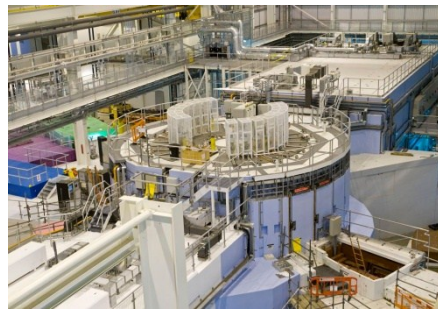




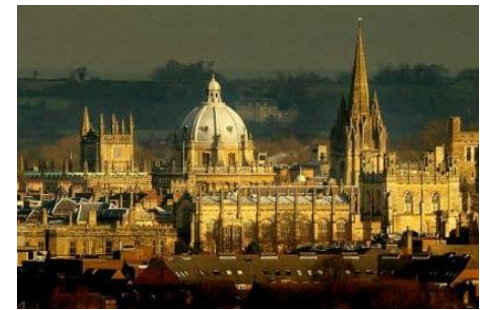
RAL: Diamond & ISIS



ISIS TSII



Oxford Chemistry



Oxford

# Powder diffraction: the best is yet to come, but...

Bill David,  
ISIS Facility, Rutherford Appleton Laboratory, UK &  
Inorganic Chemistry Laboratory, University of Oxford, UK



REPORT for Decade ending ..... April 2013 .....

Name: Powder diffraction

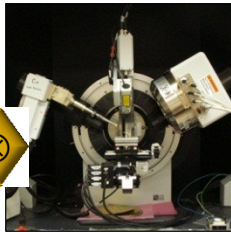
Age: 97

General observations	Excellent progress.
Technical subjects	Impressive new instruments with particular excellence in detectors and electronics. Has taken full advantage of Moore's Law.
Computer studies	Existing programs continue to perform well. Some extremely impressive new programs. Dabbling with new concepts.
Creative studies	Comes up with significant new creative ideas.
Attitude	Has matured and now has broadened interests.
Social skills	Very popular but can attract some unlikely characters with limited crystallographic skills.
Future prospects	Great potential - sure to go far.

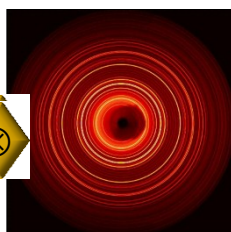
# Accuracy in Powder Diffraction



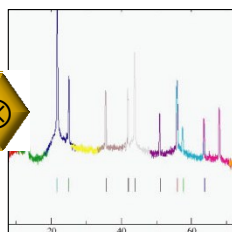
Sample preparation



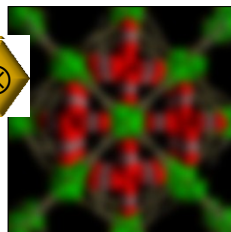
Instrument calibration



Data collection



Data reduction

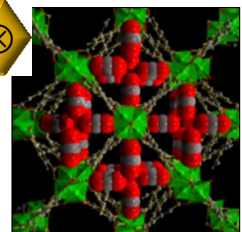


Structural model

```

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R4 = 0.015
R5 = 0.015
R6 = 0.015
R7 = 0.015
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R10 = 0.015
R11 = 0.015
R12 = 0.015
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R85 = 0.015
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R88 = 0.015
R89 = 0.015
R90 = 0.015
R91 = 0.015
R92 = 0.015
R93 = 0.015
R94 = 0.015
R95 = 0.015
R96 = 0.015
R97 = 0.015
R98 = 0.015
R99 = 0.015
R100 = 0.015
    
```

Data analysis



Validation

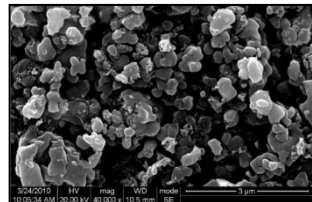




# Real Crystallography of Real Materials under Real Conditions



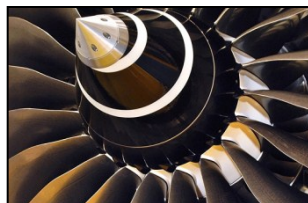
ball milling –  
a black art!



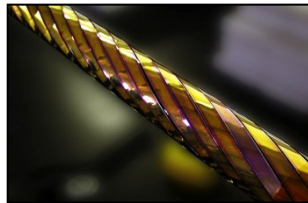
Li battery cathode



pharmaceuticals



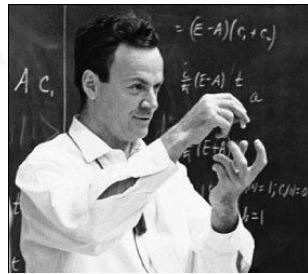
turbine blade



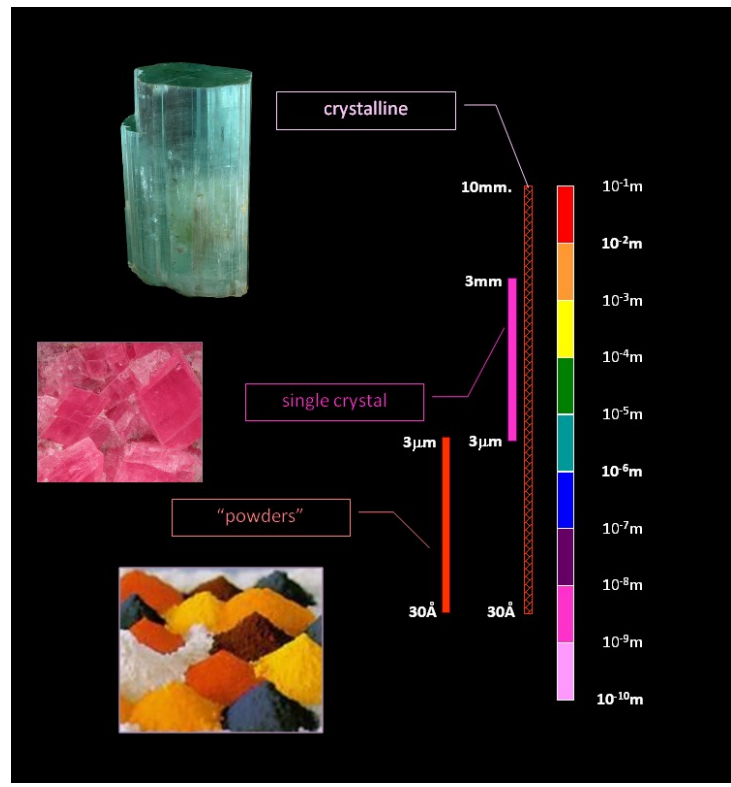
superconducting cable



pencil "lead"



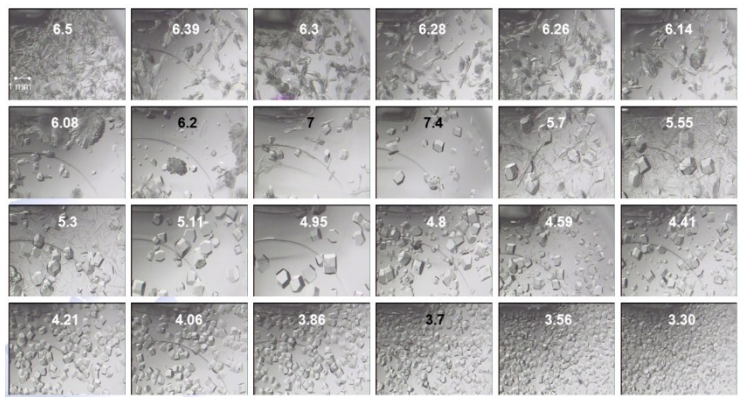
Richard P. Feynman (Dec 1959)



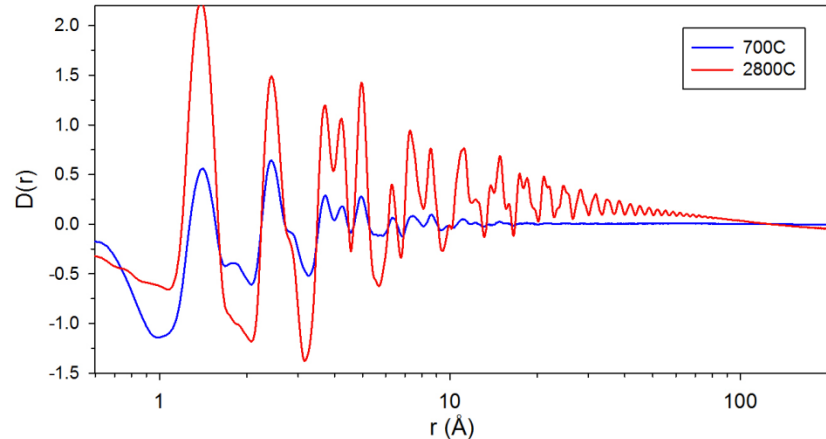
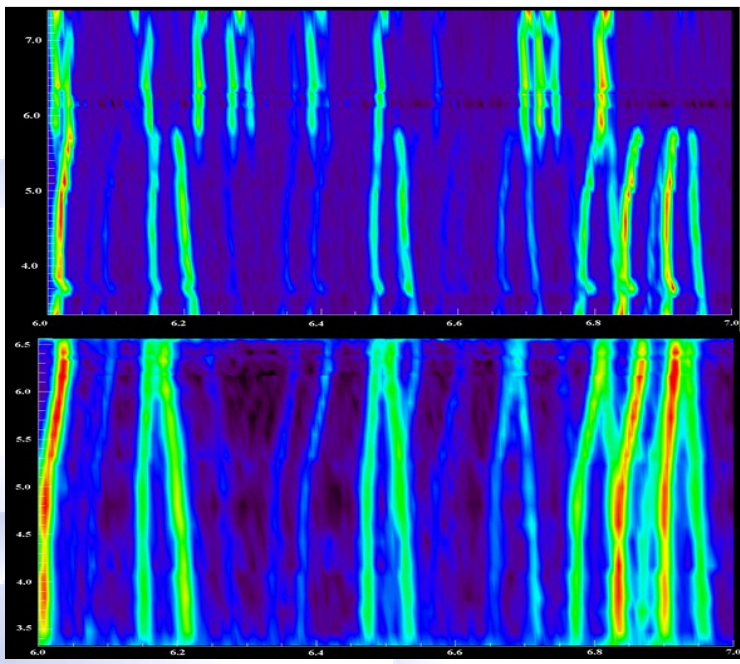
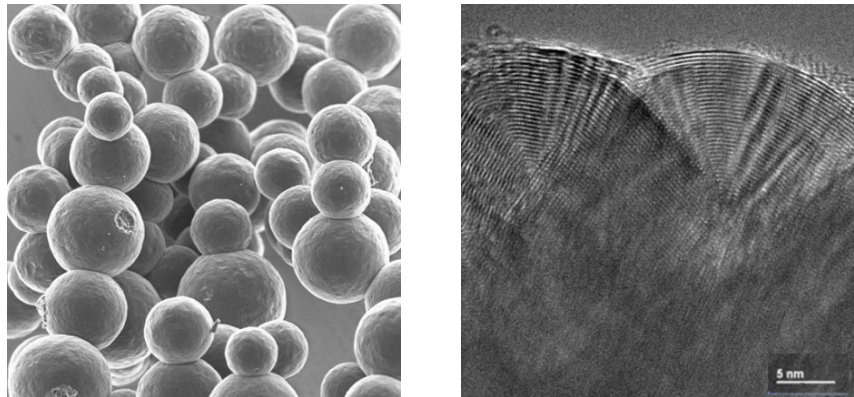
**There's Plenty of Room at the Bottom**  
An invitation to explore  
21st century science and technology.

# Real Crystallography of Real Materials under Real Conditions

Parametric proteins (Margiolaki & Wright)



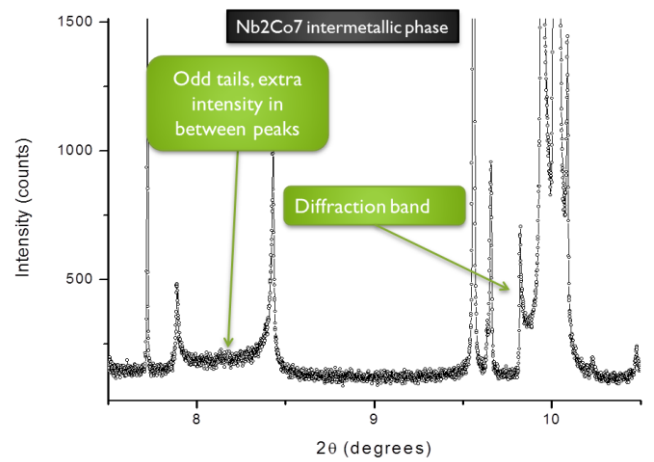
Diamond-hard graphite



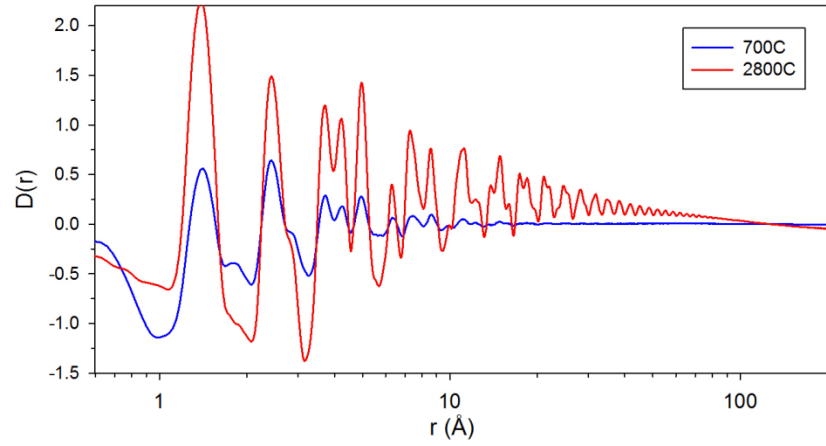
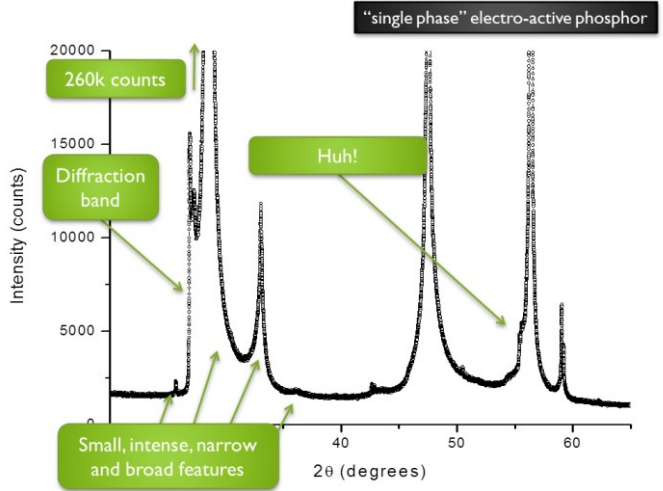
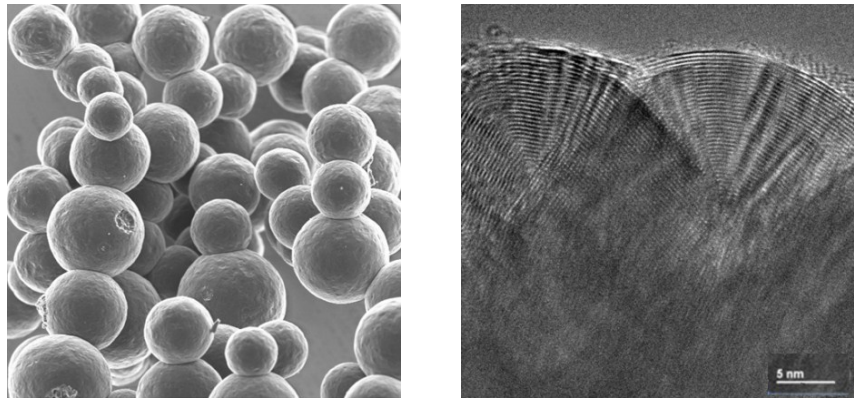
Pol, Wen, Lau, Callear, Bowron, Lin, Deshmukh, Sankaranarayanan, Curtiss, David, Miller & Thackeray, Carbon (submitted)

# Real Crystallography of Real Materials under Real Conditions

Structure & microstructure (Leoni)



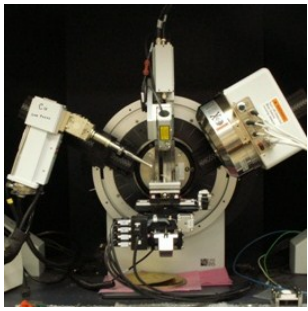
Diamond-hard graphite



Pol, Wen, Lau, Callear, Bowron, Lin, Deshmukh, Sankaranarayanan, Curtiss, David, Miller & Thackeray, Carbon (submitted)



# Instrumentation



X-ray diffractometer



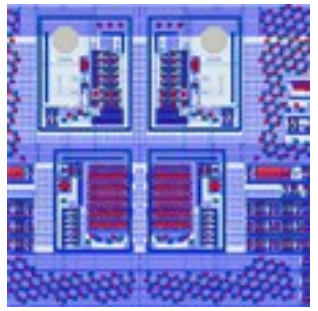
WISH detectors



PILATUS



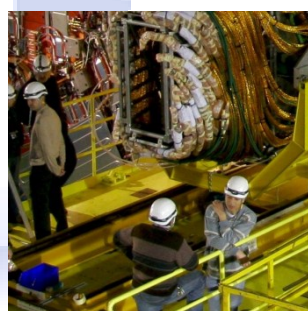
ISIS electronics



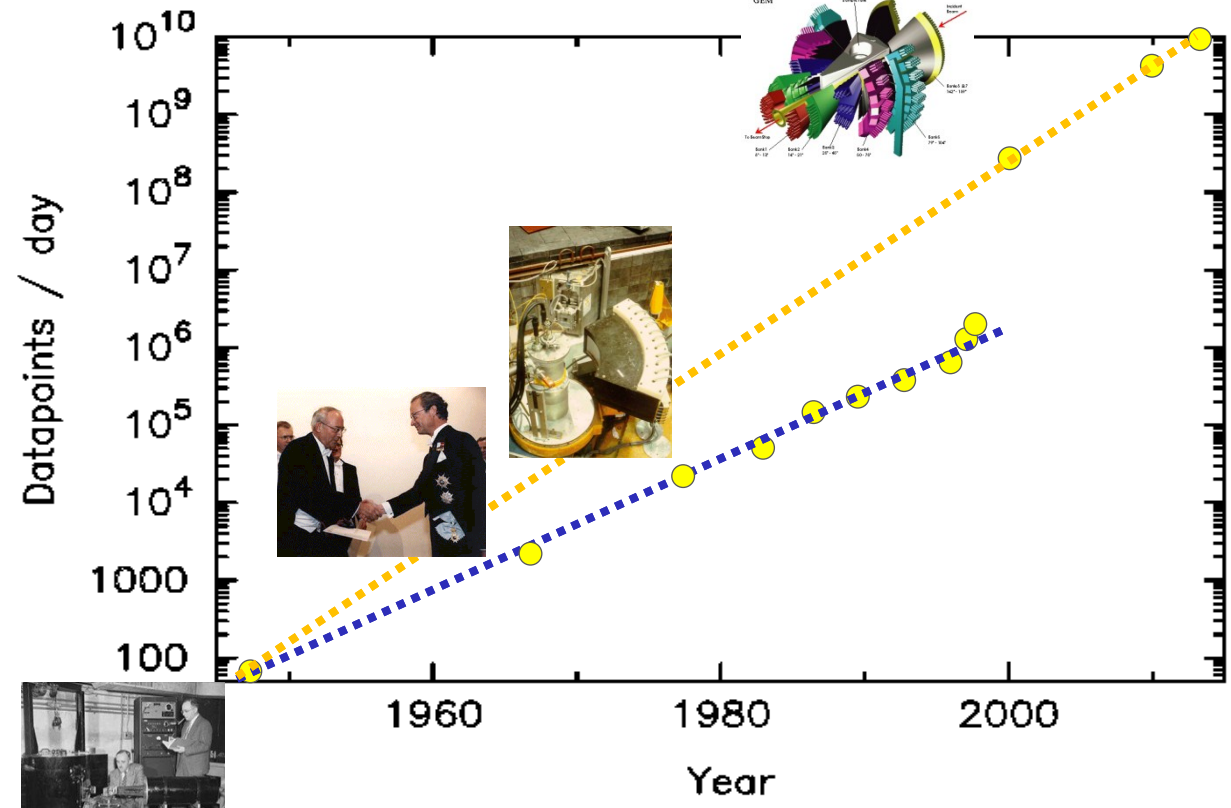
PILATUS electronics



CMS @ CERN

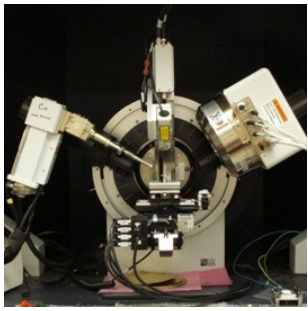


CMS @ CERN (II)



APD IV, 22-25 April 2013, NIST

# Instrumentation



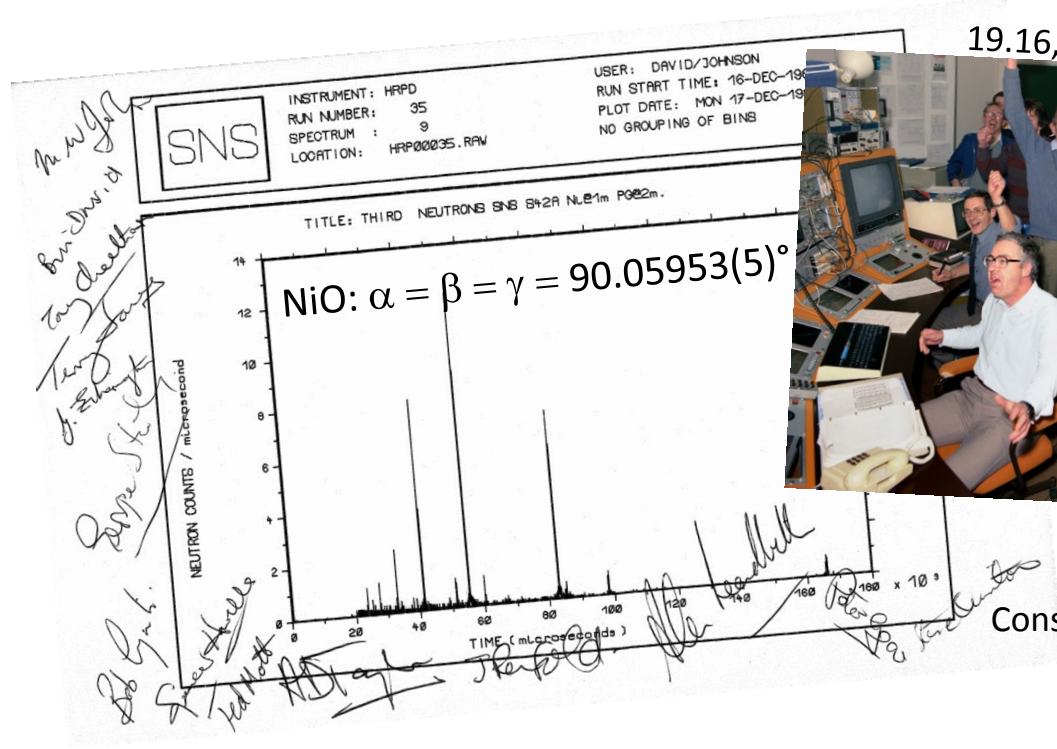
X-ray diffractometer



Diamond and ISIS



ISIS TS2

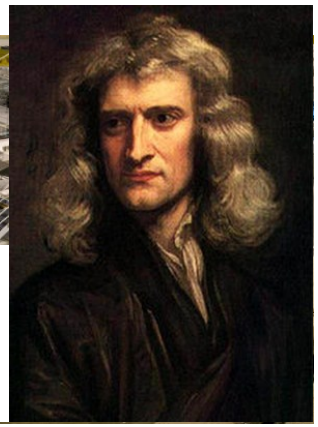


19.16, 16<sup>th</sup> December 1984



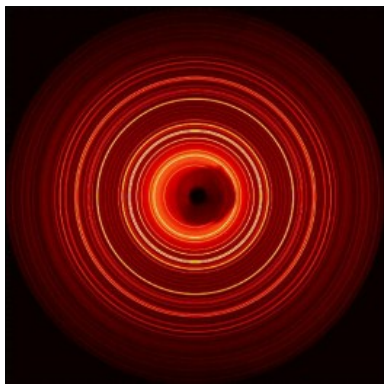
Consider the magnitude of the endeavour ...

Isaac Newton





# Data collection



Exploring the limits

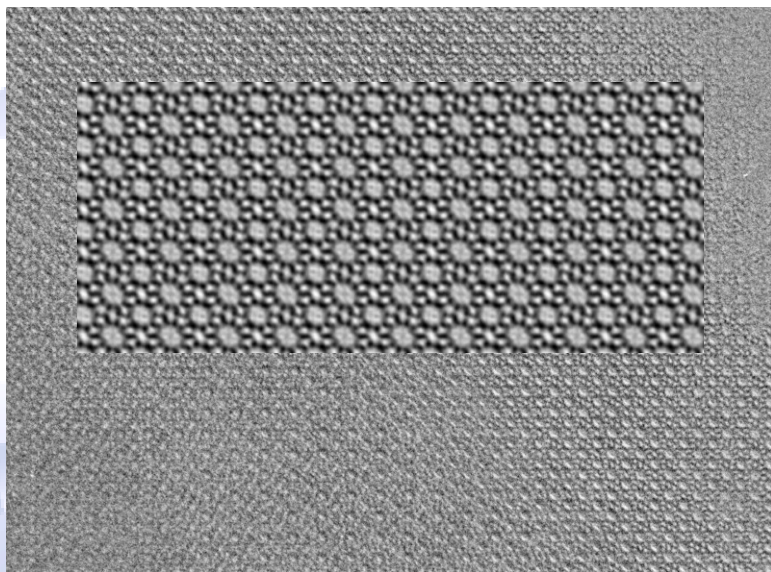
How complicated a structure can I obtain from a powder diffraction pattern? Is there a limit?

How many peaks are there in a powder diffraction pattern?

Jon Wright

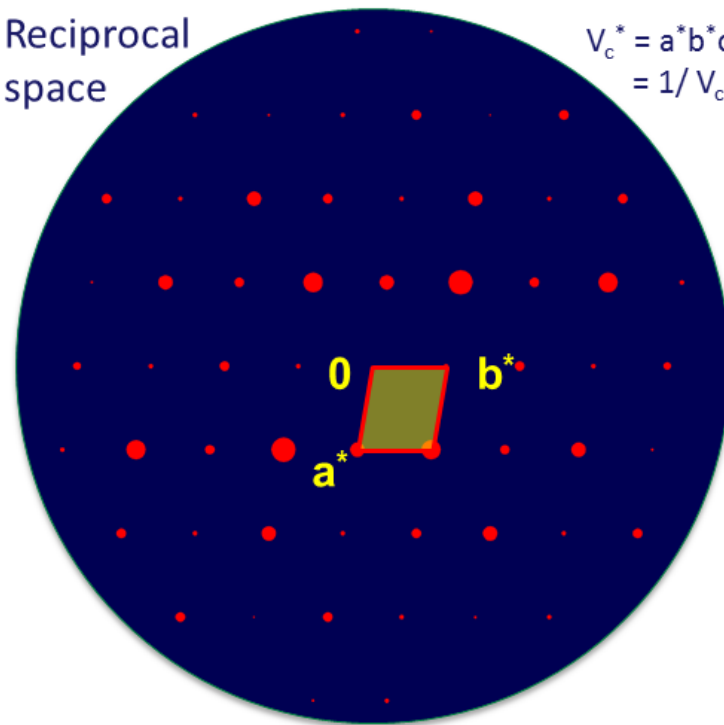
Real space

$$V_c = abc \sin(\gamma)$$



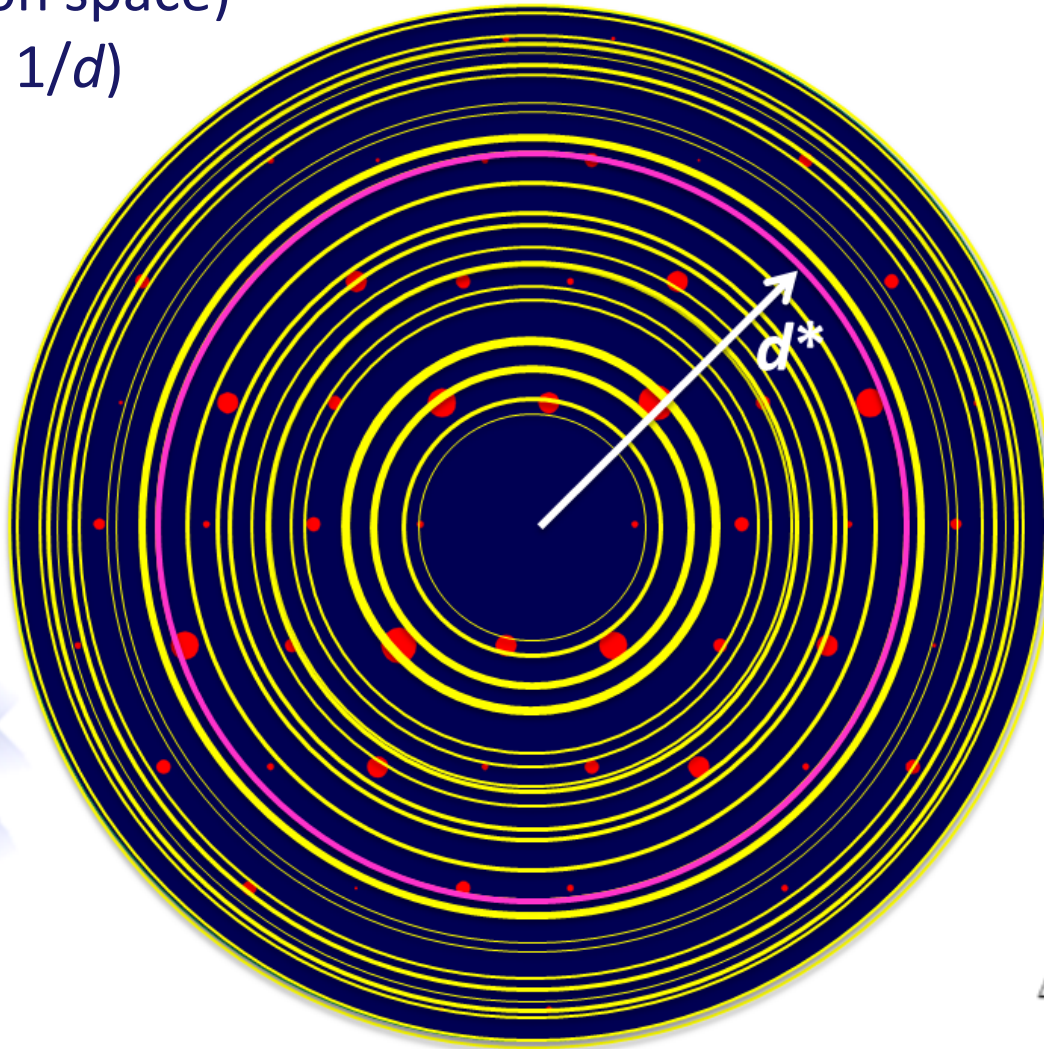
Reciprocal space

$$V_c^* = a^*b^*c^* \sin(\gamma^*) = 1/V_c$$



# Limits

Reciprocal space  
(diffraction space)  
( $d^* = 1/d$ )



$$V^* = \frac{4}{3} \pi d^{*3}$$

$$N_{\text{ref}} = \frac{4}{3} \pi d^{*3} / V_c^*$$

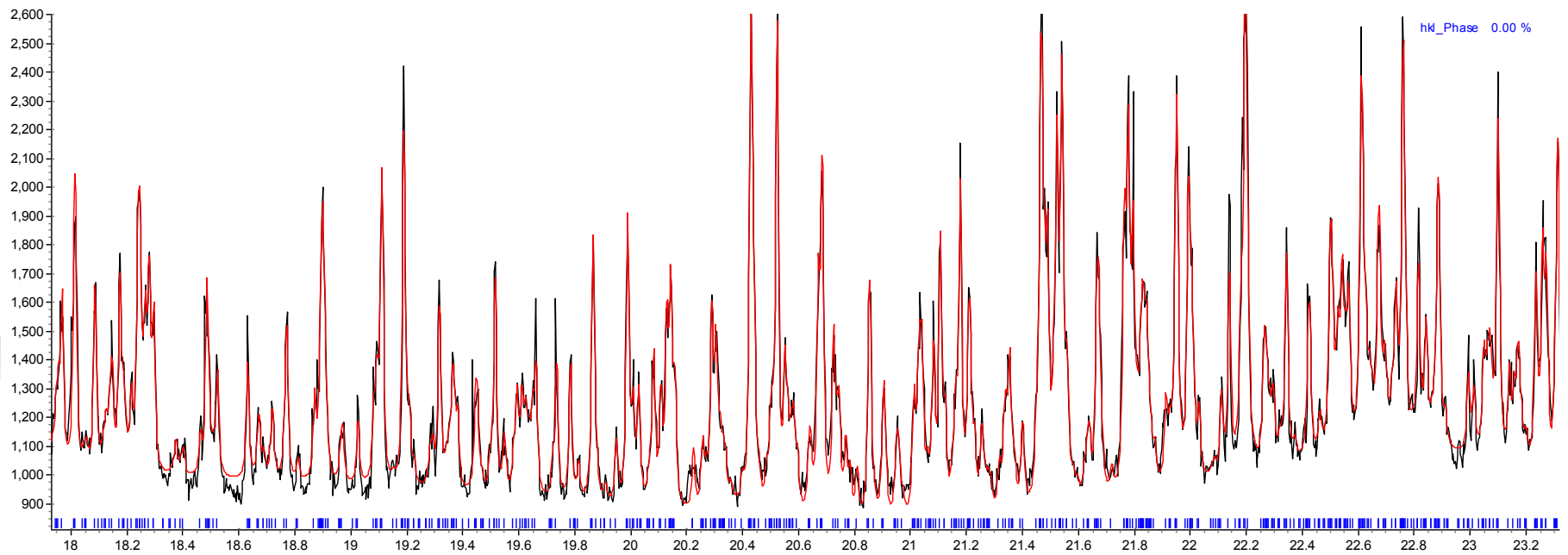
$$= \frac{4}{3} \pi V_c d^{*3}$$

$$N_{\text{ref}} = \frac{2}{3} \pi V_a d^{*3}$$

$$\Delta N = 2\pi V_a d^{*2} \Delta d^*$$



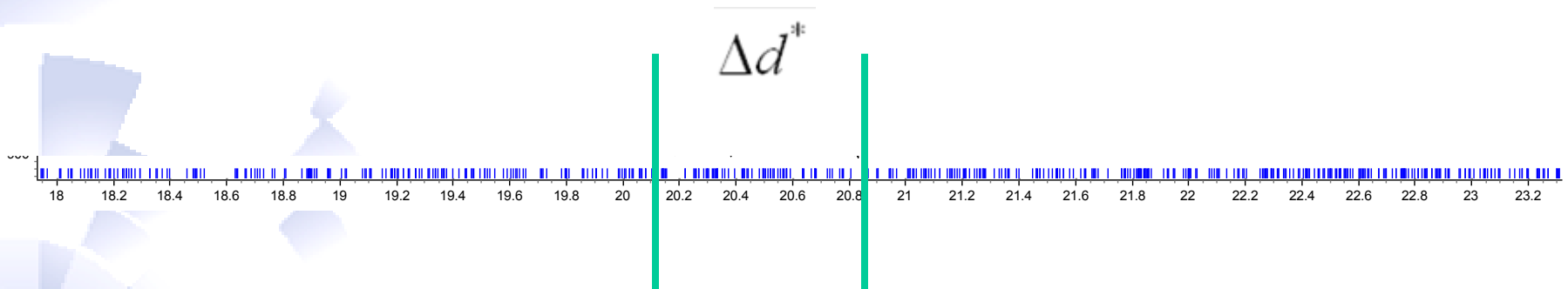
# Limits



# Limits

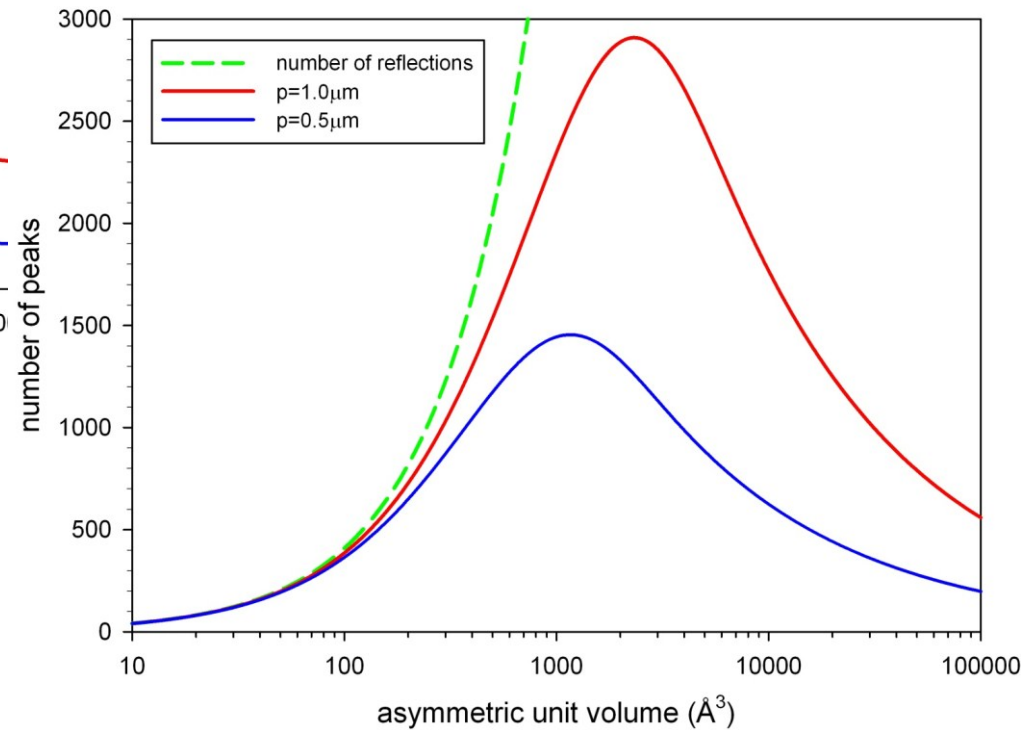
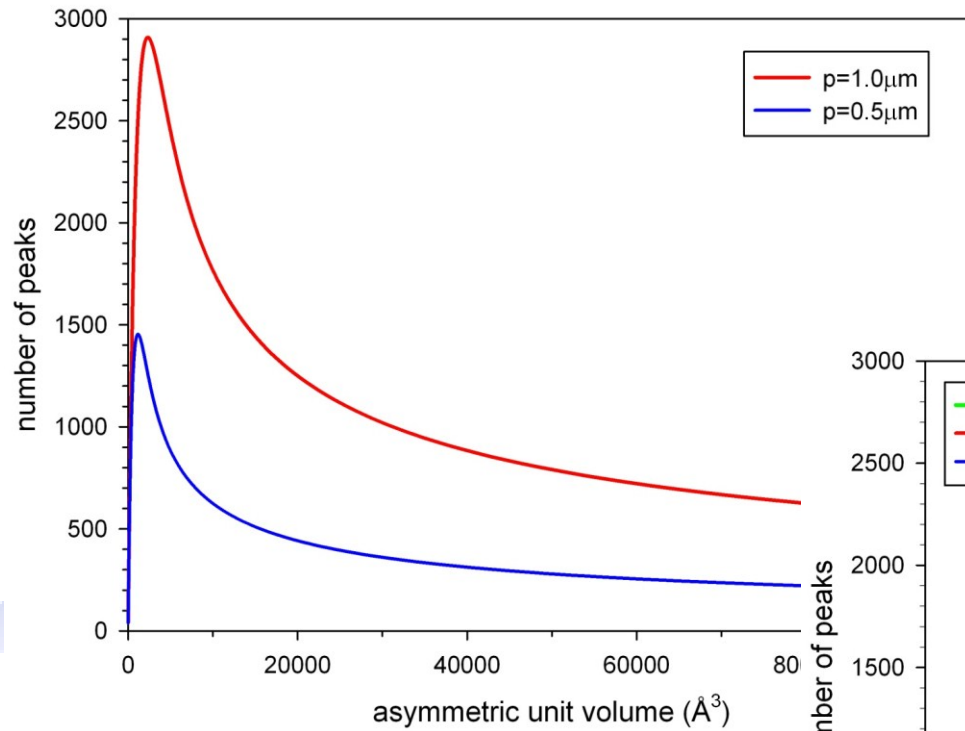
$$N_{peaks} \approx \int_0^{d_{max}^*} \Delta N(d^*) \exp(-\Delta N(d^*)/p) dd^*$$

$$p(\delta d^*) = \exp(-\Delta N \delta d^*) \quad \Delta N = 2\pi V_a d^{*2} \Delta d^*$$





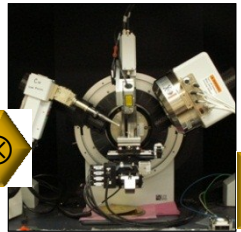
# Limits



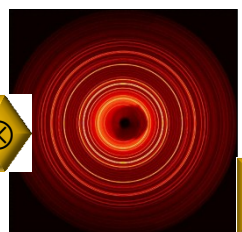
# Achieving precision and accuracy



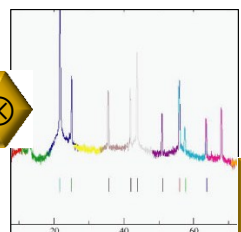
Sample preparation



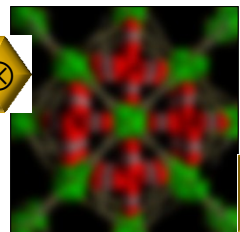
Instrument calibration



Data collection



Data reduction

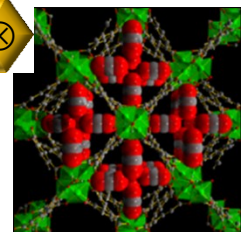


Structural model

A screenshot of a software interface for data analysis, showing a list of parameters and their values.

Cell	cell_001_000_000	=	unit1
Cell	cell_002_000_000	=	unit1
Cell	cell_003_000_000	=	unit1
Cell	cell_004_000_000	=	unit1
Cell	cell_005_000_000	=	unit1
Cell	cell_006_000_000	=	unit1
Cell	cell_007_000_000	=	unit1
Cell	cell_008_000_000	=	unit1
Cell	cell_009_000_000	=	unit1
Cell	cell_010_000_000	=	unit1
Cell	cell_011_000_000	=	unit1
Cell	cell_012_000_000	=	unit1
Cell	cell_013_000_000	=	unit1
Cell	cell_014_000_000	=	unit1
Cell	cell_015_000_000	=	unit1
Cell	cell_016_000_000	=	unit1
Cell	cell_017_000_000	=	unit1
Cell	cell_018_000_000	=	unit1
Cell	cell_019_000_000	=	unit1
Cell	cell_020_000_000	=	unit1
Cell	cell_021_000_000	=	unit1
Cell	cell_022_000_000	=	unit1
Cell	cell_023_000_000	=	unit1
Cell	cell_024_000_000	=	unit1
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Cell	cell_026_000_000	=	unit1
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Cell	cell_028_000_000	=	unit1
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Cell	cell_032_000_000	=	unit1
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Cell	cell_098_000_000	=	unit1
Cell	cell_099_000_000	=	unit1
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Data analysis



Validation



# The structural (and microstructural) model

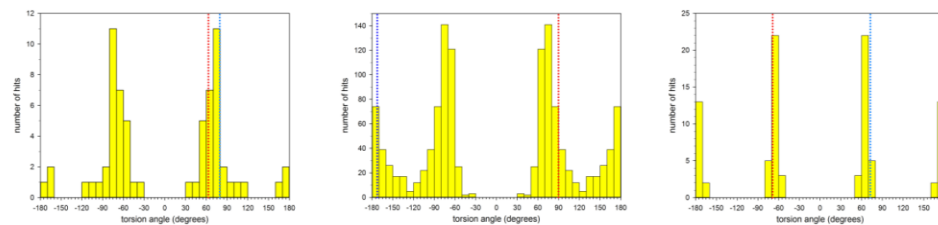
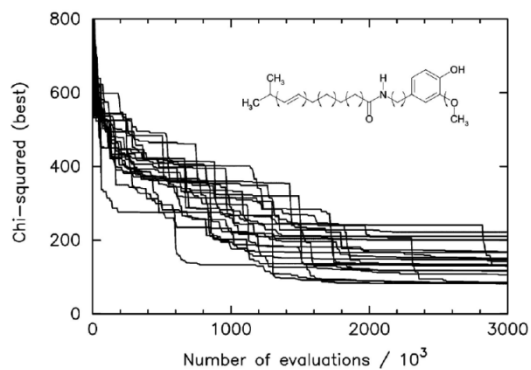
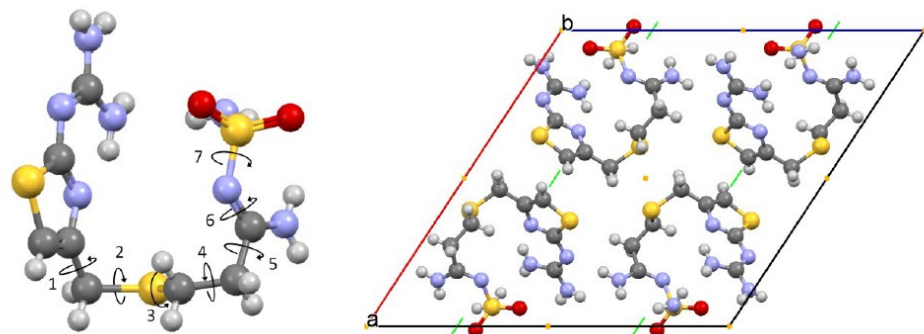
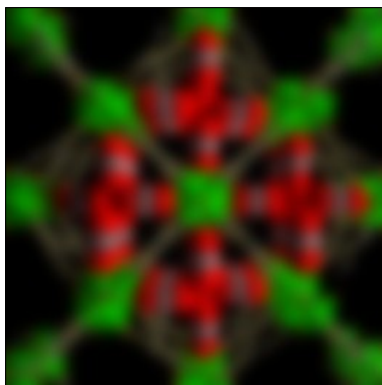


Fig. X.Z.6.3. Frequency distributions for torsion angles 1, 3 and 4 in famotidine as illustrated in Figs. X.Z.4.2 and X.Z.6.1. The values for form A and form B famotidine are indicated by red and blue vertical lines respectively.

# Maximum likelihood techniques

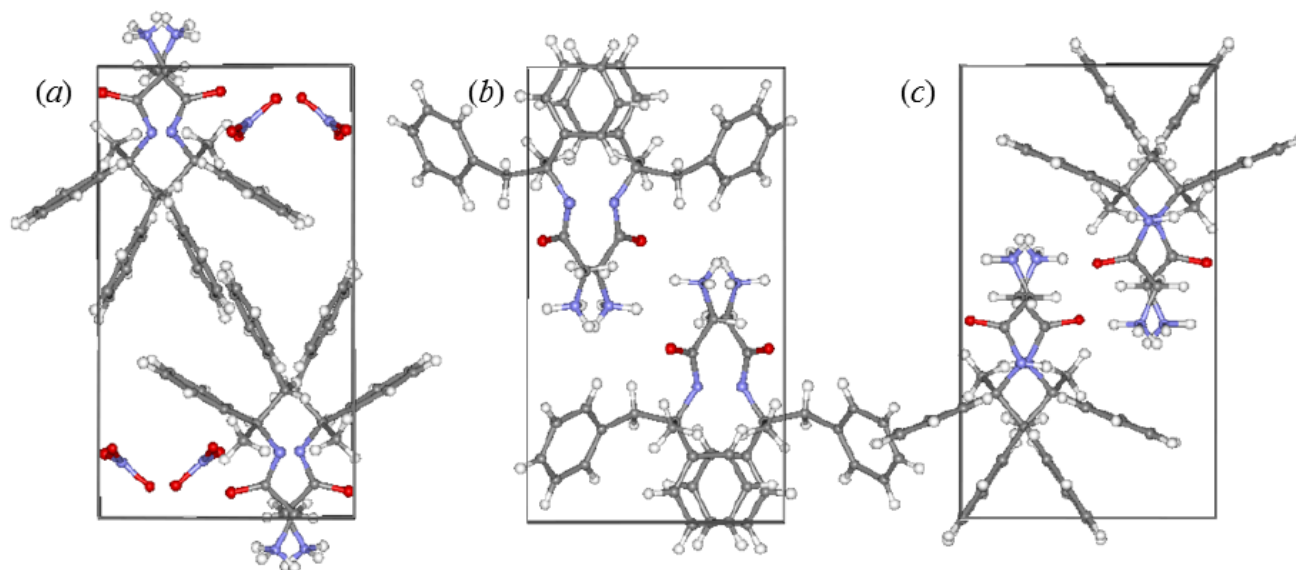


Fig. X.Z.6.7. (a) The correct crystal structure of remacemide nitrate. (b) The best structure determination using a least-squares analysis to compare observed and calculated diffraction data with only the remacemide ion used in the structural model. Note that, although the structural arrangement is completely incorrect, it is clear that the solution has resulted in an optimal correlation of observed and calculated electron density. Note, in particular, that the phenyl group maps closely on to the scattering density associated with the nitrate ion. (c) The best structure determination using a maximum likelihood analysis to compare observed and calculated diffraction data with only the remacemide ion used in the structural model. The structure illustrated in (c) is enantiometrically related to correct solution shown in (a). The agreement between the remacemide molecular position, orientation and conformation in (a) and (c) is as close as obtained in a standard least squares analysis with the nitrate ion included.

Markvardsen, A.J., W.I.F. David, and K. Shankland, *A maximum likelihood method for global optimization based structure solution from powder diffraction data*. *Acta Cryst. A*, 2002. **58**: p. 316-326



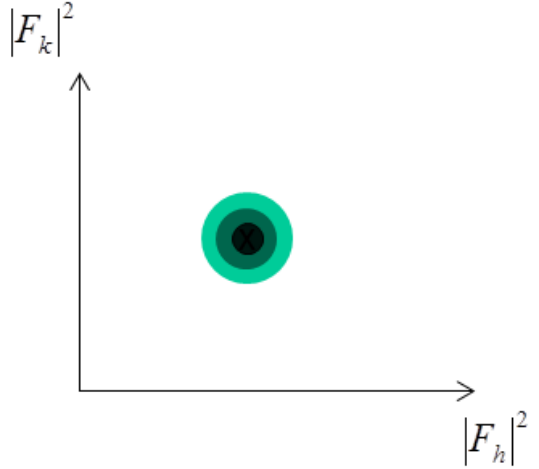
# Maximum entropy (likelihood) techniques

- Rietveld method – assumes the observed and calculated phases of the reflections are the same
- In some cases, this can lead to a biased model.
- Combined Fourier difference map and maximum entropy approach:

$$\chi^2_{CI} = \sum_h \sum_k \left[ |F_{obs}(h)|^2 - |F_{known}(h) + \Delta F(h)|^2 \right] \times (C_{hk}^{-1}) \left[ |F_{obs}(k)|^2 - |F_{known}(k) + \Delta F(k)|^2 \right]$$

data
host

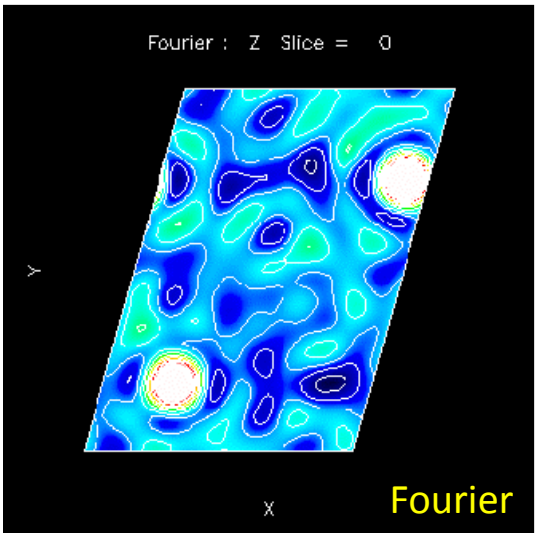
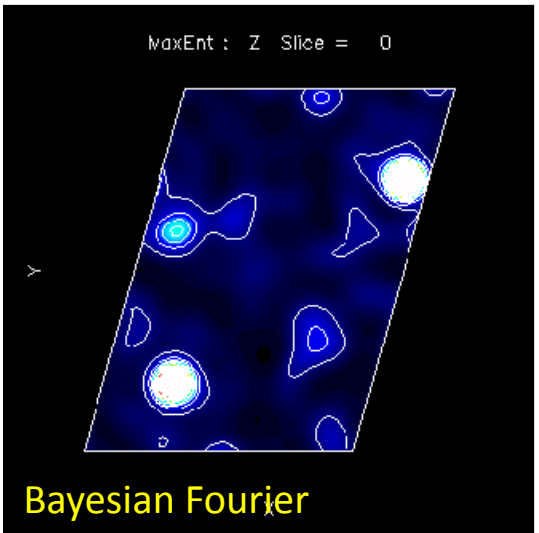
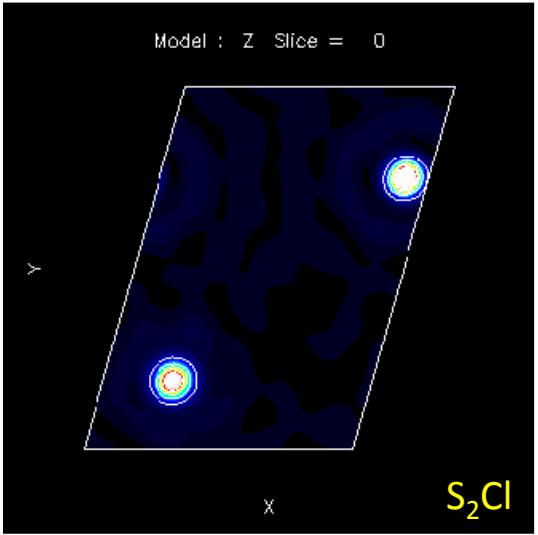
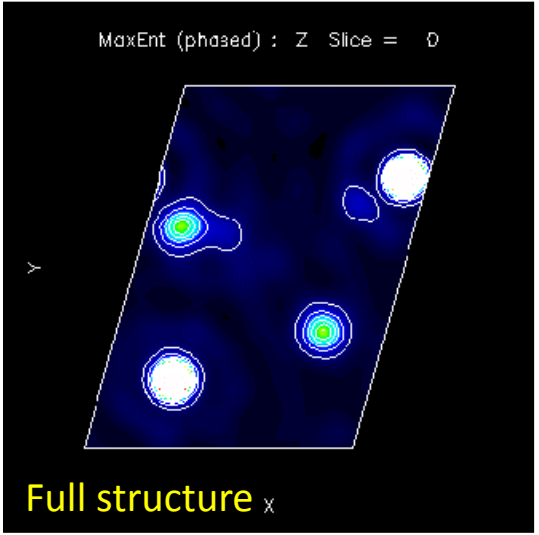
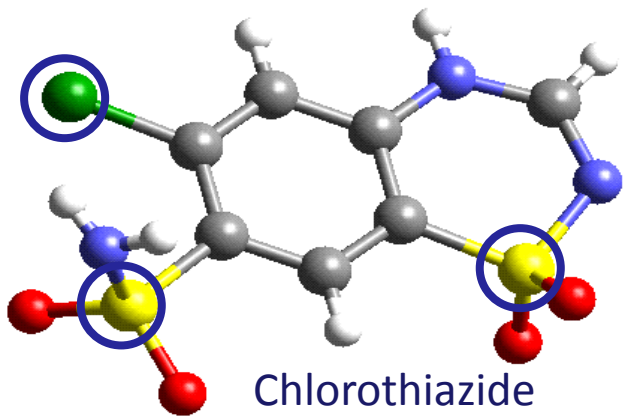
Correlation between reflections



- Does not assume phases of the reflections
- Minimises  $\chi^2$  with the minimum number of features that are consistent with the data.

W.I.F. David and D.S. Sivia, *Extracting intensities from powder diffraction patterns in Structure Determination from Powder Data*, OUP, 2002.

# Maximum entropy (likelihood) techniques







# The heroes (cont.)

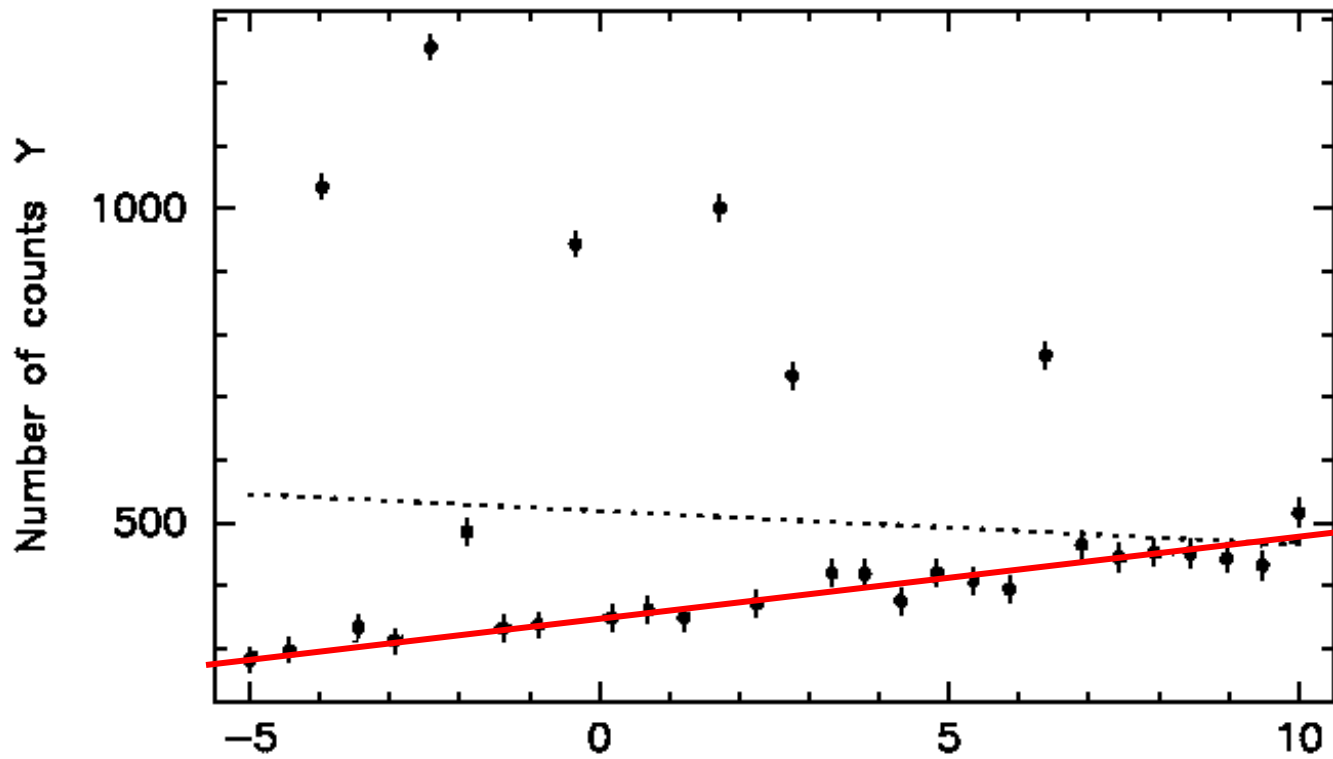


Ted Prince

Be **rigorous** – **do it properly**  
Excellent instrumentation  
Fundamental parameters  
Fundamental statistics

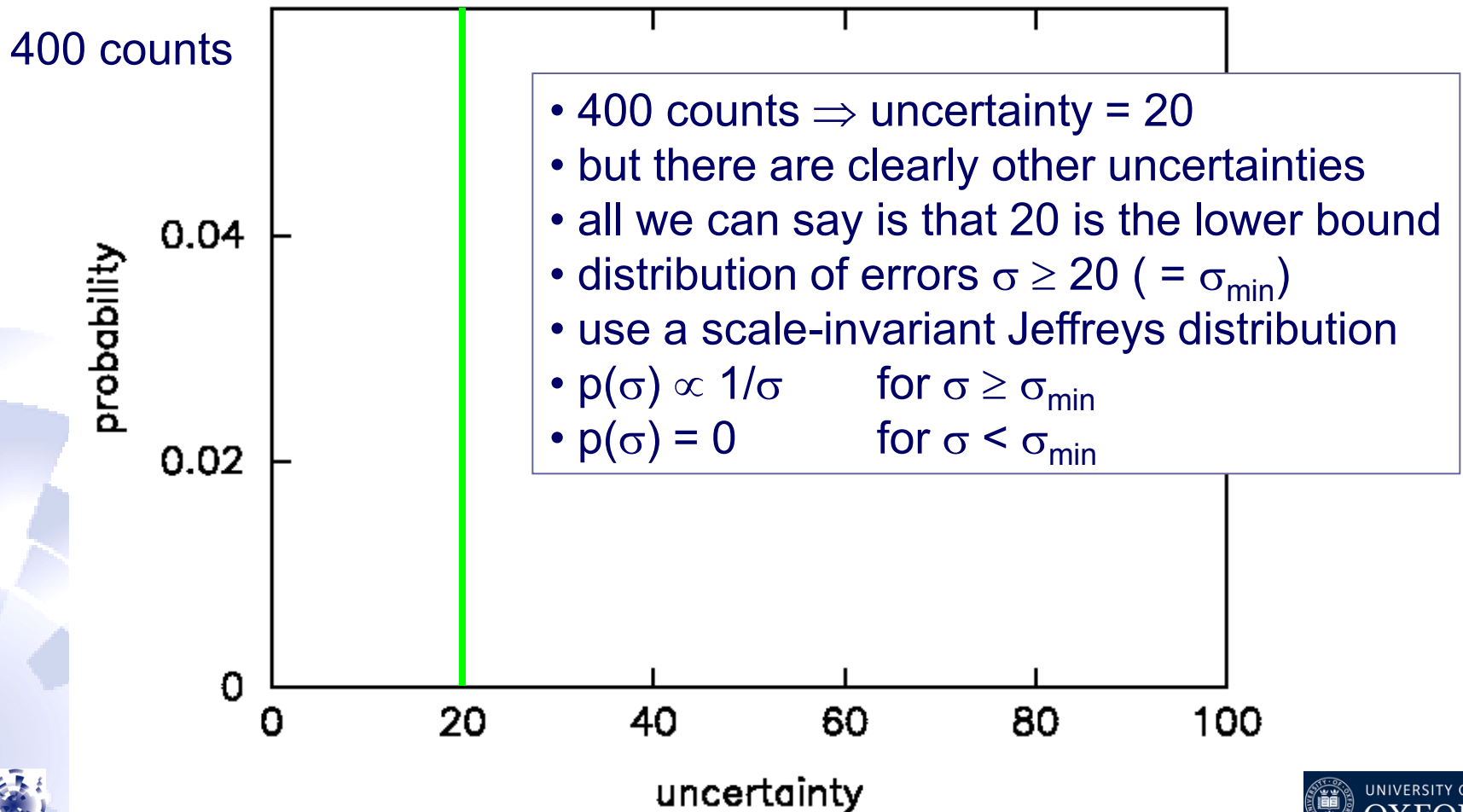
What if the fit is not as good as it could be

- Is it wise to have 150,000 counts in the biggest peak and 5000 counts in a very highly structured background?
  - No! Redo the experiment!
- Collect all Bragg peaks with similar fractional accuracy
  - variable counting time to give  $E/\sigma$  (E) constant
- If accuracy and precision are required be prepared to
  - comprehensively model structure and microstructure
  - perform fundamental line-shape analysis
  - undertake detailed “fundamental” background analysis
- If all else fails - use statistics / plausible reasoning!



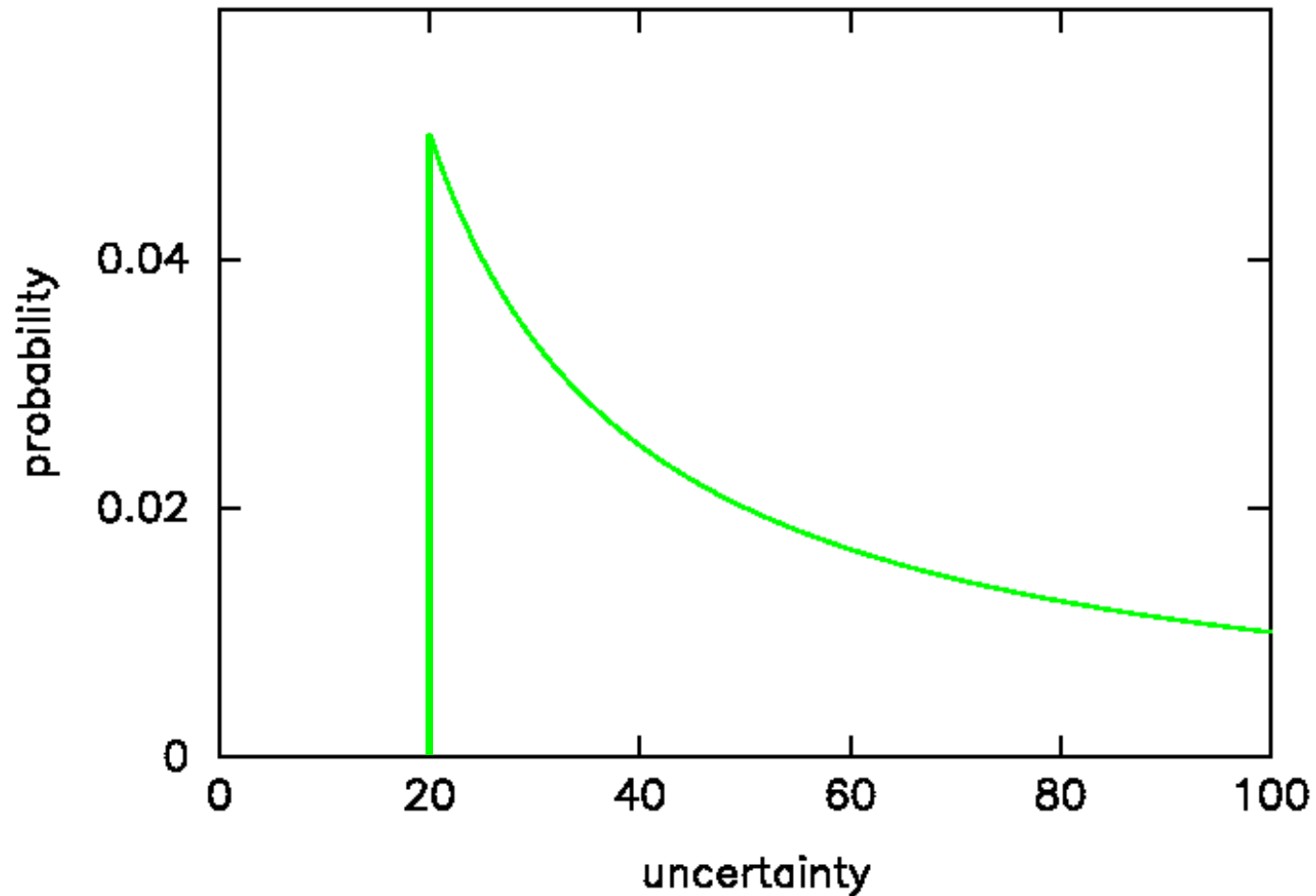
# What's gone wrong?

- We've performed a least-squares analysis and implicitly assumed that all errors follow a Gaussian PDF
- We've been certain about our uncertainties!

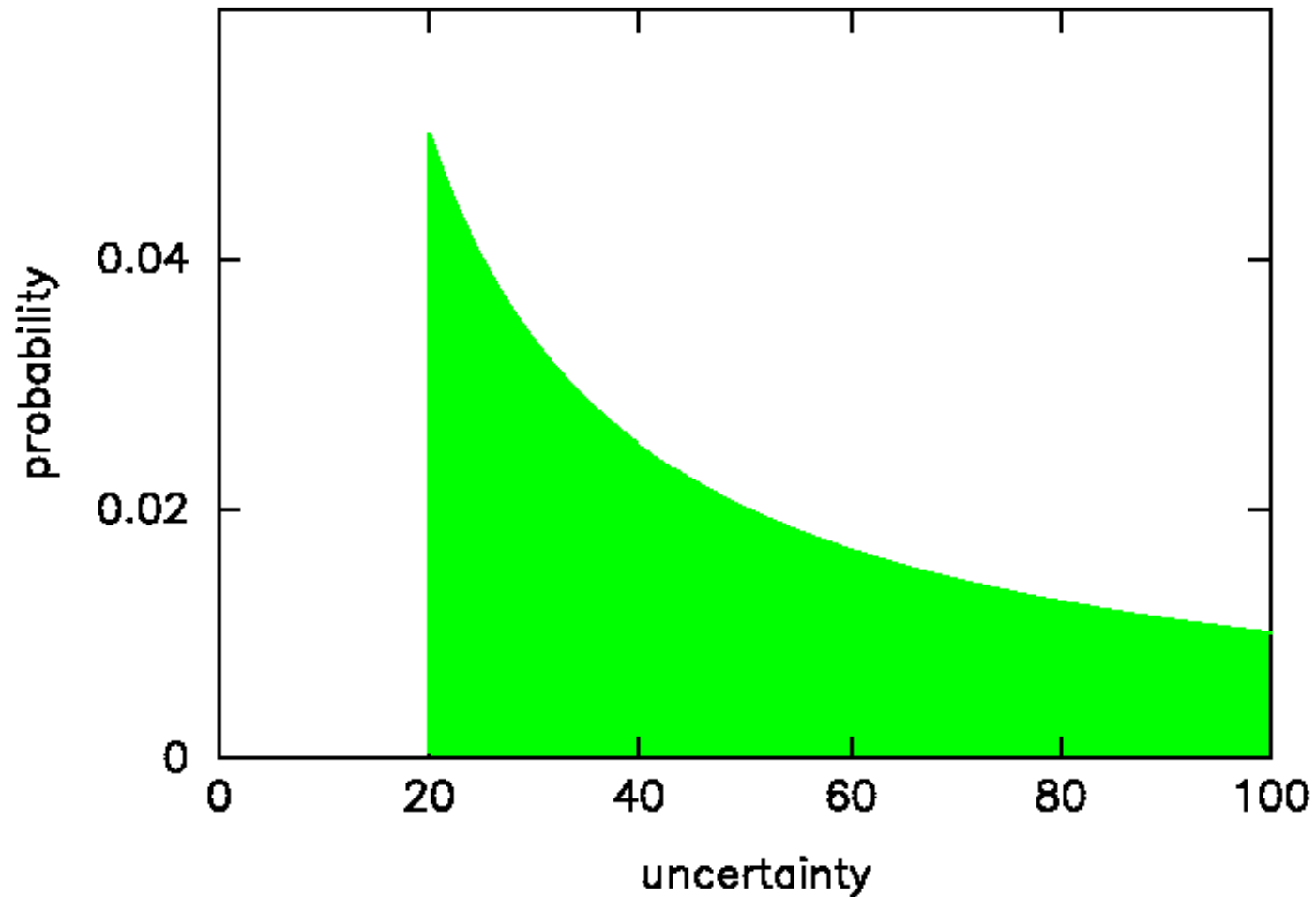




- Jeffreys prior
- $p(\sigma) \propto 1/\sigma$  for  $\sigma \geq \sigma_{\min}$
- $p(\sigma) = 0$  for  $\sigma < \sigma_{\min}$

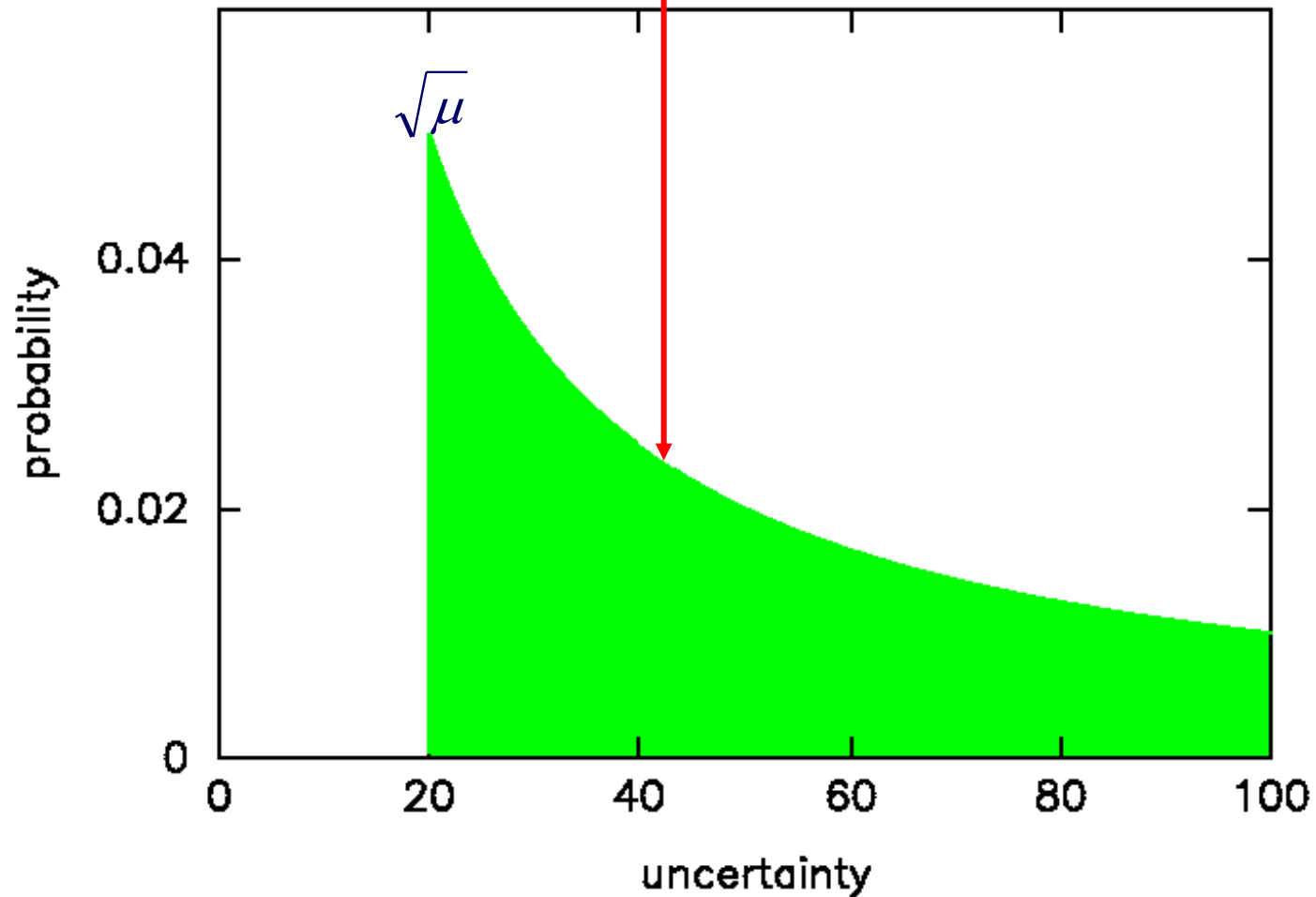


- Jeffreys prior
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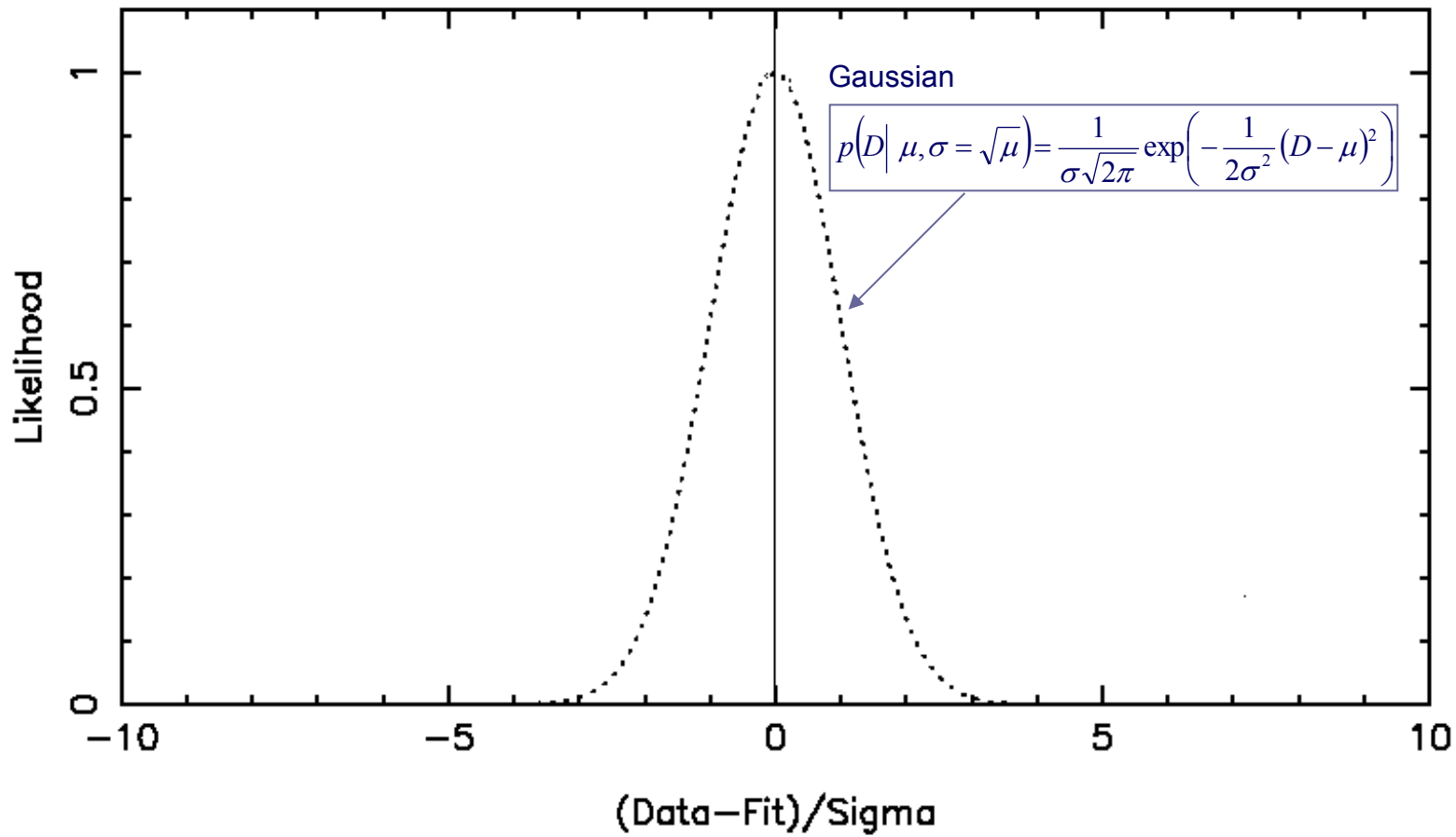


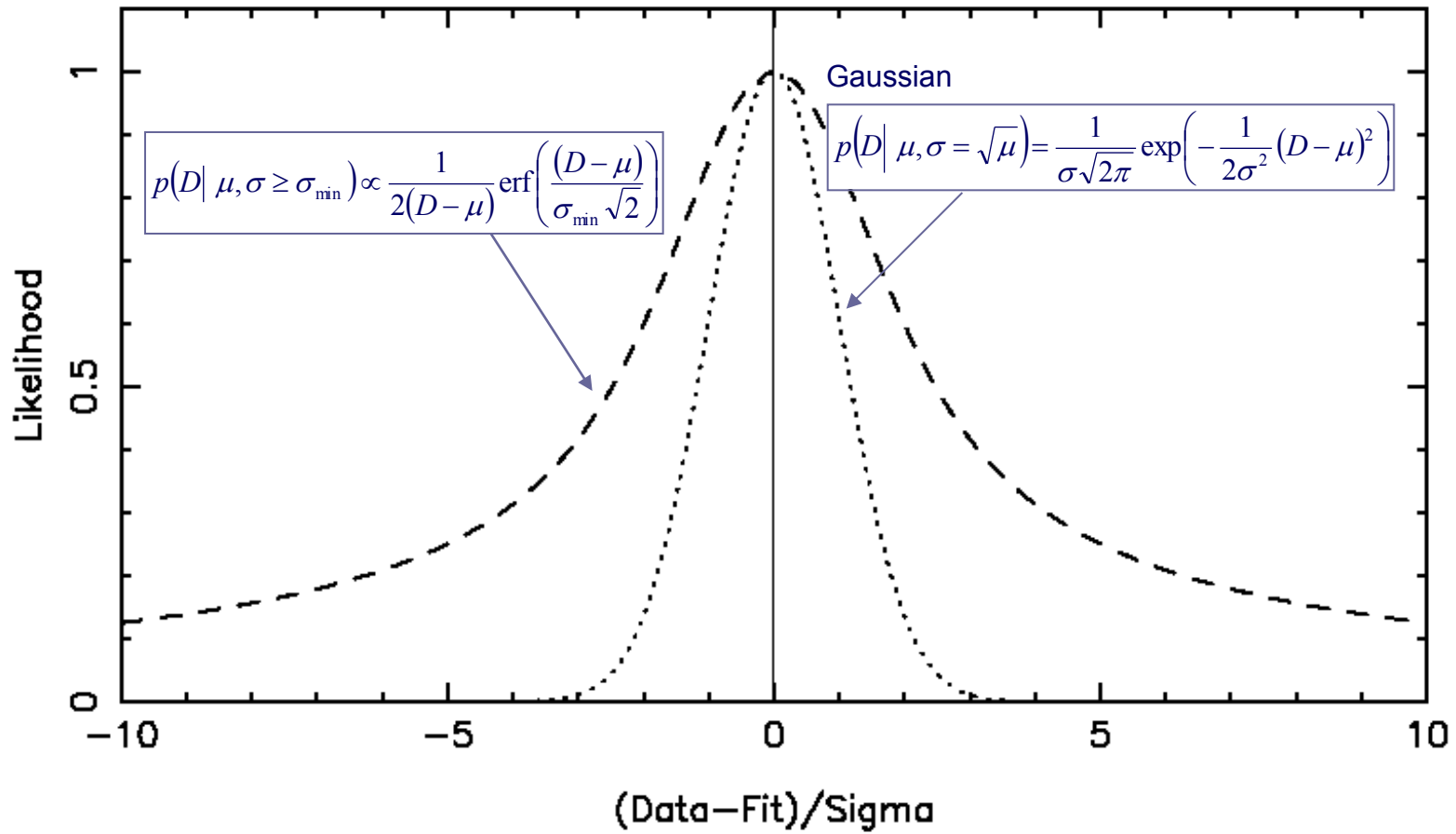
## Gaussian

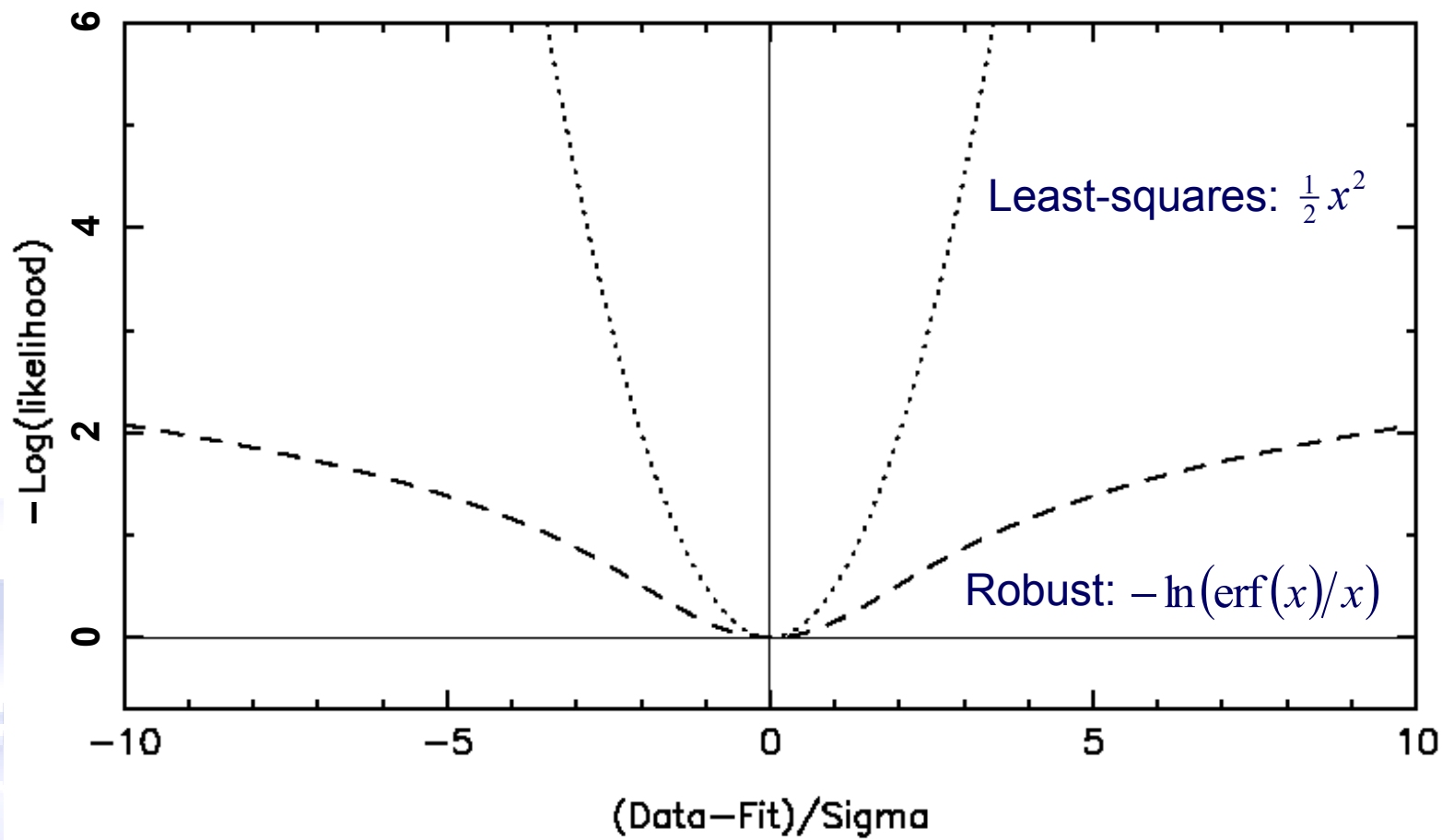
$$p(D | \mu, \sigma \geq \sqrt{\mu}) = \int_{\sigma_{\min} = \sqrt{\mu}}^{\infty} \text{prob}(\sigma) \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{1}{2\sigma^2}(D-\mu)^2\right) d\sigma$$



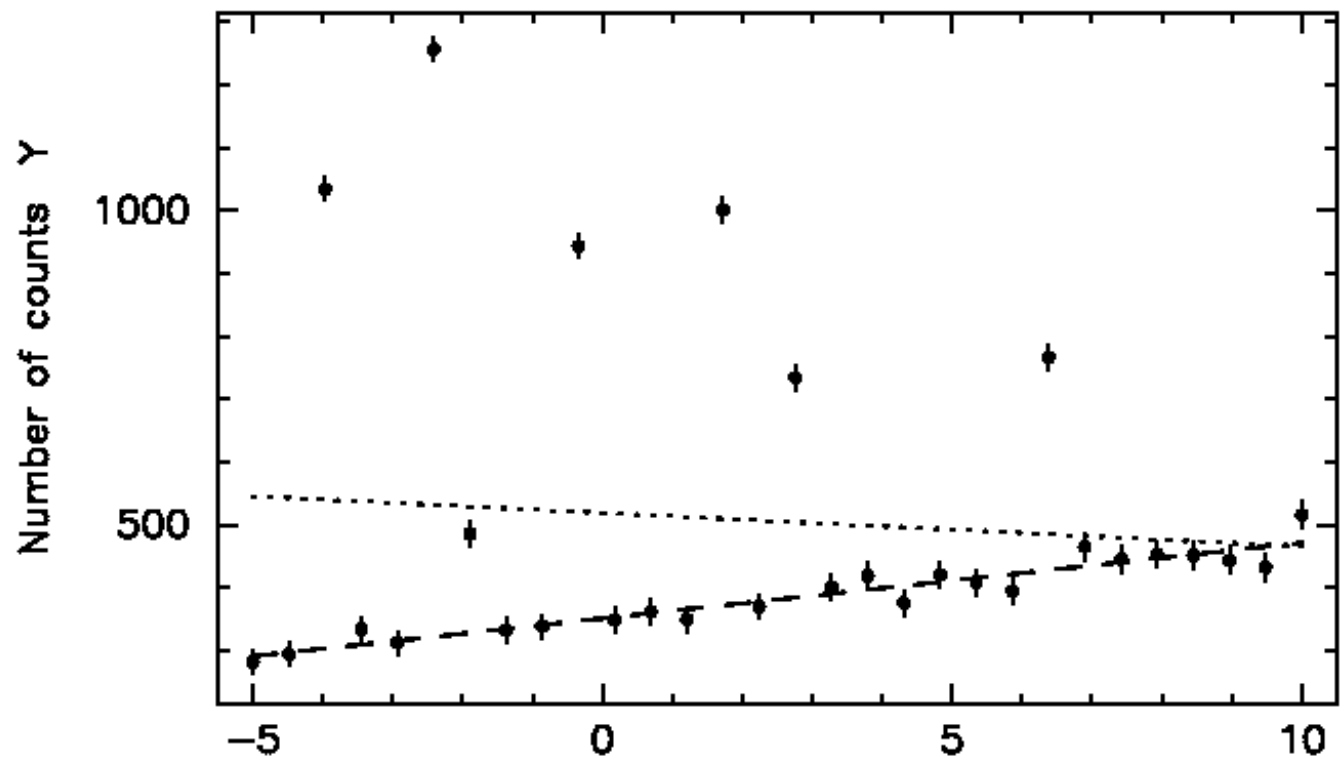




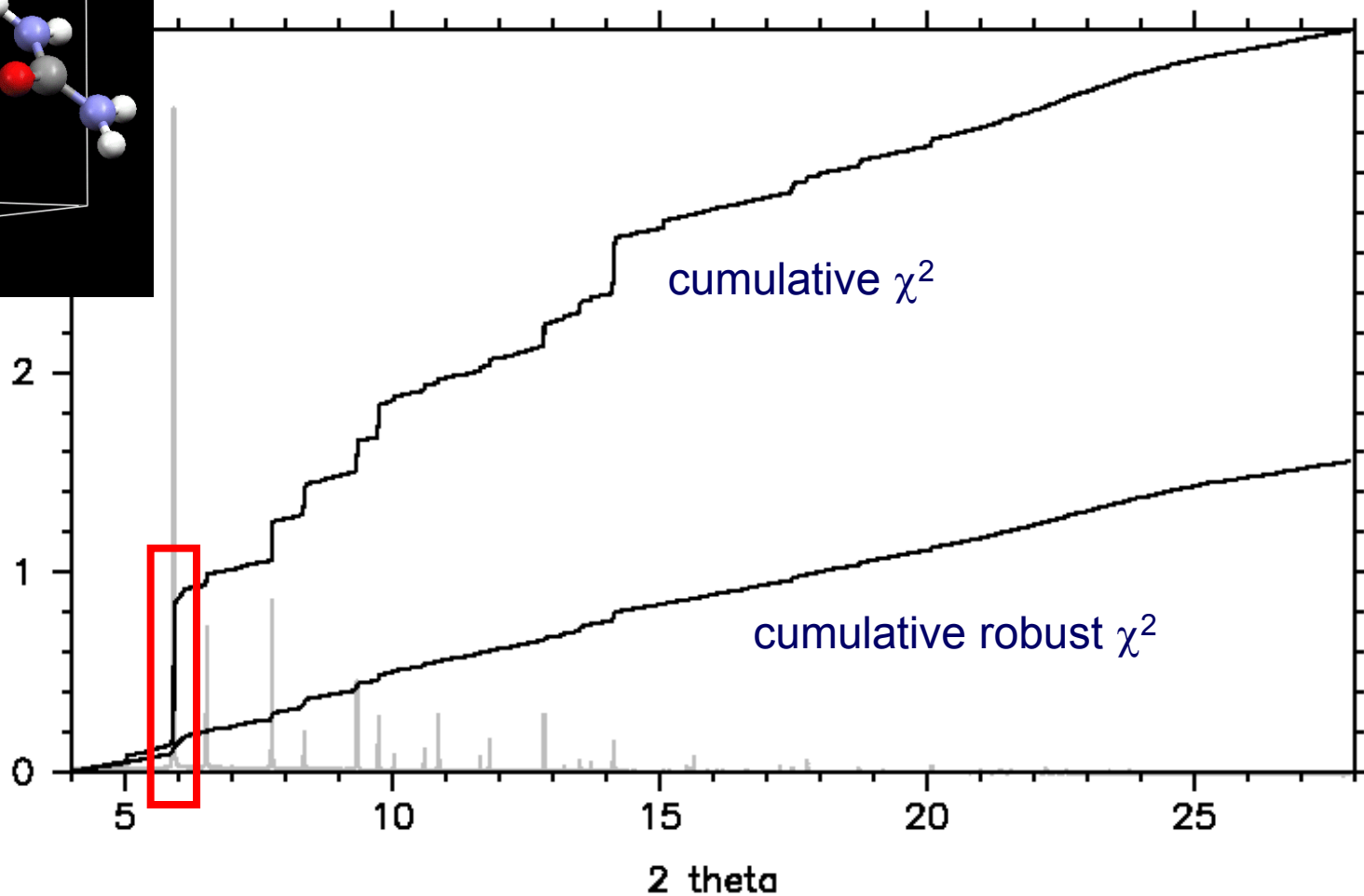
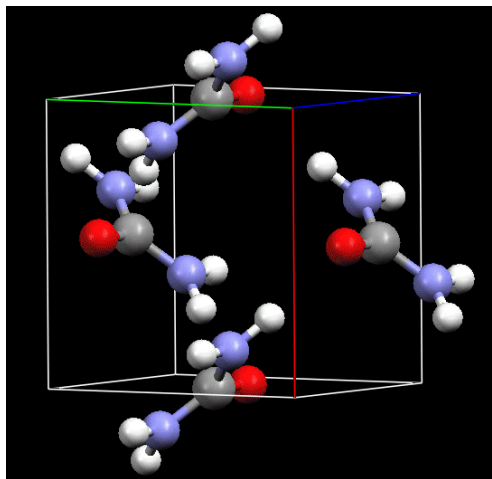








# Urea (BM16 ESRF)



# Urea (BM16 ESRF)

	SXXD	Least Squares	LS-SXXD	Robust	R-SXXD
C1 z	0.3328(3)	0.3236(9)	-0.0092(10)	0.3319(13)	-0.0009(14)
O1 z	0.5976(4)	0.6013(5)	0.0037(6)	0.5984(7)	0.0008(8)
N1 x	0.1418(2)	0.1405(3)	-0.0013(4)	0.1423(7)	0.0005(7)
z	0.1830(2)	0.1807(5)	-0.0023(6)	0.1813(7)	-0.0017(7)
C1 U11	0.0353(6)	0.0348(20)	-0.0005(20)	0.0329(40)	0.0024(40)
U33	0.0155(5)	0.0396(30)	0.0241(30)	0.0413(40)	0.0258(40)
U12	0.0006(9)	0.0205(30)	0.0199(30)	0.0128(40)	0.0122(40)
O1 U11	0.0506(9)	0.0749(16)	0.0243(18)	0.0617(30)	0.0111(30)
U33	0.0160(6)	0.0080(14)	-0.0080(15)	0.0090(20)	-0.0070(20)
U12	0.0038(18)	0.0052(20)	0.0014(30)	-0.0011(35)	-0.0049(35)
N1 U11	0.0692(6)	0.0627(15)	-0.0065(18)	0.0697(25)	0.0005(25)
U33	0.0251(4)	0.0460(22)	0.0211(22)	0.0365(30)	0.0114(30)
U12	-0.0353(7)	-0.0252(18)	0.0101(20)	-0.0361(30)	-0.0008(30)
U13	-0.0003(3)	-0.0015(11)	-0.0012(12)	-0.0029(15)	-0.0026(15)



= diff > 4σ

9/14 > 4σ

1/14 > 4σ

David, W.I.F., J. Res. Natl. Inst. Stand. Technol. **109** (2004) 107-123





# Inaccuracy and invalidation:

The image shows a screenshot of the CCDC ConQuest software interface. The main window is titled "CCDC ConQuest (1)" and has a menu bar with "File", "Edit", "Options", "View Databases", "Results", and "Help". Below the menu bar are tabs for "Build Queries", "Combine Queries", "Manage Hitlists", and "View Results". On the left side, there is a vertical list of search criteria: Draw, Peptide, Author/Journal, Name/Class, Elements, Formula, Space Group, Unit Cell, Z/Density, Experimental, All Text, and Refcode (entry ID). At the bottom of this list are "Search" and "Reset" buttons.

The main area of the window shows a search setup for "Query 1" with the name "famotidine". There are "Edit..." and "Delete" buttons next to it.

A "Search Setup" dialog box is open in the foreground. It has a "Search Name" field containing "search1" and a "Show Updates separately" checkbox. The "Available Databases" section lists "CSD version 5.34 (November 2012) + 2 updates" with a checked checkbox. Below this, there are "Select Subset" and "Clear Subset" buttons. A text box indicates "Single query being used. Search will find structures: where this query is true:" with "Query 1" entered. The "Filters" tab is active, showing various options: "3D coordinates determined", "R factor" (with radio buttons for <math>\leq 0.05</math>, <math>\leq 0.075</math>, and <math>\leq 0.1</math>), "Not disordered", "No errors", "Not polymeric", "No ions", "No powder structures" (highlighted with a red box), and "Only" (with radio buttons for "Organics" and "Organometallic"). At the bottom of the dialog are "Start Search", "Cancel", and "Reset" buttons.

# Inaccuracy and invalidation

Re: About the space group Pmcn - Message (HTML)

File Message

Social skills

*Very popular but can attract some unlikely characters with limited crystallographic skills.*

Happy new year from the hot side of the world (this days).

A good ... wrote:

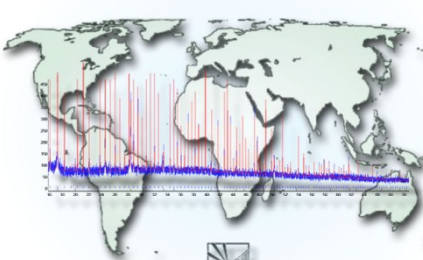

> On 7 January 2013 02:34, [redacted] wrote:  
 >> Dear [redacted]  
 >>  
 > In addition, many of us find it tiresome that these days it is easy to use the internet to ask people to explain things that basic classwork would have covered.

Nicky Scarlett

- Encourage best practice
- Awareness of limitations
- Prescriptive procedures
- Authenticated labs

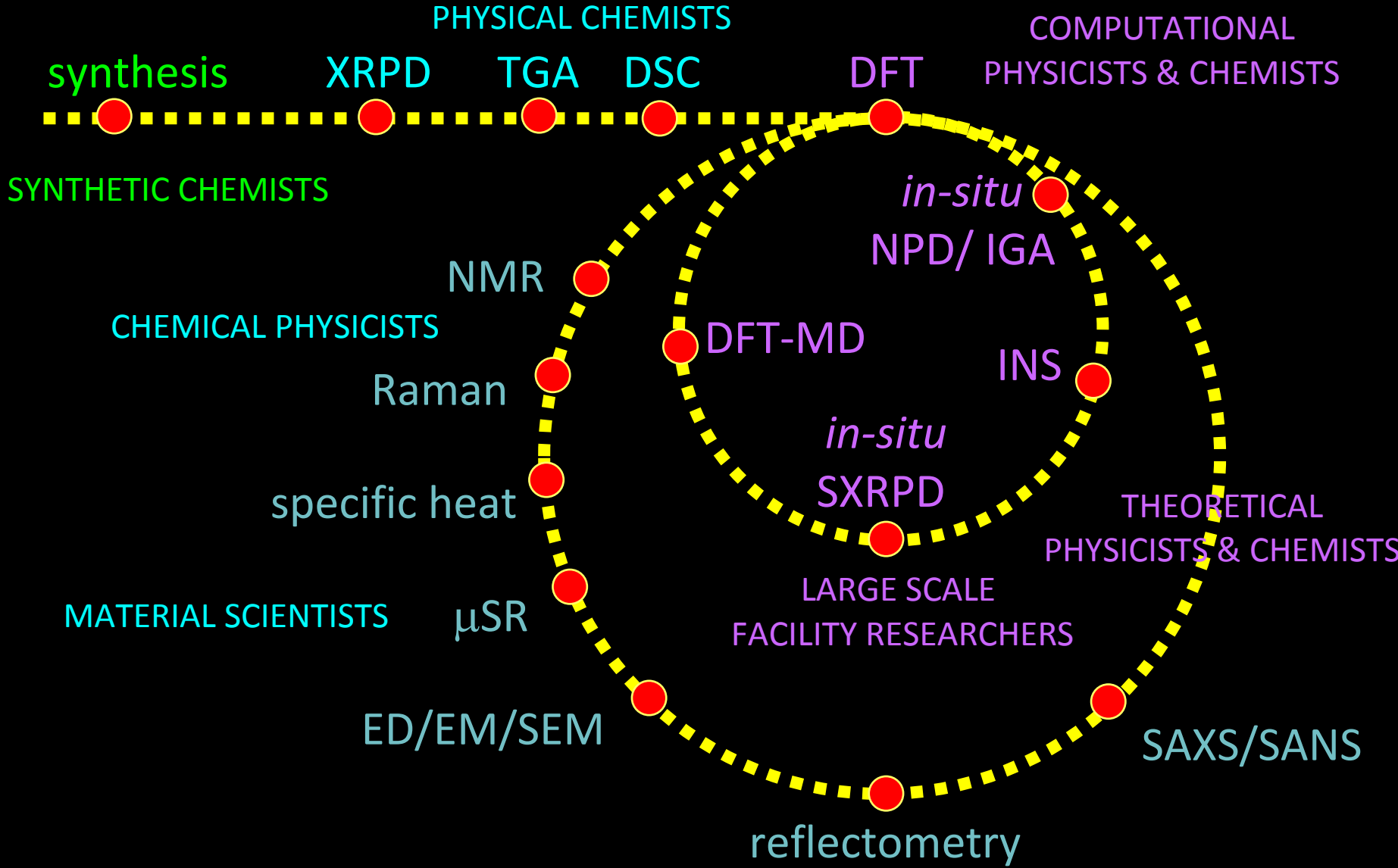
Raising the bar: journals & databases

Commission on Powder Diffraction

each school's web page, maybe someone looking for basic knowledge on IYCr, but we should also multiply the number of schools, undergraduate and more complex and black-box-like programs that are coming out get g to do... volunteers needed :-).

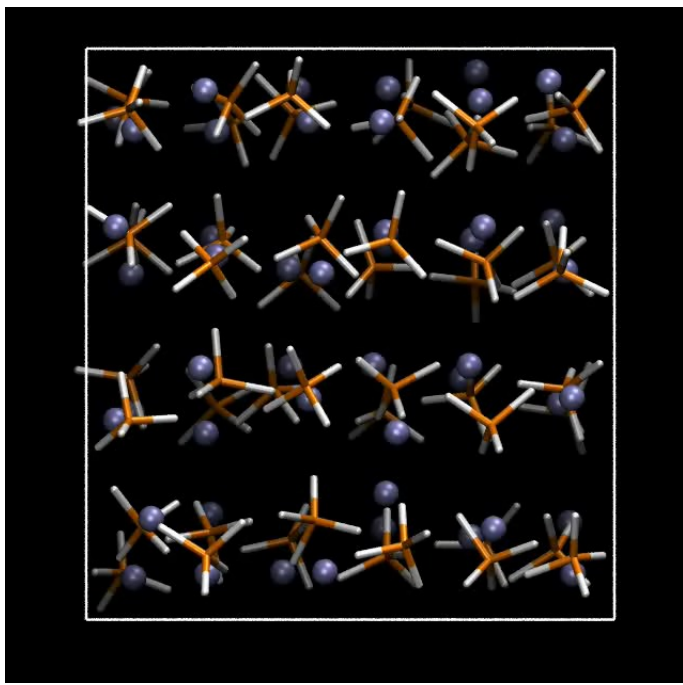
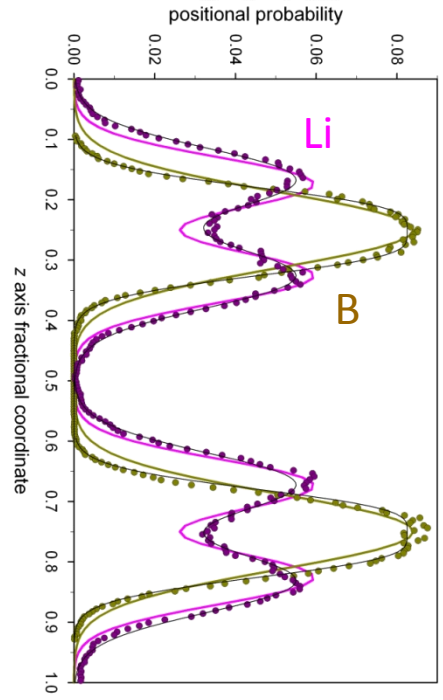
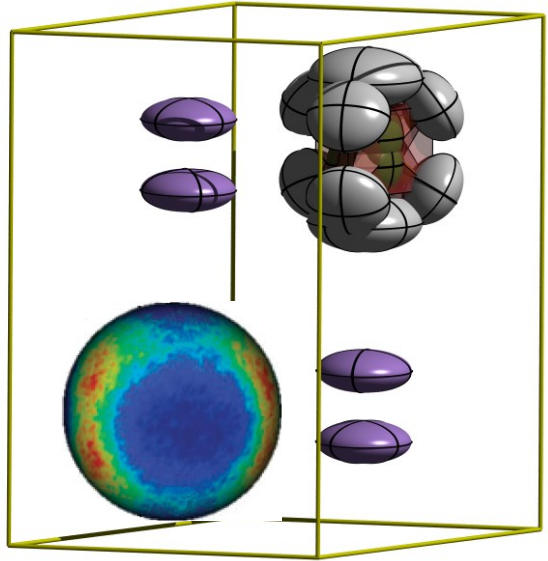
# Energy materials research ...



THE FUTURE IS COLLABORATIVE ...

# From one dimension to four ...

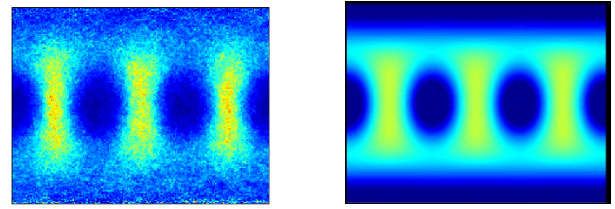
$\text{LiBH}_4$  : superionic conductor



$\text{LiBH}_4$  : DFT-MD  
PRL 108 095901 (2012)

$^7\text{Li}^{11}\text{BD}_4$  : GEM (ISIS)

Hydrogen MODF in  $\text{BH}_4$  (DFT MD)



Hydrogen MODF in  $\text{BH}_4$  (neutron powder diffraction)( $\ell = 5$  spherical harmonic fit)





- Excellent
- Good
- Average
- Poor

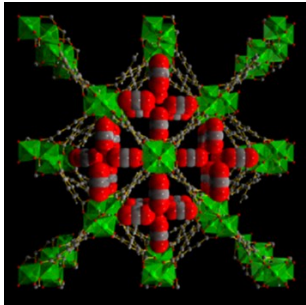
REPORT for Decade ending ..... April 2013 .....

Name: Powder diffraction

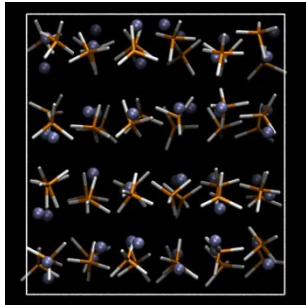
Age: 97

General observations	Excellent progress.
Technical subjects	Impressive new instruments with particular excellence in detectors and electronics. Has taken full advantage of Moore's Law.
Computer studies	Existing programs continue to perform well. Some extremely impressive new programs. Dabbling with new concepts.
Creative studies	Comes up with significant new creative ideas.
Attitude	Has matured and now has broadened interests.
Social skills	Very popular but can attract some unlikely characters with limited crystallographic skills.
Future prospects	Great potential - sure to go far.

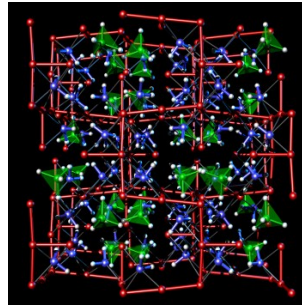
# The best is yet to come ...



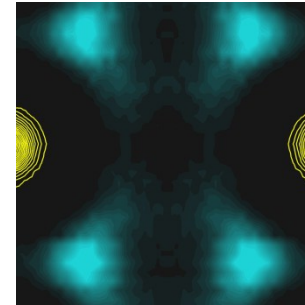
CO2 sequestration



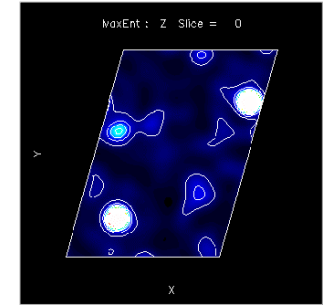
hydrogen stores



lithium batteries



fuel cells



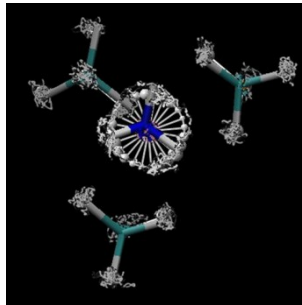
structure determination



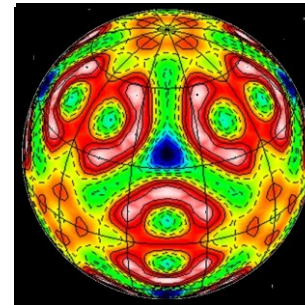
pharmaceuticals



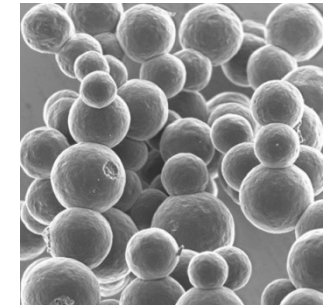
turbine blade



gas storage



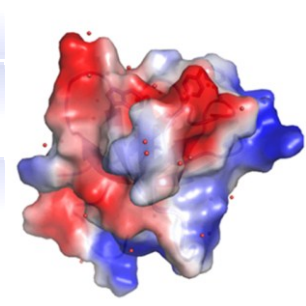
C<sub>60</sub>



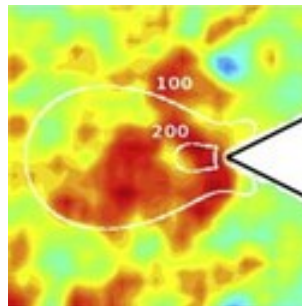
nanomaterials



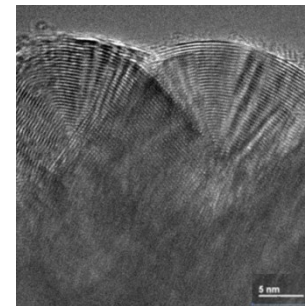
pencil "lead"



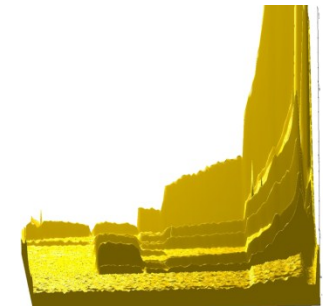
proteins



tensile stress



superhard graphite



paracetamol