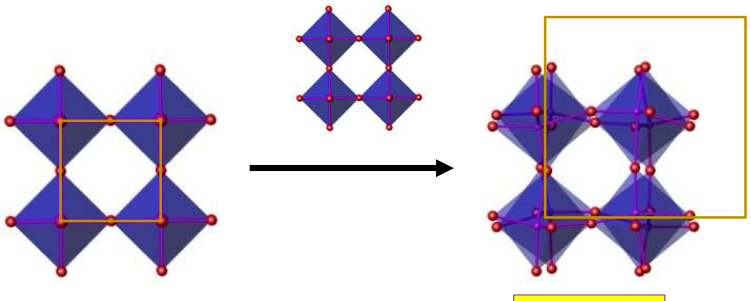
24 *xyz* parameters



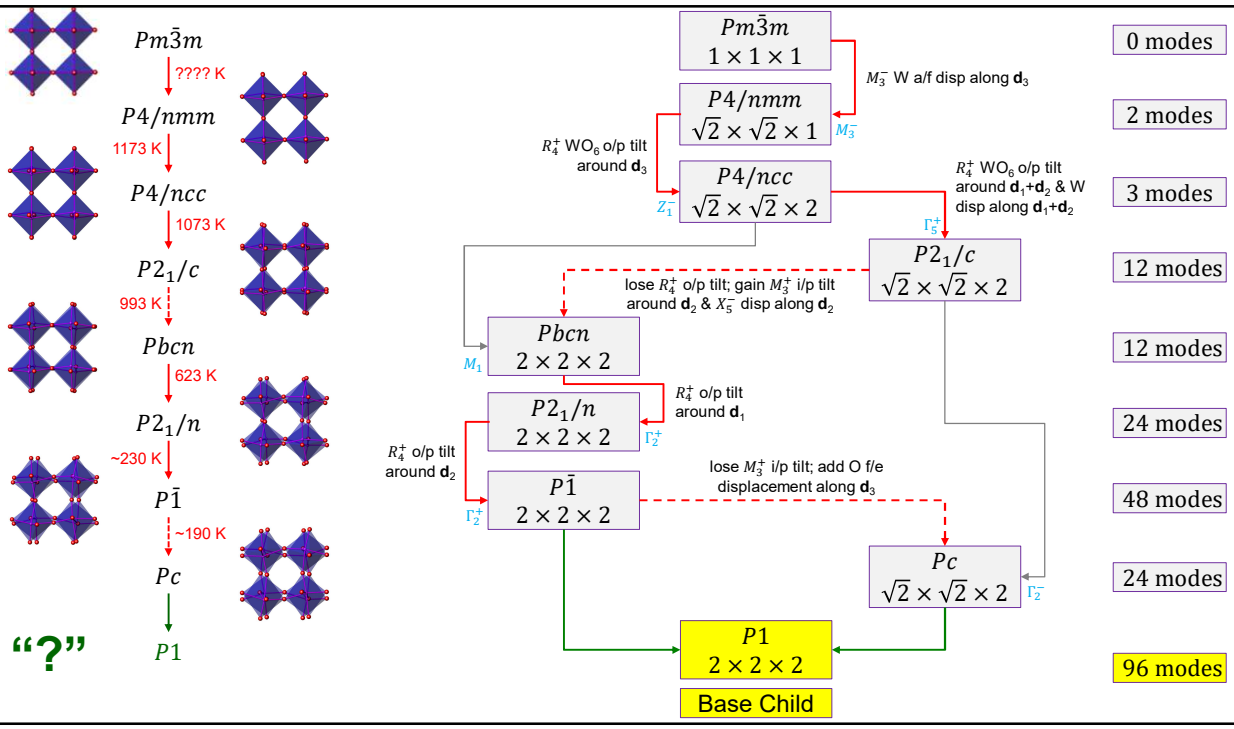
www tutorial example

Forget about symmetry (for a minute)

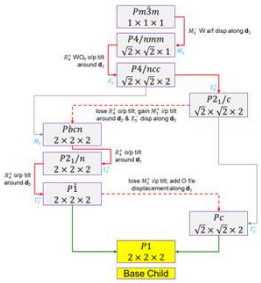
- $P2_1/_n$ monoclinic structure has 24 modes possible
- If we went all the way to a $P1$ $\sim 2a \times \sim 2a \times \sim 2a$ cell there are 96 modes possible
- Can we explore parameter efficiency in this space group?
- Could we work out the true symmetry of a structure using distortion modes?

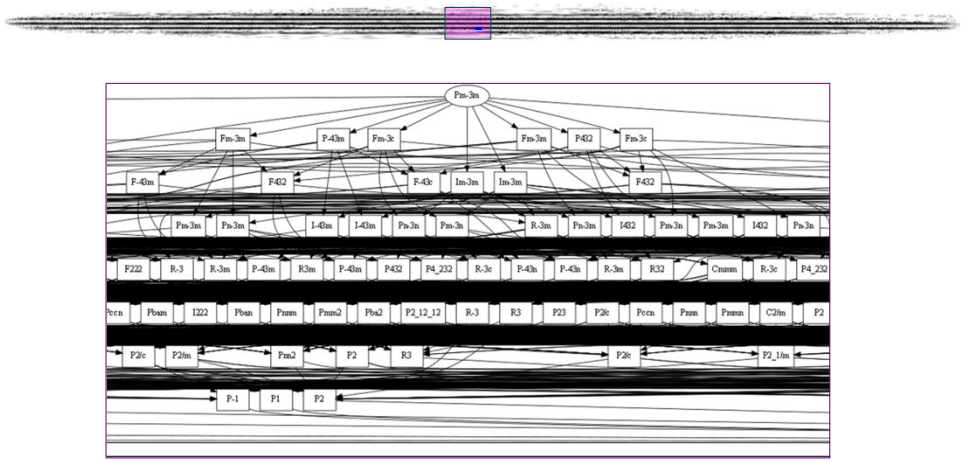


$P1$
$2 \times 2 \times 2$
Base Child

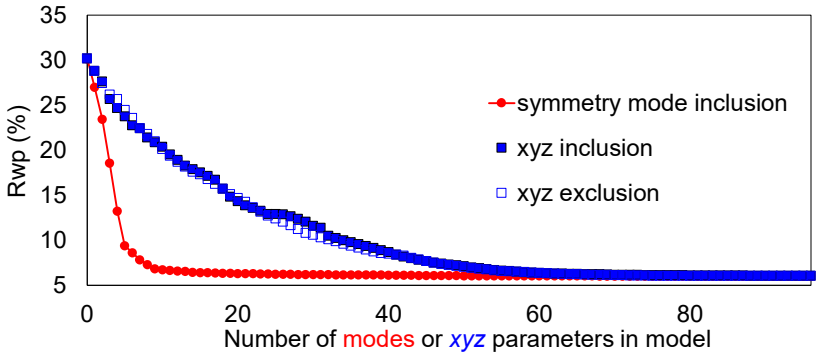


Space group choice – 1427 possibilities



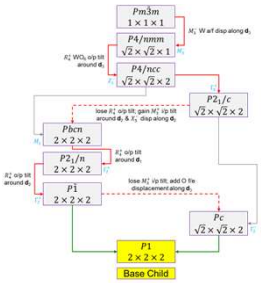


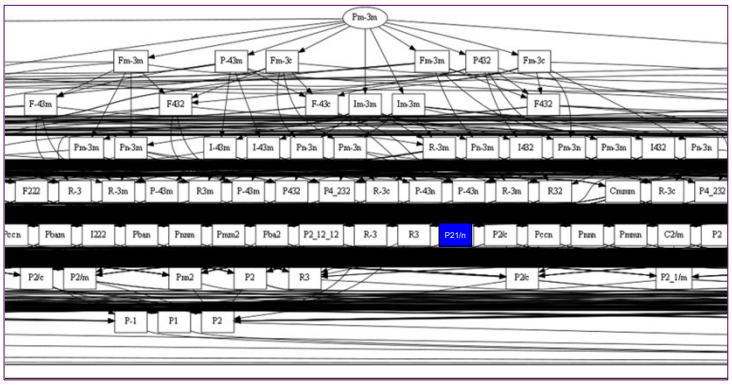
Which space group plus parameter efficiency



- The best R_{wp} you can get with *n* parameters using symmetry modes or standard *xyz* fractional coordinates
- 4657×4 Rietveld refinements – X-ray and neutron combined
- Most important modes turn out to be $R_4^+, M_3^+, M_3^-, X_5^+, X_5^-$
- Does this let us work out the true space group?

Space group – 1427 possibilities only one consistent with data



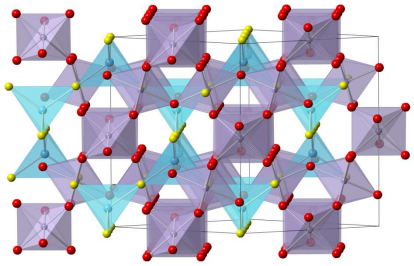


$Parent\ Pm\bar{3}m + R_4^+, + M_3^+ + M_3^- + X_5^+ + X_5^- + order\ parameter\ directions \Longrightarrow P2_1/n$

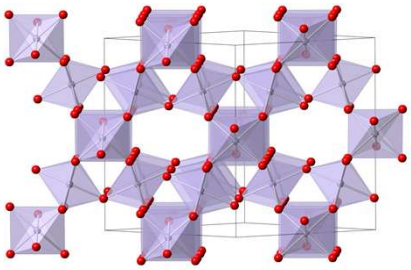
Exhaustive group-subgroup searches

- Can we systematically try all the possible space groups, origin choices and unit cell combinations?
- Systematic group-subgroup tree search

Systematic subgroup searches: $Bi_2Sn_2O_7$ pyrochlore



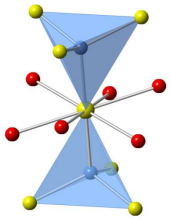
Cubic γ-$Bi_2Sn_2O_7$



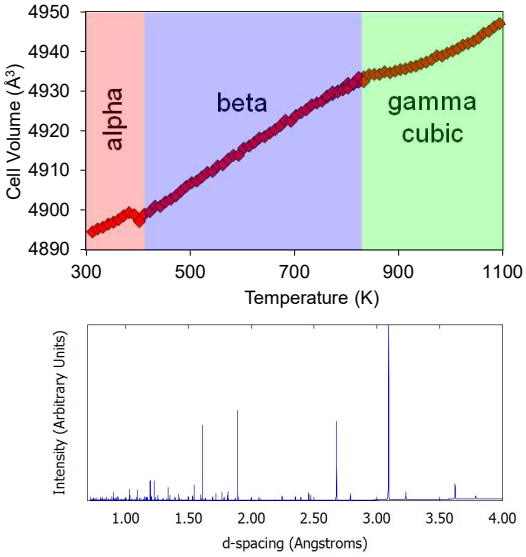
Interpenetrating Sn_2O_6 and Bi_2O' frameworks

Cubic *Fd*-3*m*
a = 10.72 Å

$BiO_6O'_2$
hexagonal
bipyramid

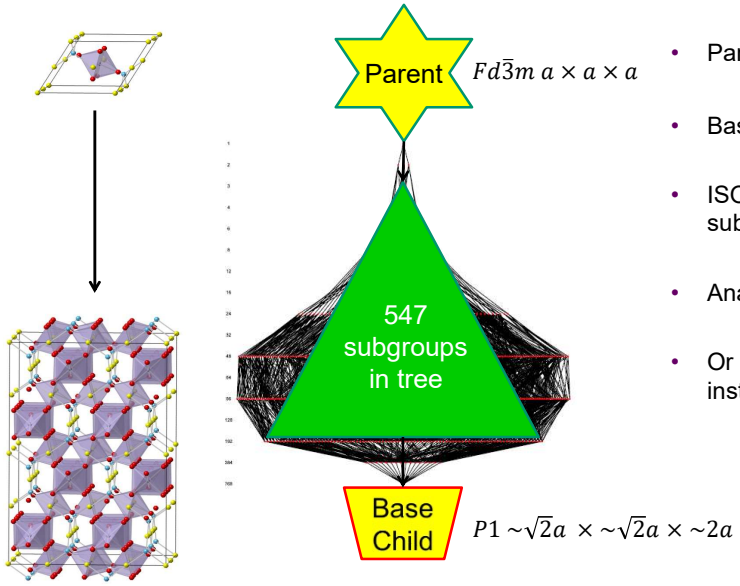


Exhaustive subgroup searches: $Bi_2Sn_2O_7$ pyrochlore



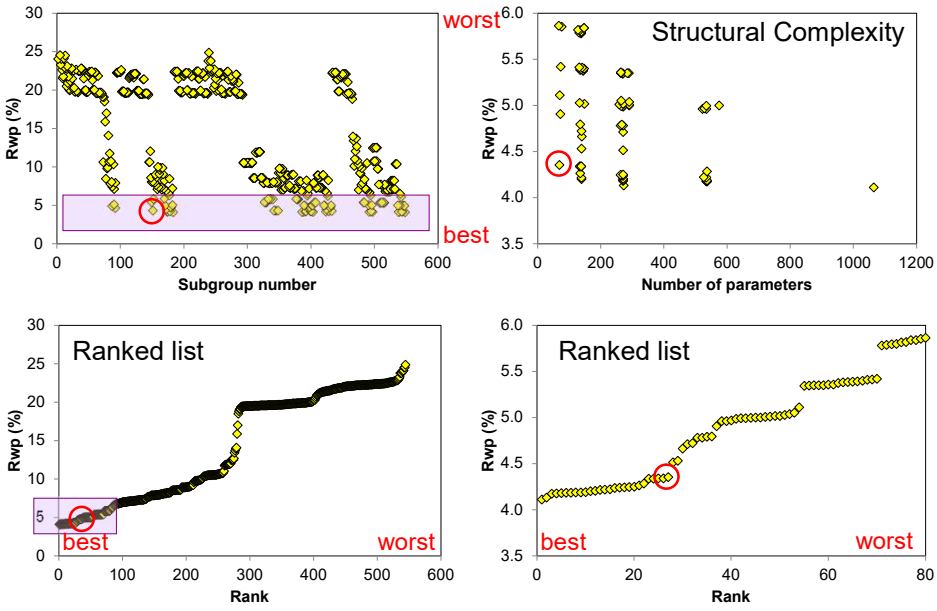
- Parent cubic *Fd*-3*m* pyrochlore
- Lots of wrong structures for alpha and beta in literature
- High quality, highest resolution synchrotron and neutron data sets
- All extra peaks and peak splittings in alpha and beta powder patterns can be fitted with a $\sqrt{2}a \times \sqrt{2}a \times 2a$ cell in *P*1

Exhaustive subgroup searches: ISODISTORT tree

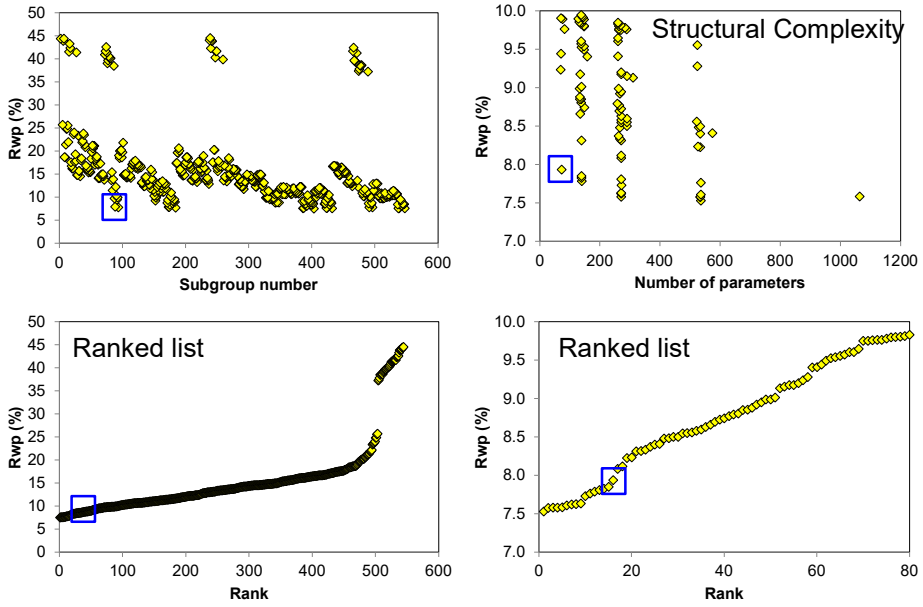


- Parent cubic *Fd*-3*m* pyrochlore
- Base child $\sqrt{2}a\ \times\sqrt{2}a \times 2a$ cell in *P*1
- ISODISTORT generates set of 547 possible subgroups
- Analyse all in TOPAS via python scripts
- Or use single TOPAS .inp file with #list instructions

β-$Bi_2Sn_2O_7$ Rietveld results – 547 subgroup models

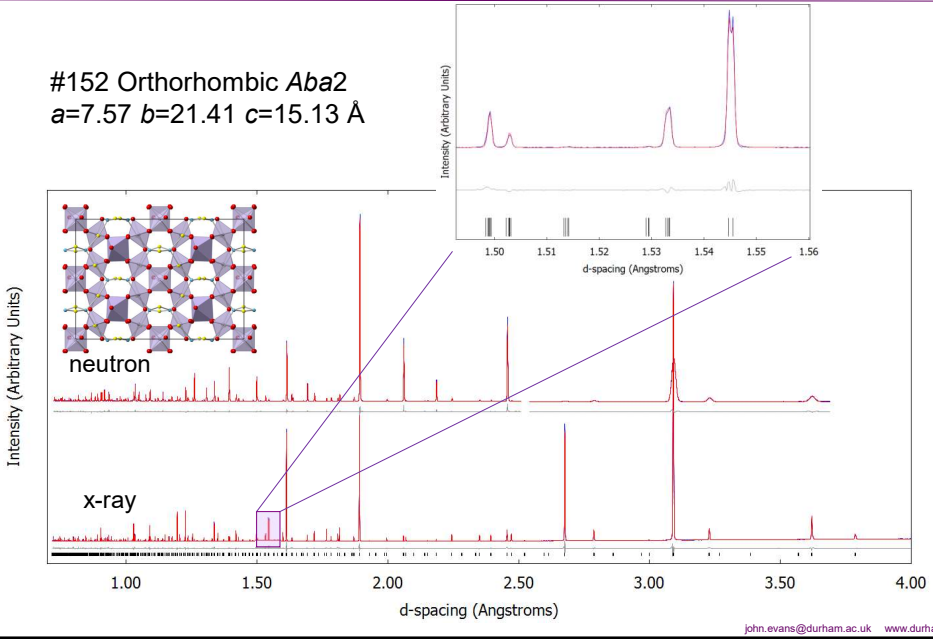


α-$Bi_2Sn_2O_7$ Rietveld results – 547 subgroup models



β-$Bi_2Sn_2O_7$ Rietveld fits

#152 Orthorhombic *Aba*2
a=7.57 *b*=21.41 *c*=15.13 Å



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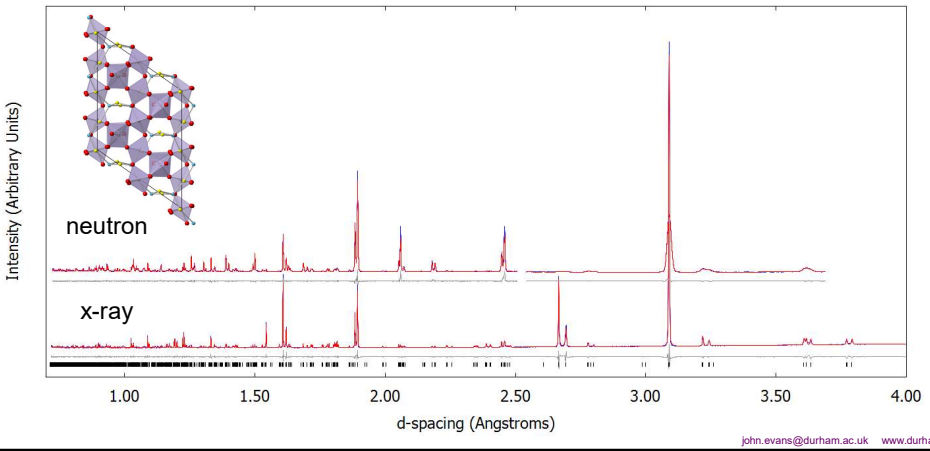
α-$Bi_2Sn_2O_7$ Rietveld fits

#88 Monoclinic *Cc*
a=7.57 *b*=21.41 *c*=15.13 Å *β*=125°



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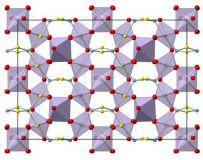
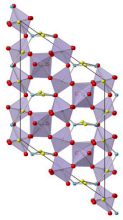
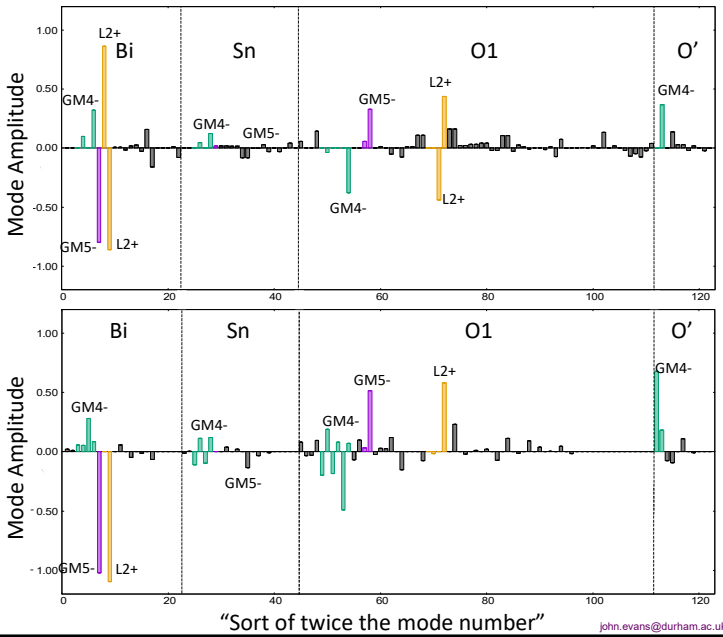
Comparing structures (OPDs hold the key)

β-$Bi_2Sn_2O_7$



α-$Bi_2Sn_2O_7$





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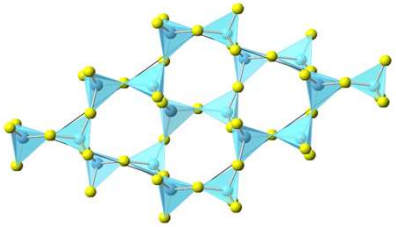
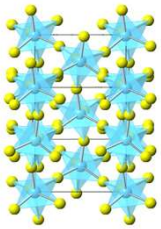
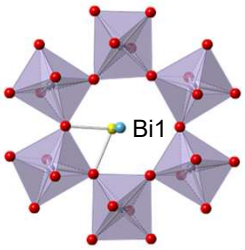
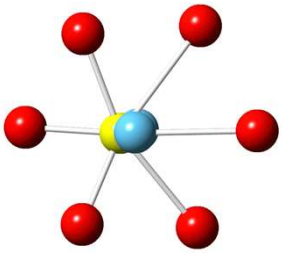
What's the local chemical driving force?

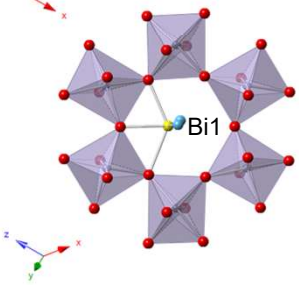




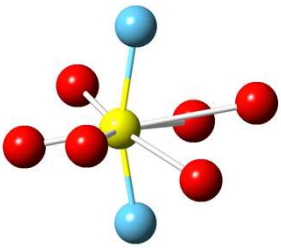


β-$Bi_2Sn_2O_7$





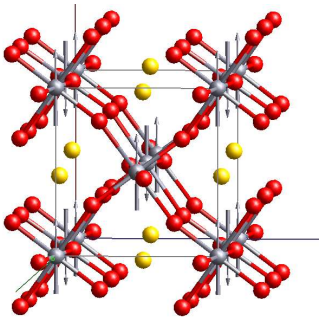
α-$Bi_2Sn_2O_7$



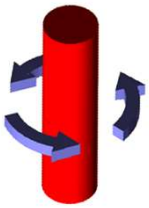
beta to alpha changes

Symmetry modes: magnetism and molecular rotations

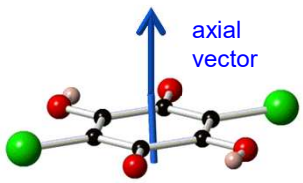
Structural distortions = displacements of atoms
Polar vectors



Similar ideas for magnetic ordering
Axial vectors



Axial vector
spinning cylinder



Similar ideas for molecular rotations
Axial vectors

cylinder: wikimedia commons

Symmetry mode conclusions?

- Symmetry modes use “extra information” that the child structure is related to the parent
- Small(?) learning curve to overcome
- Can be quick and efficient way of understanding phase transitions in functional materials

Acknowledgements

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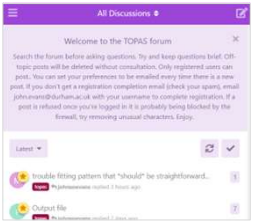
Tom Vogt, Doug Blom
Shiv Halasyamani
ILL: Bernard Frick, Mark Johnson, Quentin Berrod

James Lewis
Branton Campbell
Harold Stokes
Huiyu Liu
Ivana Evans

Resources?

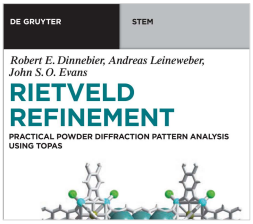
wiki site

forum

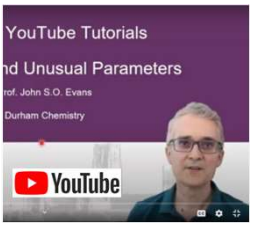


web tutorials

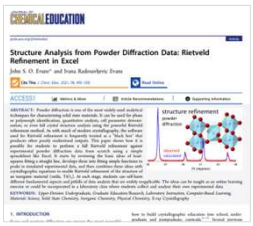
book



YouTube



Rietveld in excel



School breaks

School page

Exercises

- Try a symmetry mode refinement of $LaMnO_3$:
  - https://topas.webspace.durham.ac.uk/tutorial_isoriet/
- Try using symmetry modes to describe the magnetic structure of $LaMnO_3$:
  - https://topas.webspace.durham.ac.uk/tutorial_lamno3_magnetic/
- Try the symmetry mode refinement and symmetry detection tutorial on WO_3:
  - https://topas.webspace.durham.ac.uk/tutorial_isoriet_wo3_simple/
  - https://topas.webspace.durham.ac.uk/tutorial_isoriet_wo3_advanced/
- Anything you fancy from yesterday morning
- We will come round and help you

Stuttgart page