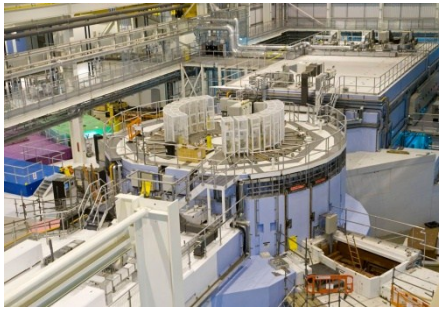
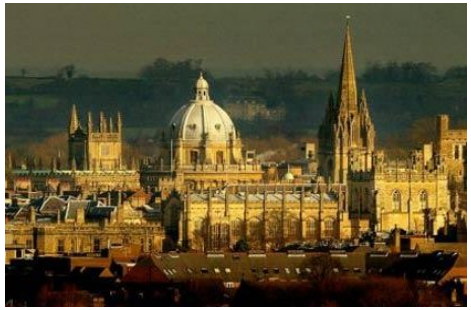
RAL: Diamond & ISIS



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

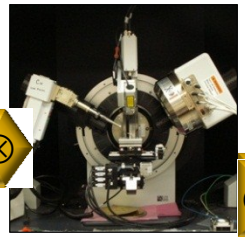
Age: 97

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.

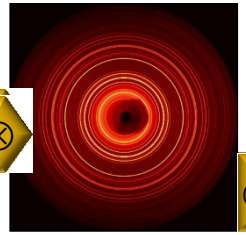
Headmaster.

Accuracy in Powder Diffraction

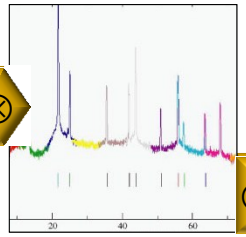
Sample preparation



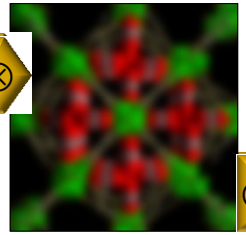
Instrument calibration



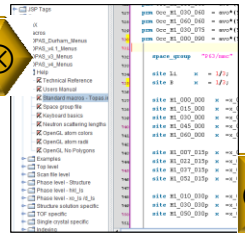
Data collection



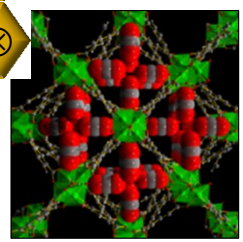
Data reduction



Structural model



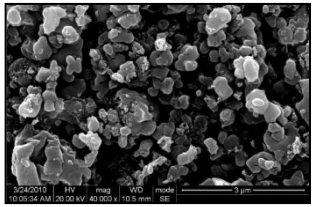
Data analysis



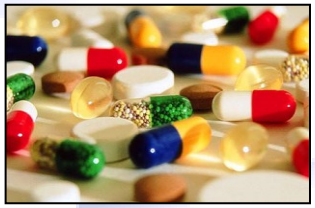
Validation

Real Crystallography of Real Materials under Real Conditions

ball milling –
a black art!

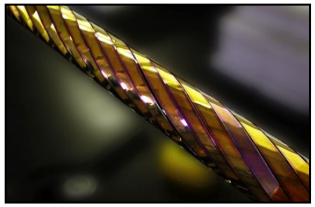


Li battery cathode



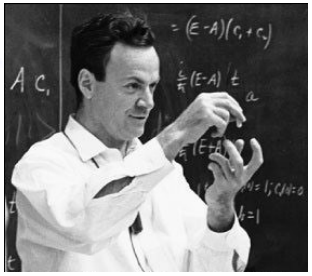
pharmaceuticals

turbine blade

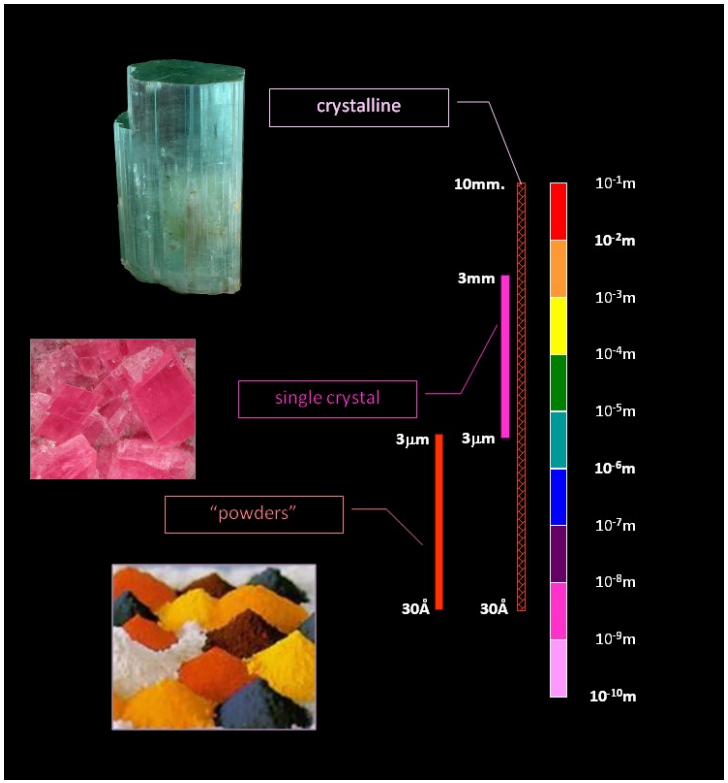


superconducting cable

pencil “lead”



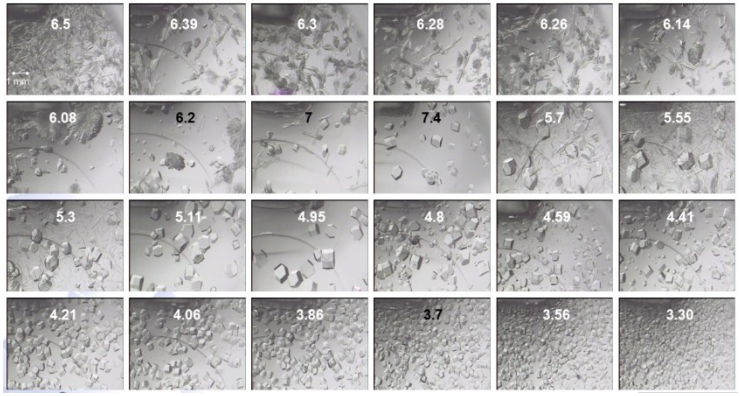
Richard P. Feynman (Dec 1959)

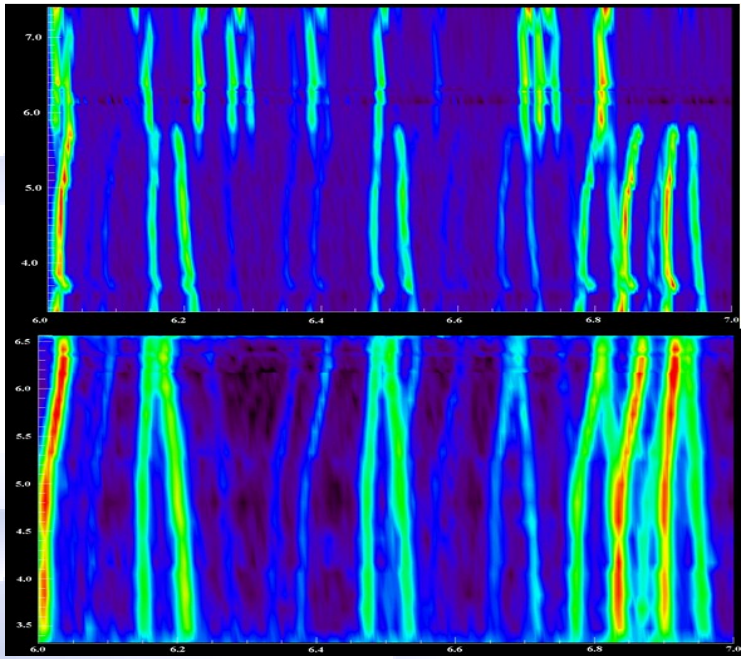


There’s Plenty of Room at the Bottom
An invitation to explore
21st century science and technology.

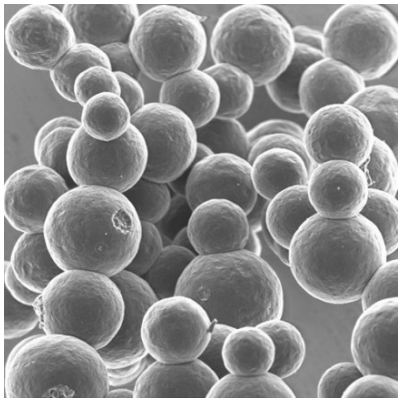
Real Crystallography of Real Materials under Real Conditions

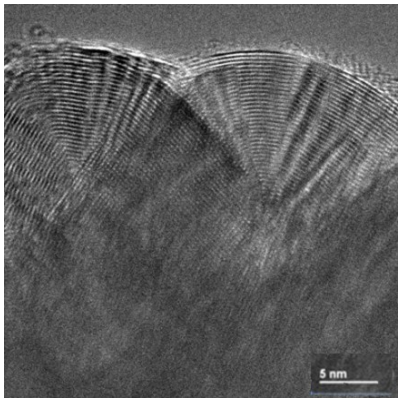
Parametric proteins (Margiolaki & Wright)

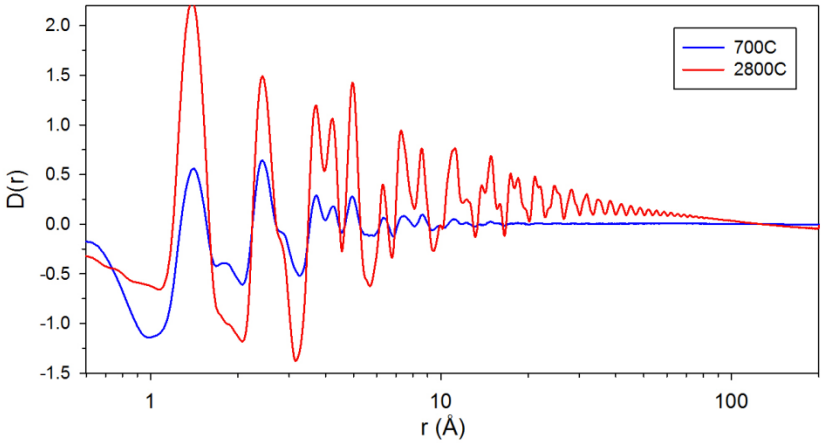




Diamond-hard graphite



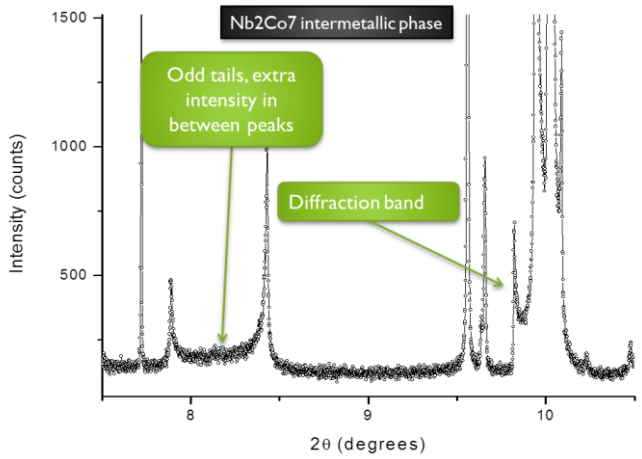


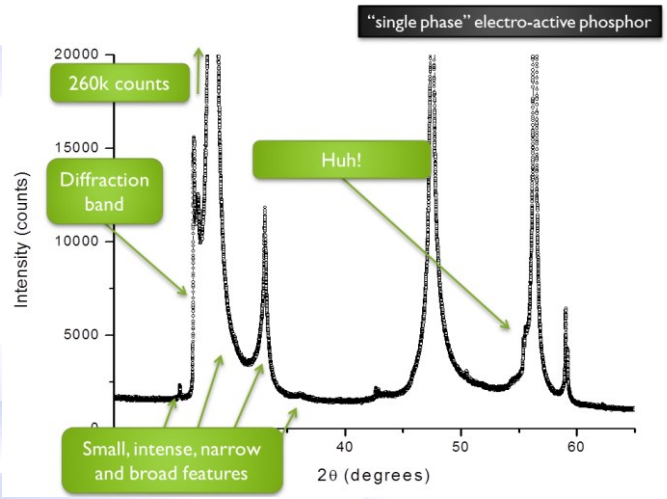


Pol, Wen, Lau, Callear, Bowron, Lin, Deshmukh, Sankaranarayanan, Curtiss, David, Miller & Thackeray, Carbon (submitted)

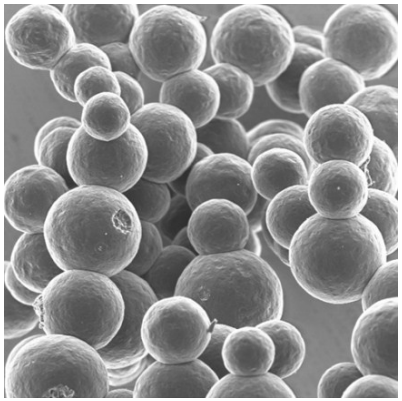
Real Crystallography of Real Materials under Real Conditions

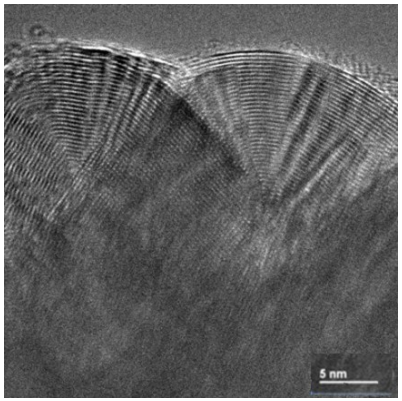
Structure & microstructure (Leoni)

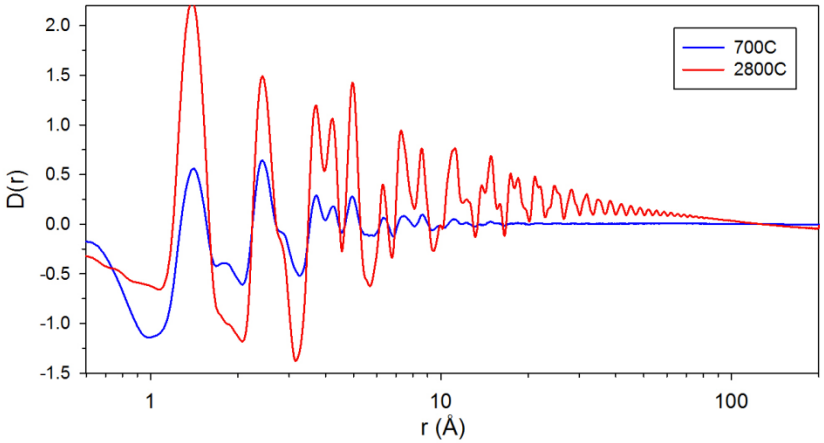




Diamond-hard graphite

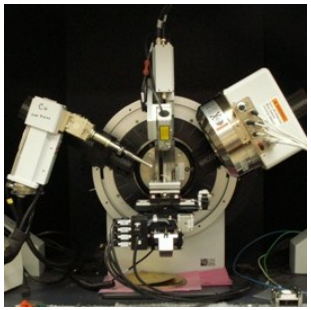






Pol, Wen, Lau, Callear, Bowron, Lin, Deshmukh, Sankaranarayanan, Curtiss, David, Miller & Thackeray, Carbon (submitted)

Instrumentation

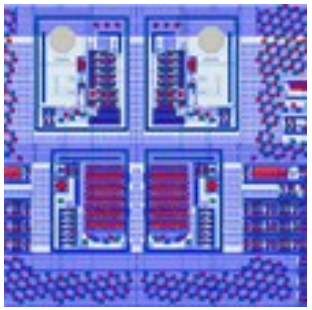


X-ray diffractometer

WISH detectors

PILATUS

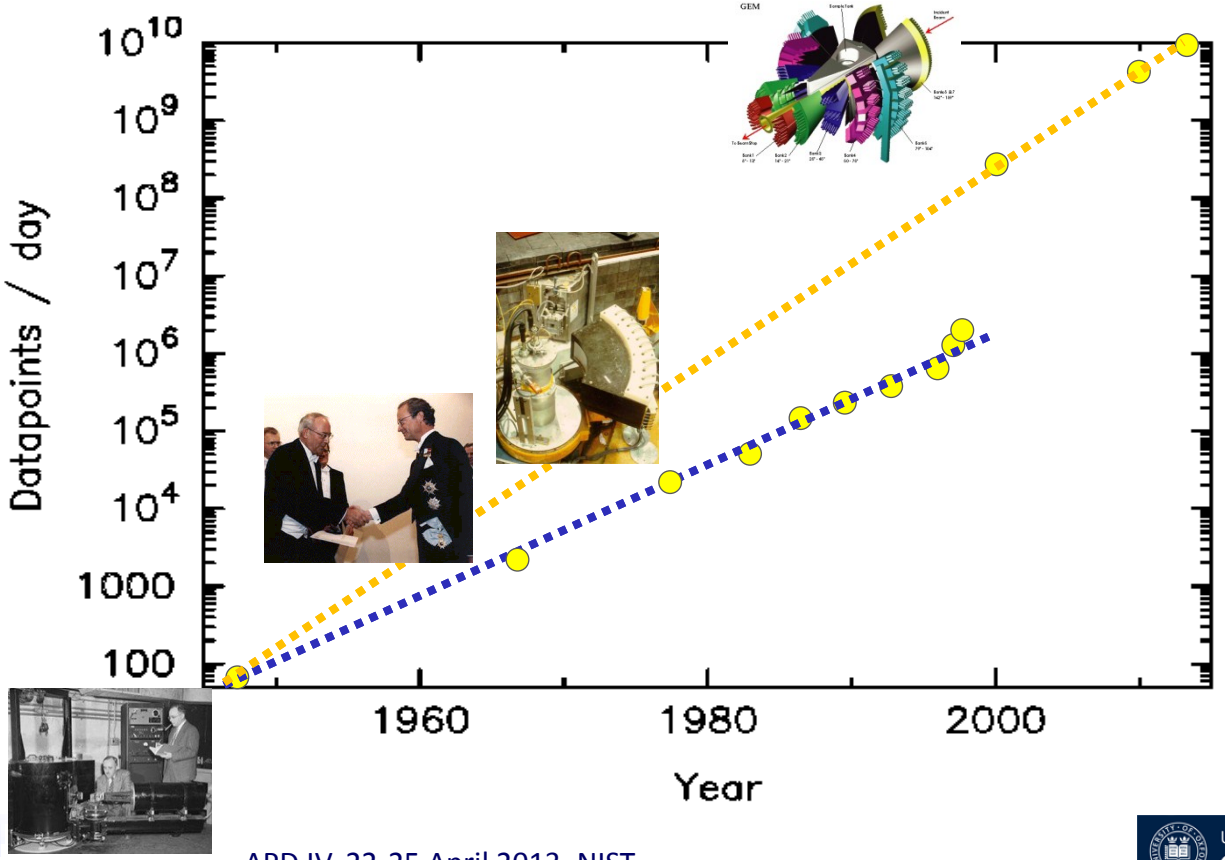
ISIS electronics



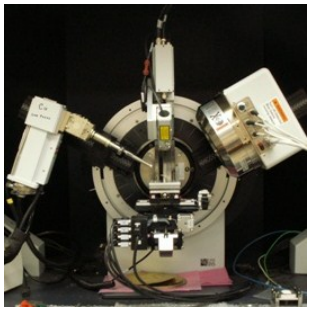
PILATUS electronics

CMS @ CERN

CMS @ CERN (II)



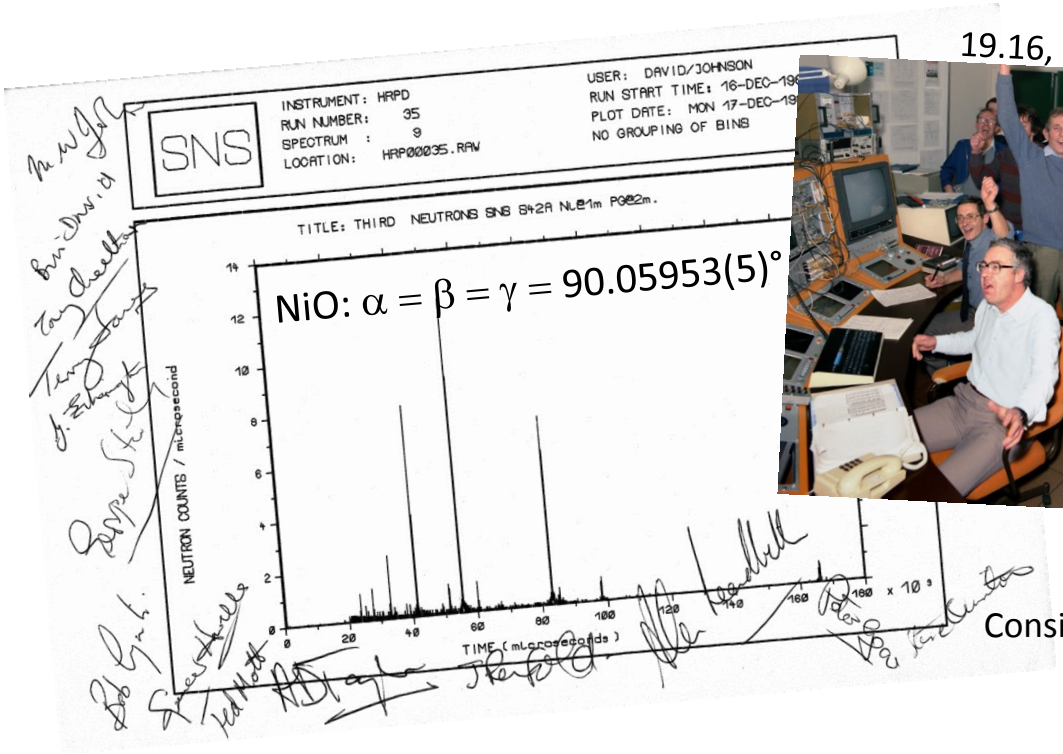
Instrumentation



X-ray diffractometer

Diamond and ISIS

ISIS TS2



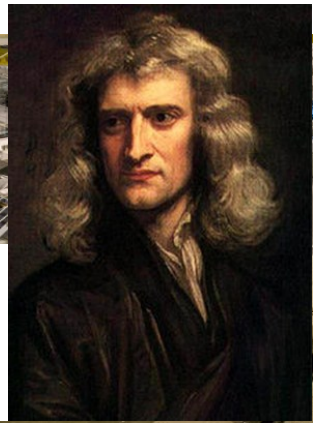
19.16, 16th December 1984

Consider the magnitude of the endeavour …

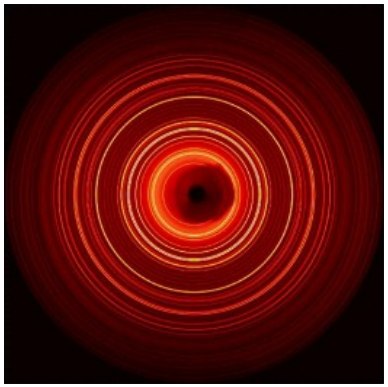
Isaac Newton

Letter to Robert Hooke (15 Feb. 1676)

"If I have seen further it is by standing on ye sholders of Giants."



Data collection



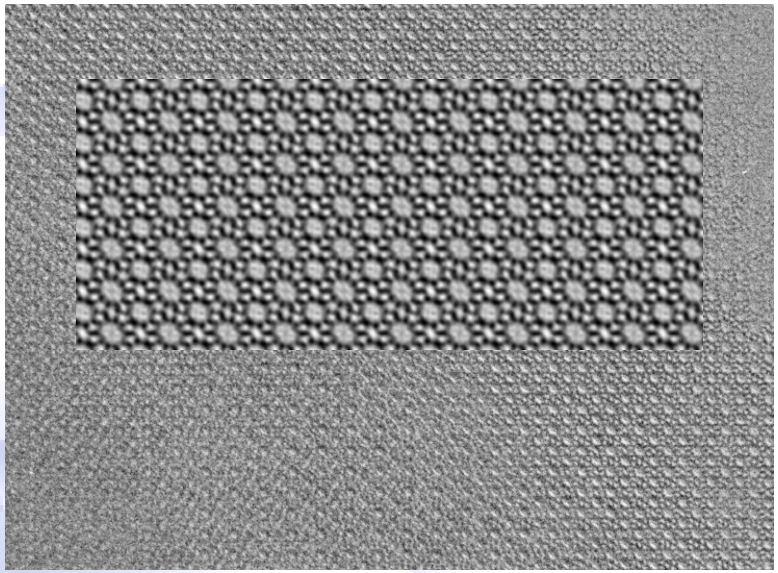
Exploring the limits

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

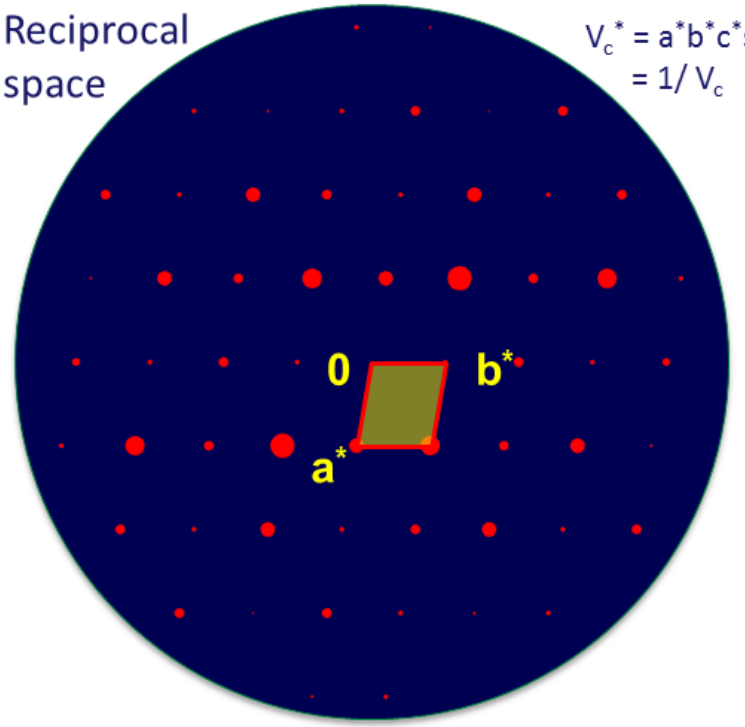
Real space

$V_c = abc \sin(\gamma)$



Reciprocal space

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



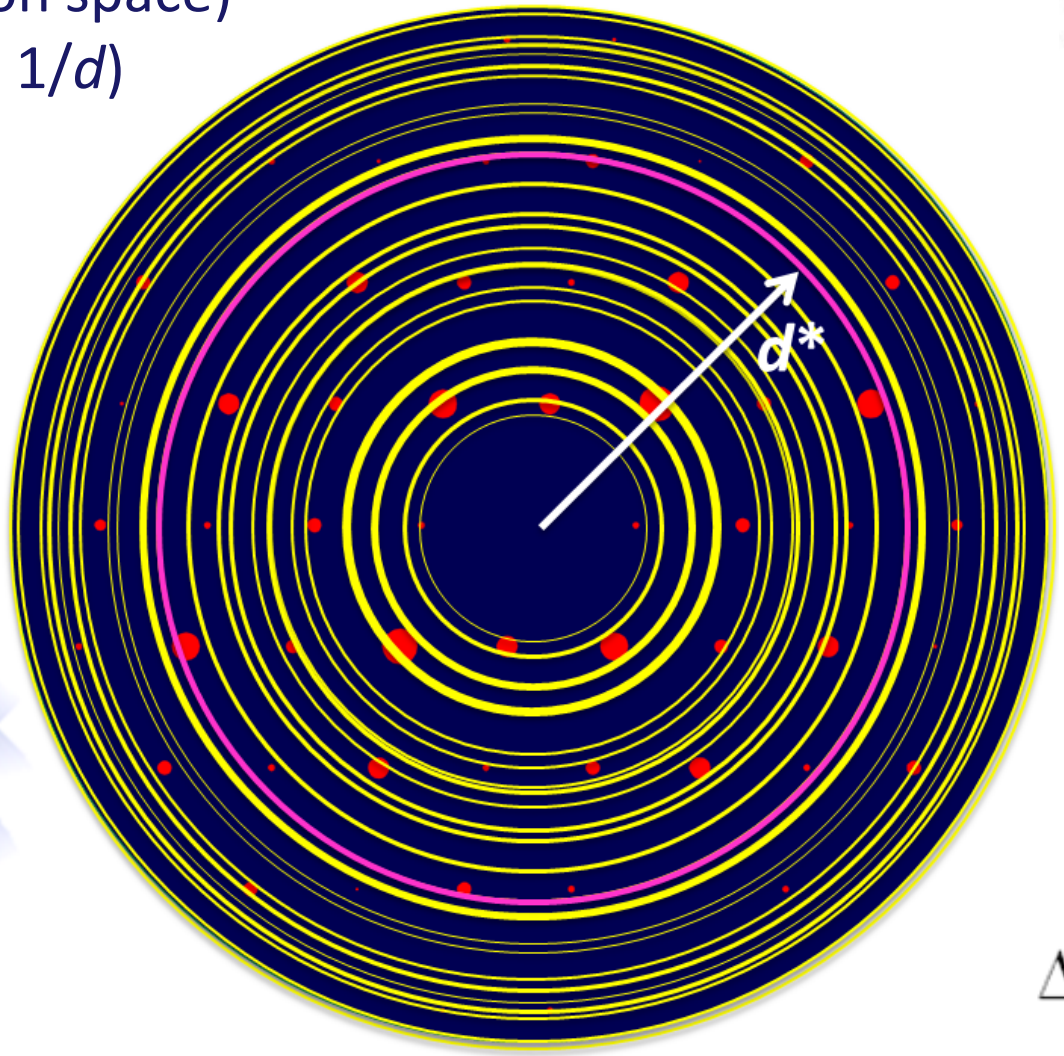
Limits

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

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

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

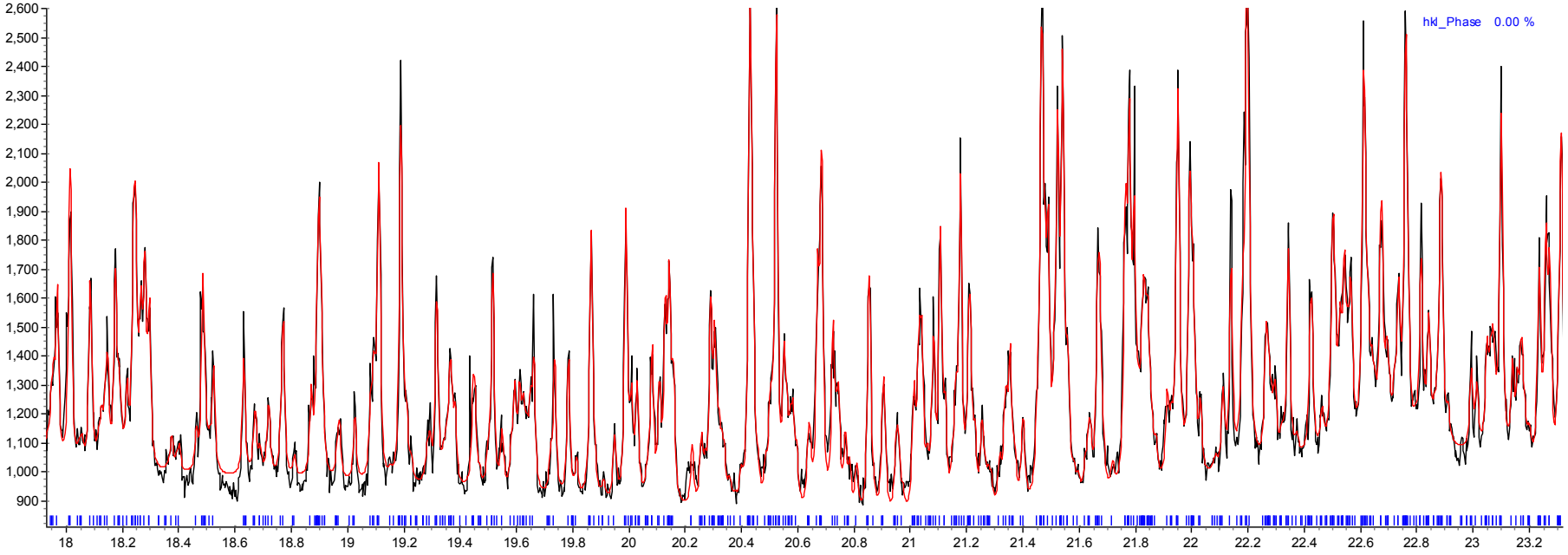
$$= \frac{4}{3}\pi V_c d^{*3}$$



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

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

Limits


hkl_Phase 0.00 %
2,600
2,500
2,400
2,300
2,200
2,100
2,000
1,900
1,800
1,700
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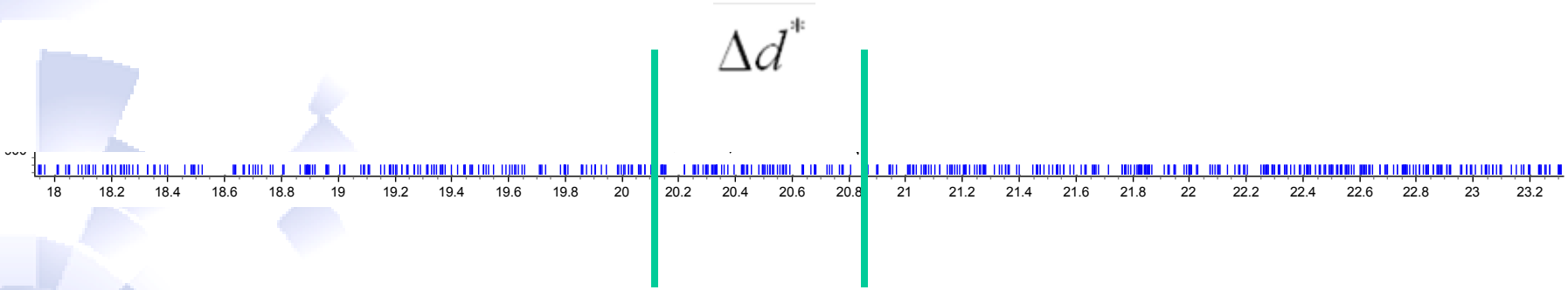
1,500
1,400
1,300
1,200
1,100
1,000
900
18
18.2
18.4
18.6
18.8
19
19.2
19.4
19.6
19.8
20
20.2
20.4
20.6
20.8
21
21.2
21.4
21.6
21.8
22
22.2
22.4
22.6
22.8
23
23.2

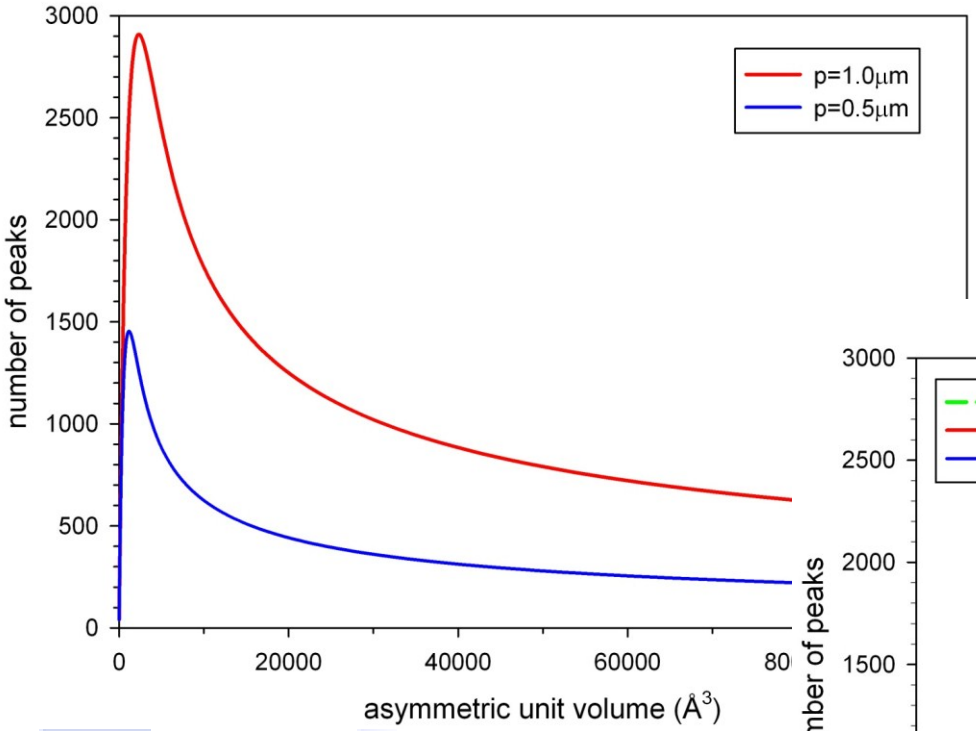
Limits

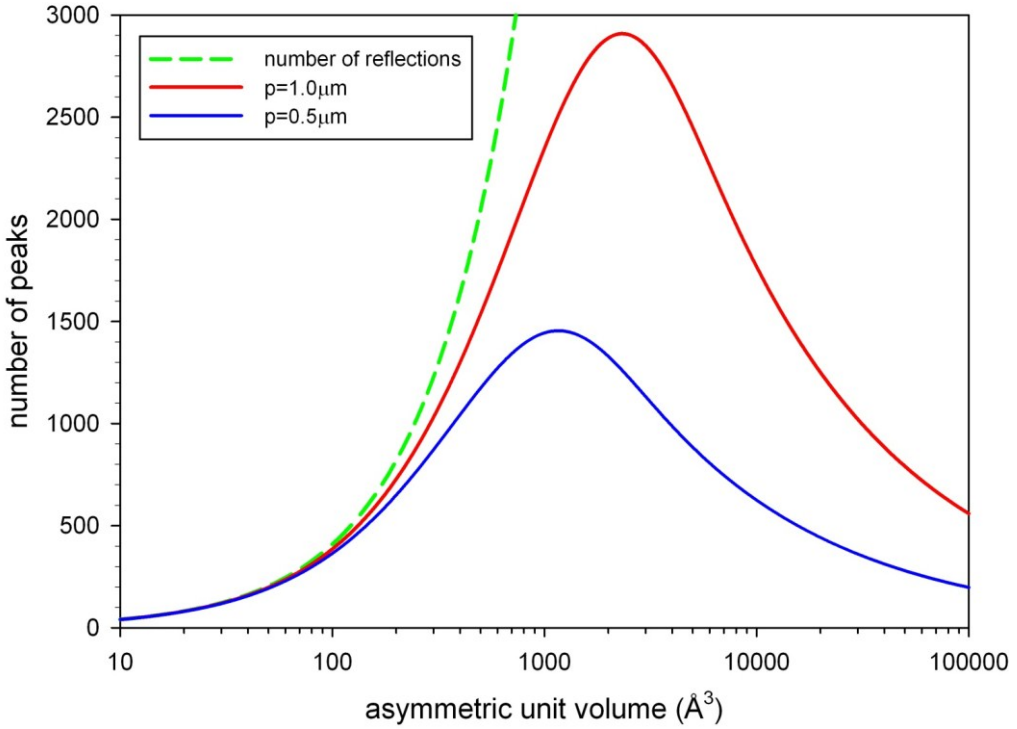
$$N_{peaks} \approx \int_0^{d^*_{max}} \Delta N(d^*) \exp(-\Delta N(d^*)/p)\, dd^*$$

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



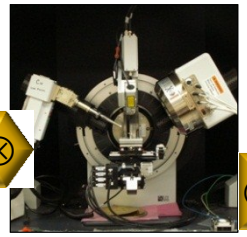
Limits


p=1.0μm
p=0.5μm
number of peaks
asymmetric unit volume (Å3)
0
500
1000
1500
2000
2500
3000
0
20000
40000
60000

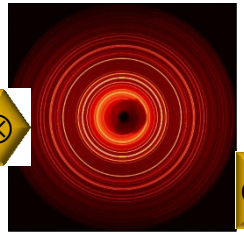

number of reflections
p=1.0μm
p=0.5μm
number of peaks
asymmetric unit volume (Å3)
0
500
1000
1500
2000
2500
3000
10
100
1000
10000
100000

Achieving precision and accuracy

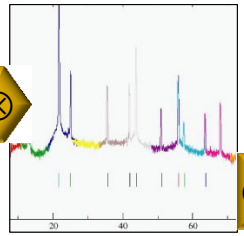
Sample preparation



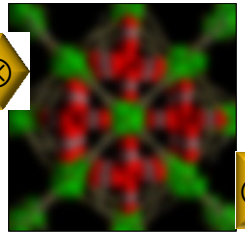
Instrument calibration



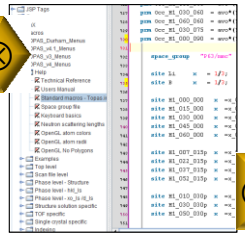
Data collection



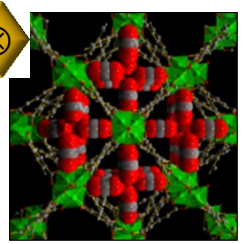
Data reduction



Structural model

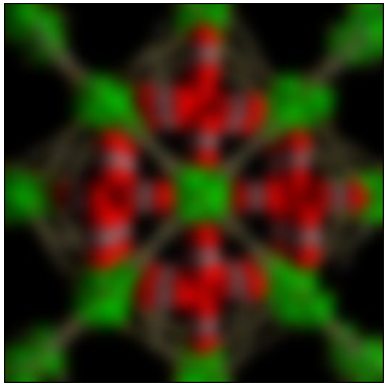


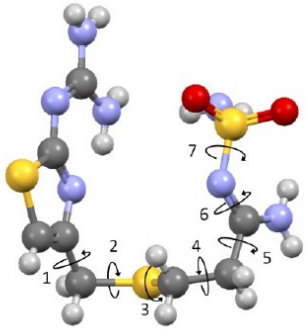
Data analysis

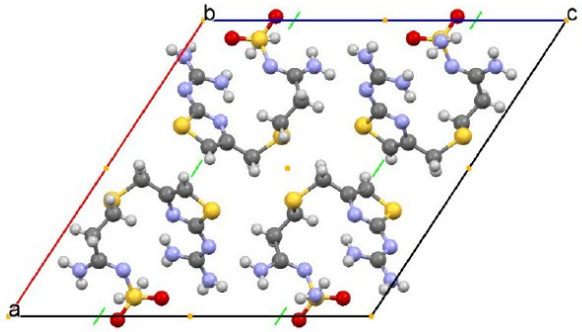


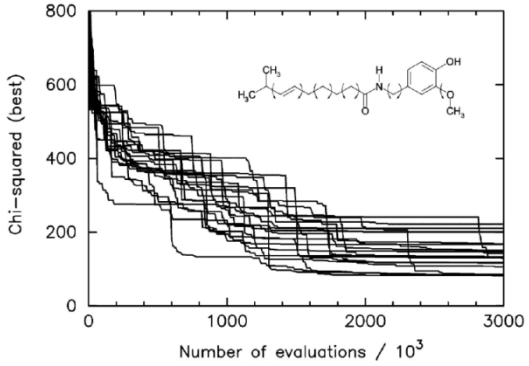
Validation

The structural (and microstructural) model









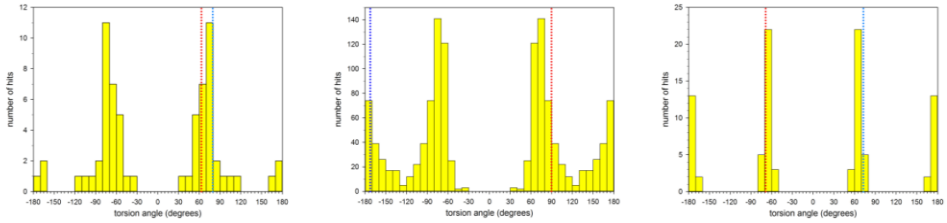


Fig. X.Z.6.3. Frequency distributions for torsion angles 1, 3 and 4 in famotidine as illustrated in Figs. X.Z.4.2 and X.Z.6.1. The values for form A and form B famotidine are indicated by red and blue vertical lines respectively.

Maximum likelihood techniques

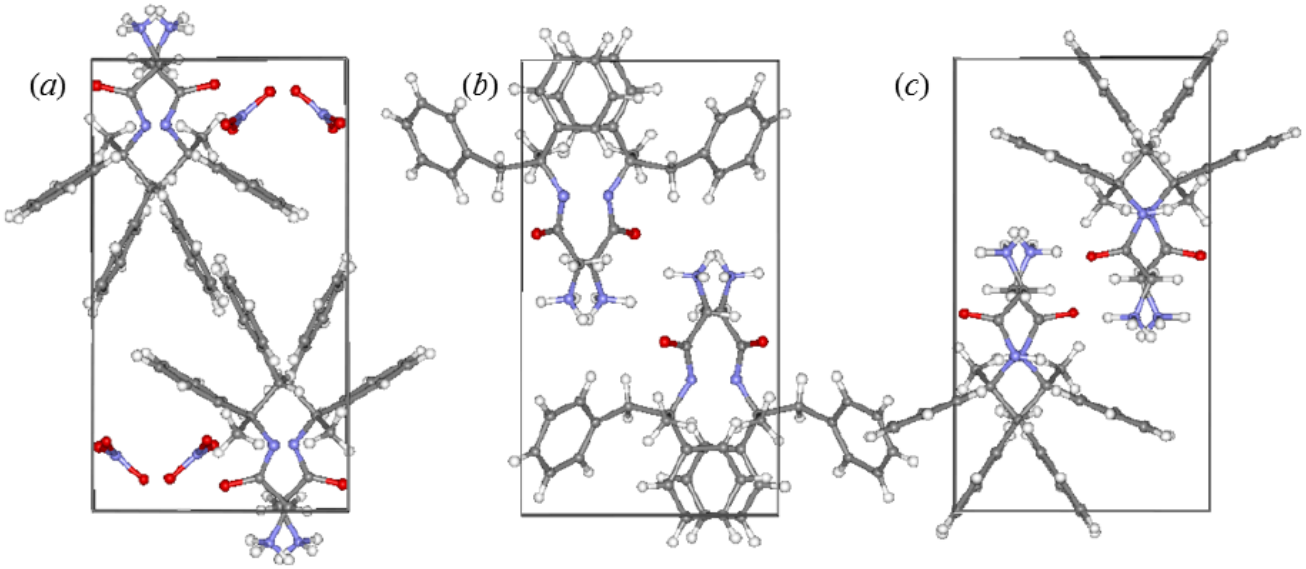


Fig. X.Z.6.7. (*a*) The correct crystal structure of remacemide nitrate. (*b*) The best structure determination using a least-squares analysis to compare observed and calculated diffraction data with only the remacemide ion used in the structural model. Note that, although the structural arrangement 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 enantioimetrically 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

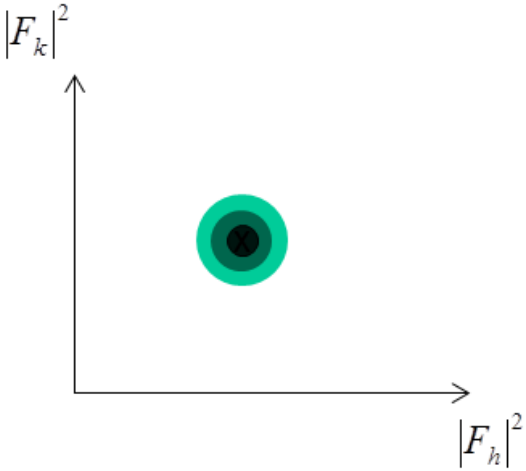
- Rietveld method – assumes the observed and calculated phases of the reflections are the same
- In some cases, this can lead to a biased model.
- Combined Fourier difference map and maximum entropy approach:

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

$$\times \left(C^{-1}_{hk} \right) \left[\left| F_{obs}(k) \right|^2 - \left| F_{known}(k) + \Delta F(k) \right|^2 \right]$$

data host

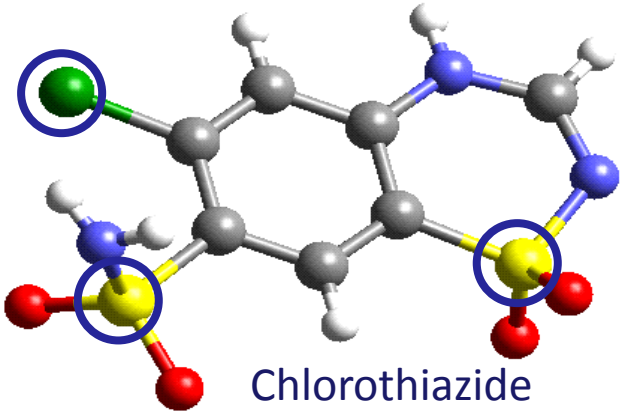
Correlation between reflections



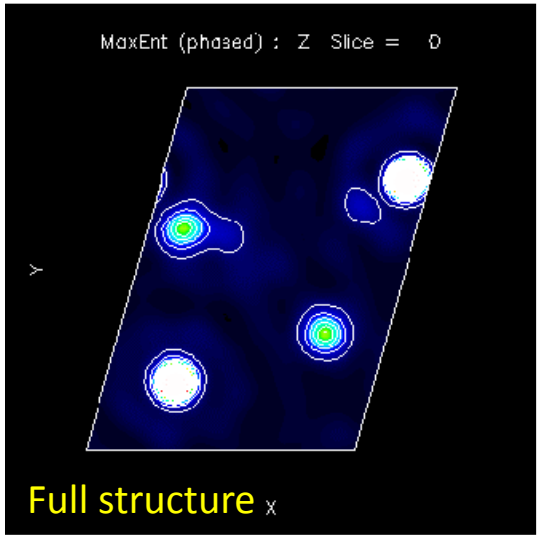
- Does not assume phases of the reflections
- Minimises χ^2 with the minimum number of features that are consistent with the data.

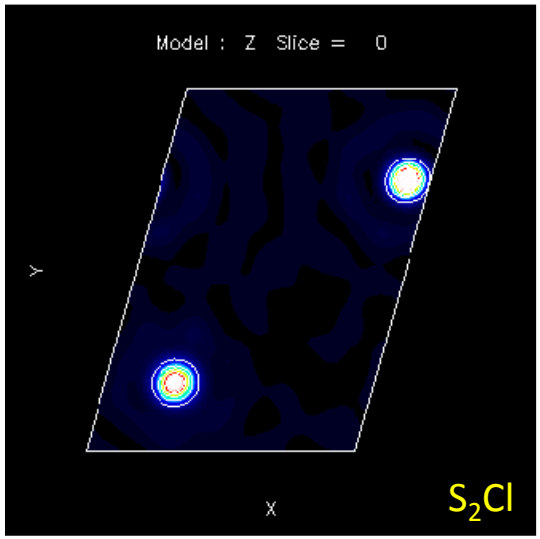
W.I.F. David and D.S. Sivia, *Extracting intensities from powder diffraction patterns* in *Structure Determination from Powder Data*, OUP, 2002.

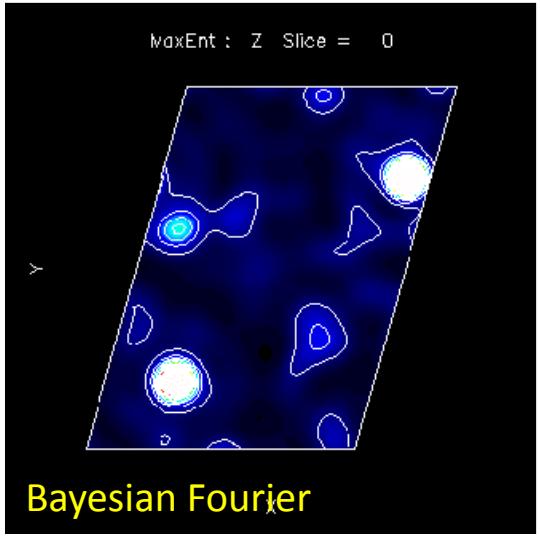
Maximum entropy (likelihood) techniques

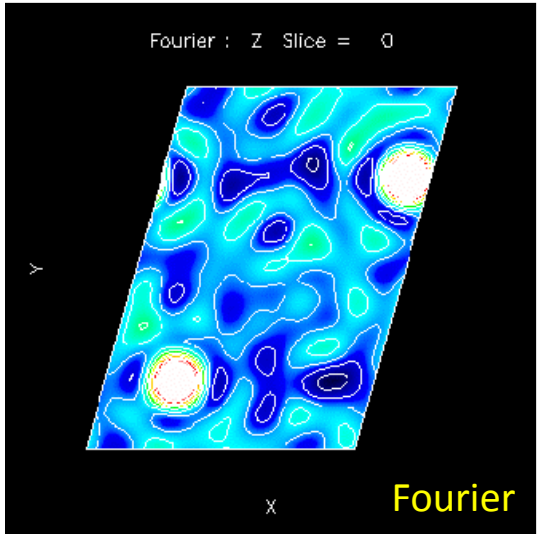


Chlorothiazide



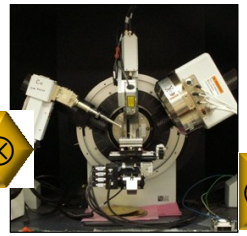




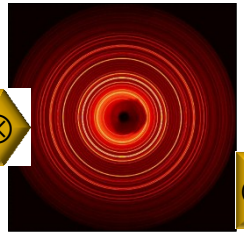


Achieving precision and accuracy

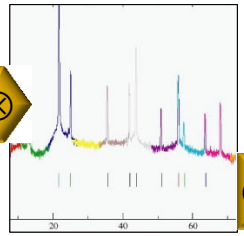
Sample preparation



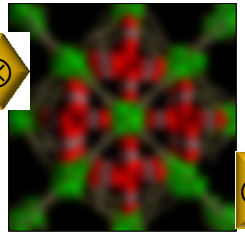
Instrument calibration



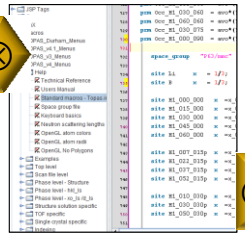
Data collection



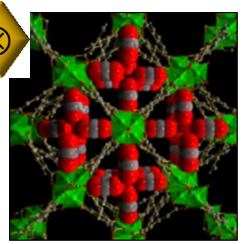
Data reduction



Structural model



Data analysis



Validation

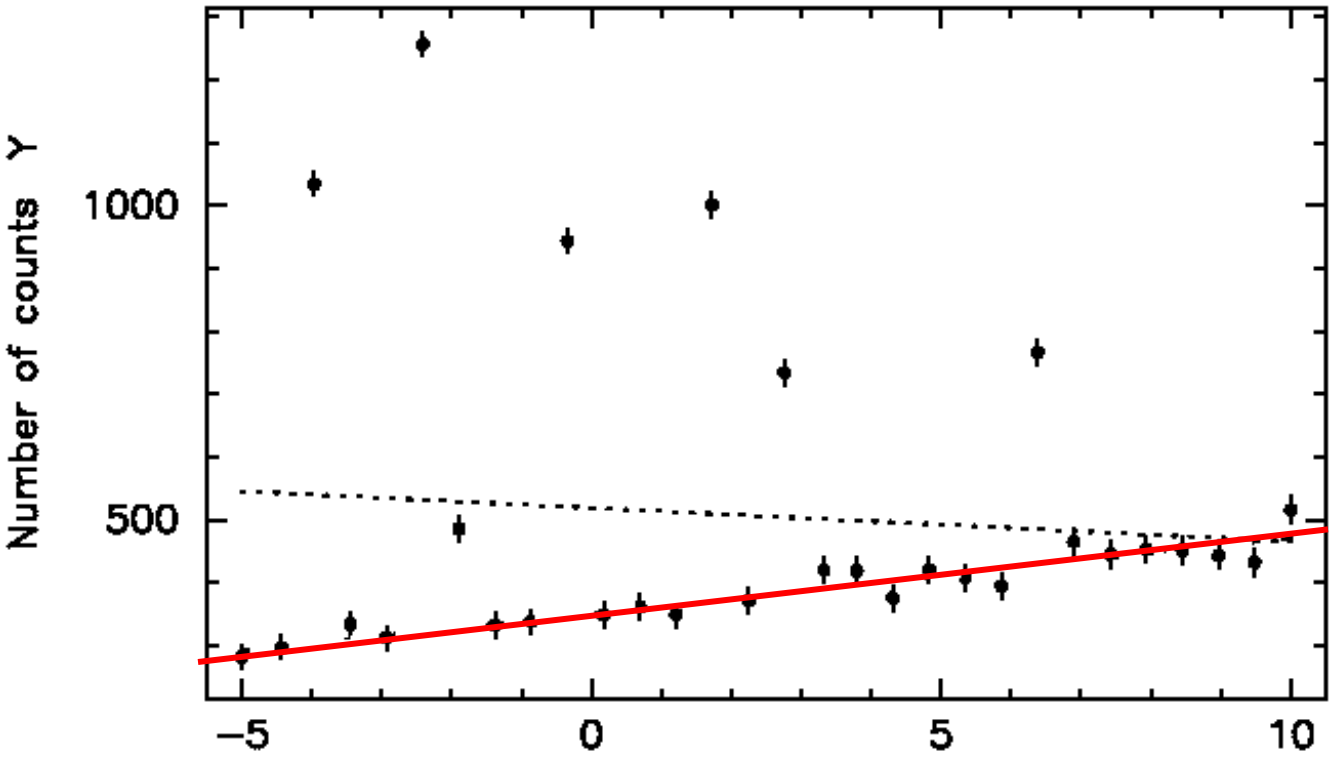
The heroes (cont.)

Ted Prince

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

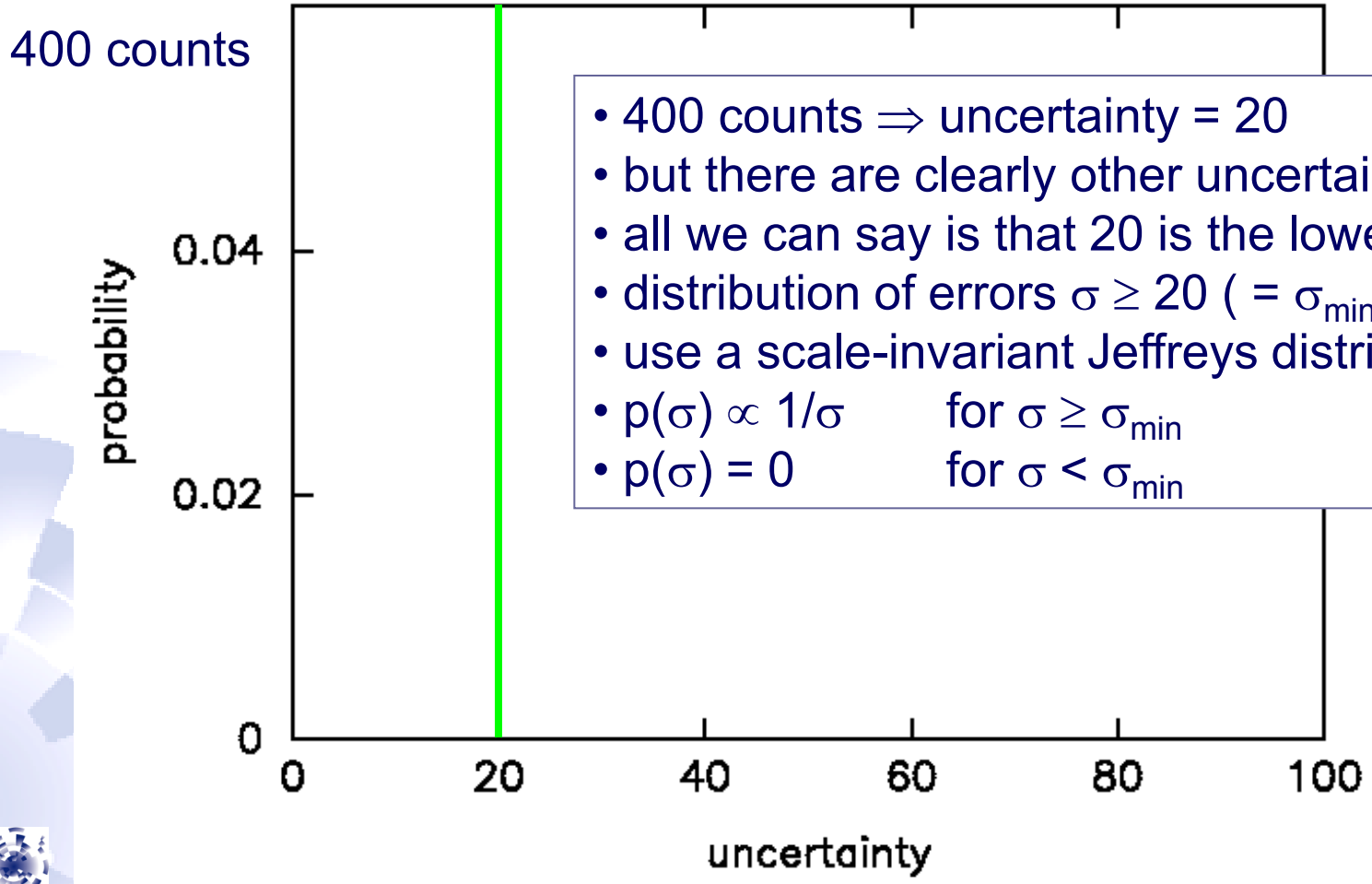
What if the fit is not as good as it could be

- 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!


Number of counts Y
1000
500
−5
0
5
10

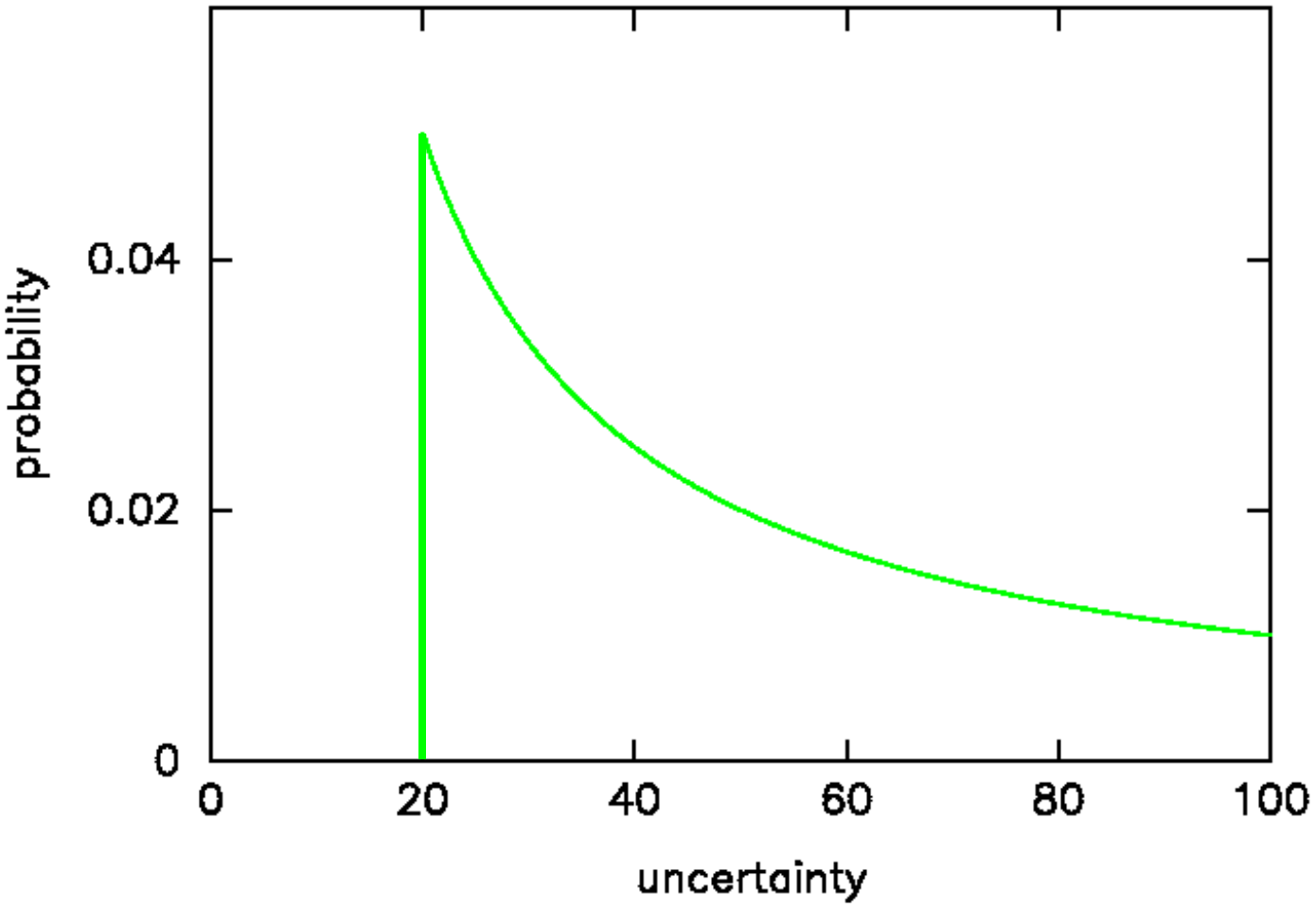
What's gone wrong?

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

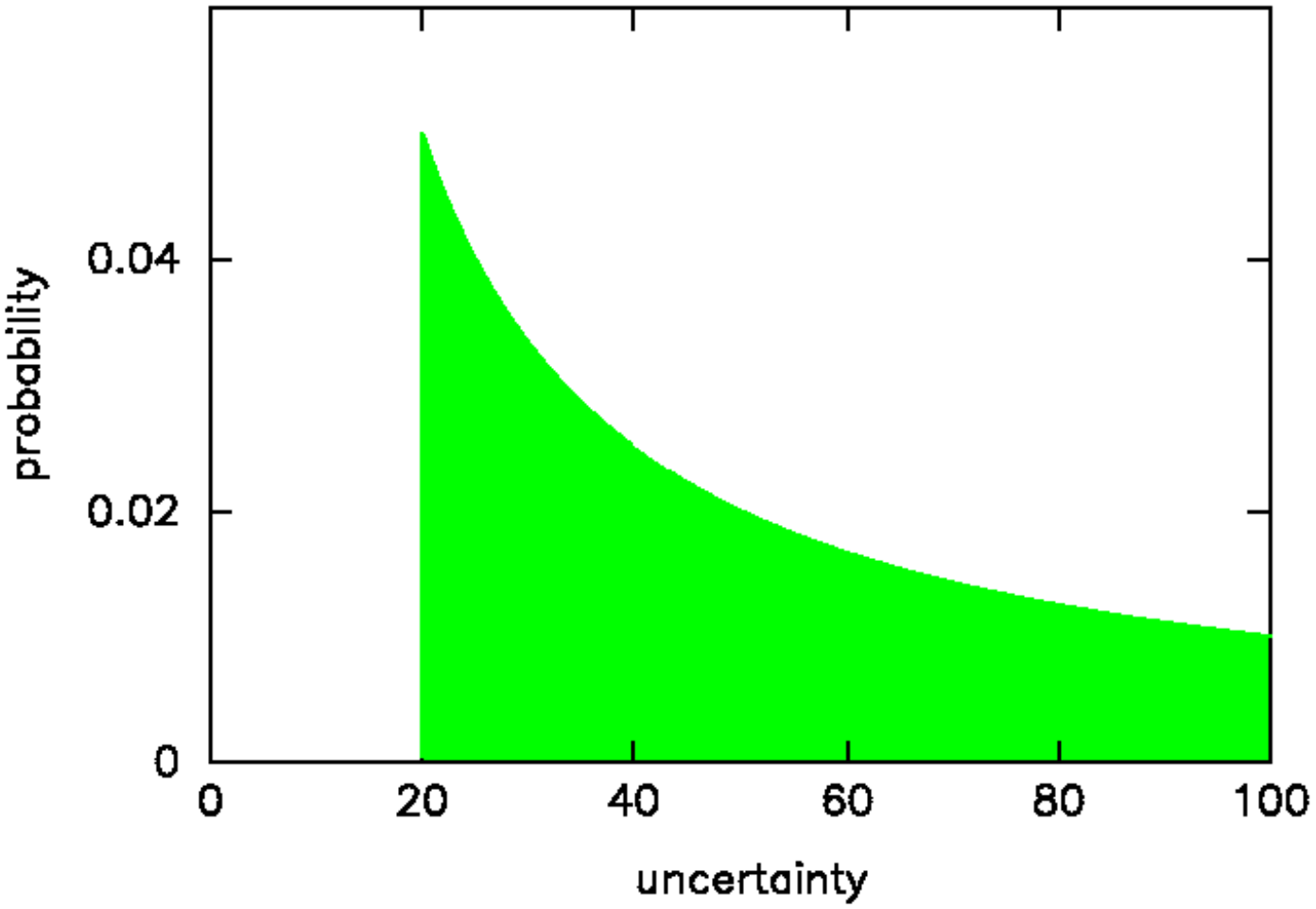


- 400 counts $\Rightarrow$ uncertainty = 20
- but there are clearly other uncertainties
- all we can say is that 20 is the lower bound
- distribution of errors $\sigma \geq 20$ (= σ_{min})
- use a scale-invariant Jeffreys distribution
- $p(\sigma) \propto 1/\sigma$ for $\sigma \geq \sigma_{min}$
- $p(\sigma) = 0$ for $\sigma < \sigma_{min}$

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

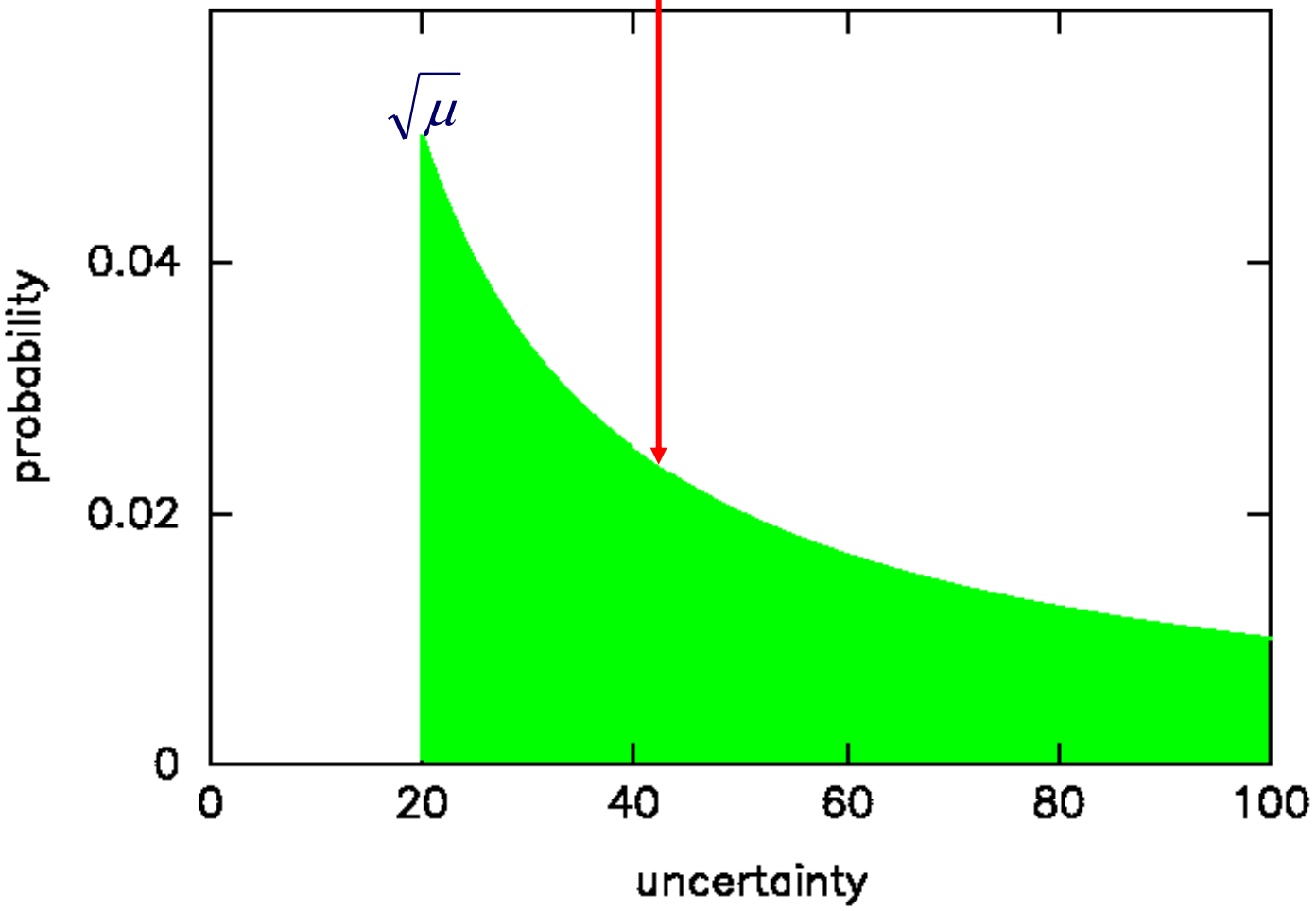


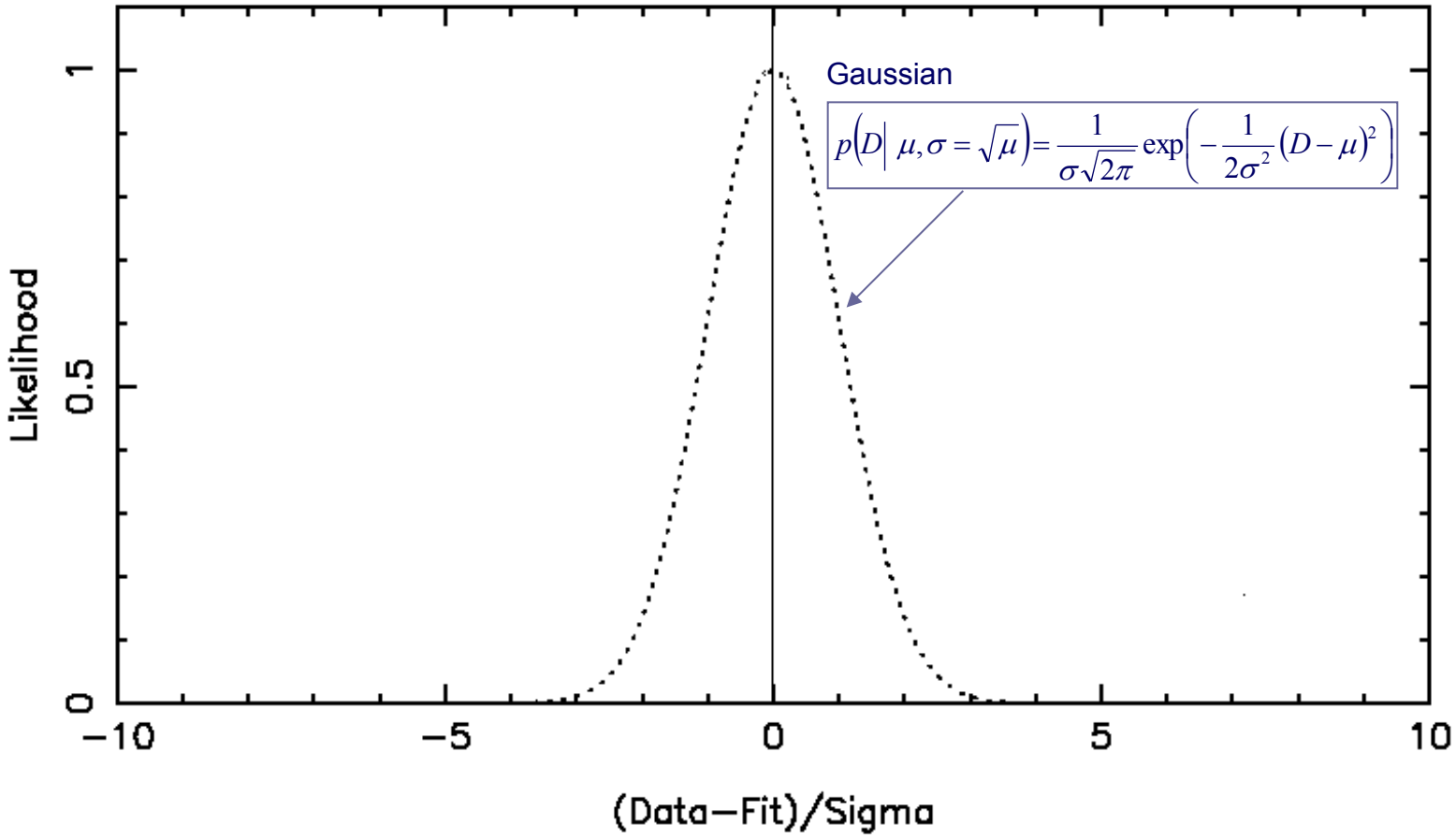
- Jeffreys prior
- $p(\sigma) \propto 1/\sigma$ for $\sigma \geq \sigma_{min}$
- $p(\sigma) = 0$ for $\sigma < \sigma_{min}$

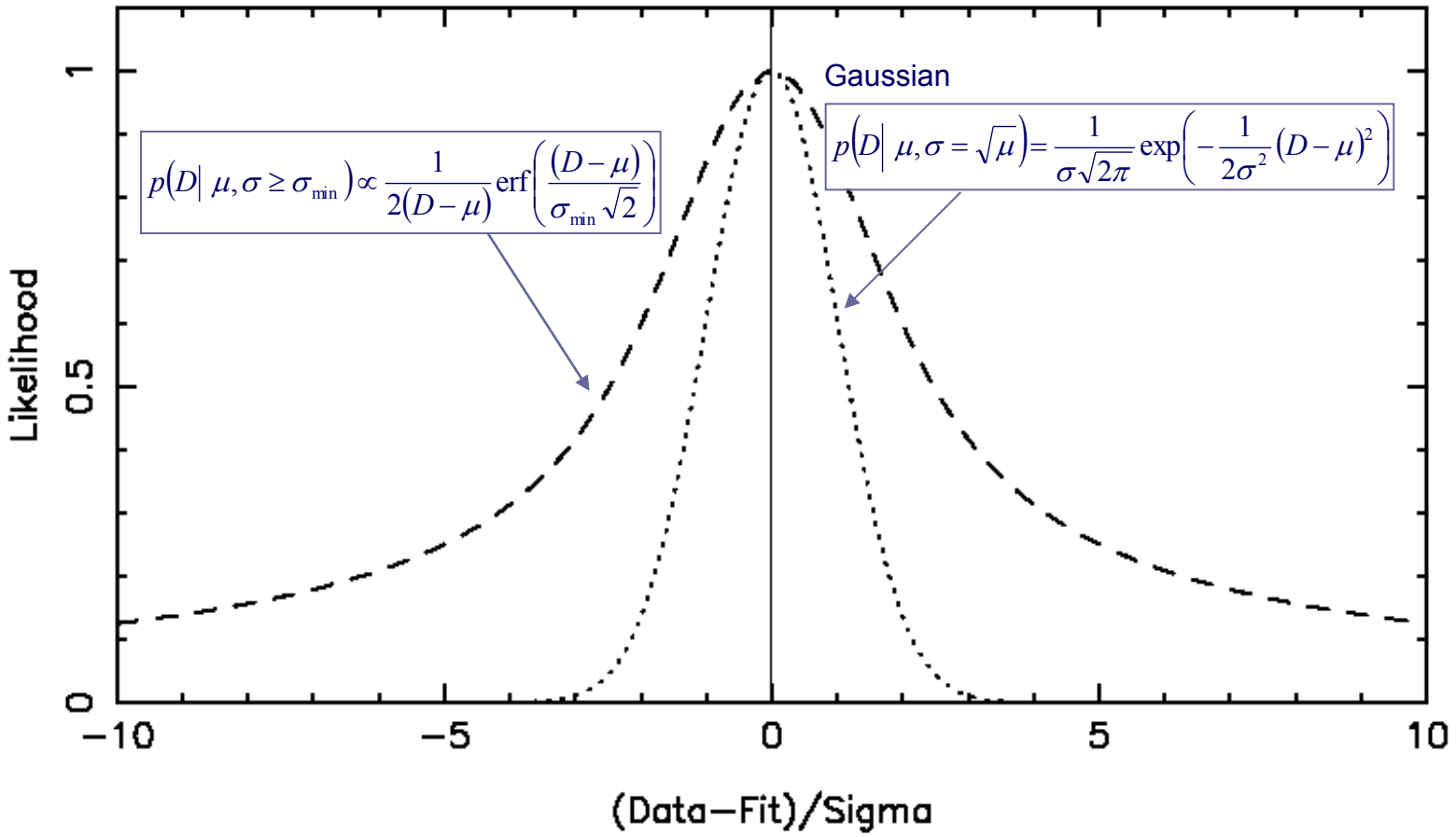


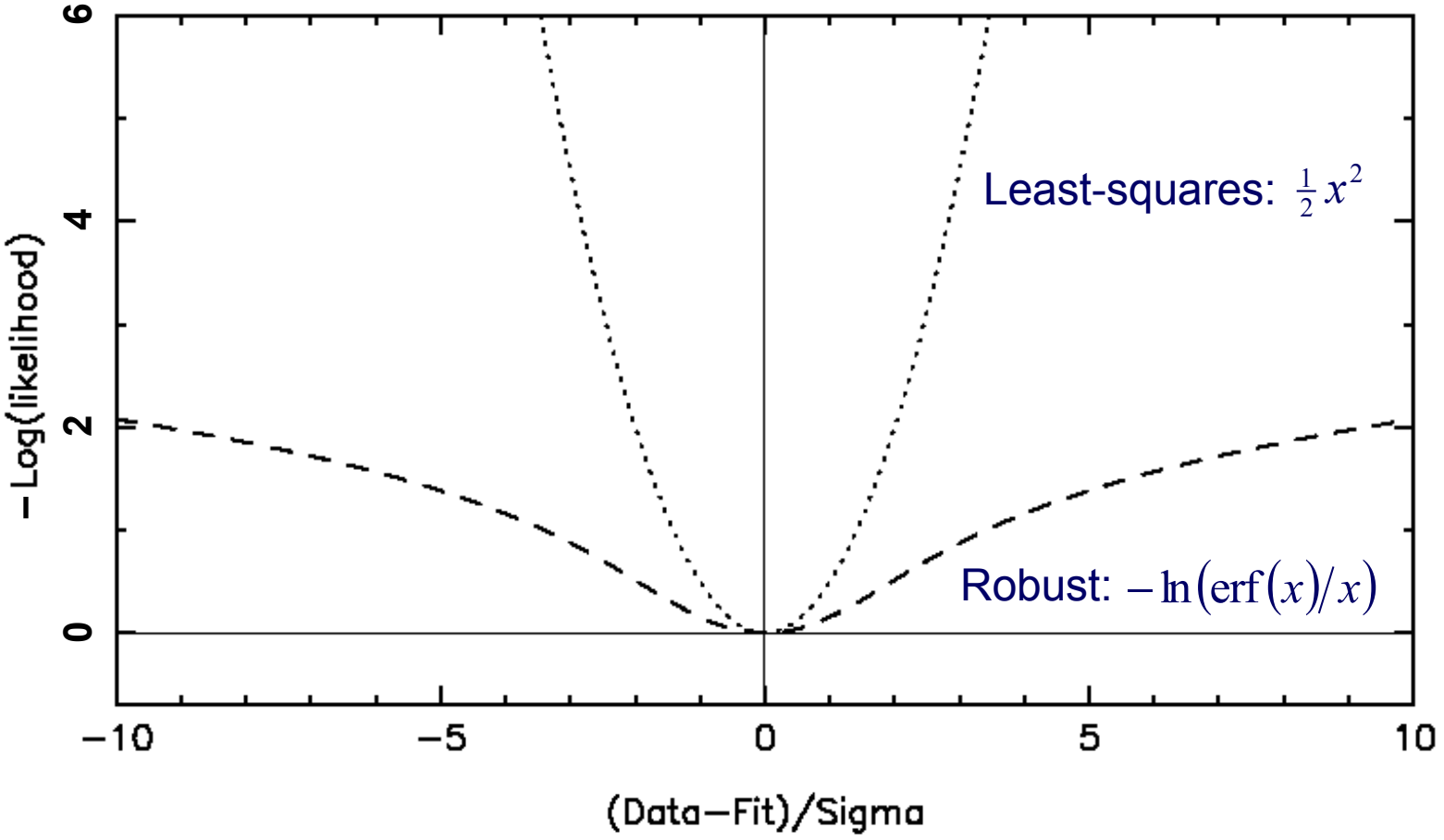
Gaussian

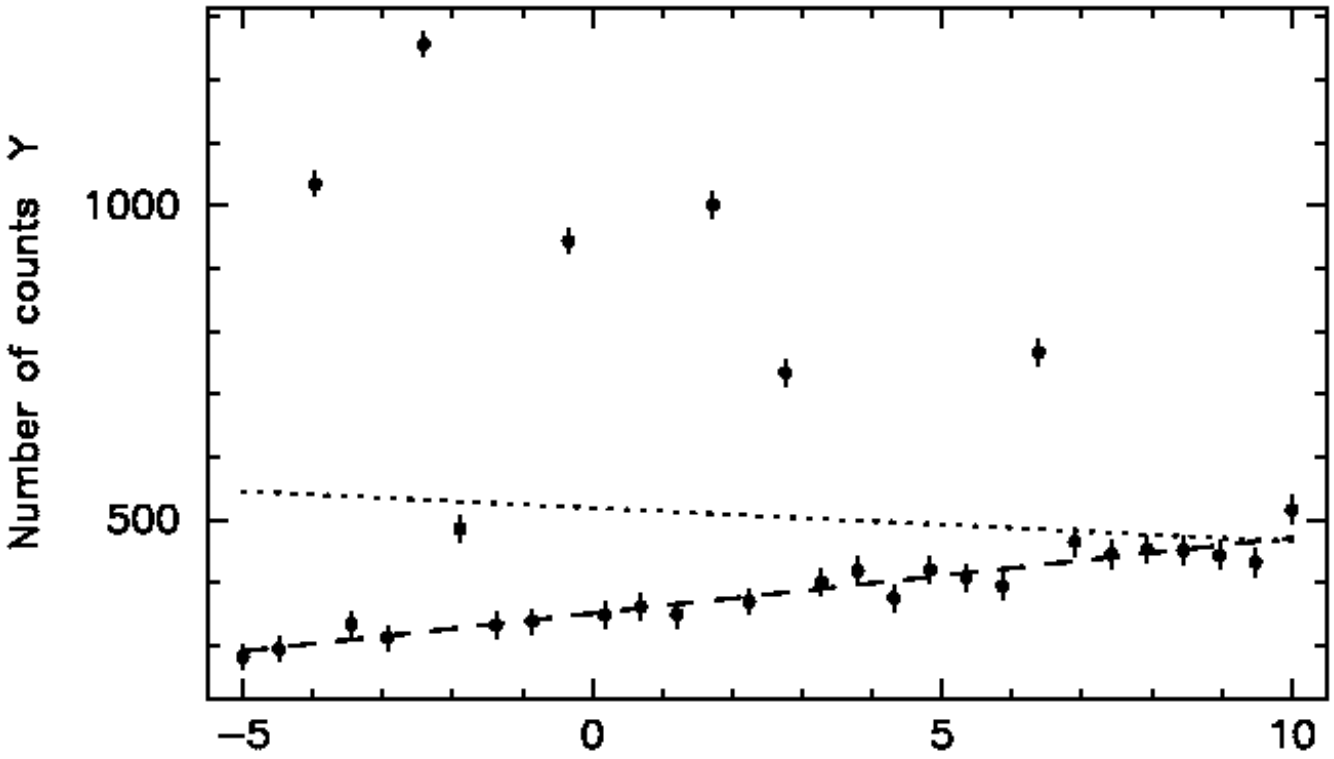
$$p\left(D \middle| \mu, \sigma \geq \sqrt{\mu}\right) = \int_{\sigma_{\min}=\sqrt{\mu}}^{\infty} prob(\sigma) \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{1}{2\sigma^2}(D-\mu)^2\right) d\sigma$$



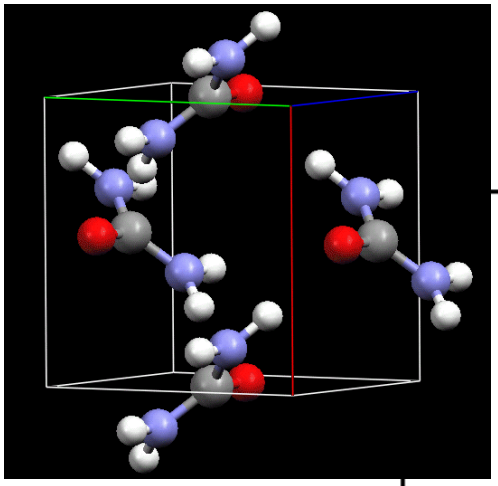

Gaussian
$p\left(D\middle|\ \mu,\sigma=\sqrt{\mu}\right)=\frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{1}{2\sigma^2}(D-\mu)^2\right)$
Likelihood
0
0.5
1
−10
−5
0
5
10
(Data−Fit)/Sigma

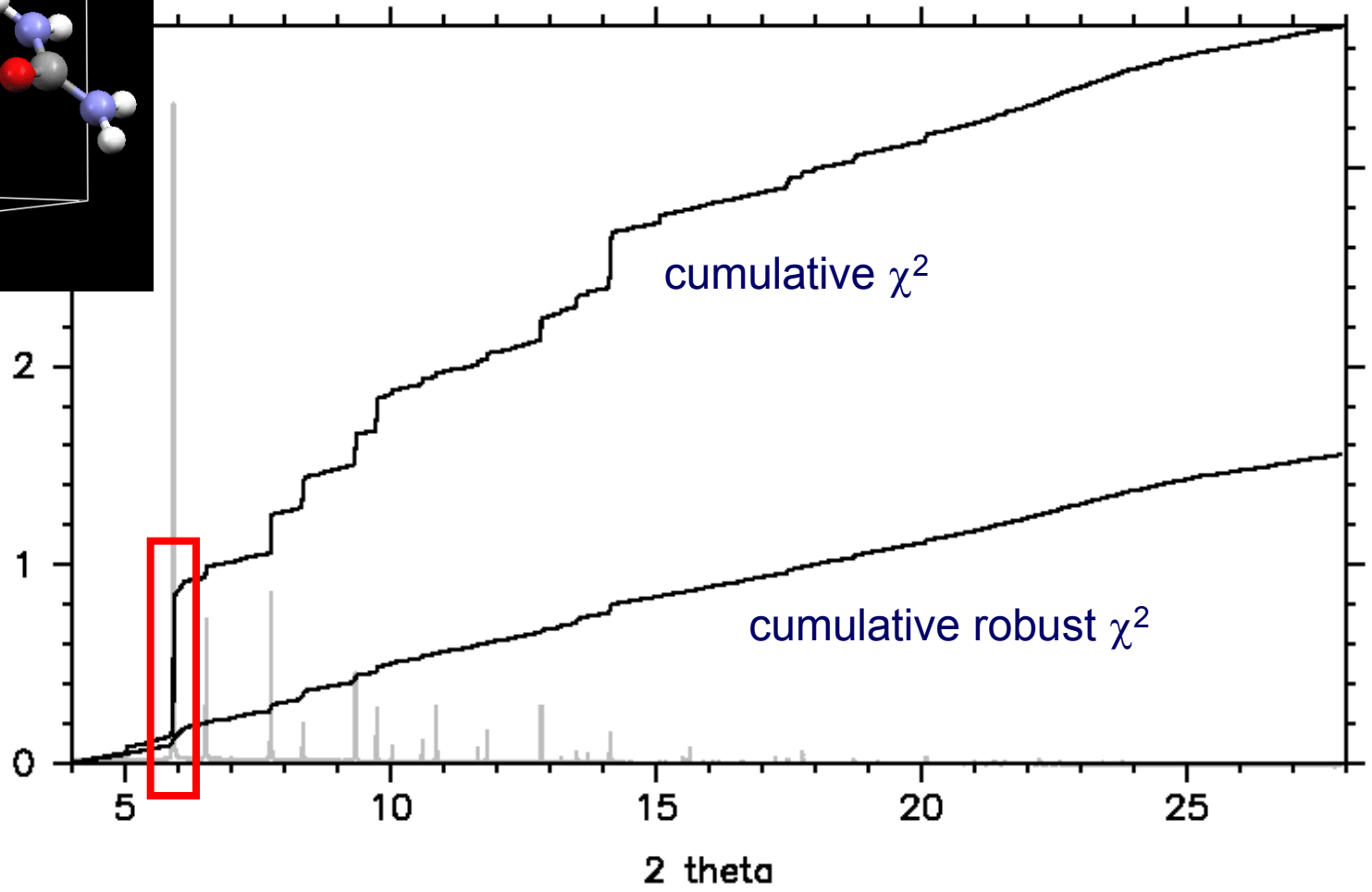

Gaussian
$p(D|\ \mu,\sigma=\sqrt{\mu})=\frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{1}{2\sigma^2}(D-\mu)^2\right)$
$p(D|\ \mu,\sigma\geq\sigma_{min})\propto\frac{1}{2(D-\mu)}\mathrm{erf}\left(\frac{(D-\mu)}{\sigma_{min}\sqrt{2}}\right)$
Likelihood
0
0.5
1
−10
−5
0
5
10
(Data−Fit)/Sigma


−Log(likelihood)
0
2
4
6
−10
−5
0
5
10
(Data−Fit)/Sigma
Least-squares: $\frac{1}{2}x^2$
Robust: $-\ln(\mathrm{erf}(x)/x)$


Number of counts Y
1000
500
−5
0
5
10

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

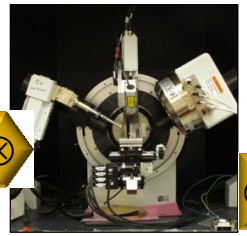
9/14 > 4σ

1/14 > 4σ

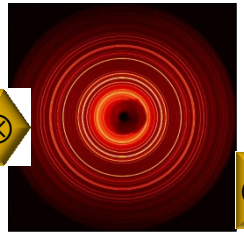
David, W.I.F., J. Res. Natl. Inst. Stand. Technol. **109** (2004) 107-123

Achieving precision and accuracy

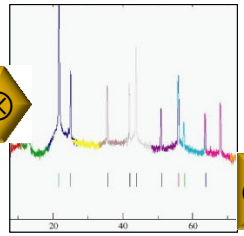
Sample preparation



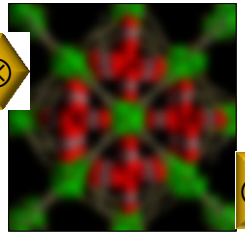
Instrument calibration



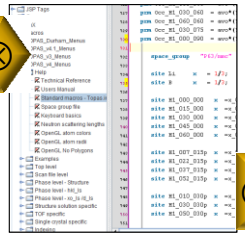
Data collection



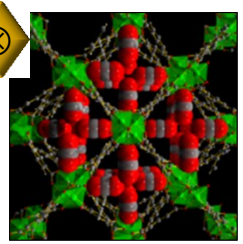
Data reduction



Structural model

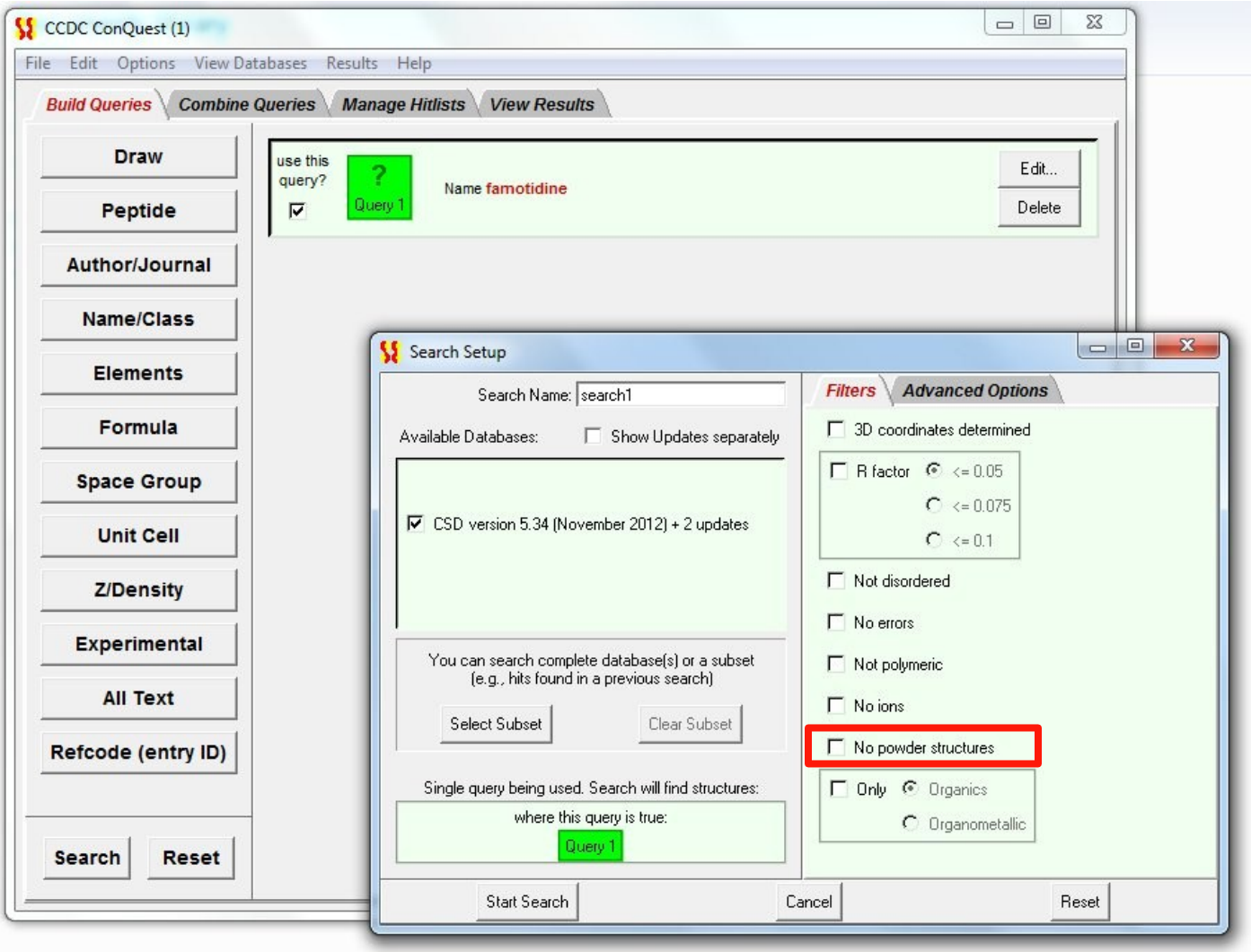


Data analysis



Validation

Inaccuracy and invalidation:



Inaccuracy and invalidation

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

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

File Message

Translate Find Related Select Editing Zoom Zoom

Sent: Wed 09/01/2013 19:20

Message message-footer.txt (347 B)

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

> wrote:

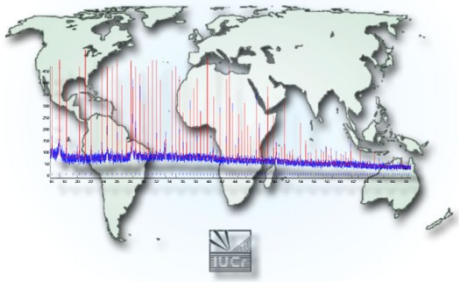
> On 7 January 2013 02:34,
>> Dear [redacted]
>>
> In
>> addition, many of us find it tiresome that these days it is easy to use the
>> internet to ask people to explain things that basic classwork would have
>> covered.
>

Nikky Scarlett

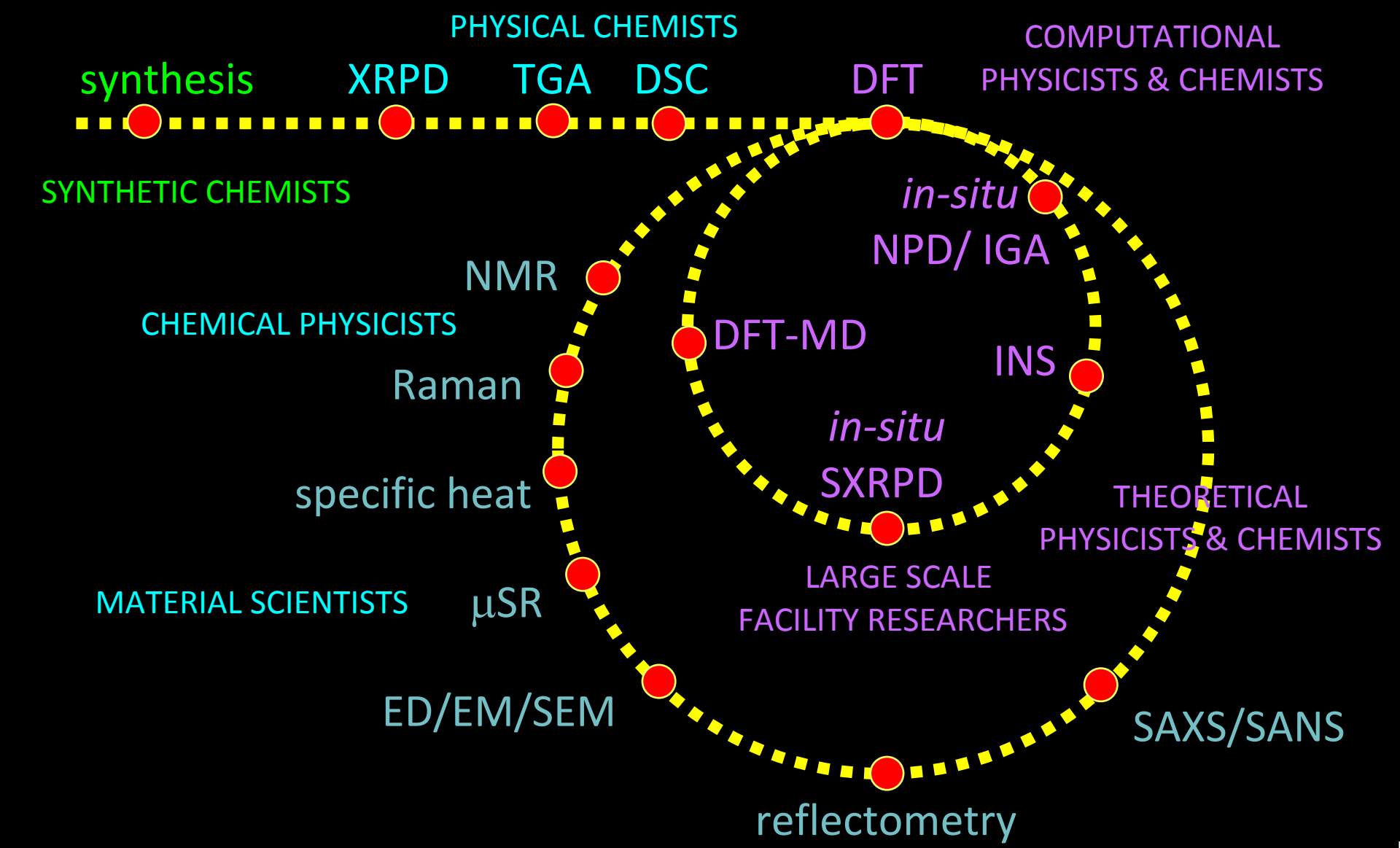
- Encourage best practice
- Awareness of limitations
- Prescriptive procedures
- Authenticated labs

Raising the bar: journals & databases

Commission on Powder Diffraction



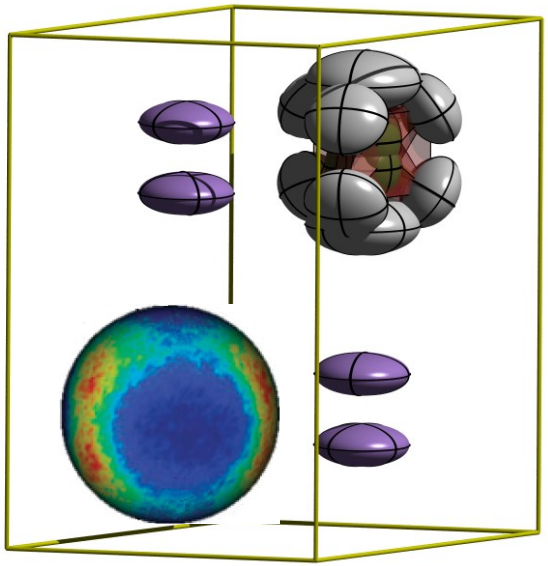
Energy materials research ...

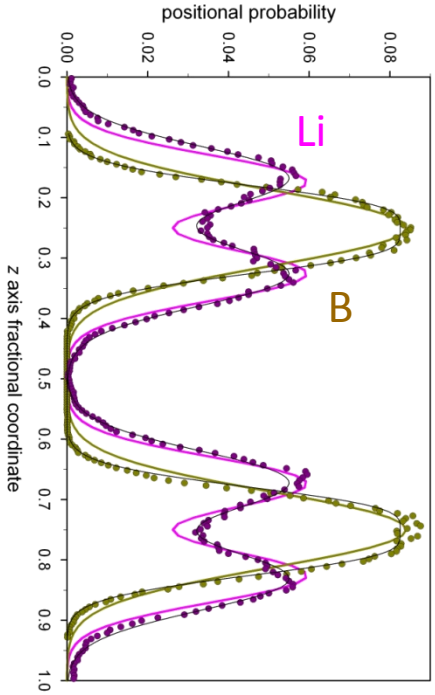


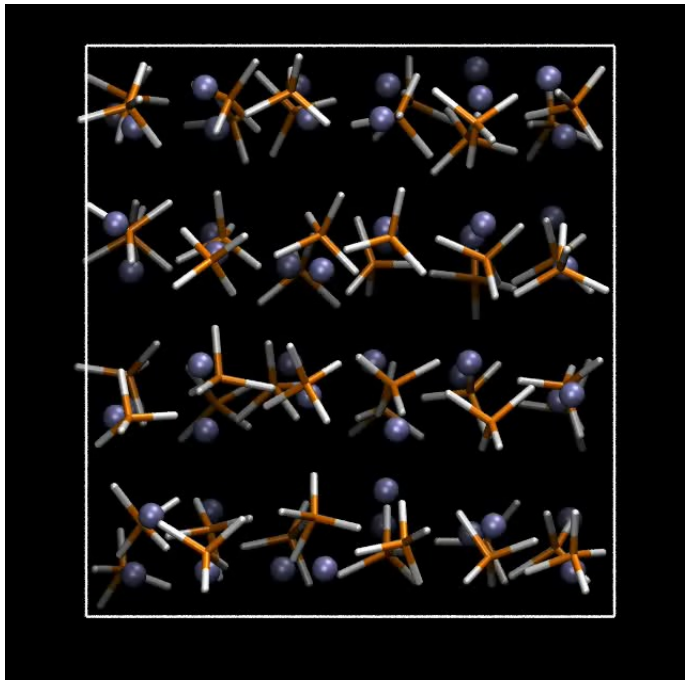
THE FUTURE IS COLLABORATIVE ...

From one dimension to four ...

$LiBH_4$: superionic conductor



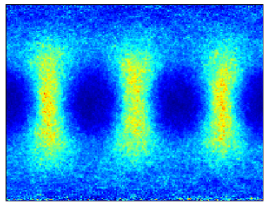


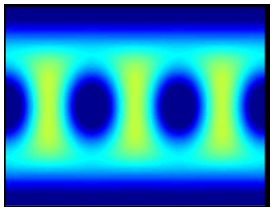


$^{7}Li^{11}BD_4$: GEM (ISIS)

$LiBH_4$: DFT-MD
PRL **108** 095901 (2012)

Hydrogen MODF in BH_4 (DFT MD)





Hydrogen MODF in BH_4 (neutron powder diffraction)(ℓ = 5 spherical harmonic fit)

☑ Excellent
☐ Good
☐ Average
☐ Poor

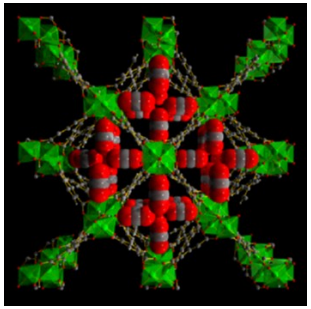
REPORT for Decade ending .....April 2013.....

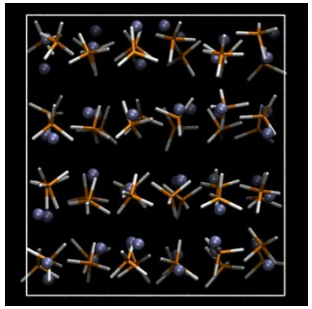
Name: Powder diffraction

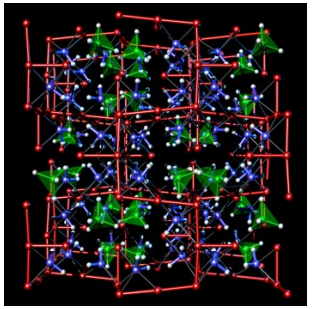
Age: 97

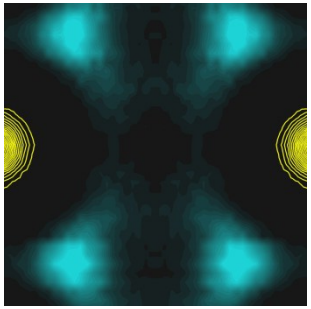
General observations	Excellent progress.
Technical subjects	Impressive new instruments with particular excellence in detectors and electronics. Has taken full advantage of Moore's Law.
Computer studies	Existing programs continue to perform well. Some extremely impressive new programs. Dabbling with new 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.

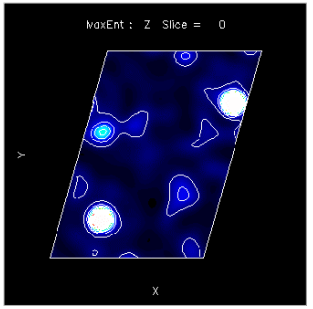
The best is yet to come …


CO2 sequestration

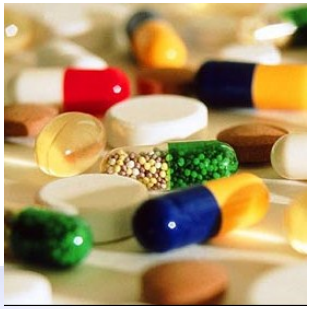

hydrogen stores


lithium batteries

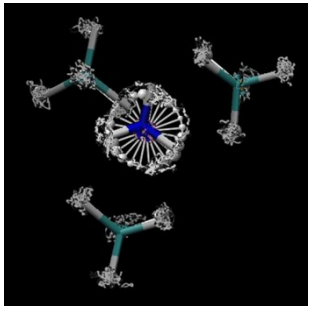

fuel cells

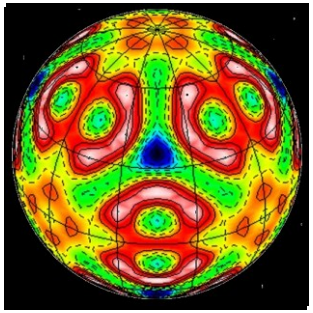


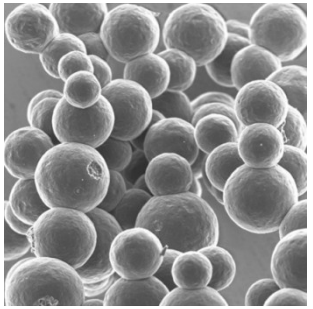
structure determination


pharmaceuticals

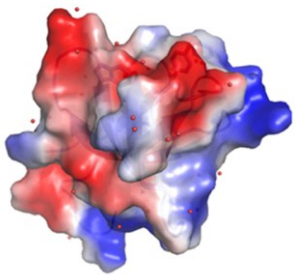

turbine blade

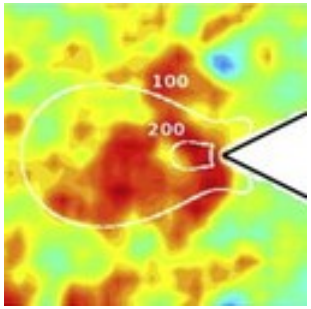

gas storage


C_{60}

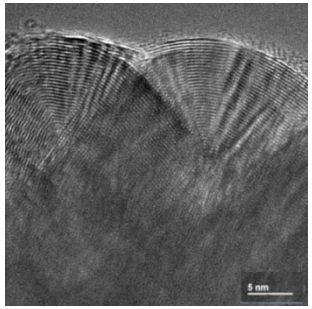

nanomaterials


pencil “lead”

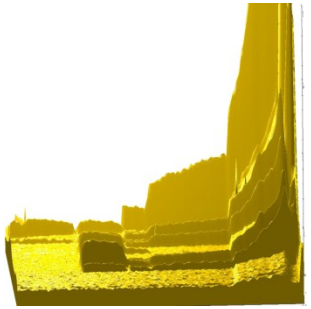

proteins



tensile stress



superhard graphite


paracetamol