University Of Durham

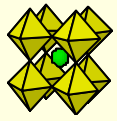
Department of Chemistry

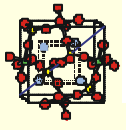
13. Refinement of Extended Structures

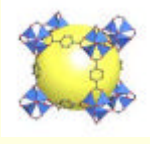
John S.O. Evans
BCA School, 2005

Extended Structures

- "Non Molecular" species
- Inorganic Compounds
  - oxides, chalcogenides, alloys
- Minerals
- Coordination polymers



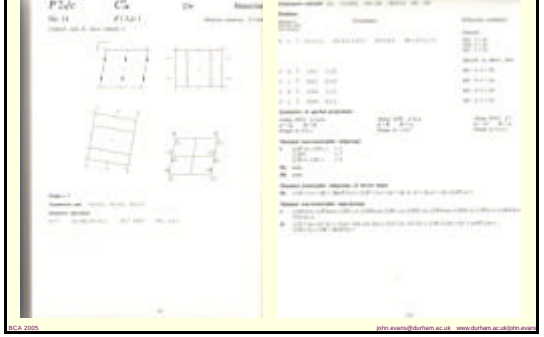




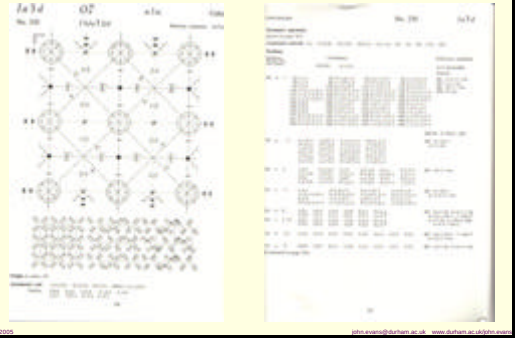
Overview of Lecture

- What is an extended structure?
- Potential pitfalls during data collection
- Potential pitfalls during solution/refinement
- Disordered materials
- Limits of Bragg Diffraction
- How to know you've got it right/wrong
- Supporting techniques
- Case histories
- Thanks to Clare, Graham, Matt, Sarah, Martin, Ivana, Thomas Proffen for data/examples!

Molecular Symmetry



Extended Symmetry



Pitfall Avoidance

Pitfall Avoidance

Data Collection – Crystal Quality, etc

- Coordination polymers and materials grown hydrothermally frequently very insoluble and form as polycrystalline powders – can't recrystallise
- Crystals frequently grown by slow cooling from melt – must be chipped away from other material
- Twinning – wait for later!

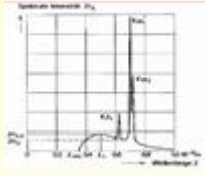
- May need to use synchrotron source or powder diffraction methods
- Good absorption corrections can become vital

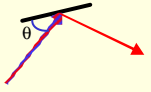
λ/2 Contamination

- Most diffractometers use graphite 001 monochromator to select a single wavelength

$$l = 2d_{001}\sin q \qquad \frac{l}{2d_{001}} = \sin q \qquad \frac{l}{2d_{001}} = \frac{(l/2)}{2(d_{001}/2)}$$

- "Monochromatic" beam will also contain λ/2

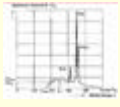




λ/2 Contamination/Solutions

$$F'_{hkl} = F_{hkl} + kF_{2h\,2k\,2l}$$

- Each reflection (2h,2k,2l) will contribute to intensity of (h,k,l) due to λ/2
- Area detectors may see extra peaks
- All reflection intensities may be effected
- Important when F_{hkl} small and F_{2h2k2l} large

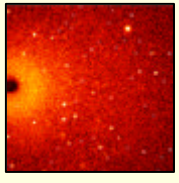


- For Mo run tube at 34.9 kV

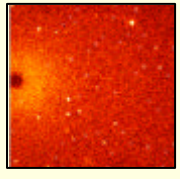
$$l_{min} = hc/eV = 1239/V$$

- Use a Si/Ge (111) monochromator – F_{222} small

λ/2 Contamination – $Bi_{4.5}CaVO_{10.5}$

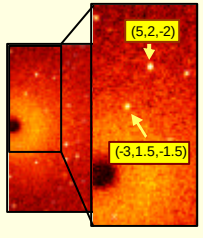


50 kV, 40 mA

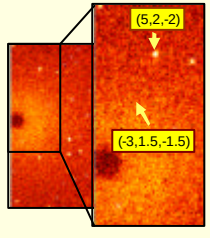


35 kV, 50 mA

λ/2 Contamination – $Bi_{4.5}CaVO_{10.5}$



50 kV, 40 mA



35 kV, 50 mA

- F^2_{-6-3-3}=498.45, 13th strongest reflection in data set

λ/2 Contamination Solutions

$$F'_{hkl} = F_{hkl} + kF_{2h2k2l} \qquad k \approx 0.001$$

" for routine data sets"….."the effect on final refinements was negligible. There was no significant change in the final agreement factors and the changes in the geometrical parameters were all smaller than 1 e.s.d."

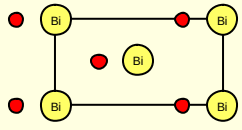
"…..it is quite easy to obtain the wrong unit cell for strongly scattering samples when pure λ/2 reflections are included….."

Kirschbaumet al, *J. Appl. Cryst.* (1997), **30**, 514-6

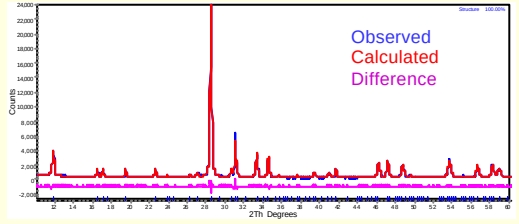
Heavy Atoms

- Heavy metal atoms may dominate diffraction
- Bi_2O_3 contains Bi (83 electrons) and O (8 electrons)
- CH_3 contains C (6 electrons) and H (1 electron)

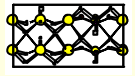
- O may have very small contribution to diffraction pattern
- Pseudo symmetry due to heavy atoms dominating



Heavy Atoms – $Pb_3O_2(PO_3H)$



$Pb_3O_2(PO_3H)$
wRp=6.612%



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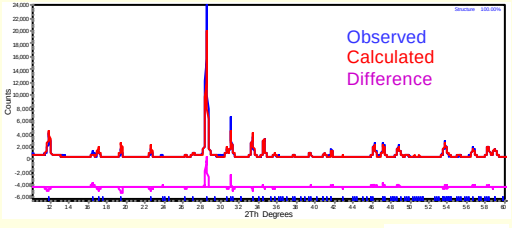
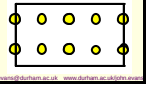


$Pb_3O_0(P_0O_0H_0)$
wRp=14.35%



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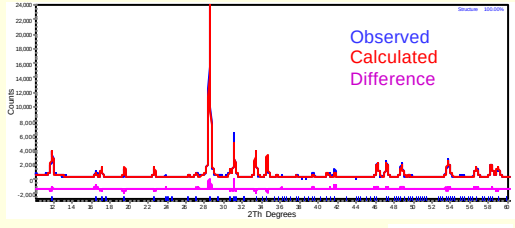
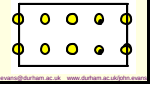
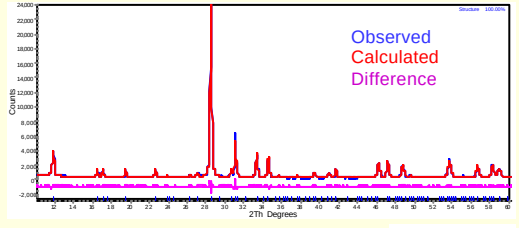


$Pb_3O_0(P_1O_0H_0)$
wRp=9.82%



Heavy Atoms – $Pb_3O_2(PO_3H)$



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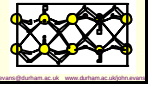
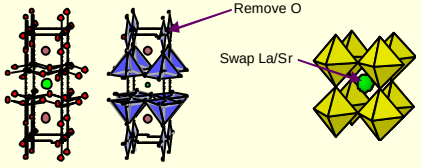
wRp=6.612%



Partial Occupancy and Disorder

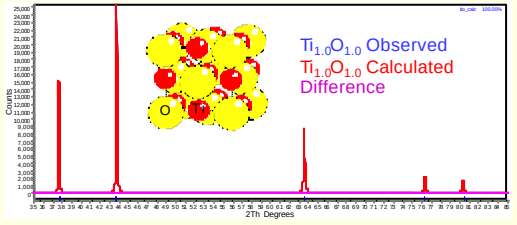
- Often crucial to the properties of materials



$YBa_2Cu_3O_{7-\delta}$
Superconductor for δ<0.6

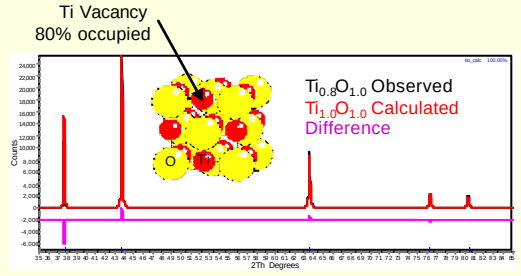
$La_{1-x}Sr_xMnO_3$
Antiferromagnetic Insulator to Ferromagnetic Metal

Ti_xO_y Disorder



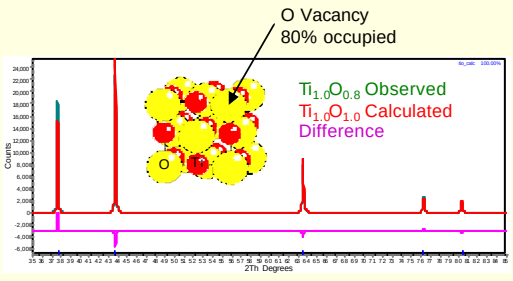
$Ti_{1.0}O_{1.0}$

Ti_xO_y Disorder



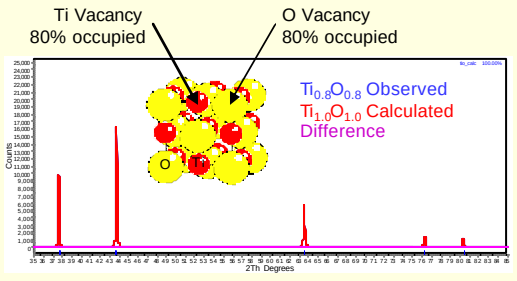
$Ti_{0.8}O_{1.0}$

Ti_xO_y Disorder



$Ti_{1.0}O_{0.8}$

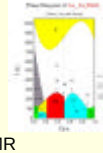
Ti_xO_y Disorder



$Ti_{0.8}O_{0.8}$

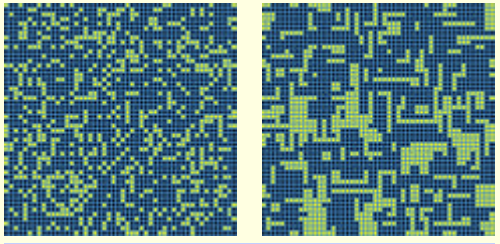
Caveats/Solutions

- Beware e.g. 2:1 disorder of H:D in neutron experiments (b=-0.373/+0.667)
- Don't try and work on MO_xF_y systems!
- $La_{1-x}Ca_xMnO_3$: Beware e.g. $La_{0.5}Ca_{0.5}MnO_3$ where cation ordering can cause complications
- Beware incommensurate superstructures



- Combine X-ray and neutron data
- Consider anomalous scattering
- Consider other techniques – e.g. solid state NMR
- Think

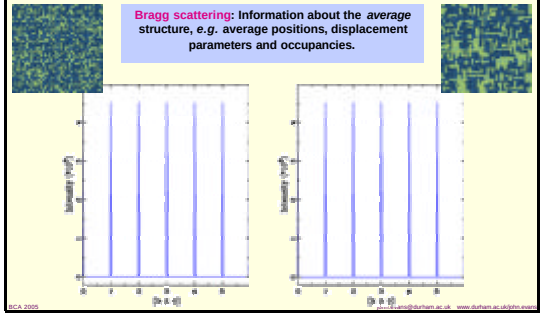
Limits of Bragg Diffraction



Cross section of 50x50x50 u.c. model crystal consisting of 70% black atoms and 30% *vacancies* !
Properties might depend on vacancy ordering !!

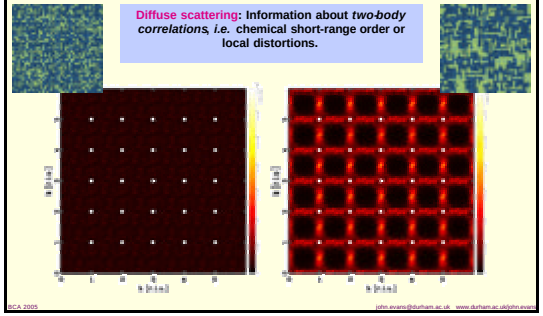
[example/calculations stolen from Thomas Proffen]

Limits of Bragg Diffraction



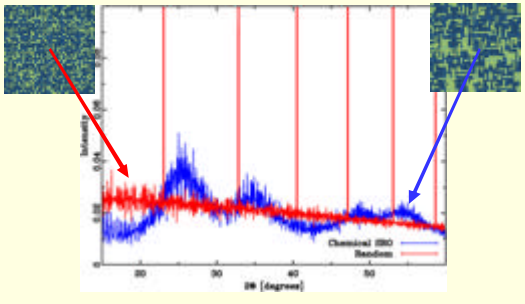
Bragg scattering: Information about the *average* structure, *e.g.* average positions, displacement parameters and occupancies.

Diffuse Scatter

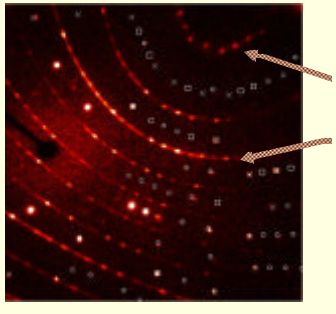


Diffuse scattering: Information about *two-body correlations*, *i.e.* chemical short-range order or local distortions.

Disorder and Powder Diffraction

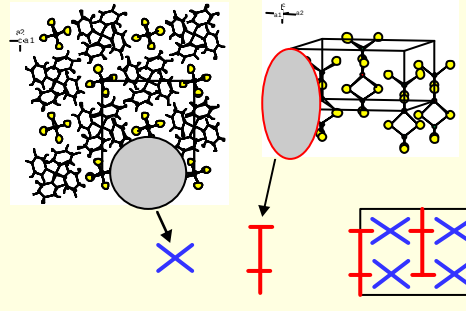


Order and Disorder?

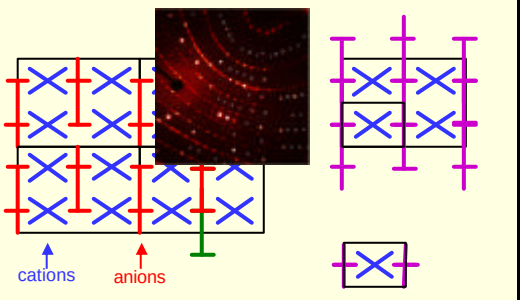


- Sharp spots showing and ordered material
- Streaks showing a disordered material
- Order on one length scale, disorder on another?

$PPh_4^+[Zn(WS_4)_2]^{2-}$



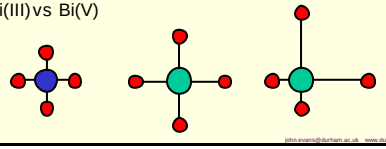
Order and Disorder



Structure Validation

- Molecular structures relatively straightforward
- C-C 1.54 ?
- C=C 1.34 ?
- CSD for more complex examples

- Metal coordination less predictable, depends on oxidation state, Jahn Teller/Lone pair distortions, etc
- e.g. Bi(III) vs Bi(V)

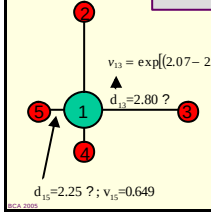


Bond Valence Sums

$$v_{ij} = \exp\left[\left(R_{ij} - d_{ij}\right)/0.37\right] \qquad V = \sum_j v_{ij}$$

Bond valence parameter From tables. e.g. $R_{Bi\text{-}O}$ = 2.07, $R_{Re\text{-}O}$ =1.79

Total Valence (*V*) for each cation/anion in structure should match expected values: Bi 3, Mg 2, V 5, O 2, etc



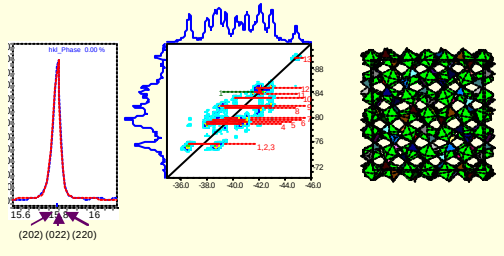
e.g. Bi(III)
4*O at 2.25 ? ? 4*v_{ij}=0.649 = 2.592
3*O at 2.80 ? ? 3*v_{ij}=0.147 = 0.441
3.033

Typical values

		O1	O1	O1	O1	O2	O3	O3	O4	Sum
Bi1	d/Å	2.199	2.199	2.236	2.236					
	v_{ij}	0.75	0.75	0.68	0.68					2.87
Mg1	d/Å			2.066	2.066		2.038	2.038		
	v_{ij}			0.36	0.36	1.980 0.46	0.39	0.39		1.98
Mg2	d/Å			2.066	2.066		2.042	2.042	1.995	
	v_{ij}			0.36	0.36		0.39	0.39	0.44	1.95
V1	d/Å					1.688	1.733	1.733	1.684	
	v_{ij}					1.36	1.21	1.21	1.38	5.16
	Sum			(2*Bi1)	2.16	1.82		1.99	1.82	

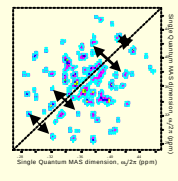
- After refinement calculate all bond valence parameters from distances
- e.g. $BiMg_2VO_6$ (see later)

Think Beyond Diffraction

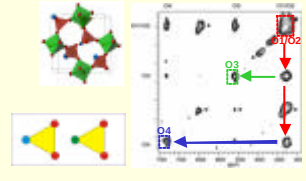


- Best diffraction data tells you ZrP_2O_7 is complicated – 50 atoms in the asymmetric unit, perhaps higher
- 2D MQ ^{31}P solid state NMR **PROVES** it has 136 (±0)

Think Beyond Diffraction



SnP_2O_7



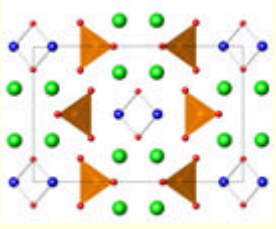
ZrW_2O_8

ZrV_2O_7

Case History 1 – $BiMg_2VO_6$

- Simple metal oxide originally published in J. Solid State Chemistry in 1992
- Space group Cmcm
- Straightforward material, simple structure, low R factor no particular reason to think anything might be wrong

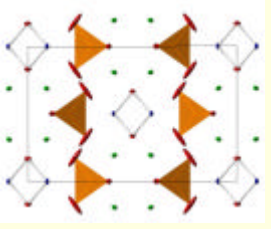
Case History 1 – $BiMg_2VO_6$



- Simple metal oxide
- Cmcm
- R=2.10%
- Bond distances etc sensible

4+n coord Bi, 5 coordinate Mg, VO_4 tetrahedra

Case History 1 – $BiMg_2VO_6$



- Simple metal oxide
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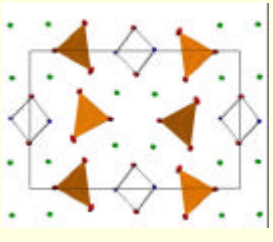
Case History 1 – $BiMg_2VO_6$



- Simple metal oxide
- Pnma
- R=2.13%
- Face index + sadabs
- Everything sensible

4+n coord Bi, 5 coordinate Mg, VO_4 tetrahedra

Tedious Detail - 1

		O1	O1	O1	O1	O2	O3	O3	O4	Sum
Bi1	d/Å	2.199	2.199	2.236	2.236					
	v_{ij}	0.75	0.75	0.68	0.68					2.87
Mg1	d/Å			2.066	2.066		2.038	2.038		
	v_{ij}			0.36	0.36	1.980 0.46	0.39	0.39		1.98
Mg2	d/Å			2.066	2.066		2.042	2.042	1.995	
	v_{ij}			0.36	0.36		0.39	0.39	0.44	1.95
V1	d/Å					1.688	1.733	1.733	1.684	
	v_{ij}					1.36	1.21	1.21	1.38	5.16
	Sum			(2*Bi1)	2.16	1.82		1.99	1.82	

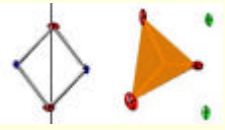
Tedious Detail - 2

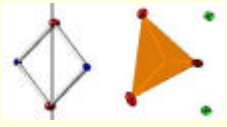
	Untreated	Face Indexed	SADABS	FI + SADABS
Rint (%)	25.8	12.8	5.2	2.9
No. Reflections	8983	8983	7680	8955
R/wR (%), istropic refinement	7.20 / 17.53	3.80 / 10.14	5.44 / 11.85	2.43 / 6.36
R/wR (%), anisotropic refinement	6.70 / 16.16	3.19 / 8.47	3.82 / 8.77*	2.21 / 6.03
R/wR (%), aniso ref + optimal weights	6.75 / 10.85	3.14 / 7.05	4.05 / 7.79**	2.13 / 5.27

Raw data vs absorption correction

Raw Data
R=6.75%

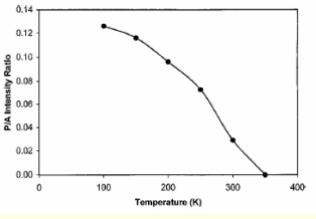
Corrected Data
R=2.13%





4+n coord Bi, 5 coordinate Mg, VO_4 tetrahedra

Phase Transition….



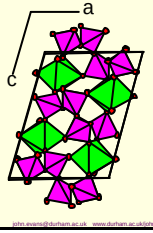
- In Cmcm structure expect h+k=even reflections only
- h+k=odd clearly visible at low T but disappear at high T

Pitfall Avoidance

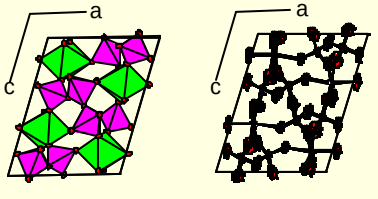
Case History 2 - $Mo_2P_4O_{15}$

- $Mo_2P_4O_{15}$ simple oxide
- Published 1992
- 11 atoms in asymmetric unit
- R= 3.6%, $P2_1/c$
- Corner sharing **MoO_6 octahedra** and **PO_4 tetrahedra**

a = 8.31 Å
b = 6.52 Å
c = 10.71 Å
β = 107.0°
V = 555 Å^3

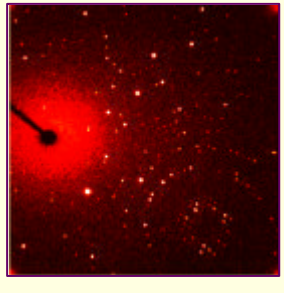


$Mo_2P_4O_{15}$ 120 K Structure



- ADP's drawn at 70% level

$Mo_2P_4O_{15}$



incorrect subcell

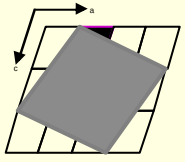
a = 8.31 Å
b = 6.52 Å
c = 10.71 Å
β = 107.0°
V = 555 Å^3

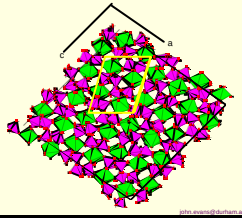
↓

correct cell

a = 24.11 Å
b = 19.53 Å
c = 25.09 Å
β = 100.0°
V = 11635 Å^3

$Mo_2P_4O_{15}$ – Structure Solution





- Space group Pn
- 441 atoms in asymmetric unit
- How to solve?

$Mo_2P_4O_{15}$

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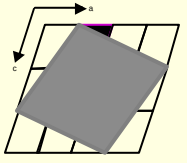
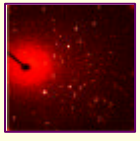
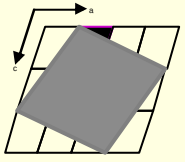
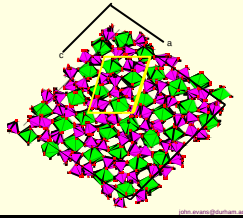




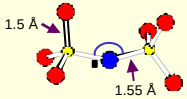
$Mo_2P_4O_{15}$ – Structure Solution



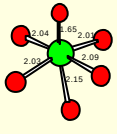


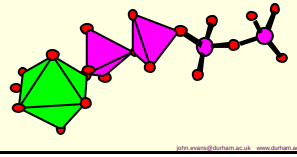
- Space group Pn
- 441 atoms in asymmetric unit
- How to solve?

Distance Least Squares



- We know a lot about the structure!
- 42 MoO_6 octahedra
- 84 P_2O_7 groups
- We know octahedra share corners with tetrahedra

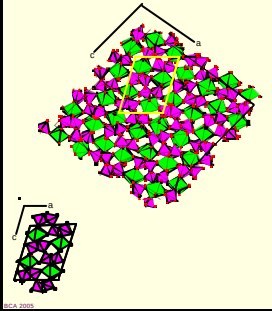




Distance Least Squares Refinement

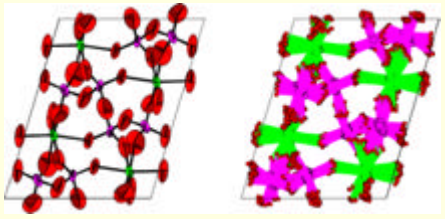
- Structural model has a bond distance of d_{model} ?
- Ideal bond distance of d_{ideal} ?
- Calculate and minimise $w(d_{ideal}-d_{model})^2$
- Do this for all the bonds/angles known in the structure

$Mo_2P_4O_{15}$ – Structure Solution



- Space group Pn
- 441 atoms in asymmetric unit
- Solved by simulated annealing approach in Topas
- R=3.49% for 43738 reflections

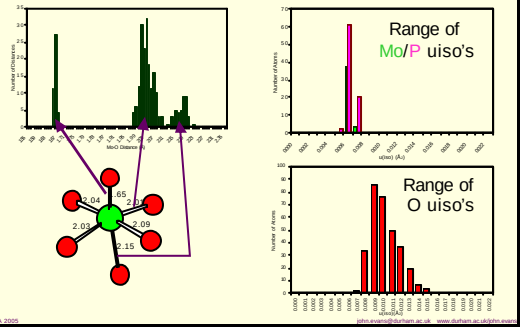
$Mo_2P_4O_{15}$ – Wrong Structure



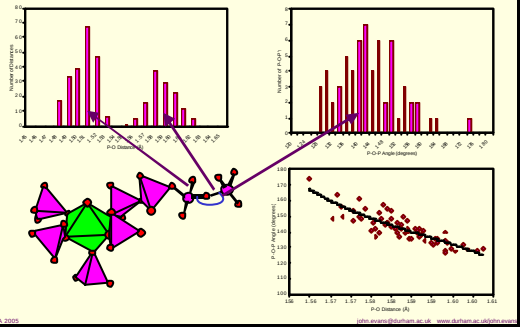
Incorrect cell/adp's
Apparent disorder

Correct cell mapped onto subcell
Ordered static superstructure

Structure Validation



P_2O_7 Structural Database?



The Problems

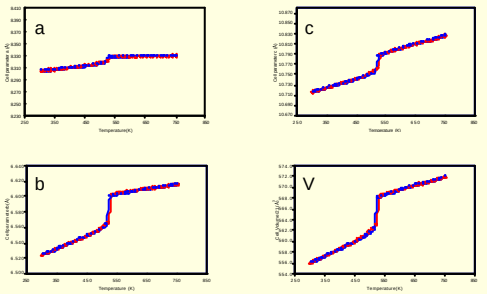
- Getting the right unit cell, pseudo symmetry
- Getting the right space group
- Transformation matrices
- Spotting a chemically nonsensical result
- Designing a good experiment

Pitfalls Avoided

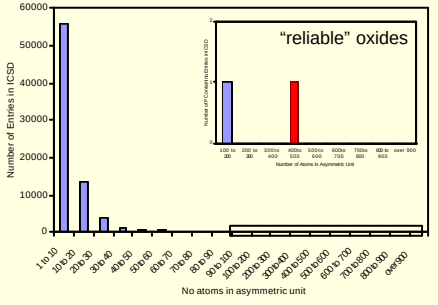
Handy Hint

- Inverse of $\begin{pmatrix} 2 & -1 & 0 \\ 2 & -1 & 1 \\ -2 & 0 & -2 \end{pmatrix}$
- is $\begin{pmatrix} 1 & -1 & -0.5 \\ 1 & -2 & -1 \\ -1 & 1 & 0 \end{pmatrix}$

$Mo_2P_4O_{15}$ – Thermal Expansion



A World Record? (!)



$Mo_2P_4O_{15}$

incorrect subcell

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b = 6.52 Å
c = 10.71 Å
β = 107.0°
V = 555 Å^3

$$\begin{pmatrix} 3 & 0 & 1 \\ 0 & 3 & 0 \\ -1 & 0 & 2 \end{pmatrix}$$

correct cell

a = 24.11 Å
b = 19.53 Å
c = 25.09 Å
β = 100.0°
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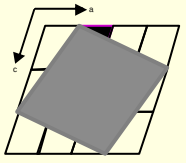
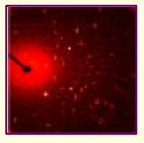
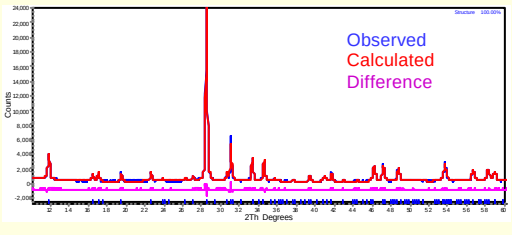




Heavy Atoms – $Pb_3O_2(PO_3H)$



$Pb_3O_{1.82(4)}(P_{1.01(2)}O_{3.18(6)}H_{0.7(4)})$
wRp=6.593%