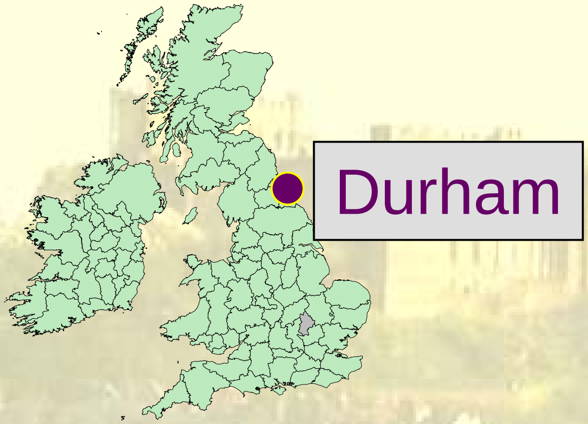
Durham University

Chemistry Department

Parametric Rietveld Refinement

Prof. John S.O. Evans

APD IV Gaithersburg, 2013



Outline

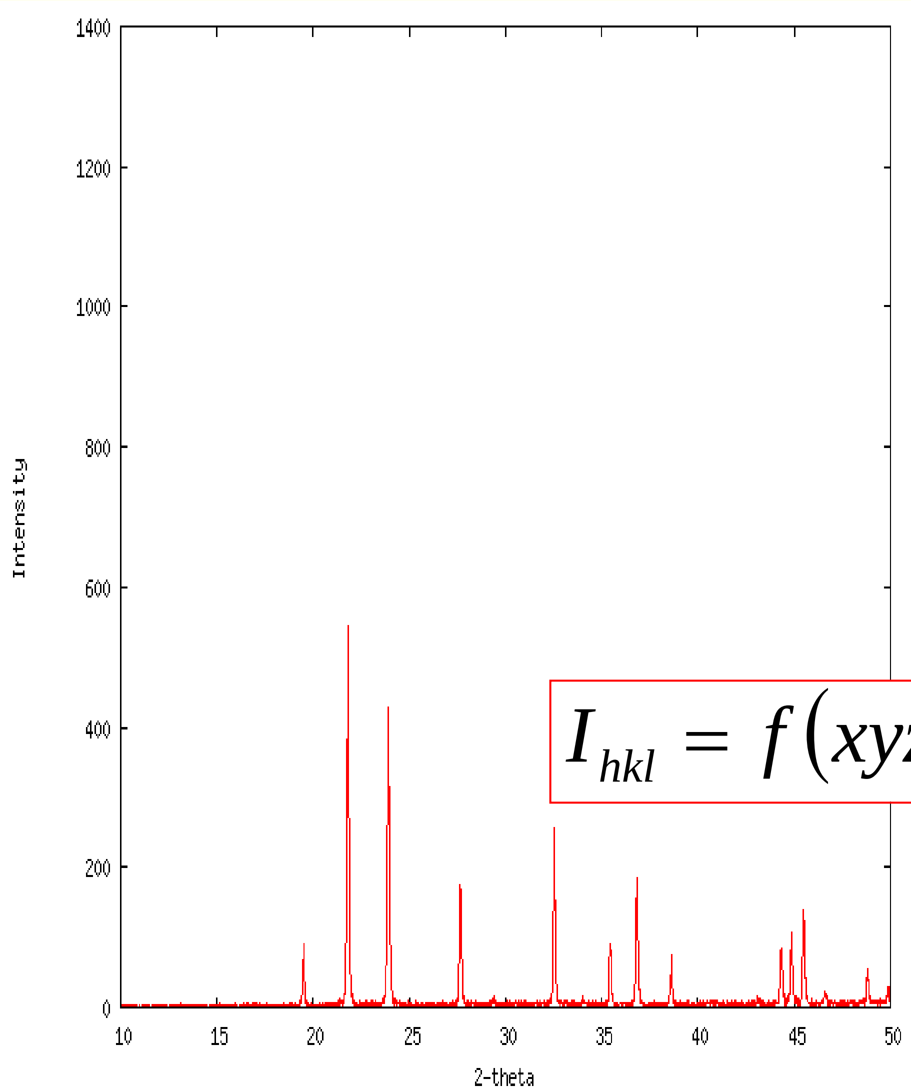
- What is parametric Rietveld refinement?
  - Should you do it?
  - How do you do it?
  - What can you parameterise?
- Examples
  - Cell parameter parameterisation
  - Subtle structural phase transitions
  - Background & amorphous content
  - Poor/low quality data
- Accuracy in Powder Diffraction
  - Accuracy – getting the answer right
  - Precision – better precision by more appropriate data analysis

Evans/Stinton, *J. Appl. Cryst.*, **40**, 2007, 87

X+N refinements

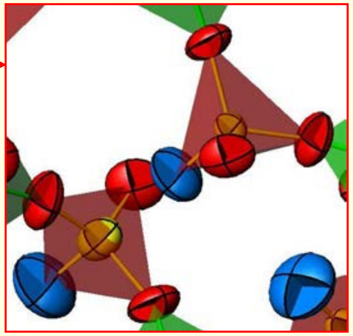
Jean Francois Berar, XND

Diffraction = f(*x*)

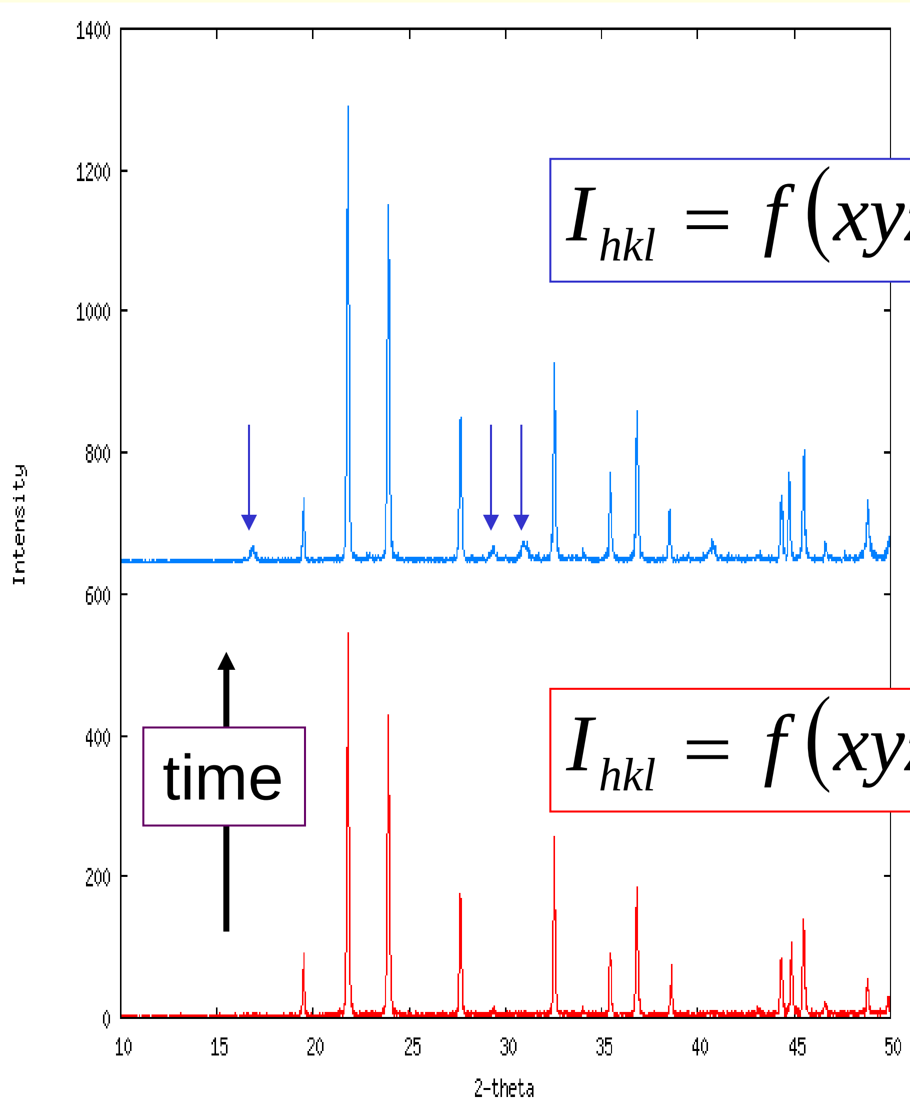


$$I \propto F_{hkl}^2; \; F_{hkl} = \sum_{j=1}^{N} f_j \exp\left[2\pi i\left(hx_j + ky_j + lz_j\right) - 8\pi^2 U_j \sin^2\theta / \lambda^2\right]$$

$$I_{hkl} = f\left(xyz, occ, adp\right)$$



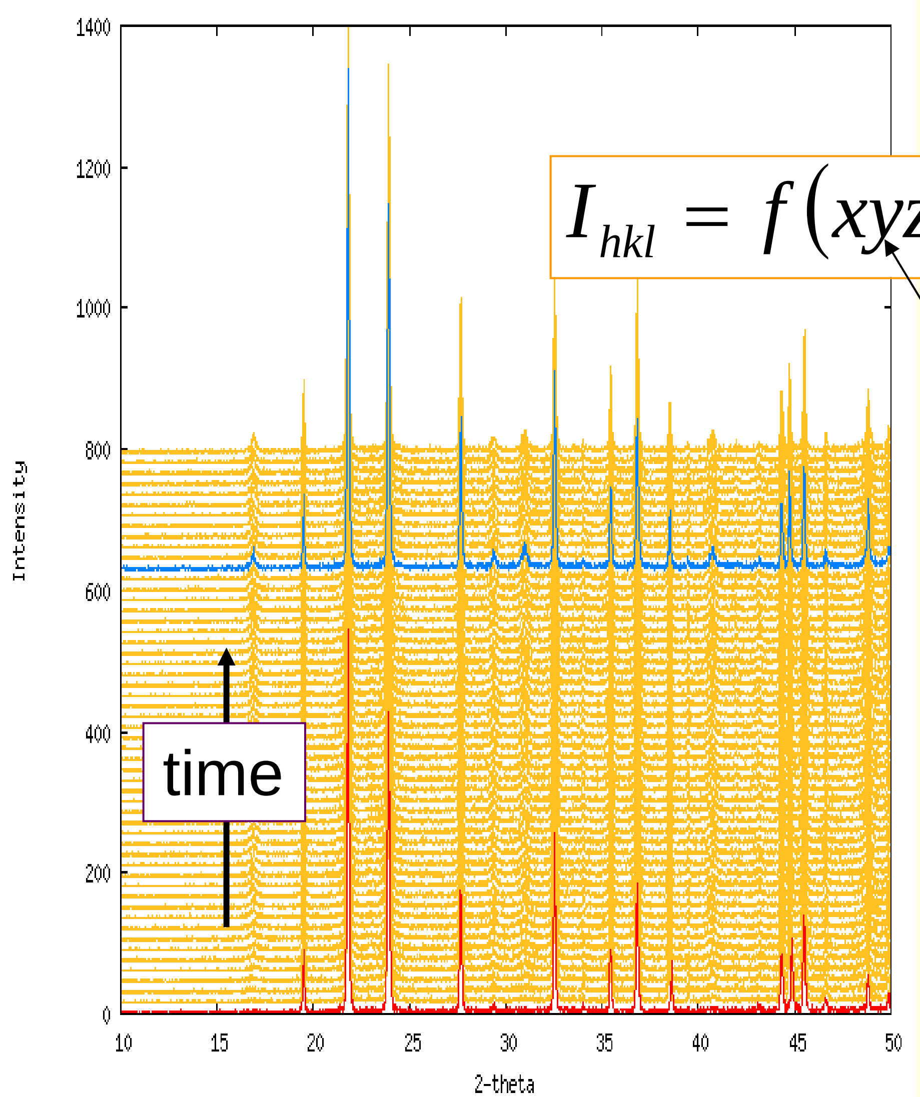
Diffraction = f(*x*)



$$I_{hkl} = f\left(xyz(t=2), occ(t=2), adp(t=2)\right)$$

$$I_{hkl} = f\left(xyz(t=1), occ(t=1), adp(t=1)\right)$$

Diffraction = f(x)



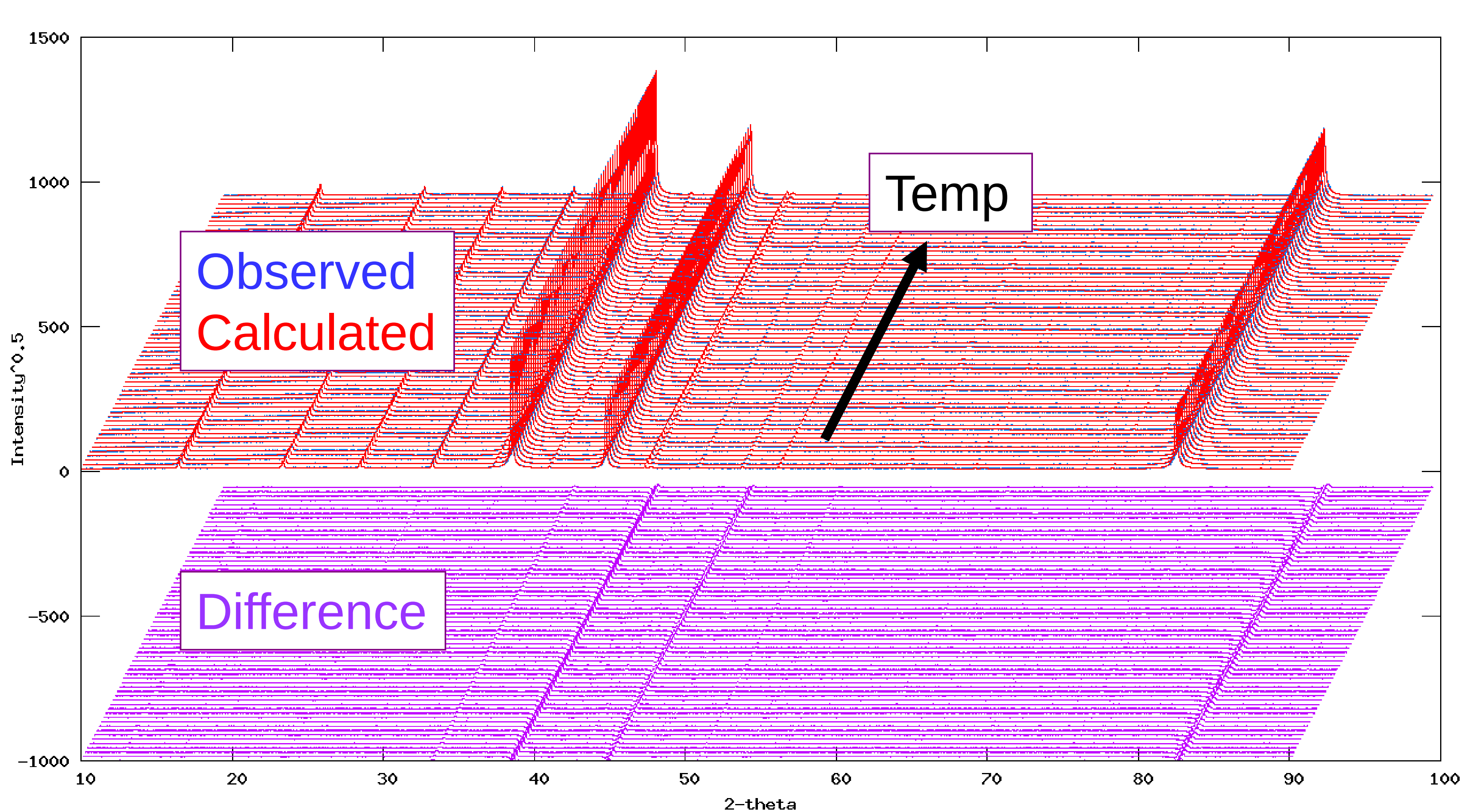
$$I_{hkl} = f\left(xyz, occ, adp\right)$$

$$adp = f(t)$$

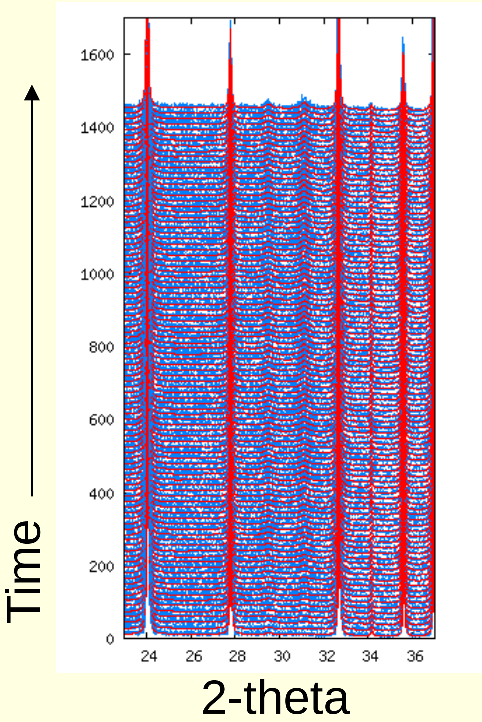
$$occ = f(t)$$

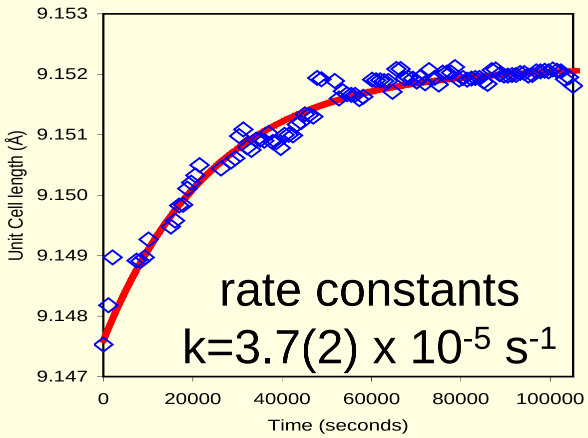
$$xyz = f(t)$$

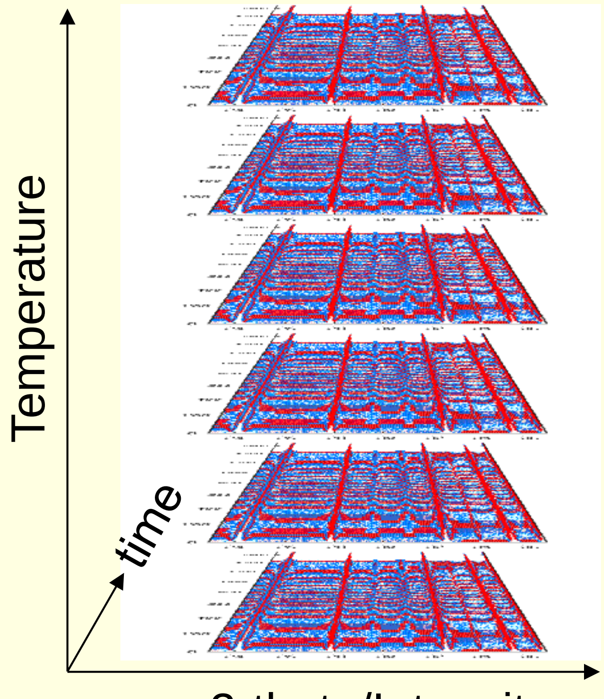
Parametric Rietveld Refinement

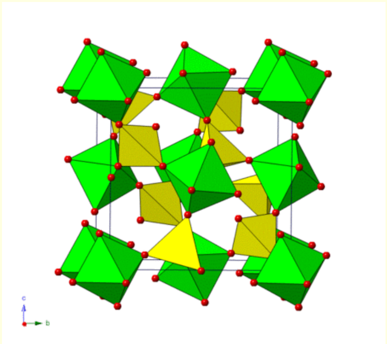


Parametric Rietveld Refinement





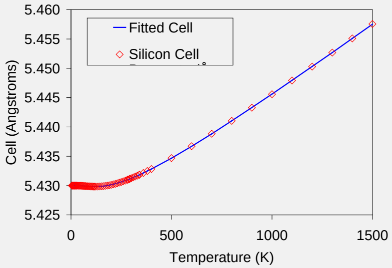




Activation Energies

Evans/Stinton, *J. Appl. Cryst.*, **40**, 2007, 87

Things you Might Parameterise….



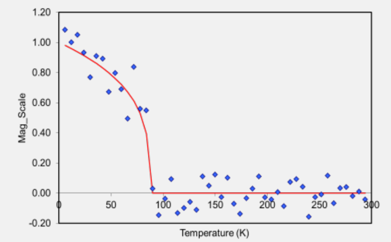
$$a(T) = Exp\left(\ln(a_0) + \frac{c_1\theta_1}{\exp(\theta_1/T) - 1}\right)$$

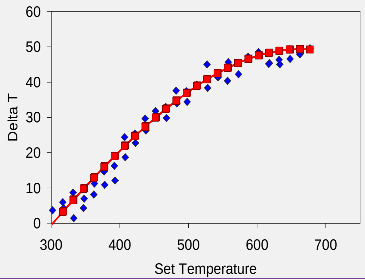
$$x(T) = x_0\left(1 + c_1T + c_2T^2 + c_3T^3\right)$$

Structural variables

Critical behaviour

$$Intensity(T) = c_1\left(1 - \frac{T}{T_C}\right)^{\beta}$$





$$\Delta T = c_0 + c_1T_{set} + c_2T_{set}^{\ 2}$$

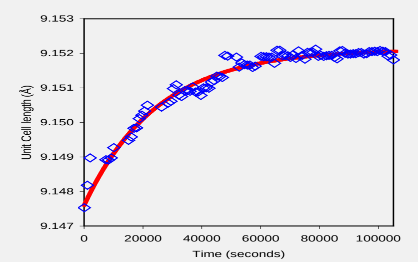
$$height(T) = h_0\left(1 + c_1T + c_2T^2\right)$$

Instrumental effects

Kinetic parameters

$$frac(t) = c_1\left[1 - \exp\left(-k_{frac}t\right)\right] + c_2$$

$$cell(t) = c_2\left[1 - \exp\left(-k_{cell}t\right)\right] + c_3$$



Parametric/Surface vs Sequential

- Parametric fitting is a specialist beast
- Sequential fitting generally much easier, easily automated, fewer assumptions

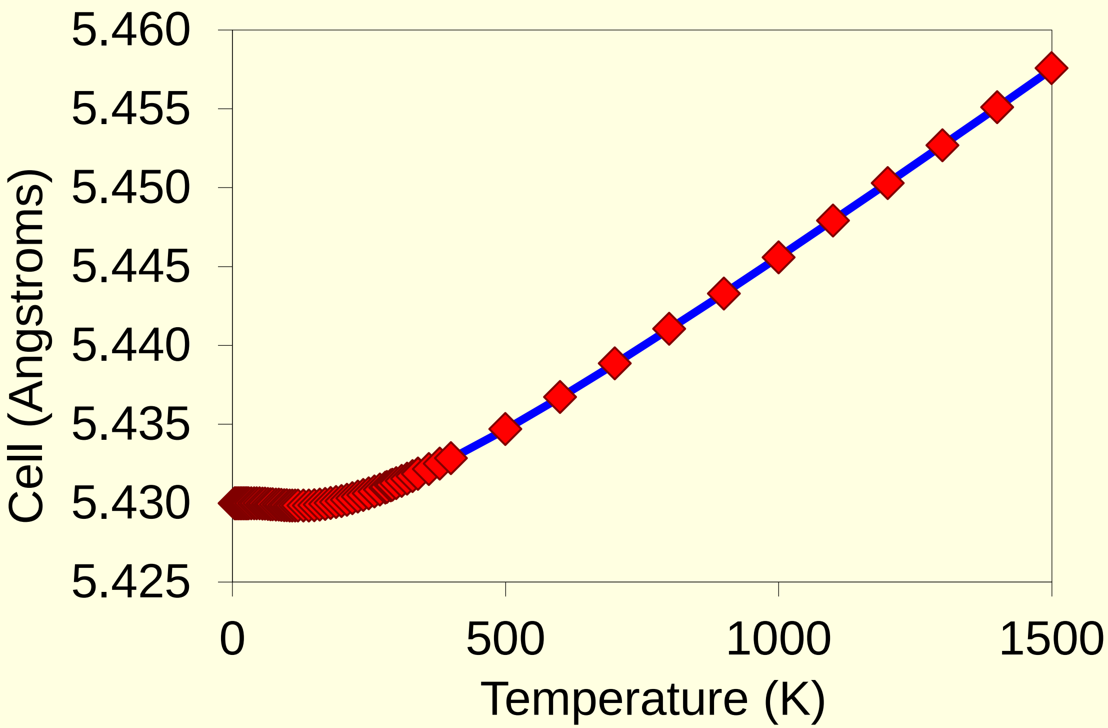
EPDIC 2012 Software Discussion

- Misquotes from “Profs F/G” EPDIC 2012:
  1. I don’t think we should be doing that.
  2. Why not just take all refined variables and variance-covariance matrices and analyse externally?
  3. What happens if you don’t choose the proper functional form?

- Misquotes in return:
  1. I agree with you 90% of the time.
  2. What piece of software do we have to do that (ANO); what if you’re in completely the wrong minimum.
  3. You learn a lot about your system.

  4. It’s really powerful when the wrong answer gives a better fit than the right answer

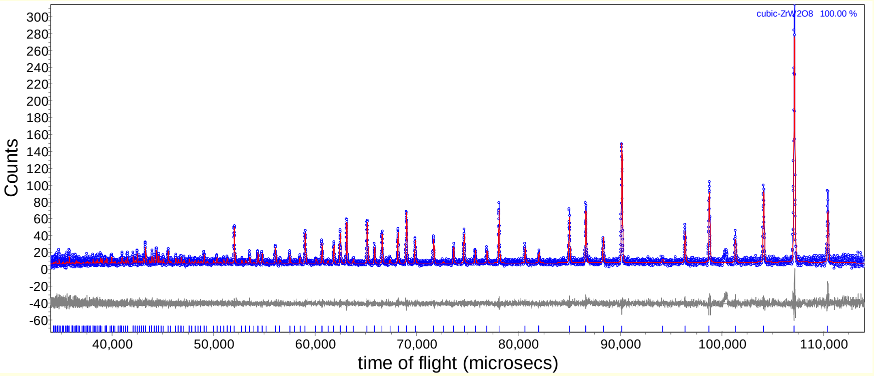
Unit Cell Parameterisation

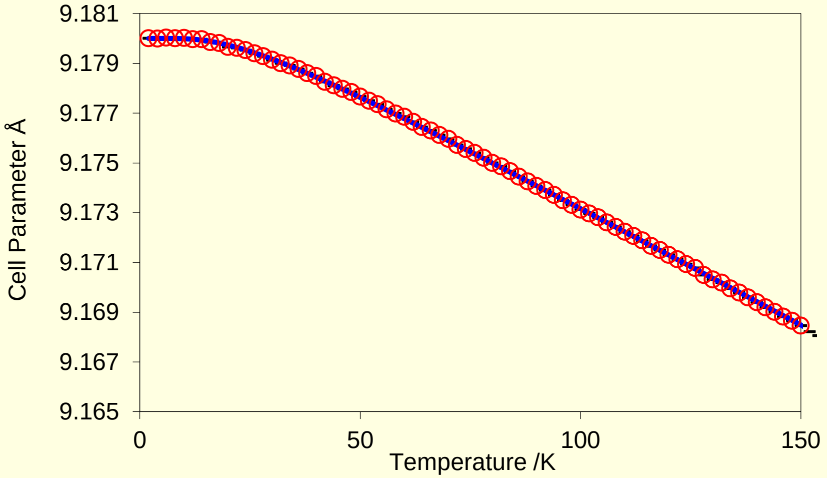


- Refine independently?
- Refine parametrically?

$$a(T) = Exp\left(\ln(a_0) + \frac{c_1\theta_1}{\exp(\theta_1/T)-1} + \frac{c_2\theta_2}{\exp(\theta_2/T)-1} + \ldots \right)$$

ZrW_2O_8 Phonons – Don't Parameterise

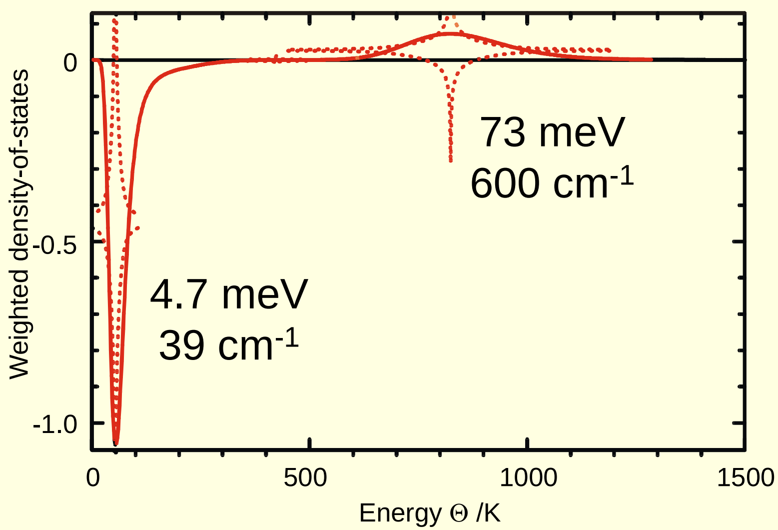




260 relatively quick diffraction patterns

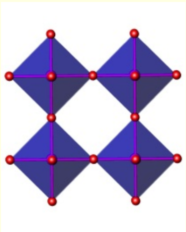
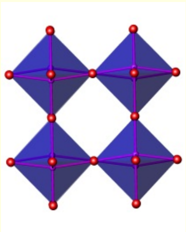
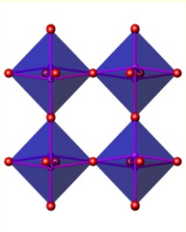
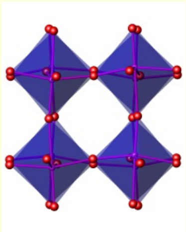
Cell Parameter at 260 temperatures

Complex physics

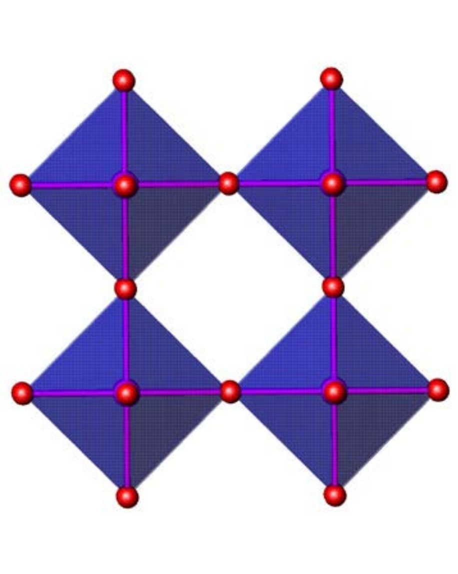


Bill David

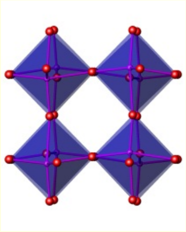
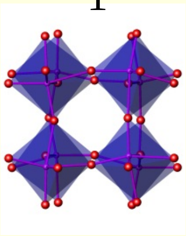
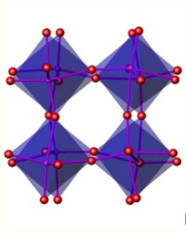
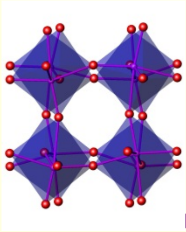
WO_3 Phase Transitions – Do Parameterise

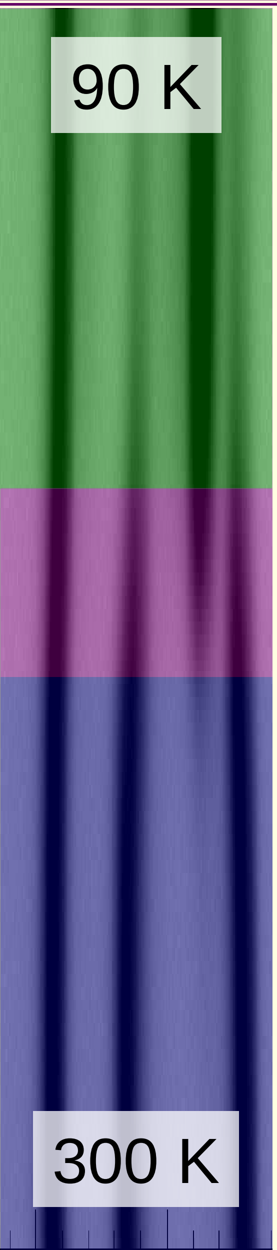
$$Pm\bar{3}m \xrightarrow{??K} P4/nmm \xrightarrow{1173K} P4/ncc \xrightarrow{1073K} P2_1/c$$

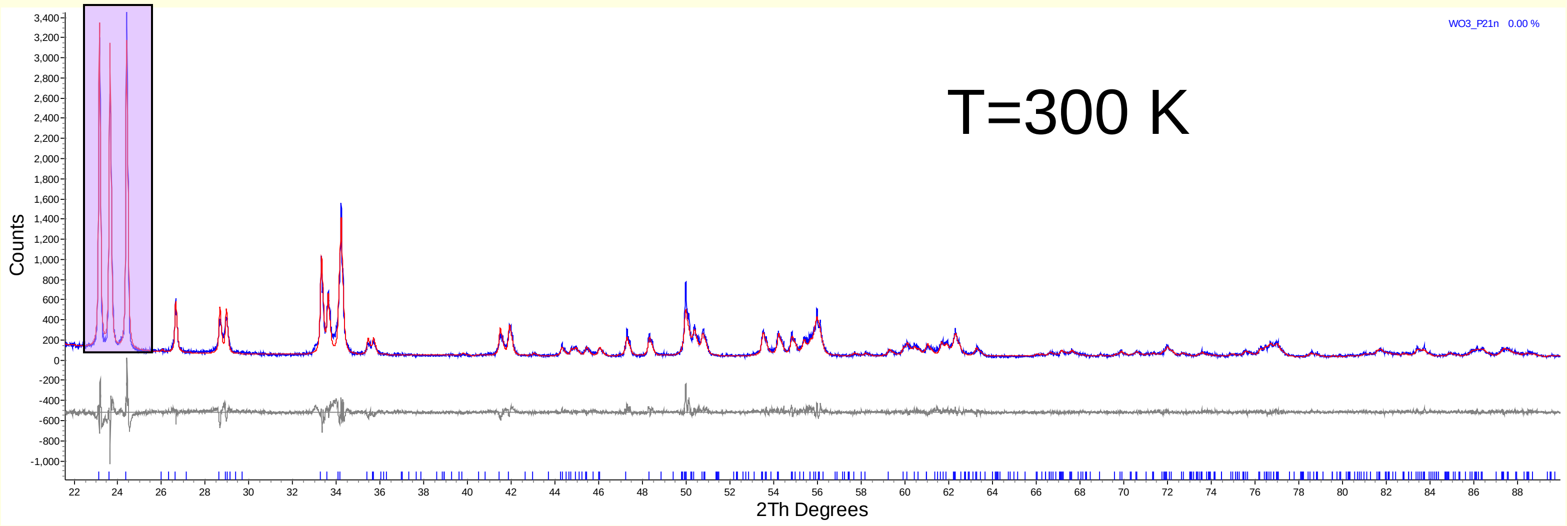


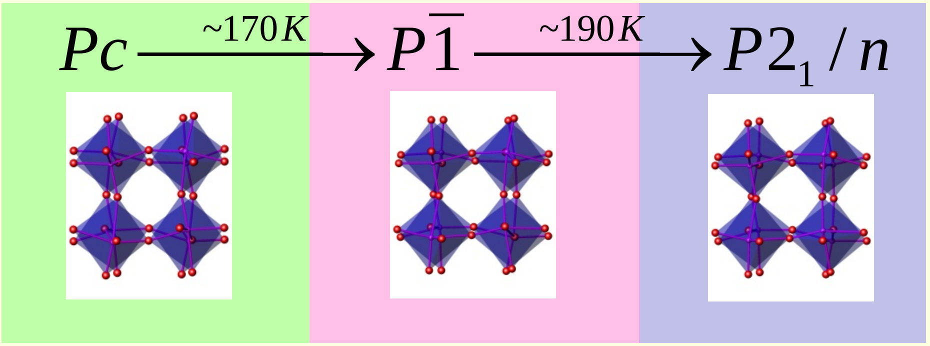
$$\xrightarrow{993K} Pbcn \xrightarrow{623K} P2_1/n \xrightarrow{\sim 230K} P\bar{1} \xrightarrow{\sim 190K} Pc$$

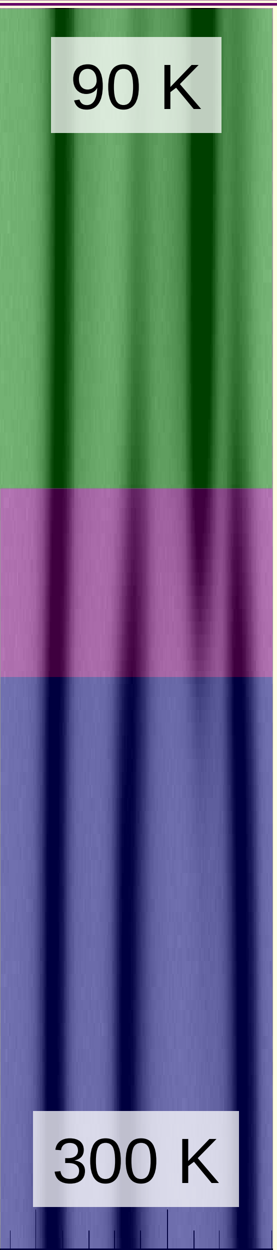
Laboratory VT Data

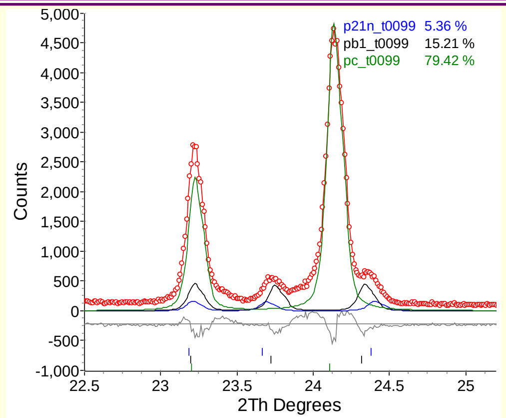


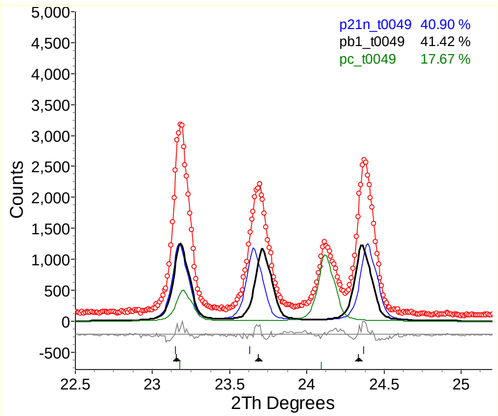


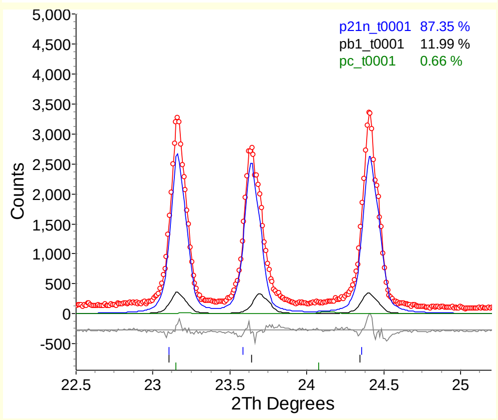


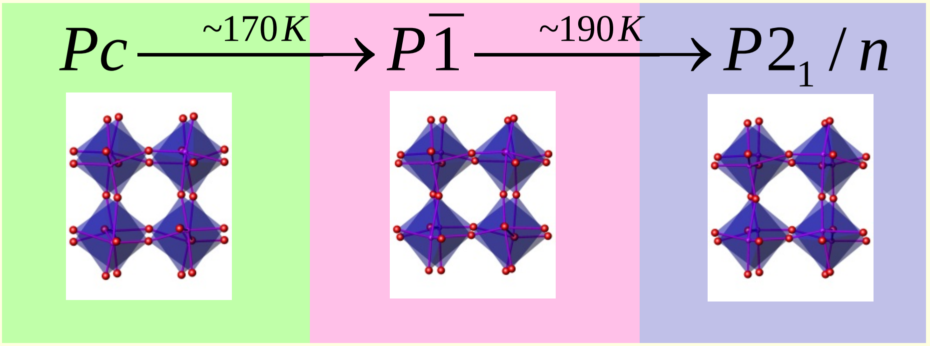
VT Lab Diffraction Data











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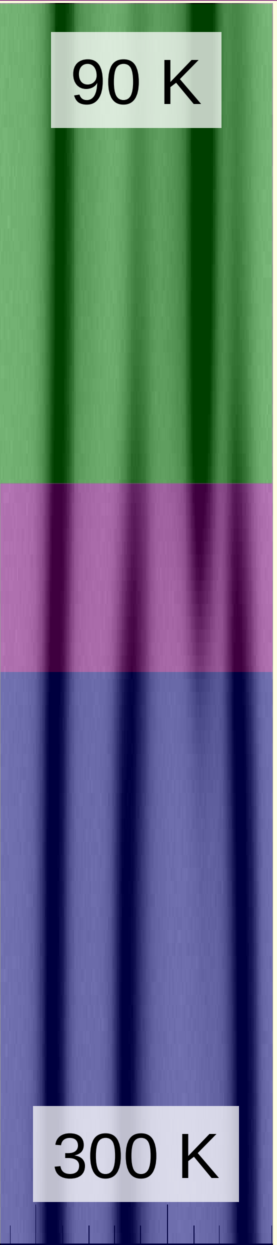
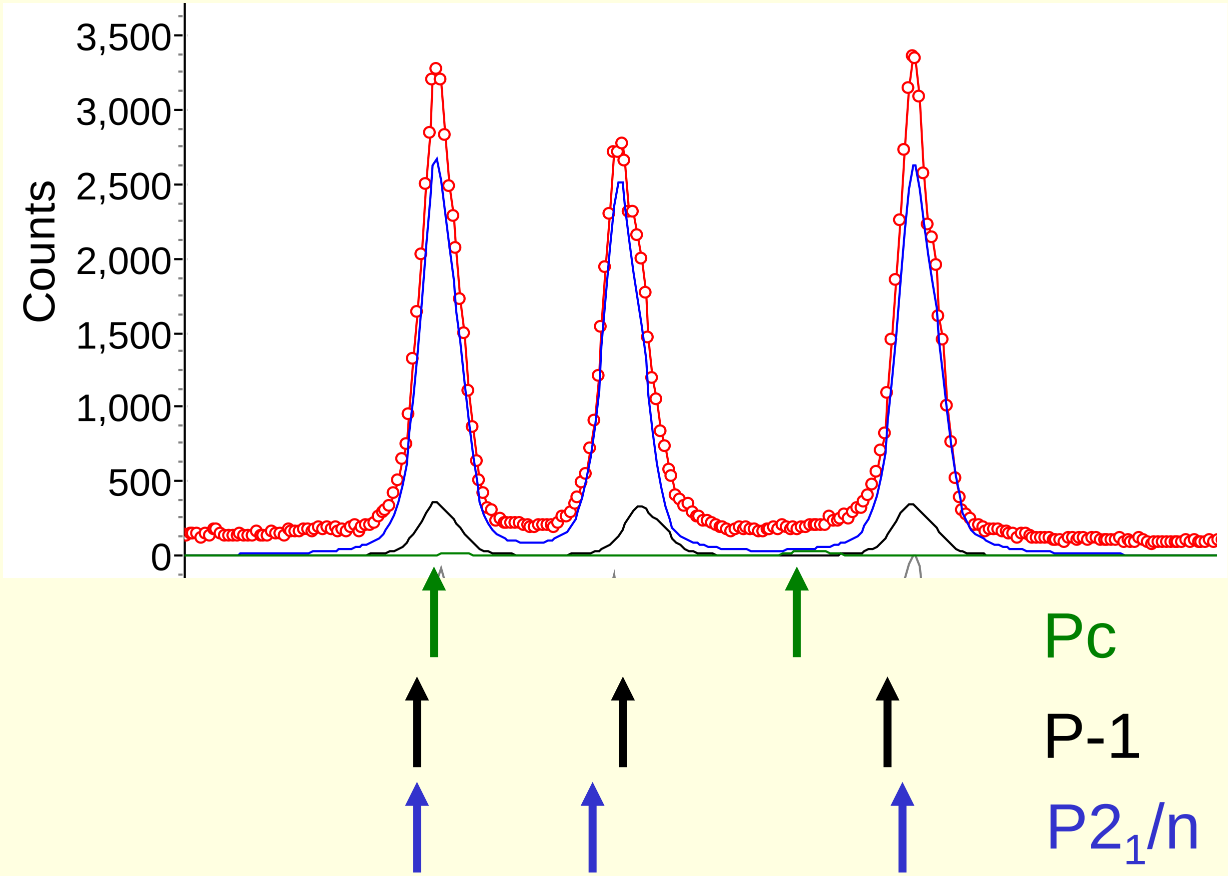
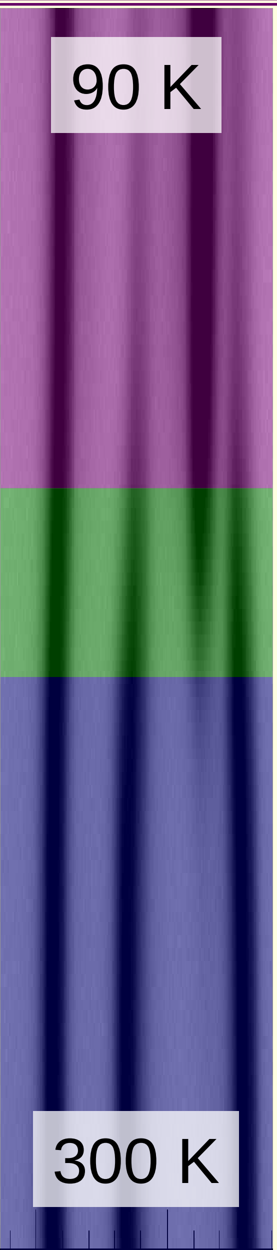
Peak Overlap/Structural Distortions

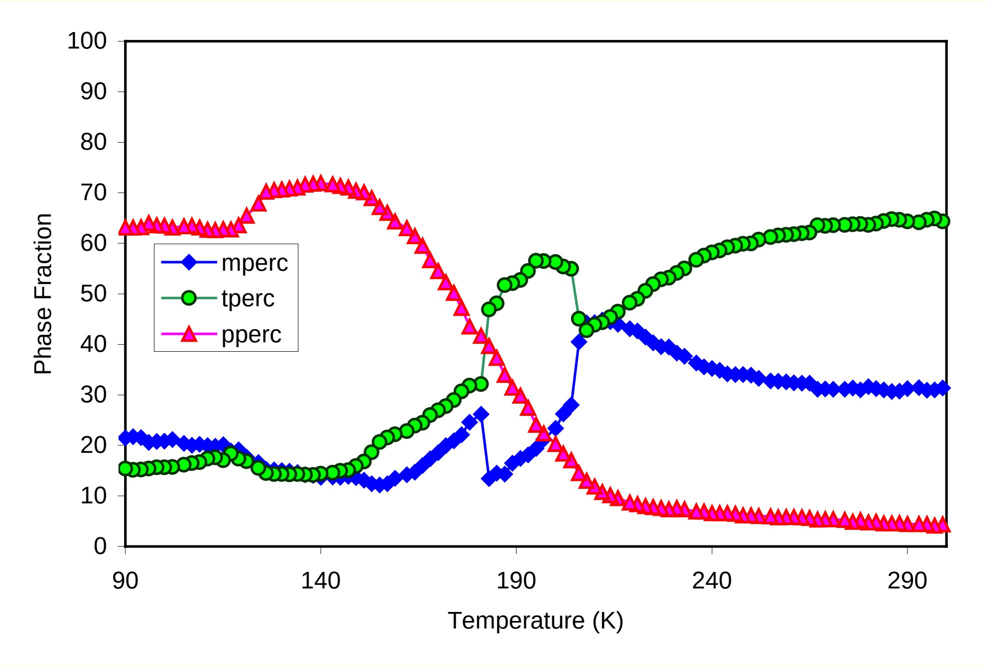


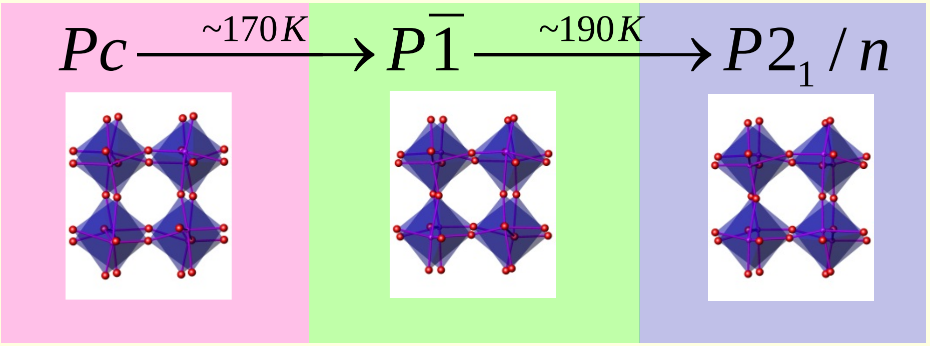


P2$_1$/n (002)/(020)/(200) reflections

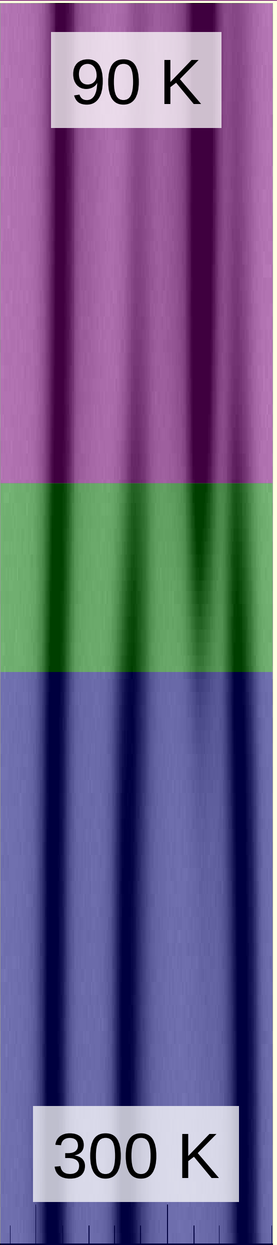
Sequential Phase Fractions

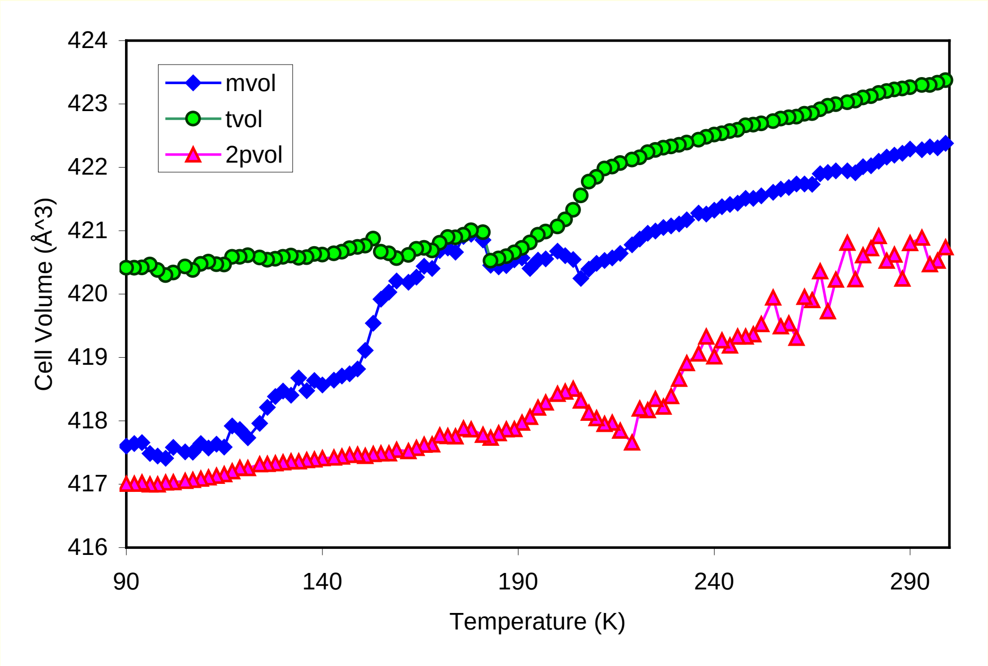


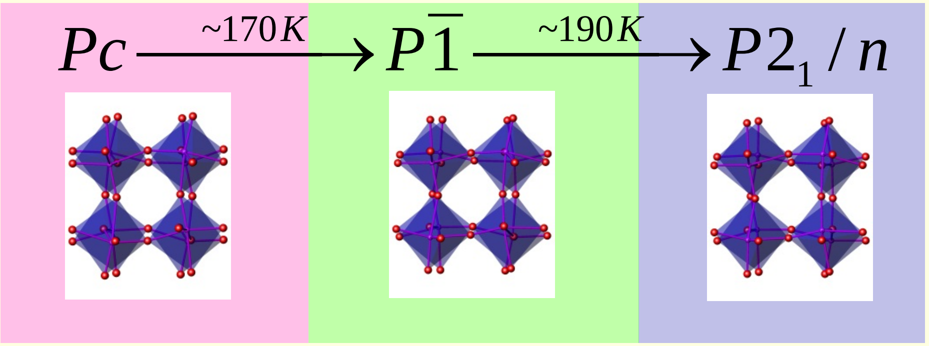




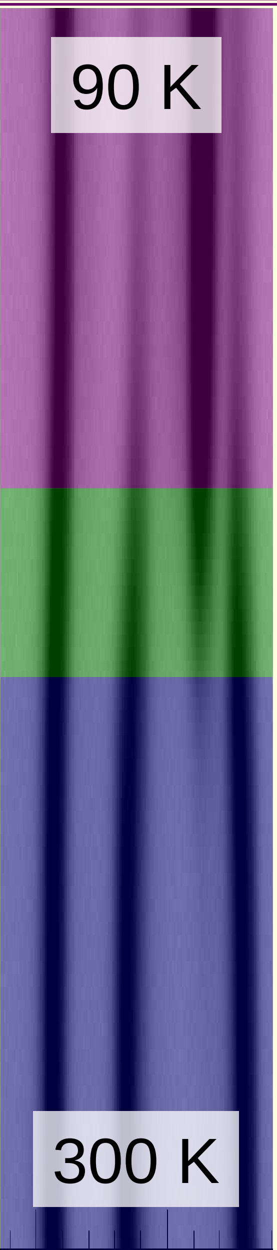
Sequential Cell Volumes







Parametric Assumptions



- Individual phases show smooth variations in a/b/c and $\alpha/\beta/\gamma$ with temperature
- Temperature factors vary smoothly with temperature
- Peak shape for each phase derived from all data
- Einstein/polynomial type expressions

- 1102 parameters not 8100

Surface Fitting – Smooth Cell

Overall Refinable Parameters:

```
a0    5.42999
c1    4.86977*10-6
θ1    570.1
.
.
.
```

Refinement info for Temperature = 300 K

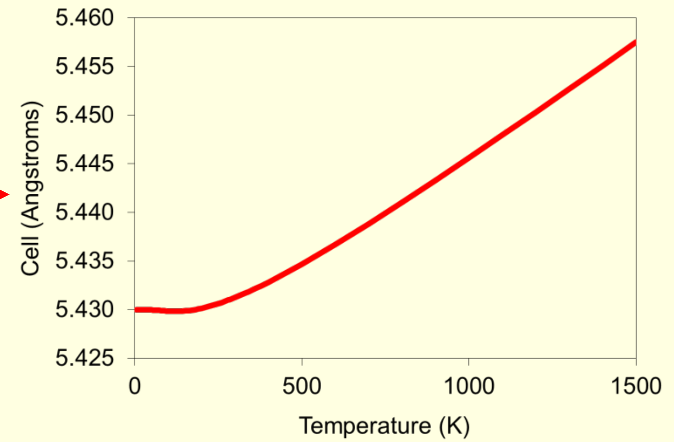
$$T = 300$$

$$a(T) = \mathrm{Exp}\left(\ln(a_0) + \frac{c_1 * \theta_1}{\exp(\theta_1 / T) - 1} + \ldots \right)$$

Refinement info for Temperature = 350 K

$$T = 350$$

$$a(T) = \mathrm{Exp}\left(\ln(a_0) + \frac{c_1 * \theta_1}{\exp(\theta_1 / T) - 1} + \ldots \right)$$



Surface Fitting – Smooth ADPs

Overall Refinable Parameters:

a0	5.42999
c1	$4.86977*10^{-6}$
θ1	570.1
b0	0.113
c2	$2.33*10^{-3}$
θ2	500

Refinement info for Temperature = 300 K

$$T = 300$$

$$a(T) = \mathrm{Exp}\left(\ln(a_0) + \frac{c_1 \theta_1}{\exp(\theta_1 / T) - 1} + \ldots\right)$$

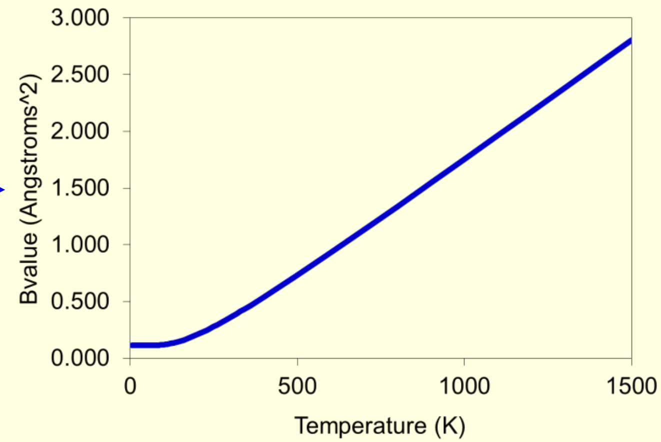
$$b(T) = b_0 + \frac{c_2 \theta_2}{\exp(\theta_2 / T) - 1}$$

Refinement info for Temperature = 350 K

$$T = 350$$

$$a(T) = \mathrm{Exp}\left(\ln(a_0) + \frac{c_1 \theta_1}{\exp(\theta_1 / T) - 1} + \ldots\right)$$

$$b(T) = b_0 + \frac{c_2 \theta_2}{\ldots}$$



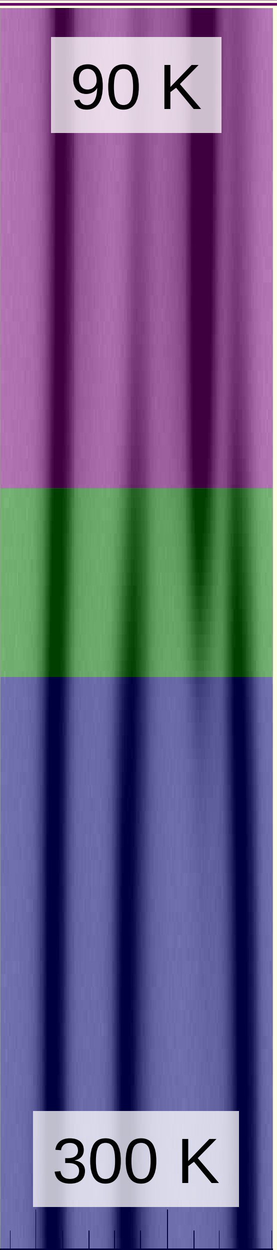
.inp file format/implementation

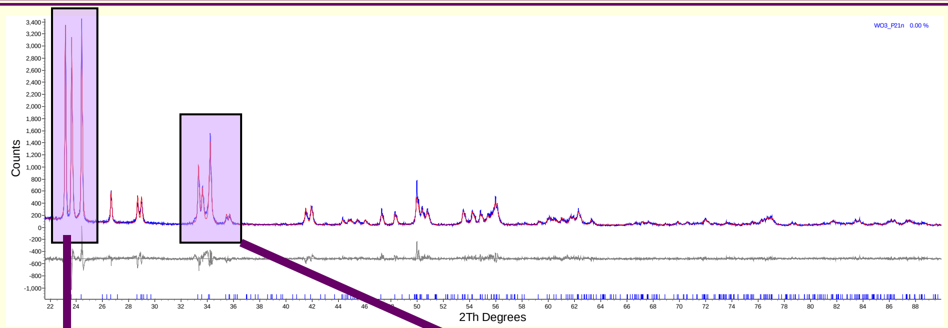
- Topas input file

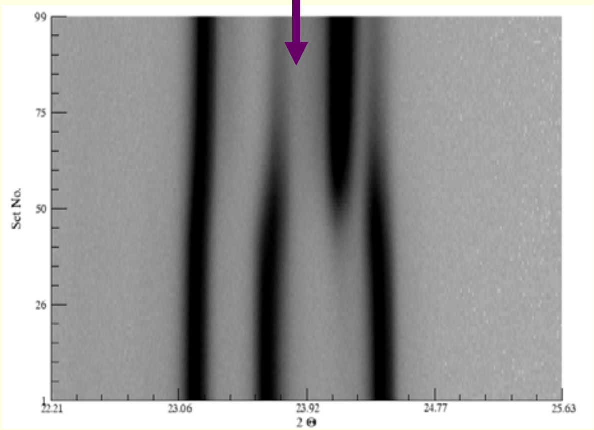
```
'a bit of the input file
prm zero_ma 7.2900
prm theta_ma 150
prm grad_ma 1.02e-5


str
   phase_name p21n_t0001
#ifdef param_cell
   prm mlpa_t_0001  = zero_ma + (grad_ma/(Exp(theta_ma/t_0001)-1));:7.30037
   a =mlpa_t_0001;:7.30037`
   ....
#else
    a mlpa_t_0001  7.30735 mlpaminmax
   ....
#endif
```

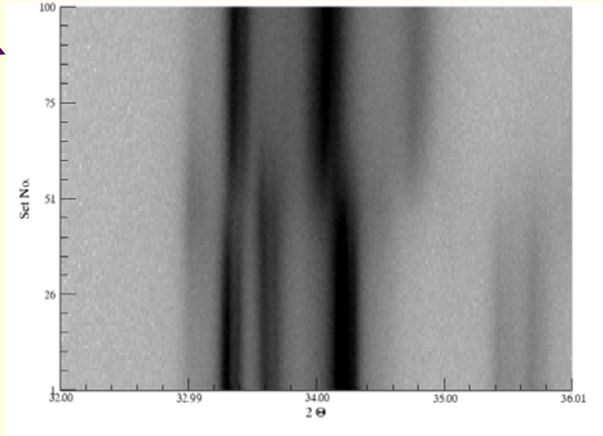
Surface Fit

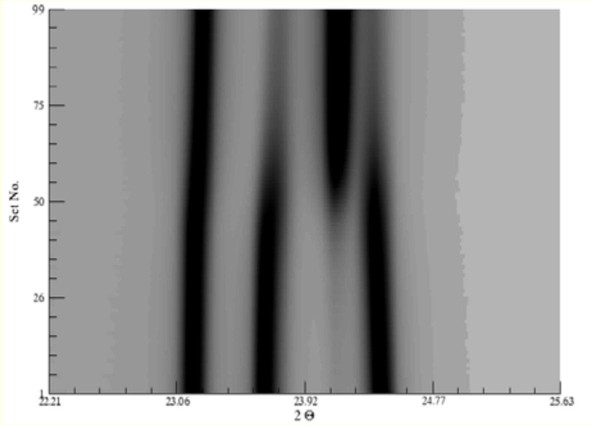




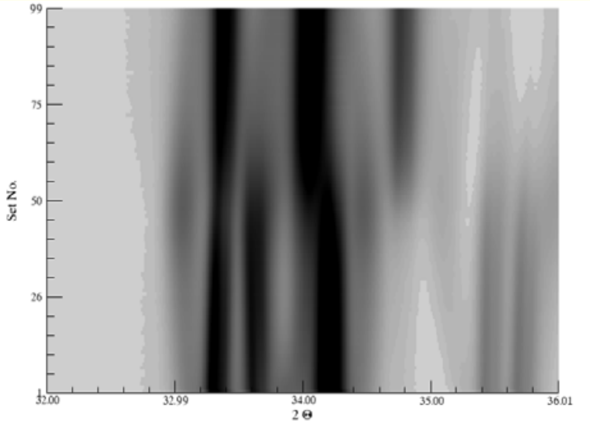


obs

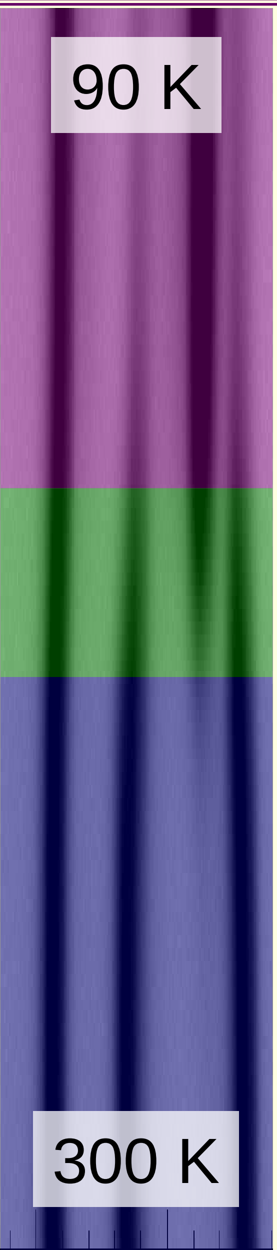


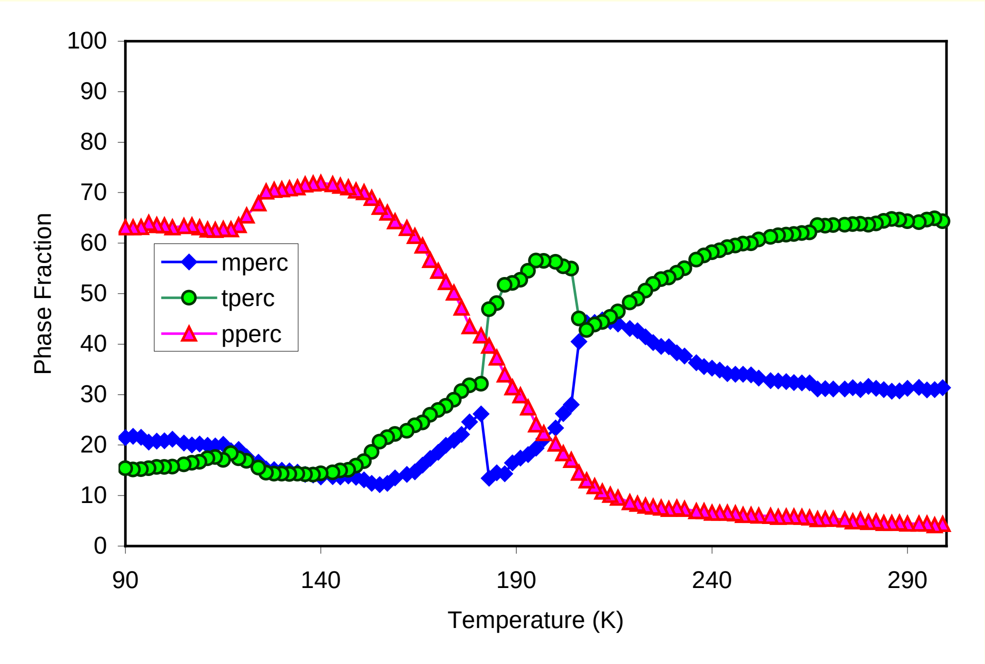


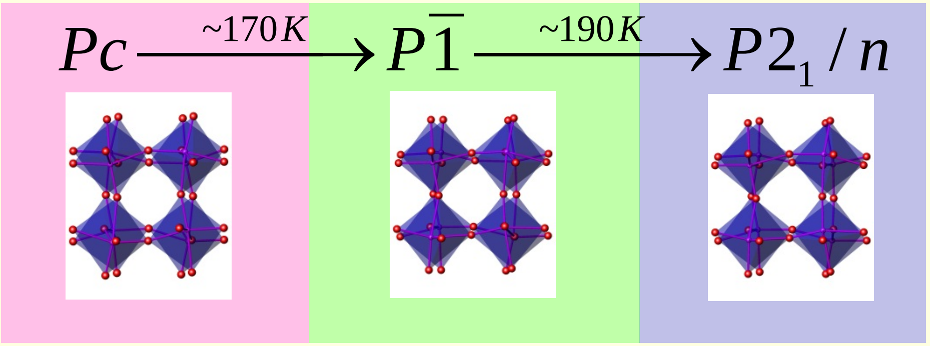
calc



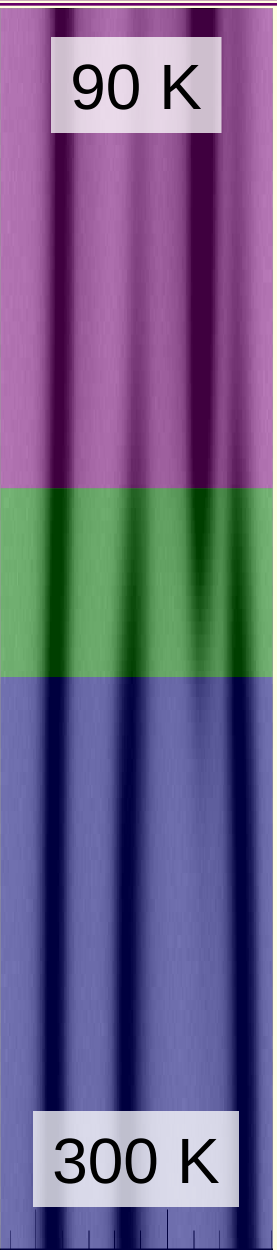
Sequential Phase Fractions

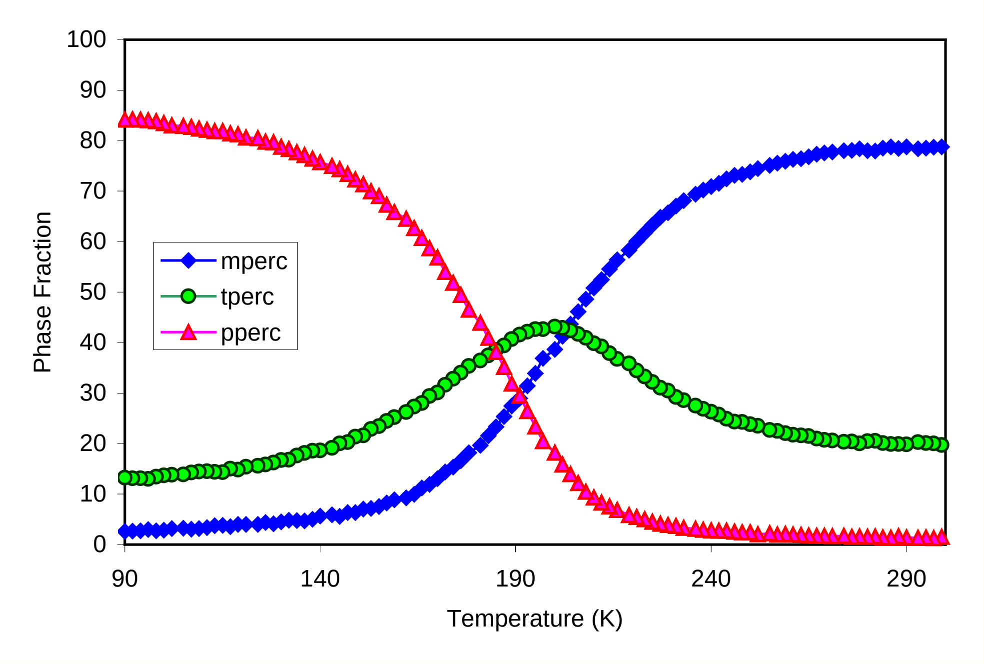


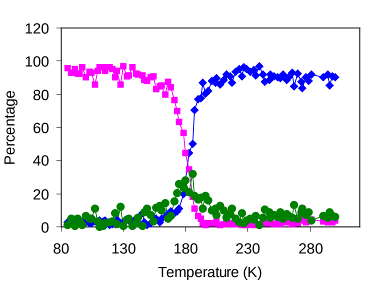




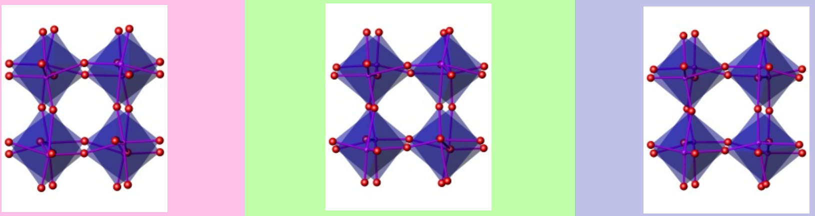
Parametric Phase Fractions





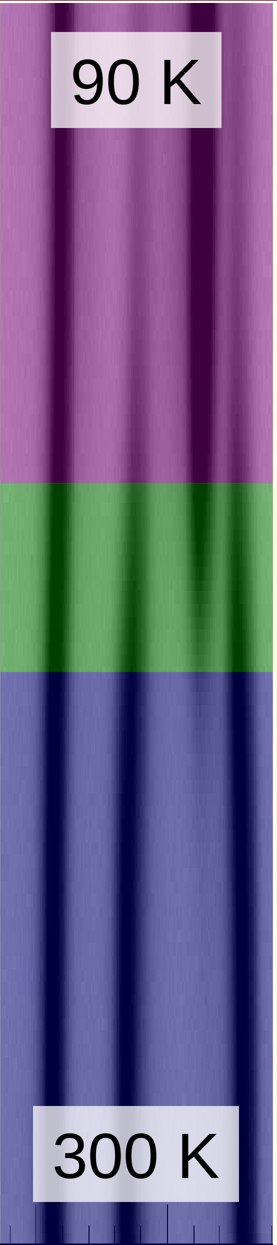


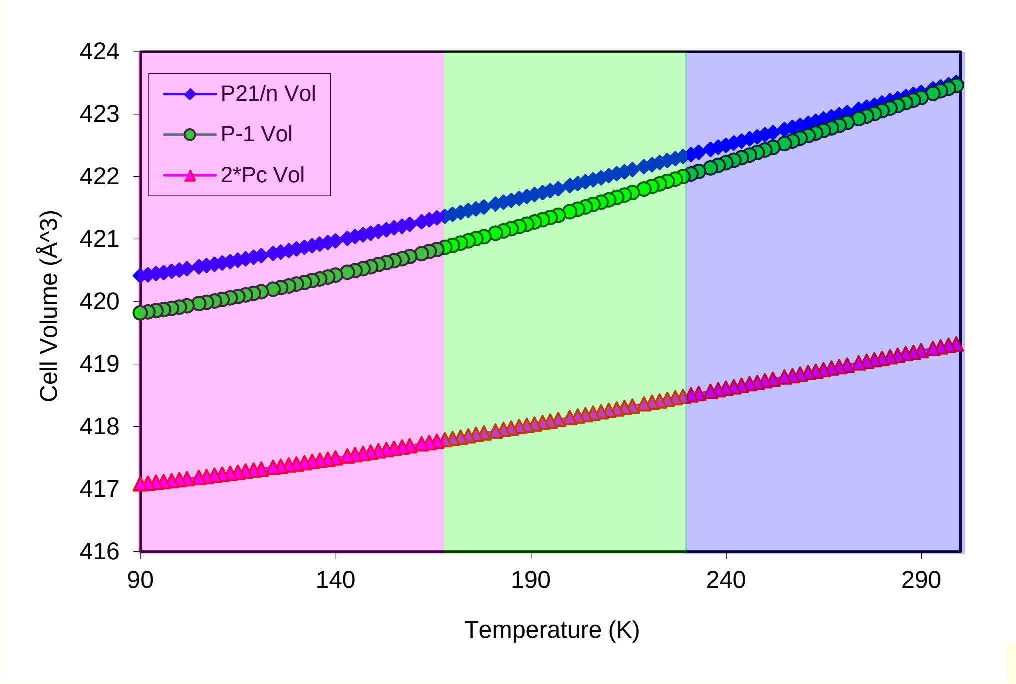
$$Pc \xrightarrow{\sim 170K} P\bar{1} \xrightarrow{\sim 190K} P2_1/n$$

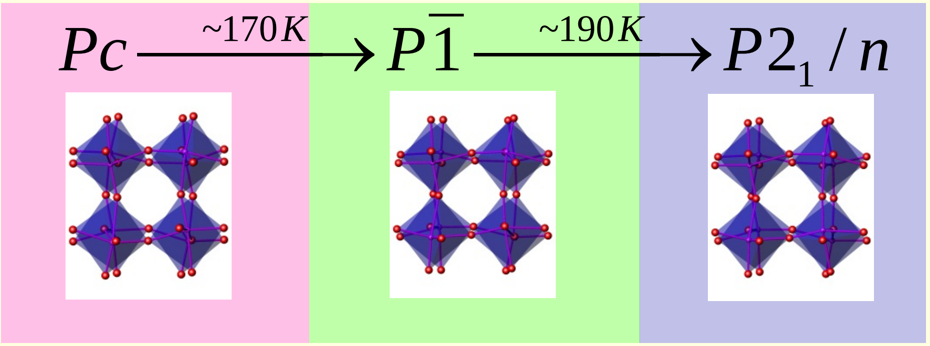


john.evans@durham.ac.uk www.durham.ac.uk/john.evans

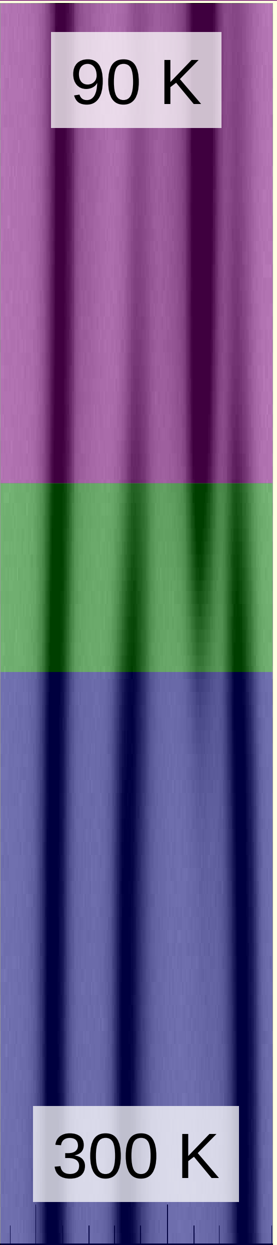
Parametric Cell Volumes

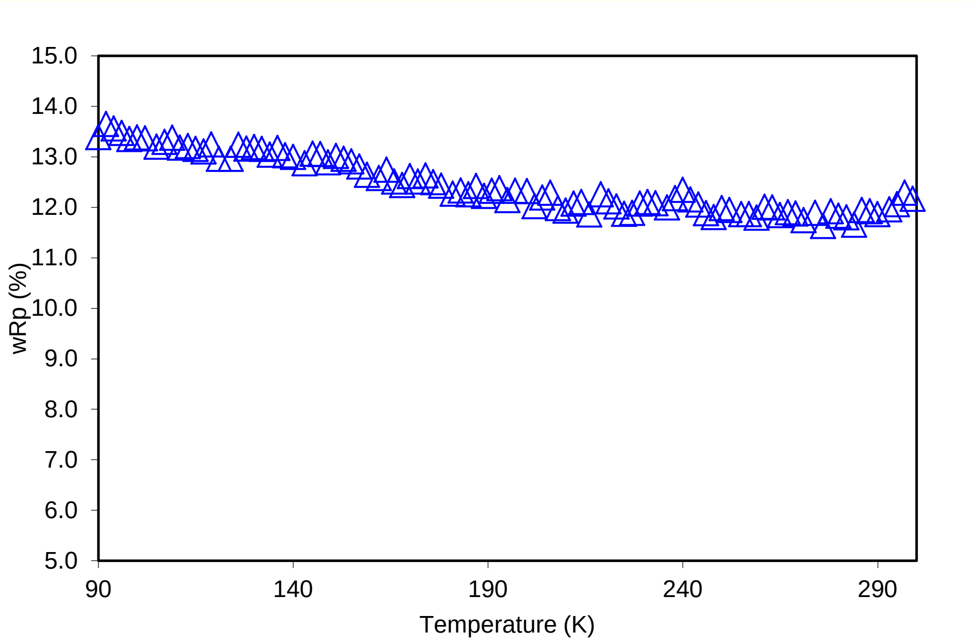


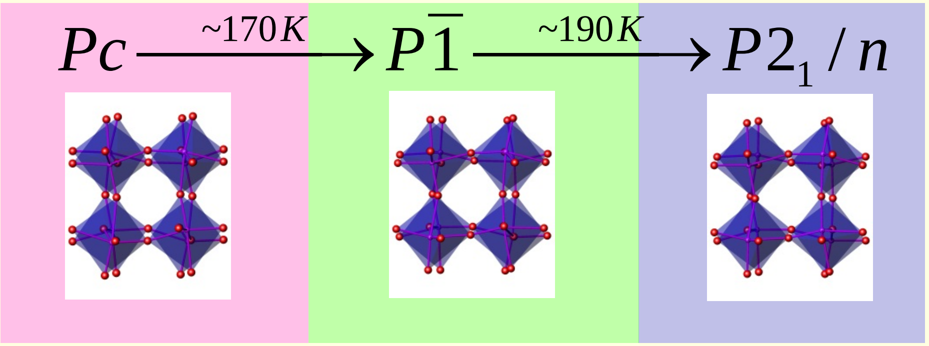




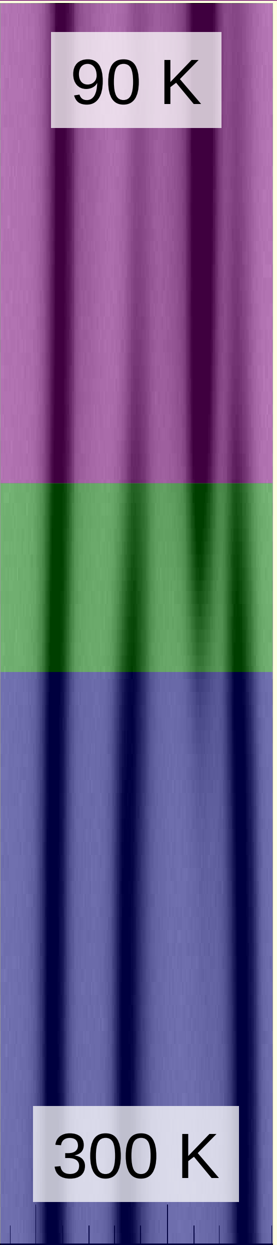
Parametric R-factors

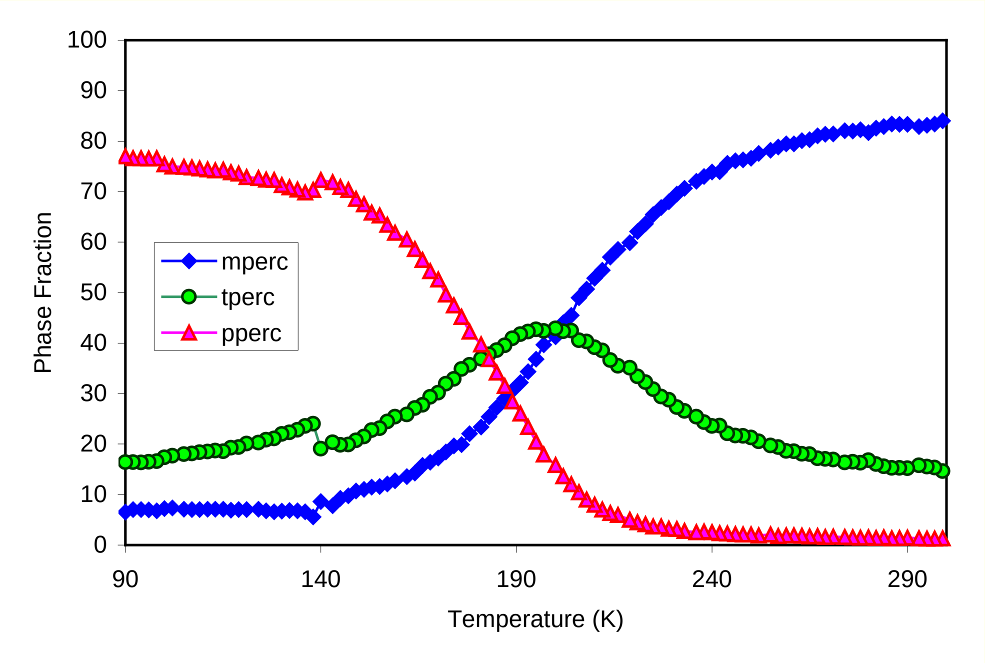






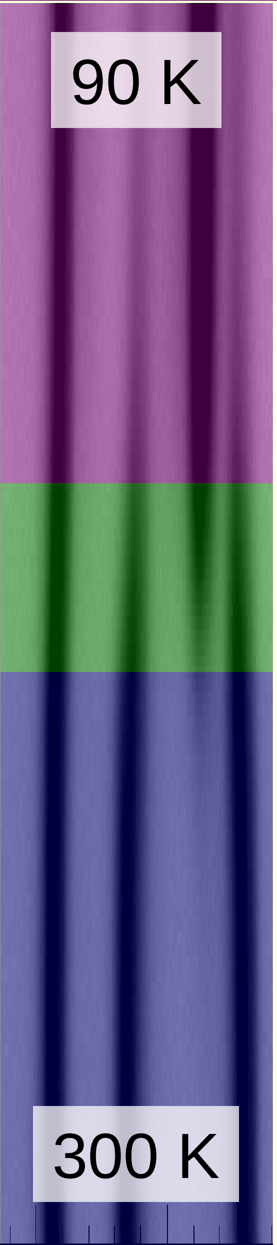
"Best Possible" Independent Fitting?



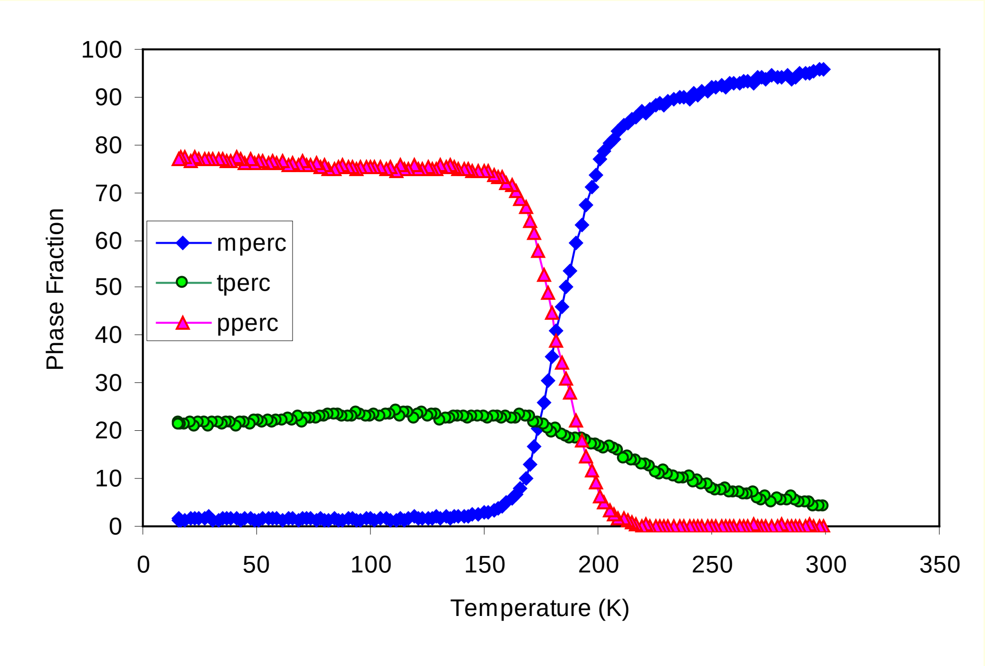


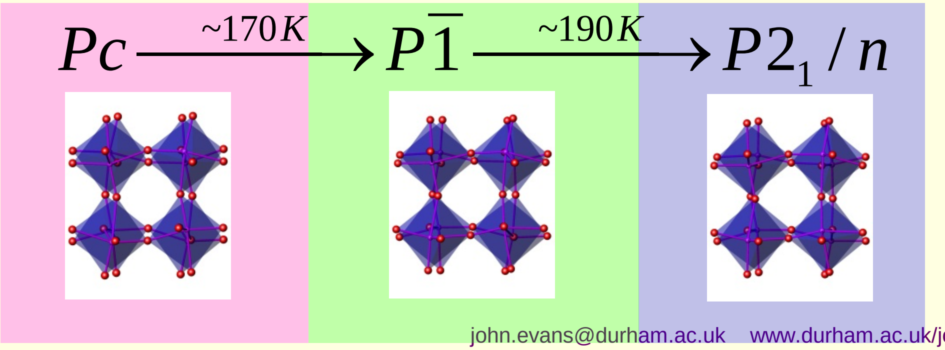
- Start all refinements at "perfect" cell parameters from parametric fit
- Minimum number of parameters (identical peak shapes etc)
- Perform limited simulated annealing at each T
- "Wrong" answer can have lower R-factor

Wrong Model?

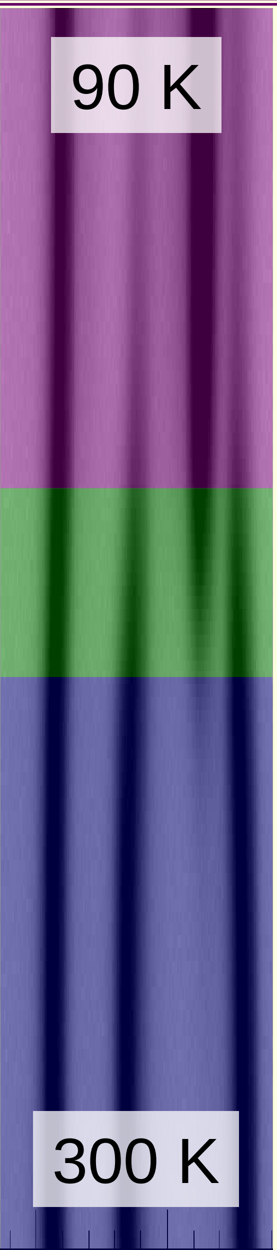


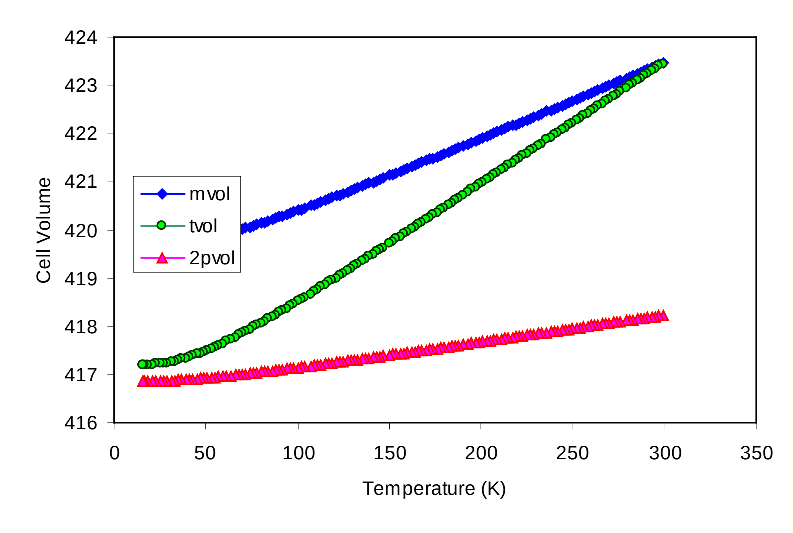
- Different sample
- Equivalent X-ray experiment

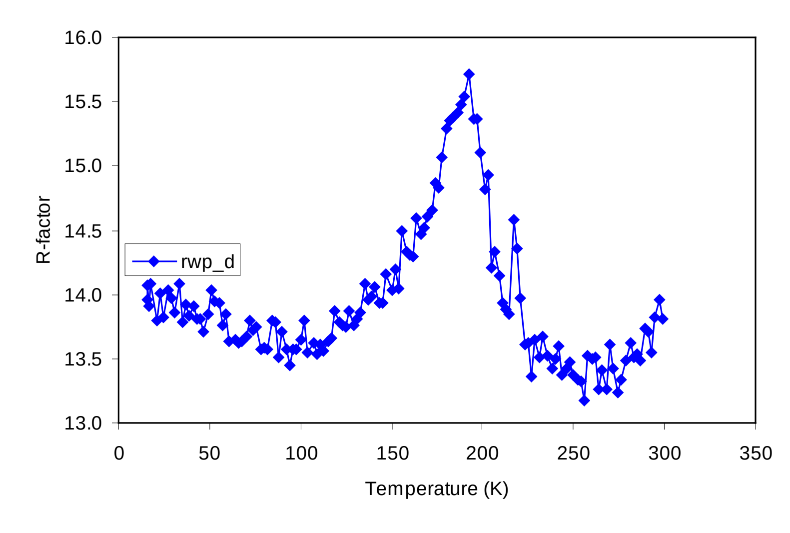




Cell volumes and R-factor

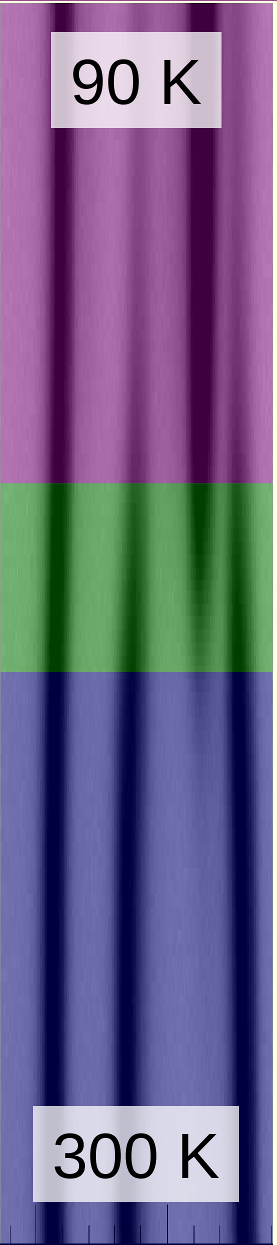


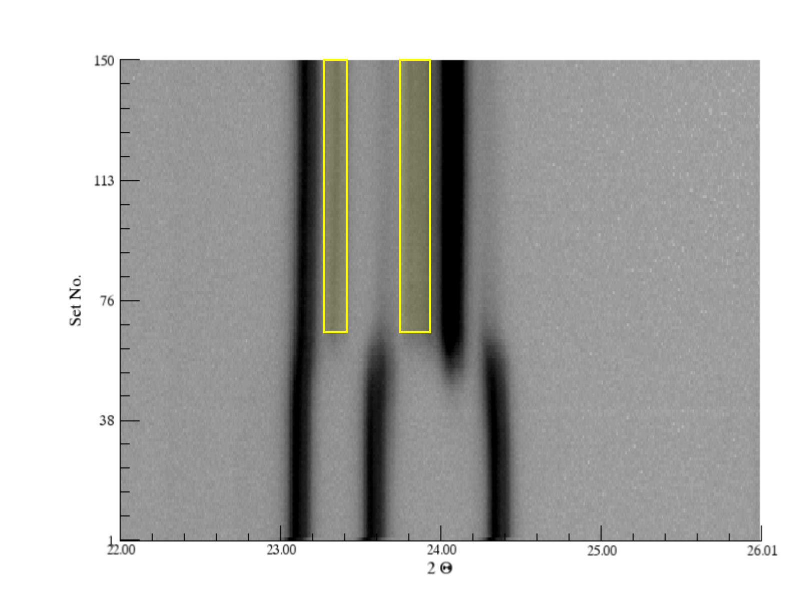




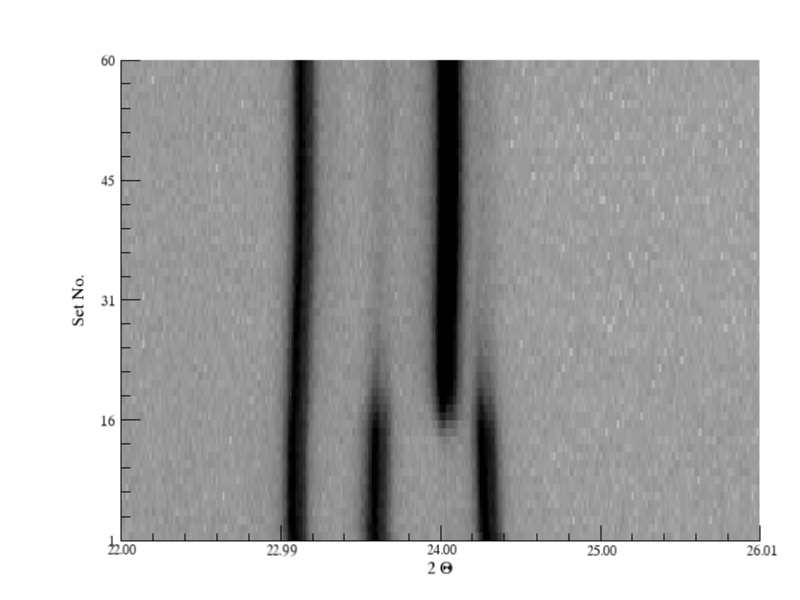
- Cell volumes with temperature very suspicious
- R-factors very suspicious
- Unusual trends suggest something wrong

Raw data – additional peaks





d9_03124



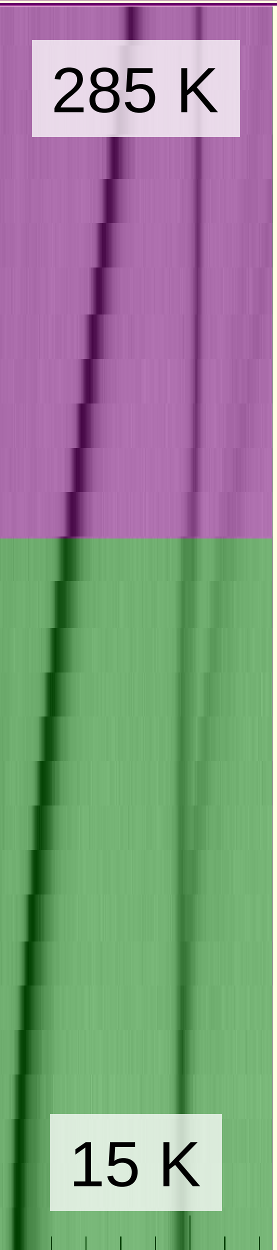
d9_03125

- Extra low temperature phase
- Without surface fitting these peaks get “mopped up” by P-1 phase
- Phase transitions very dependent on thermal history

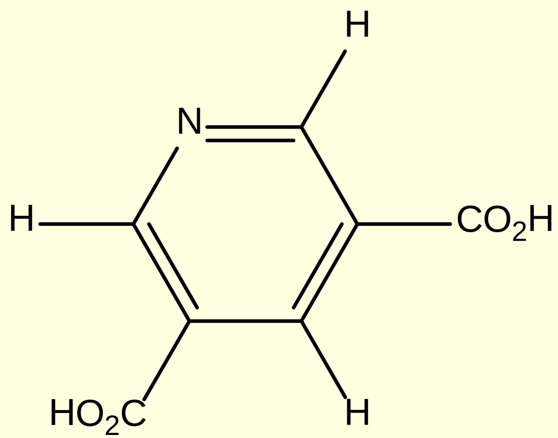
Quantitative Analysis – Advantages

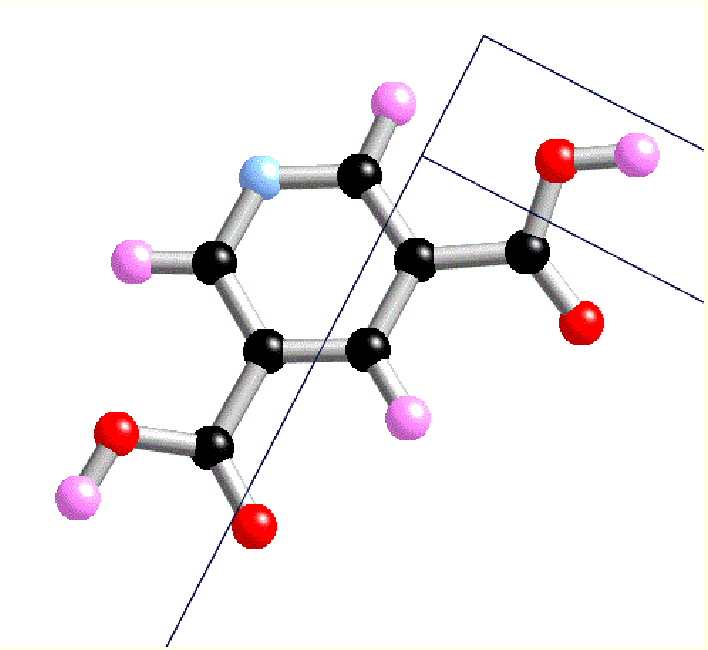
- Impose “physically sensible model” on well understood quantities
- Prevent “wrong solutions” fitting data
- Prevent peaks becoming infinitely broad and correlating with background
- Unbiased way to refine data?

Example 2 – Proton Migration

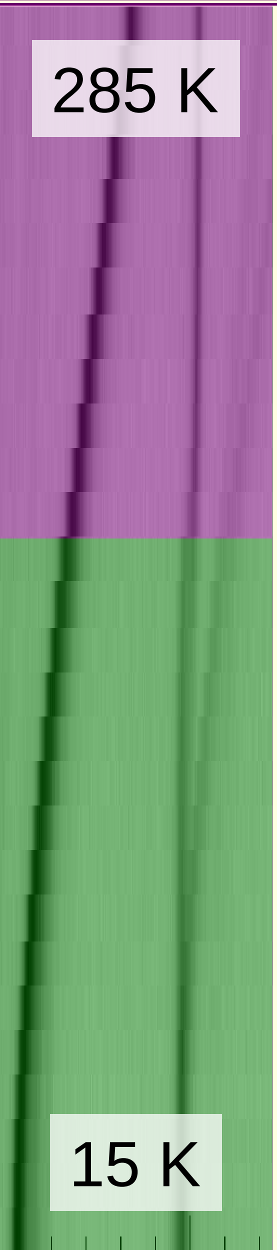


- Subtle structural change in the organic solid state
- 3,5 pyridine dicarboxylic acid (3,5 PDCA)

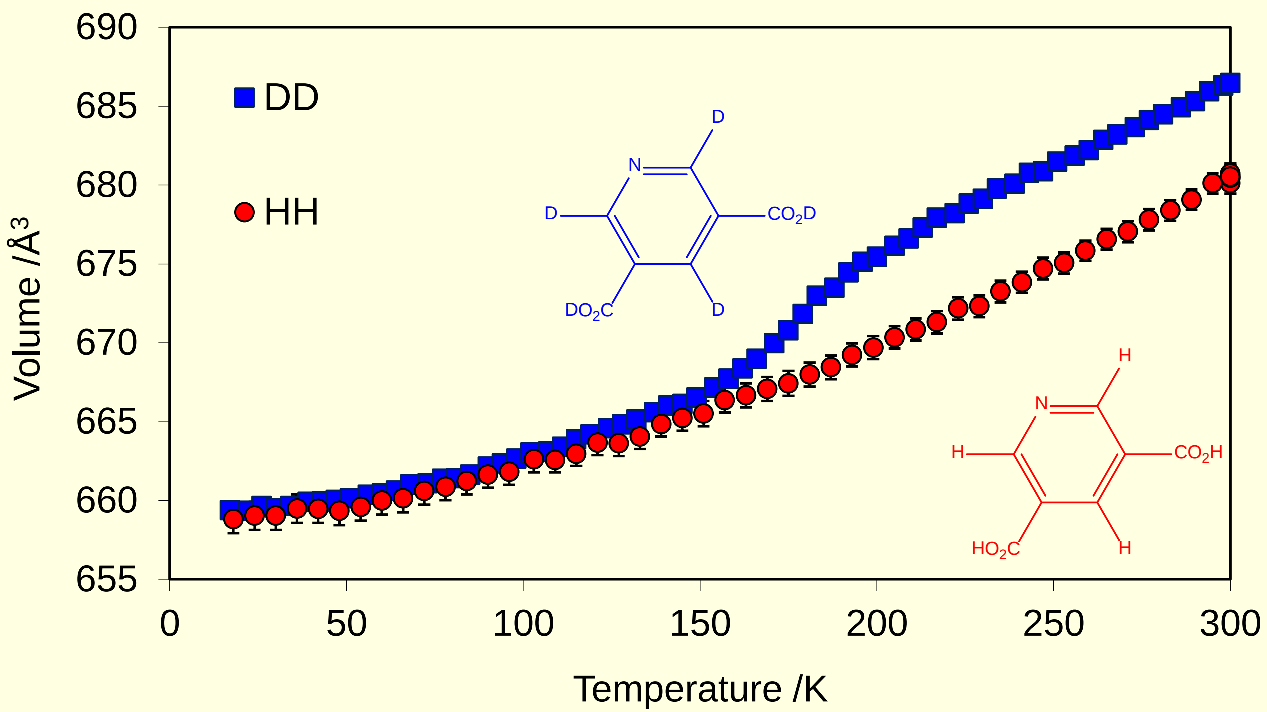




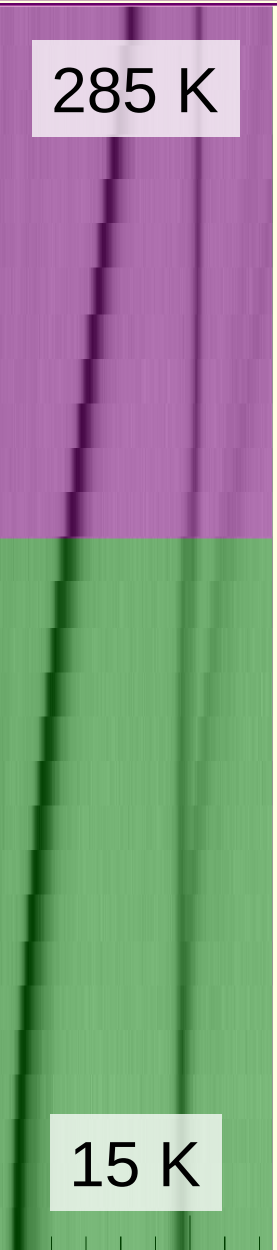
3,5-PDCA

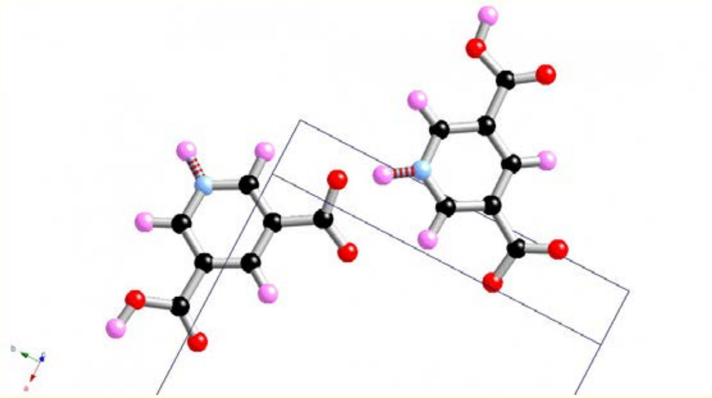


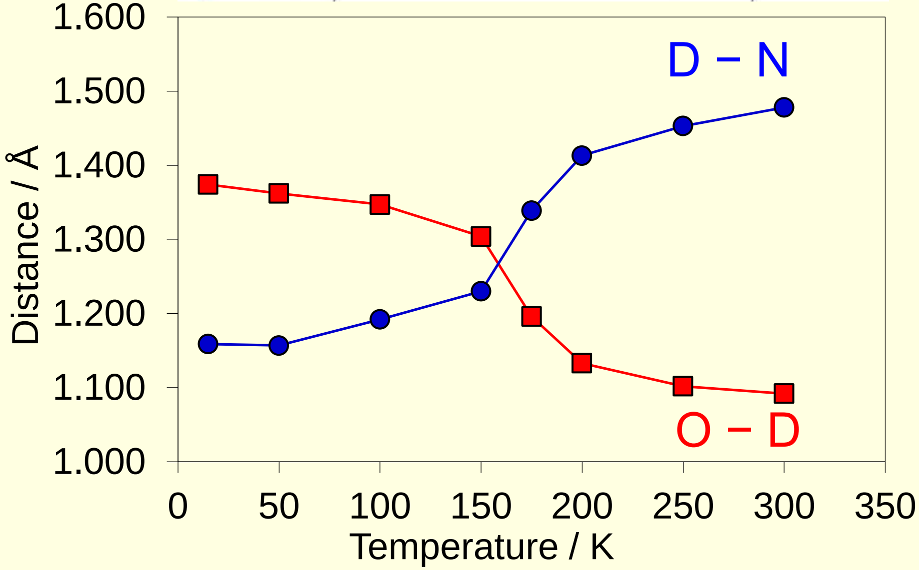
- 3,5 pyridine dicarboxylic acid
- Unusual difference between cell volumes of H and D isotopologues

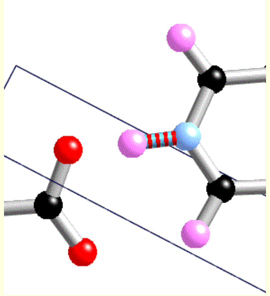


Single Crystal neutron diffraction

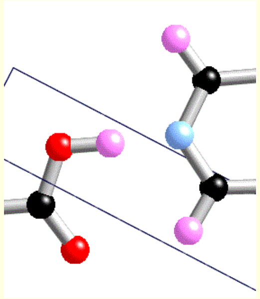








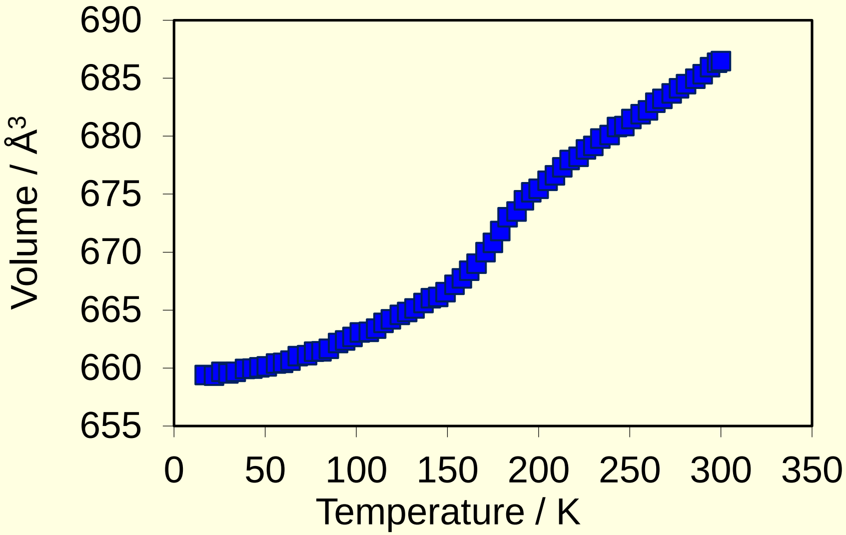
O · · · · D – N

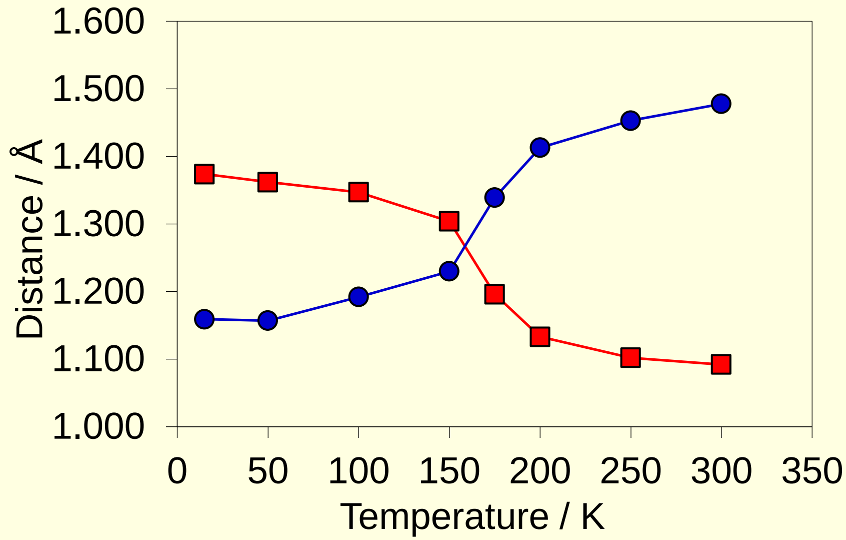


O – D · · · ·N

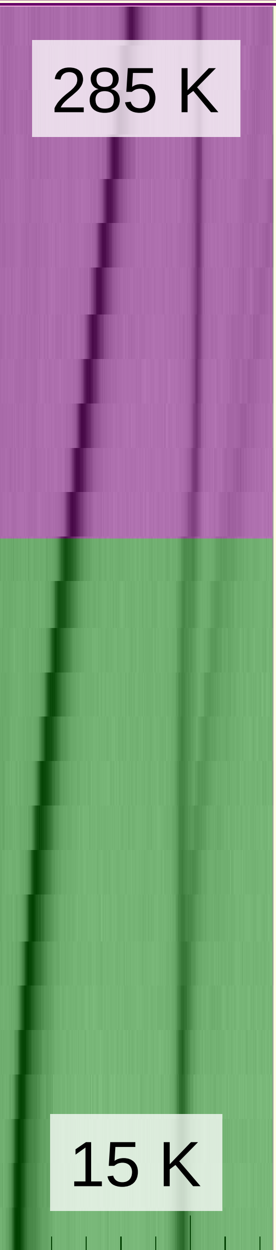
35-PDCA - Questions

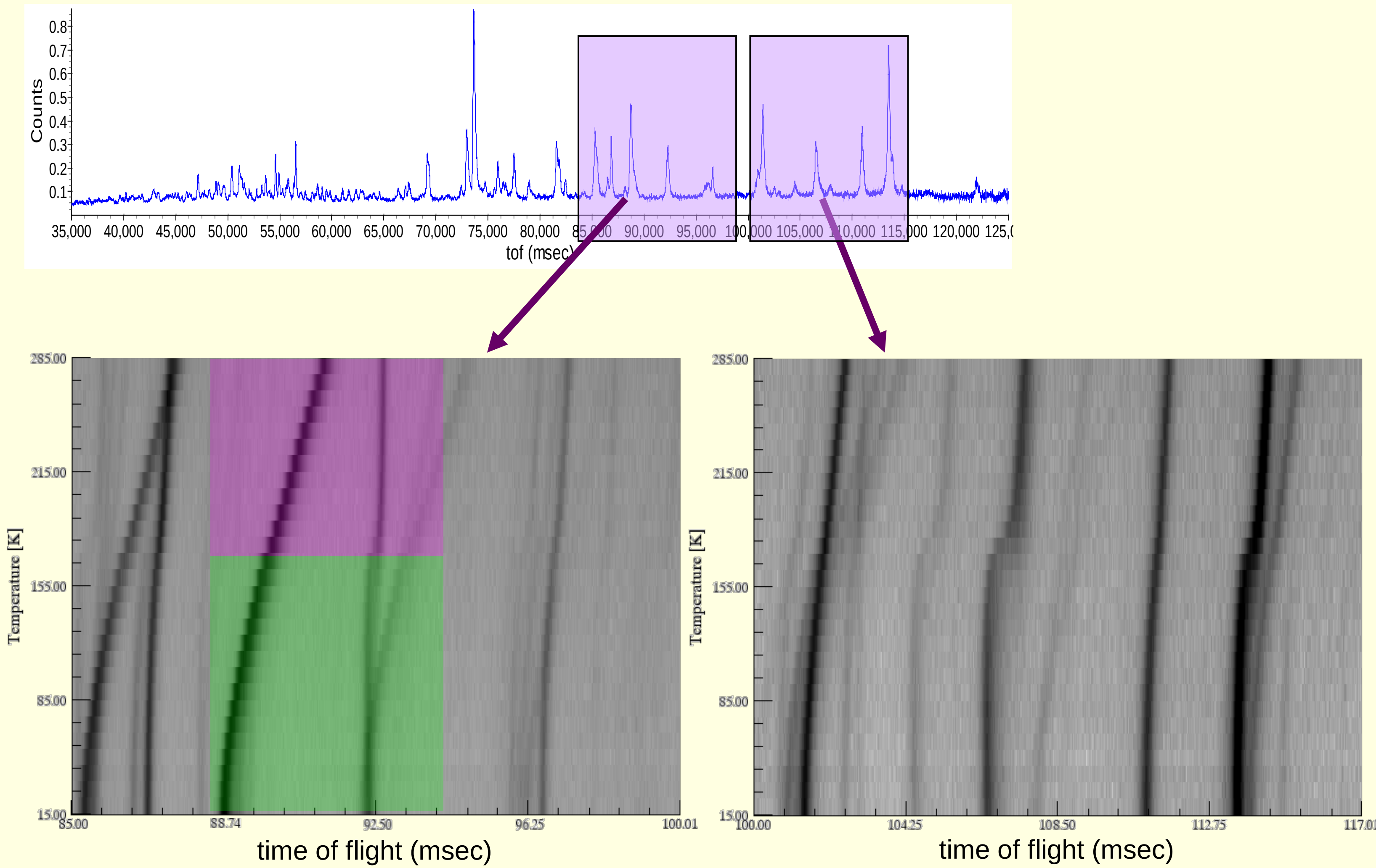
- Smooth effect or sharp phase transition?
- 1st or 2nd order?
- Isosymmetric phase transition



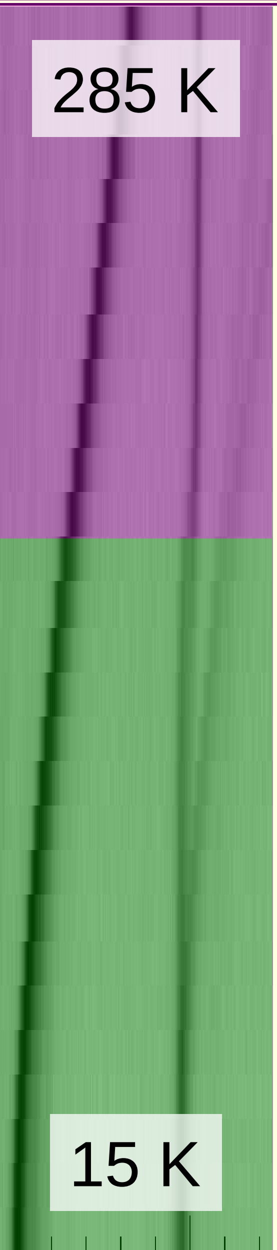


HRPD Observed Powder Data

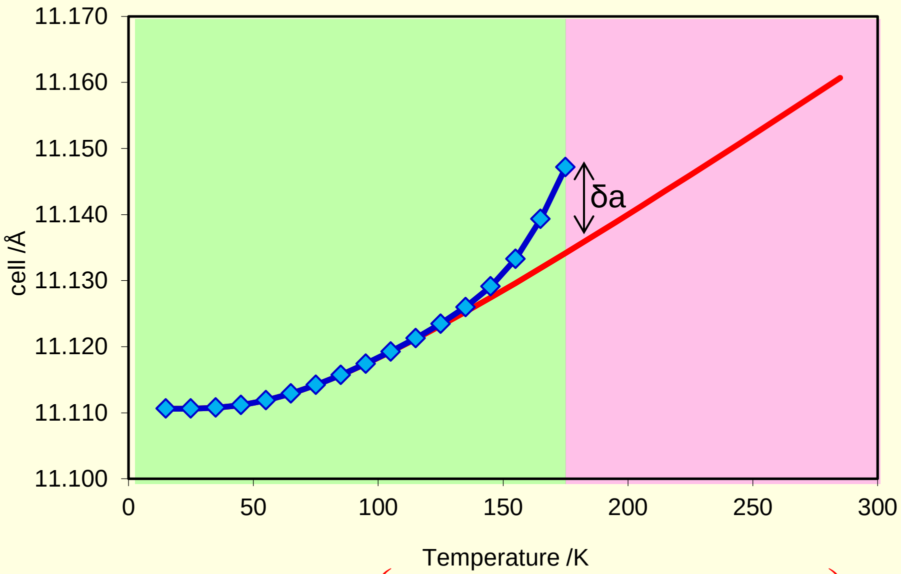




Parametric fitting

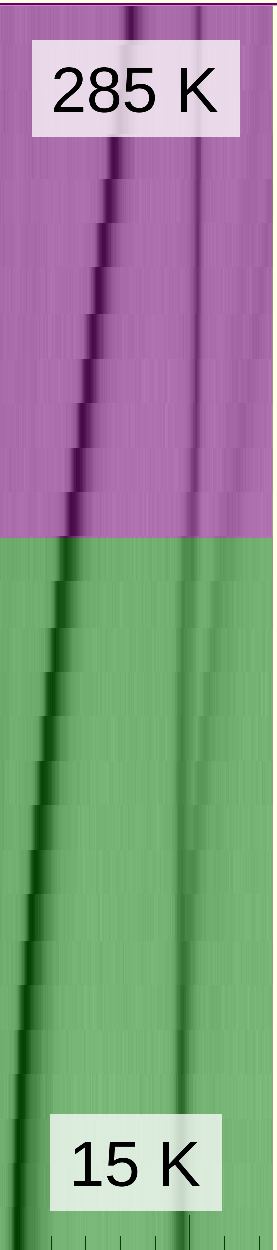


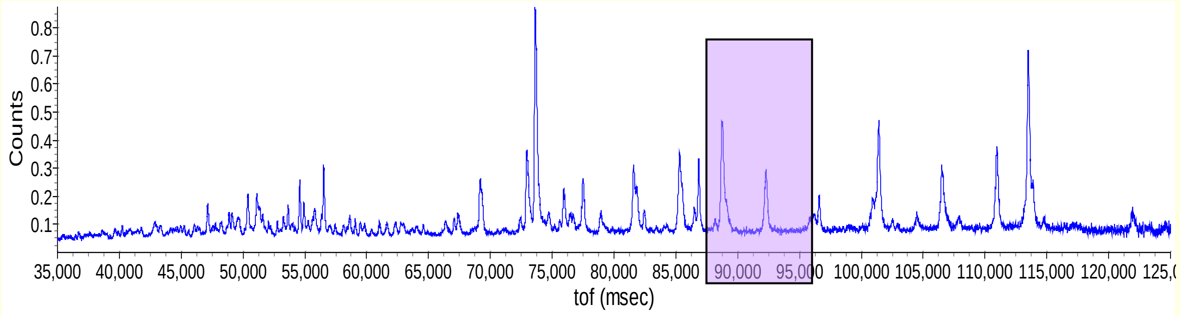
- 2 phase Rietveld refinement
- Assume each phase has a smooth evolution of cell parameters away from T_c
- Allow a critical excess cell close to T_c



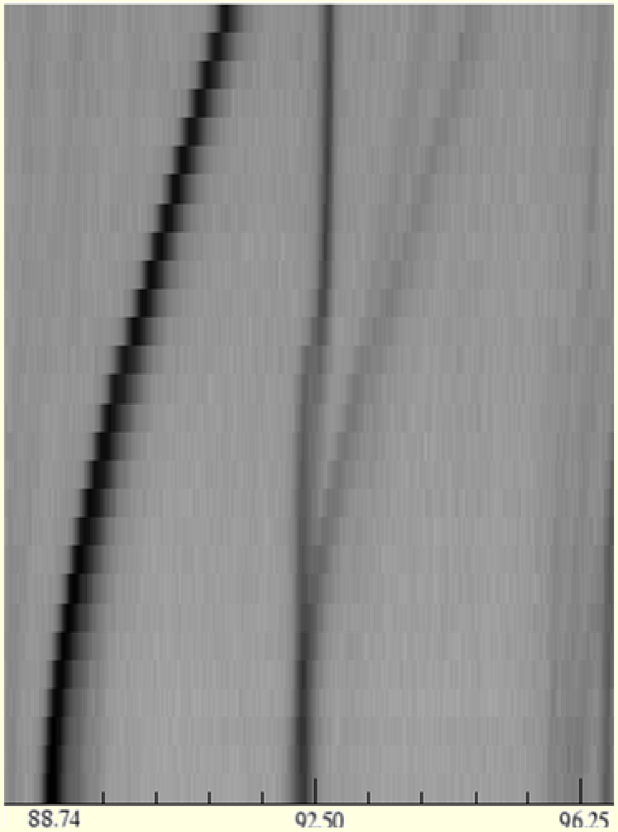
$$a(T) = Exp\left(\ln(a_0) + \frac{c_1\theta_1}{\exp(\theta_1/T)-1}\right) + c_2\exp\left(-c_3\left|T-T_c\right|^{\beta}\right)$$

Surface Rietveld

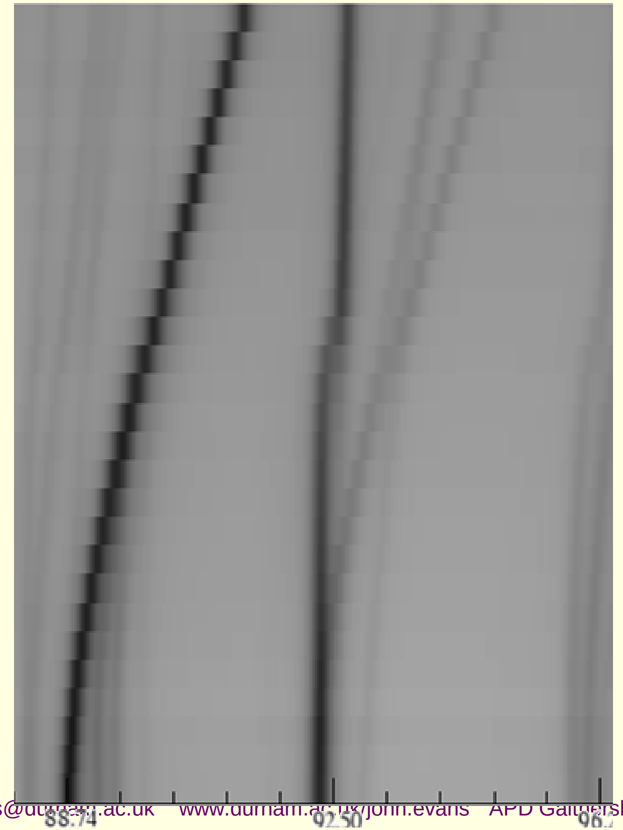




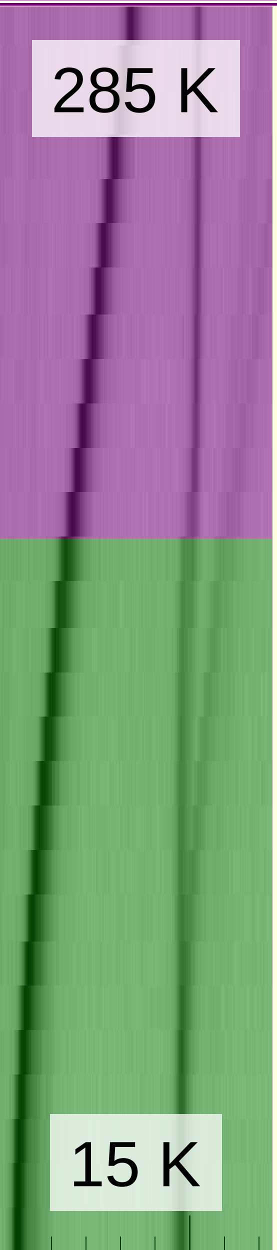
observed

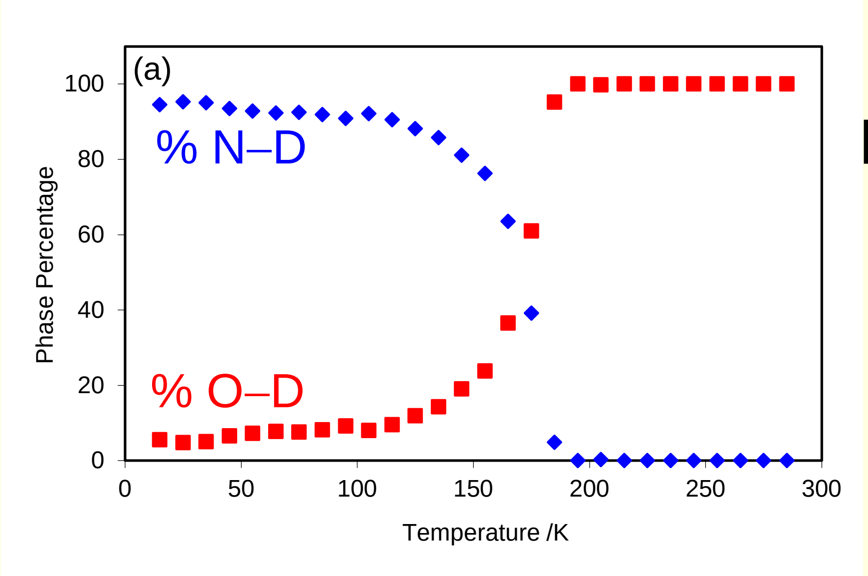


calculated

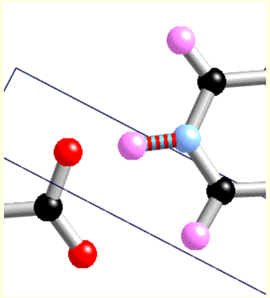


Results - 1

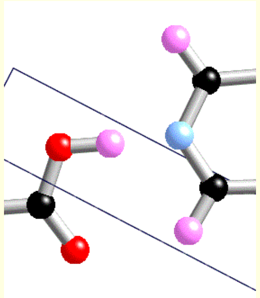




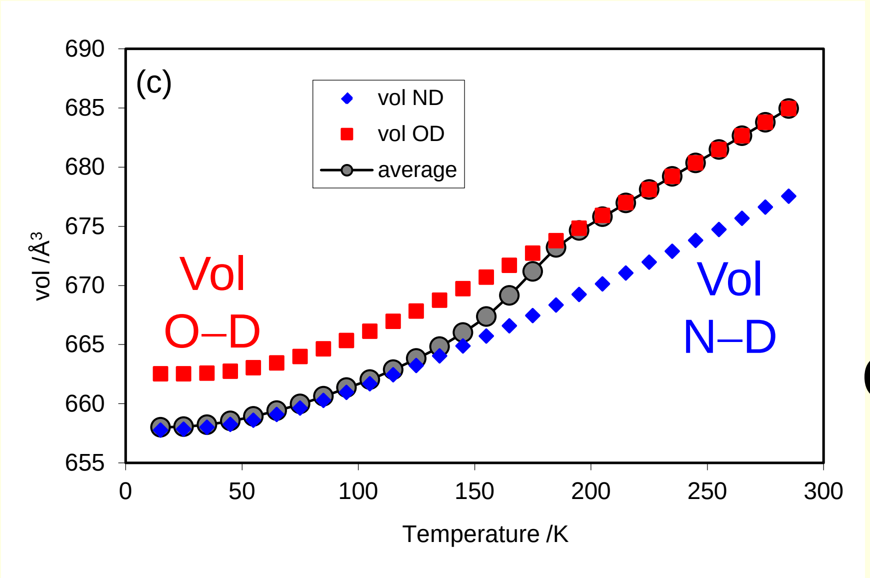
Phase Fractions



N–D

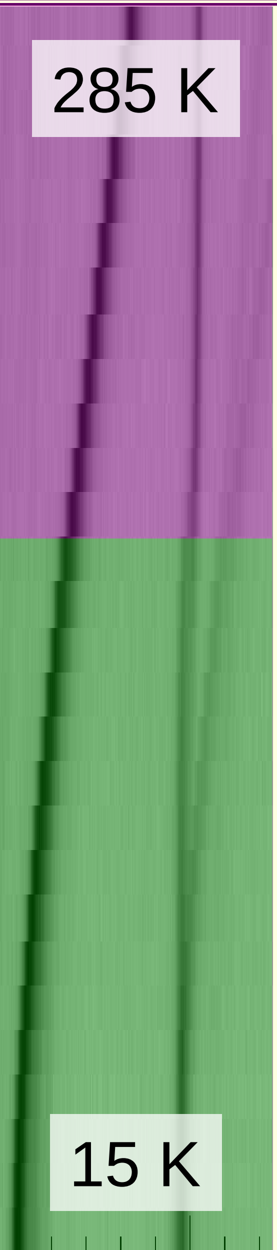


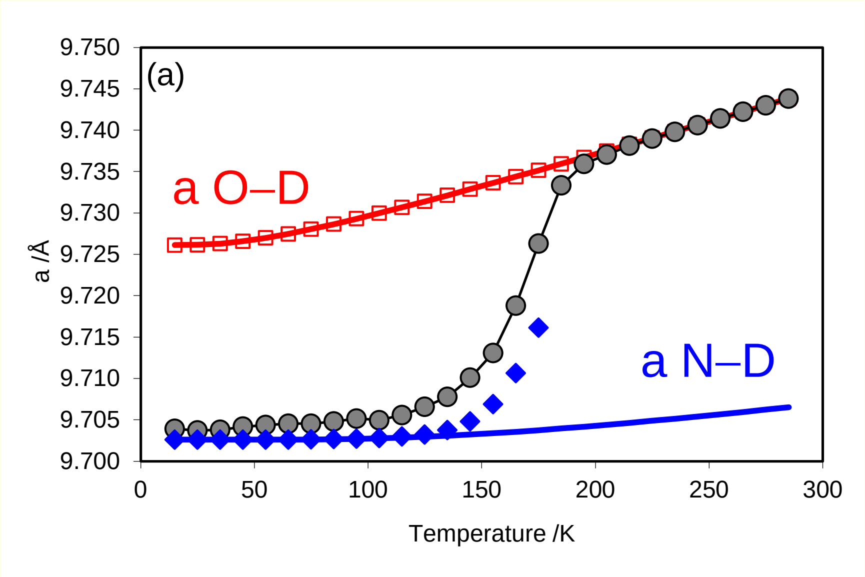
O–D



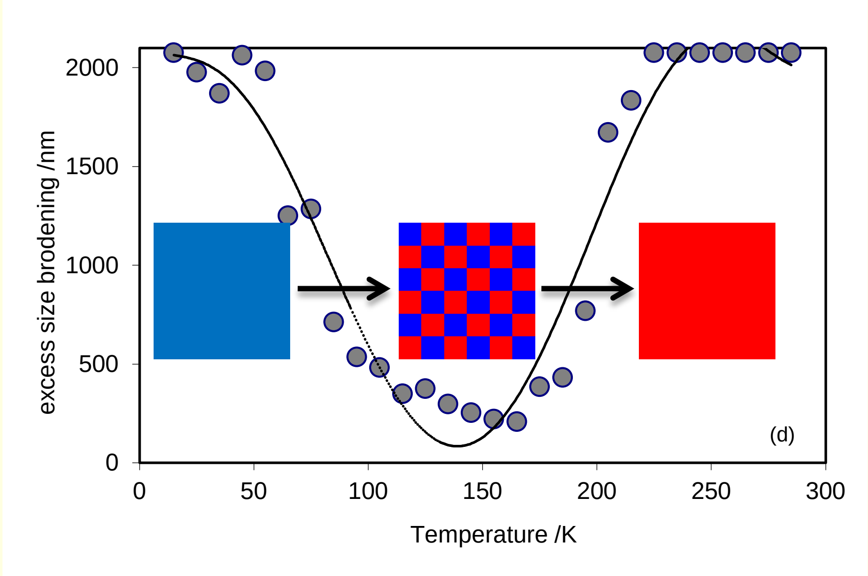
Cell Volumes

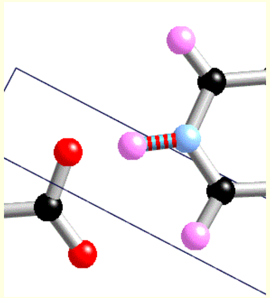
Results - 2



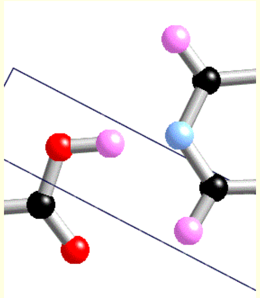


Unit cell param a





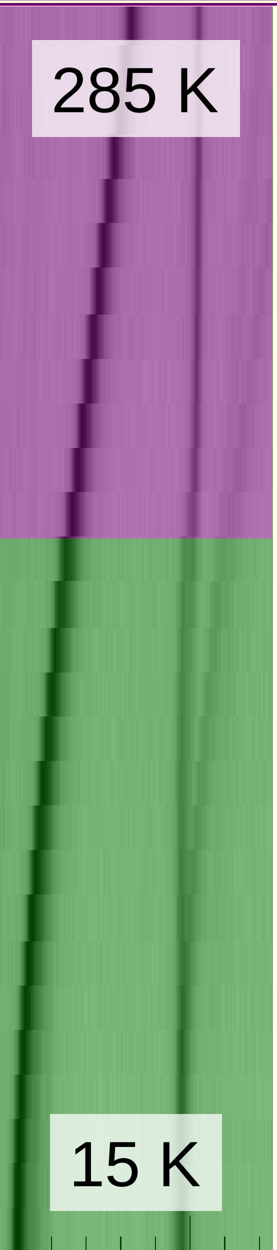
N–D



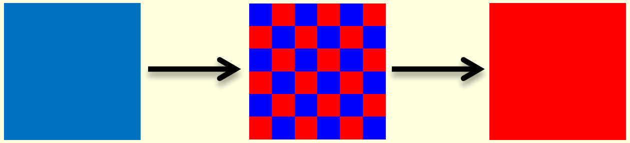
O–D

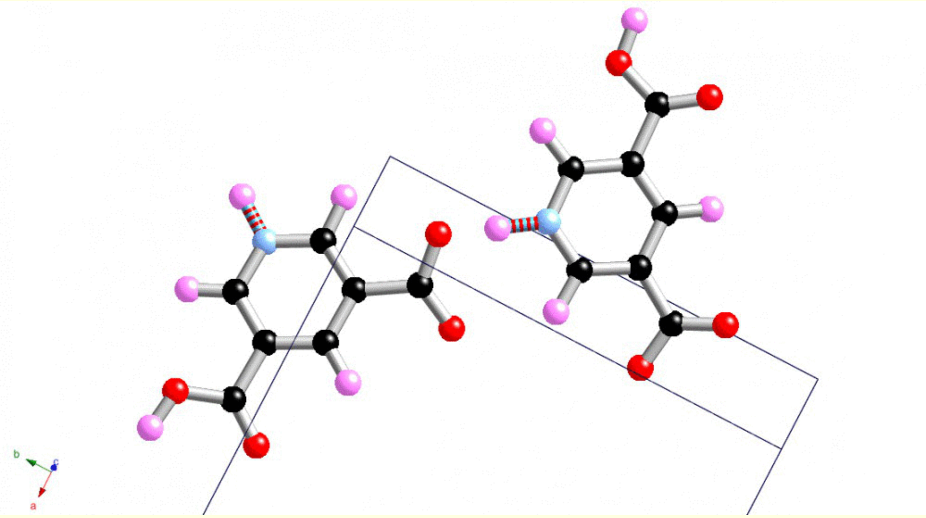
Size broadening

3,5-PDCA Summary



- 3,5 pyridine carboxylic acid
- Unusual proton migration
- Unusual isotopologue polymorphism

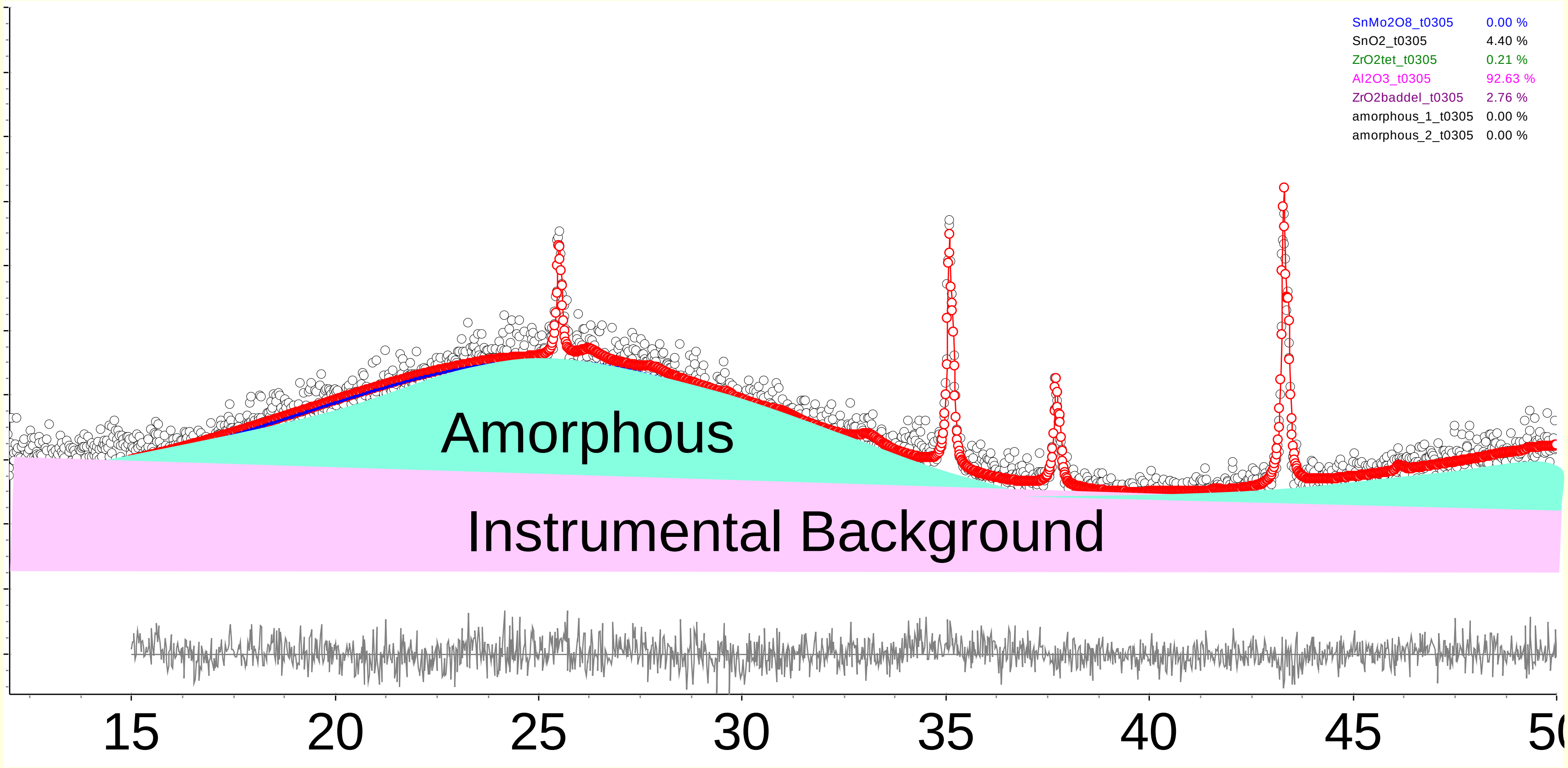




Example 3 – in situ synthesis

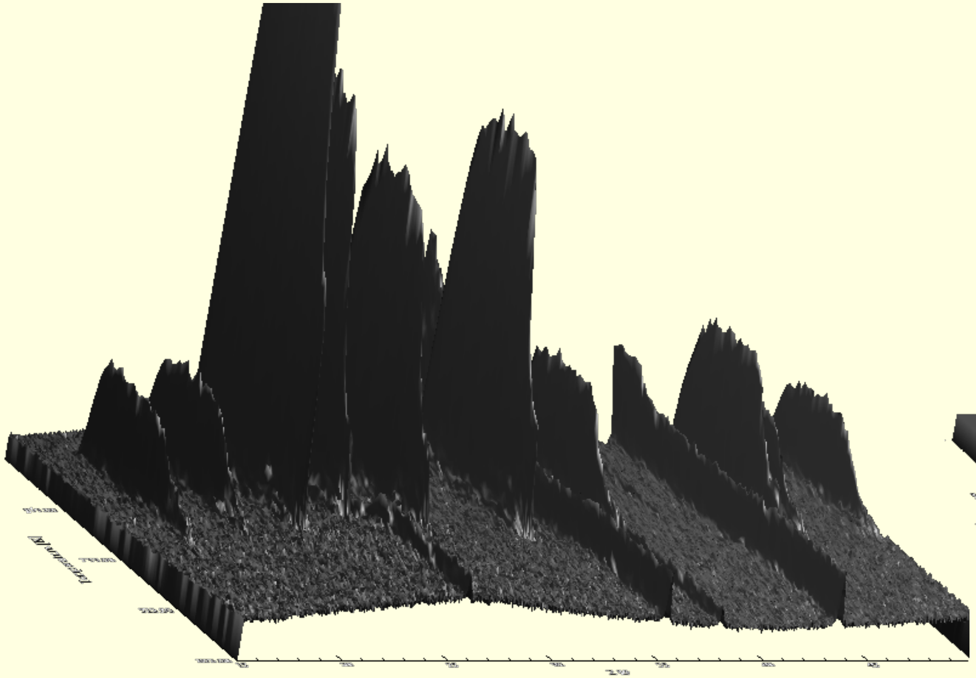
- Lab data following in situ synthesis
- Short 2-theta range
- Relatively quick data collections
- Several hundred data sets on each of 10 compositions
- Need to quantify several crystalline phases
- Need to quantify amorphous content

Quantify Amorphous Background?

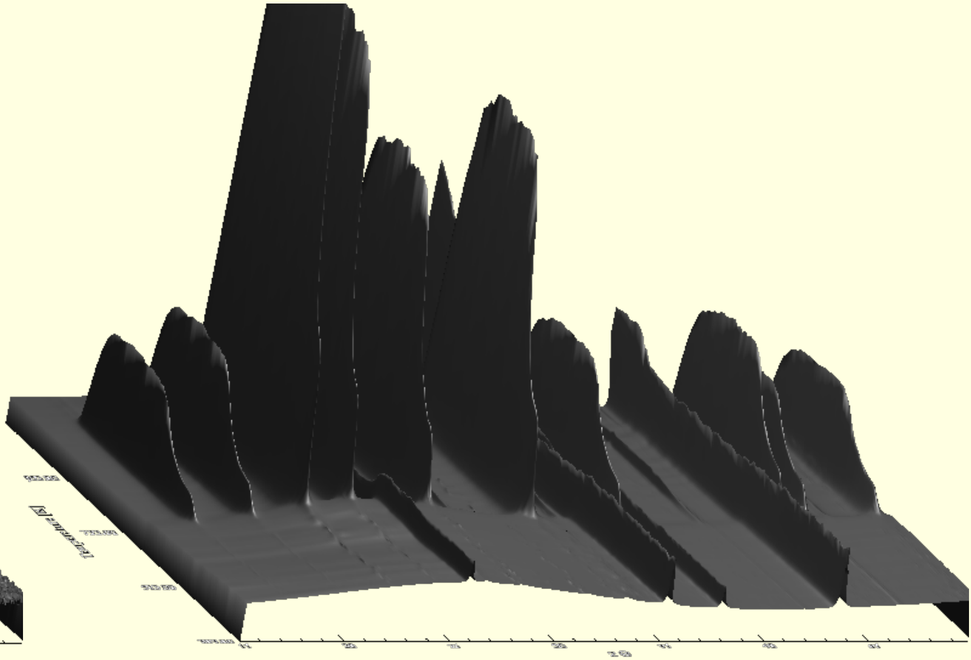


- Separate instrumental and amorphous (sample + diffuse) contributions to background?

Parametric Fitting

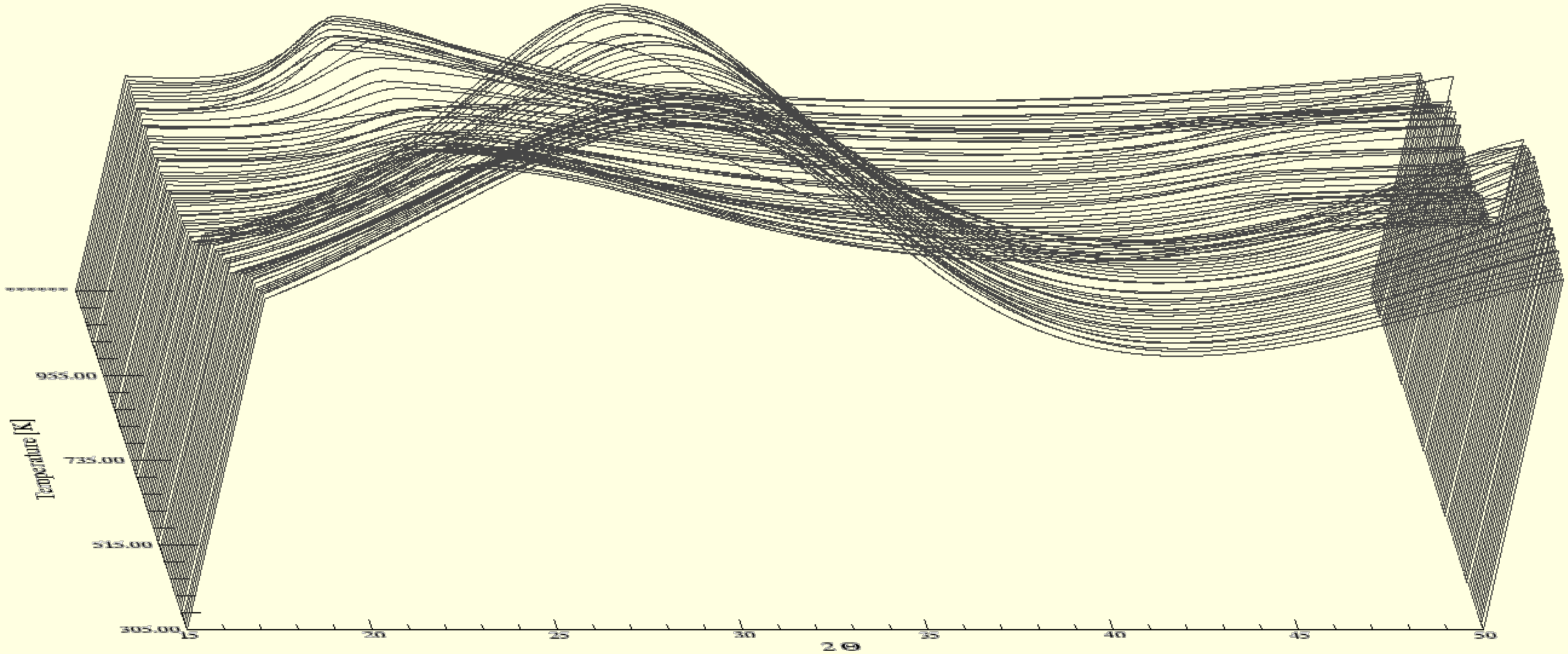


observed



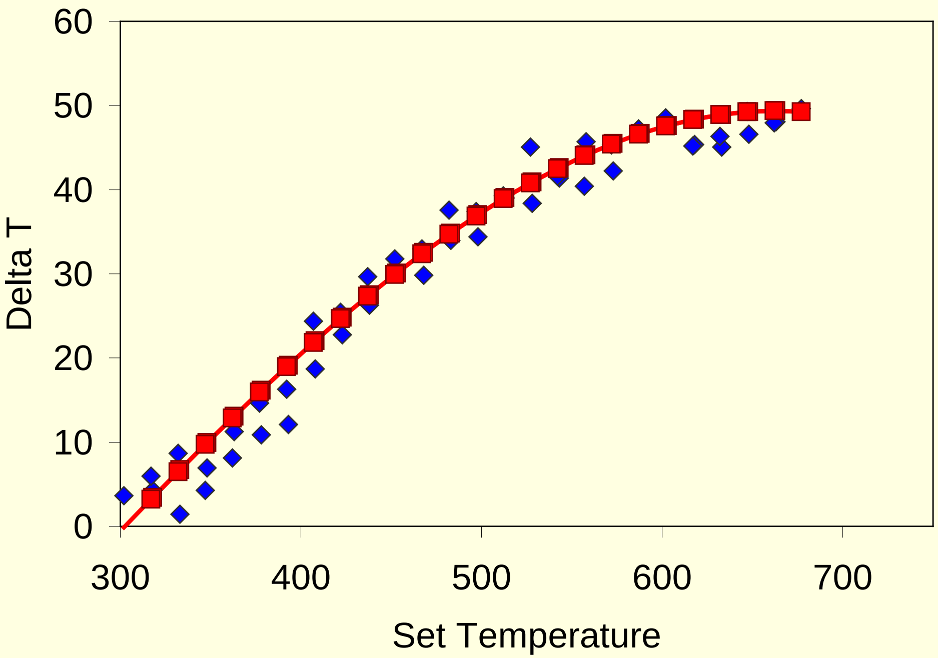
calculated

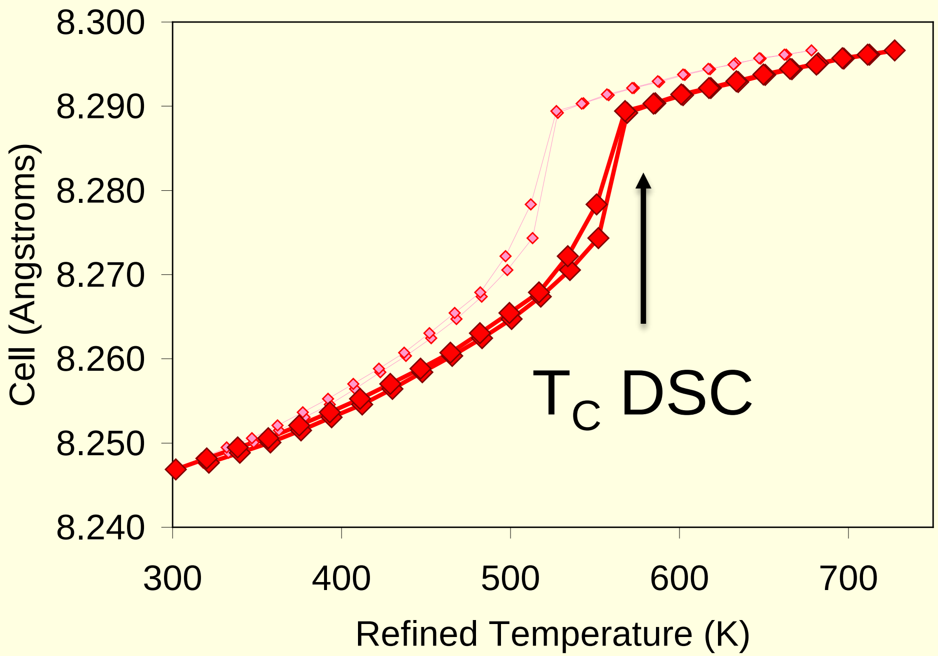
Parametric Fitting



Overall + Individually refined background

Temperature Calibration/Internal Standards





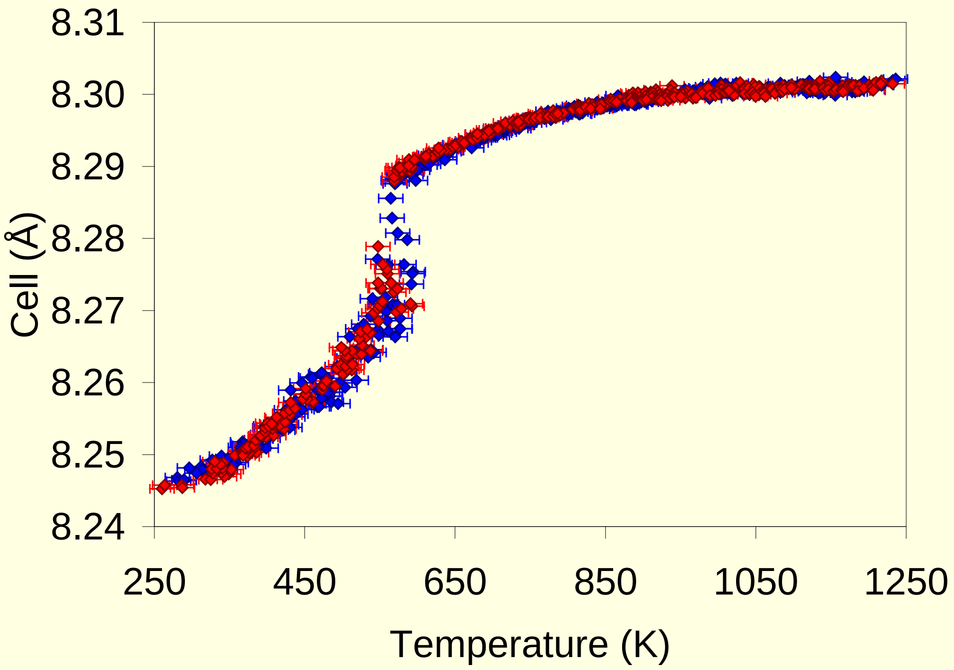
ΔT fit all data sets

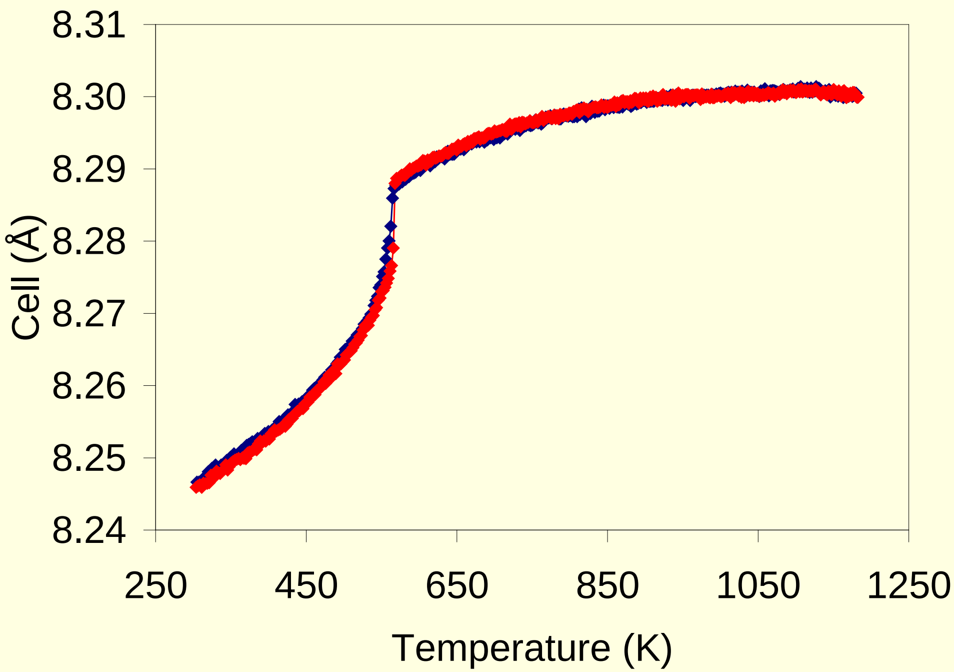
ΔT individual data sets

X-ray T_C < 567 K

DSC T_C = 565 K

Better Precision from Bad Data"

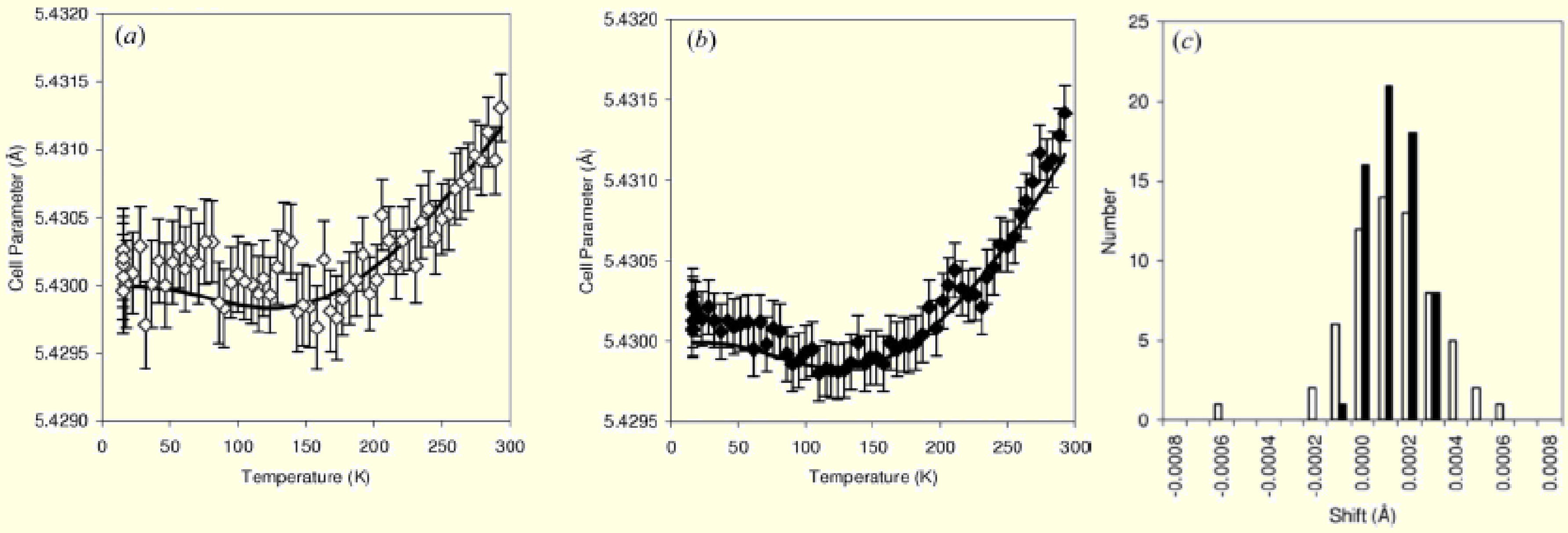




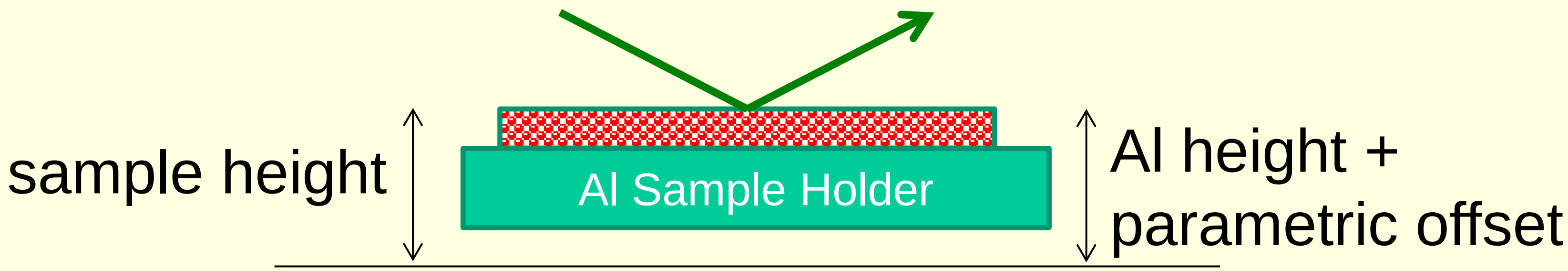
Individual Fitting
4.75 minutes

Surface Fitting
871*4.75 minutes
(~3 days)

Better Precision from Data



Parameterising sample height offset improves precision
Average esd 0.00028 to 0.00017 Å



When/What Should you Parameterise?

- When should you parameterise?
  - Rarely……5-10% of systems?
  - When you have poor data
  - When you have significant correlations
  - When you know the wrong answer
  - When you want to quickly test a model against 1000s of data sets
  - When you want to test if you're assumption is right/wrong

- What should you parameterise?
  - Information you're not particularly interested in
  - Information for which you're sure of model to apply

Acknowledgements!

Durham

Graham Stinton
Ivana Evans
Sam Ford
Anne Soleilhavoup
Ian Fall
Felicity Child
Sarah Tallentire
Liana Vella-Zarb

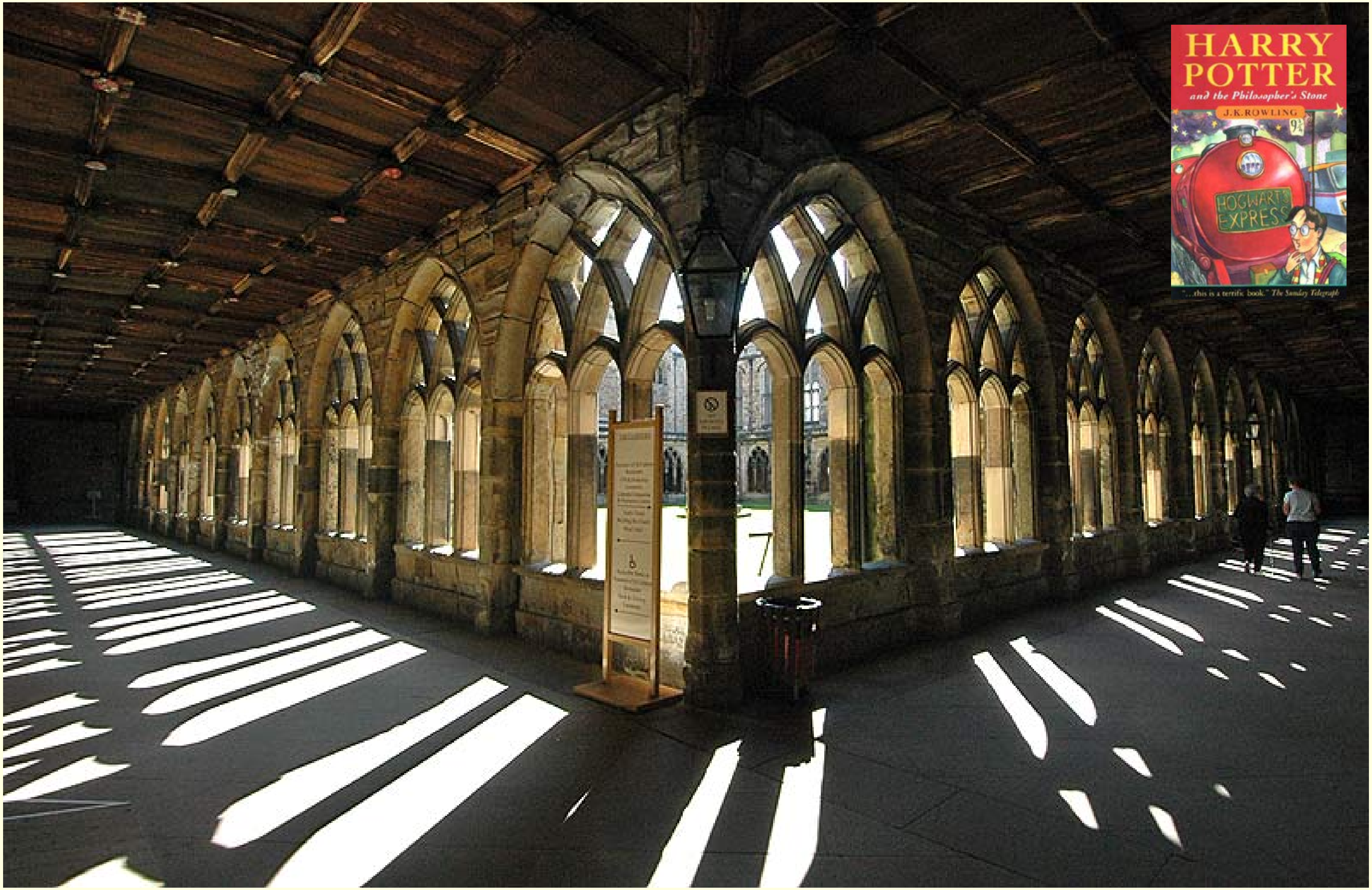
Elsewhere

Alan Coelho
Dave Billings
Mark Johnson
Garry McIntyre

Funding

EPSRC
University of Durham

Thank you!


HARRY
POTTER
and the Philosopher's Stone
J.K.ROWLING
HOGWARTS
EXPRESS
"...this is a terrific book." The Sunday Telegraph