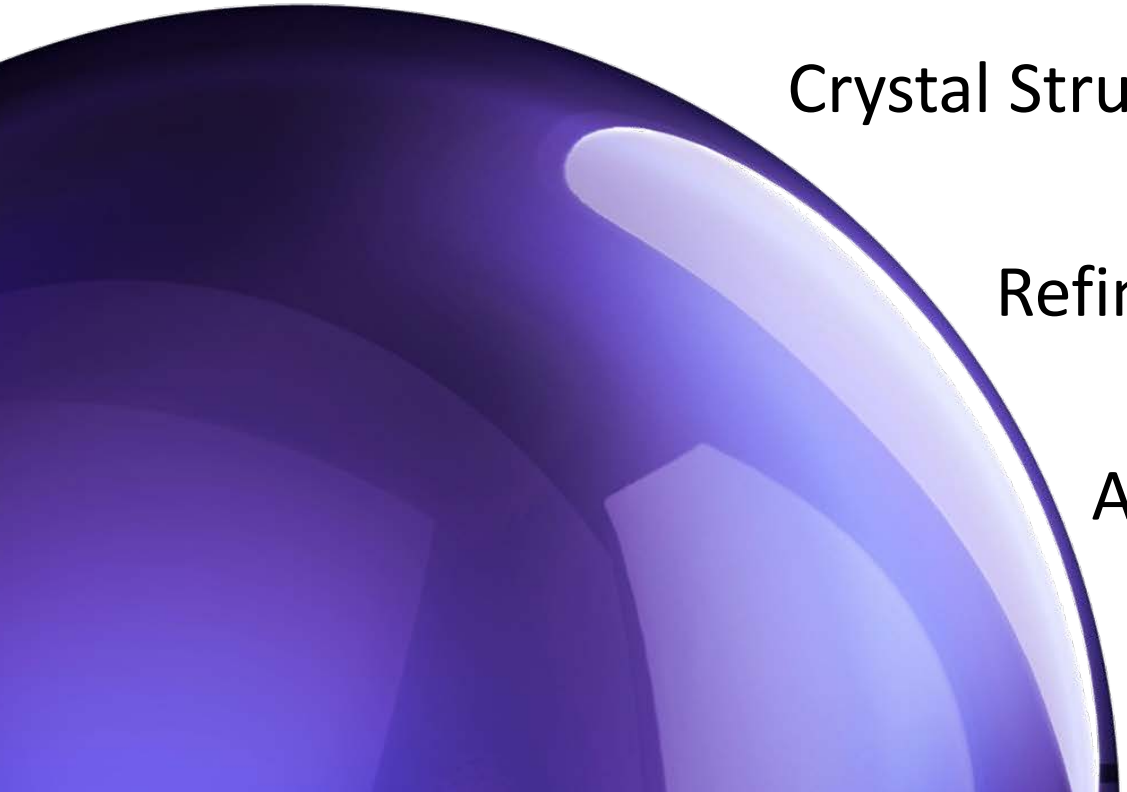
A Bayesian Approach to Crystal Structure Refinement

Dylan Quintana

Carnegie Mellon University / NIST Center for Neutron Research

Preview



Crystal Structure

Refinement

A Bayesian Approach

Image: topdefinitions.com

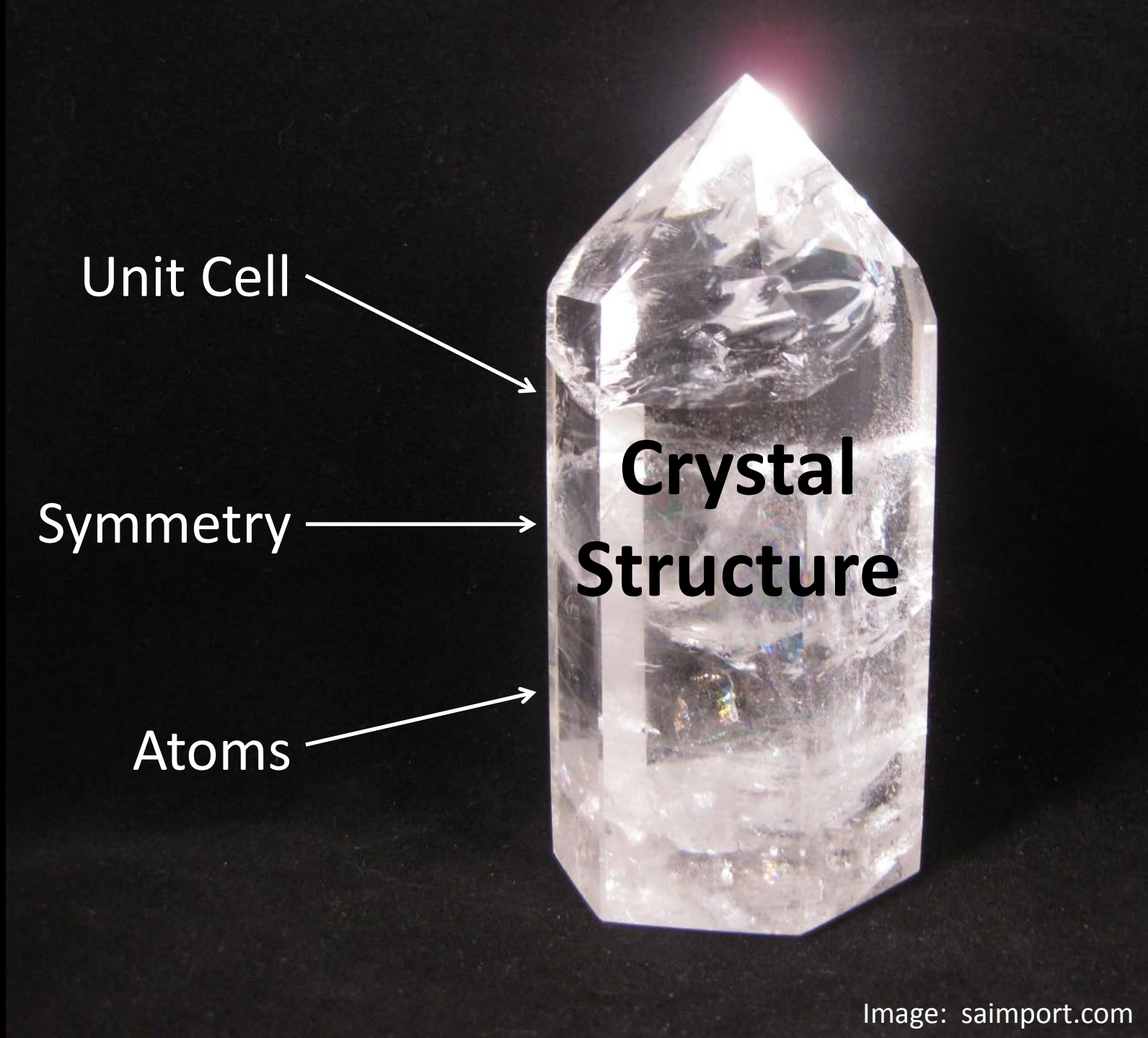
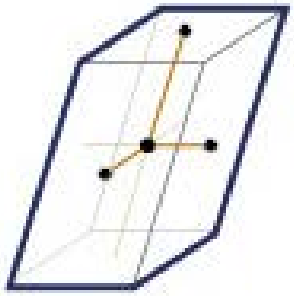
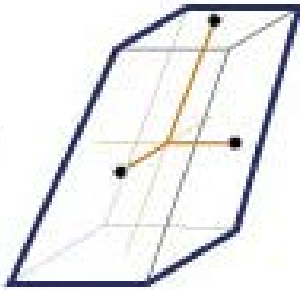


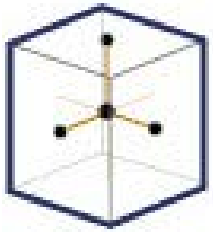
Image: saimport.com



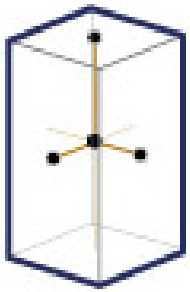
Monoclinic



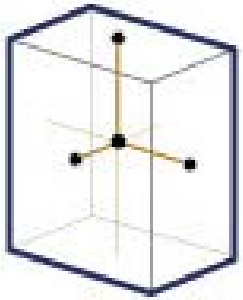
Triclinic



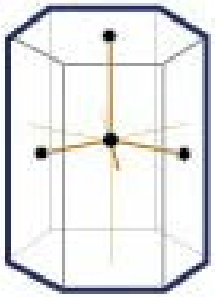
Cubic



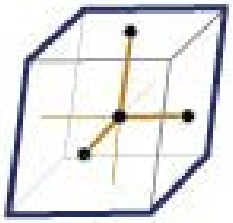
Tetragonal



Orthorhombic



Hexagonal

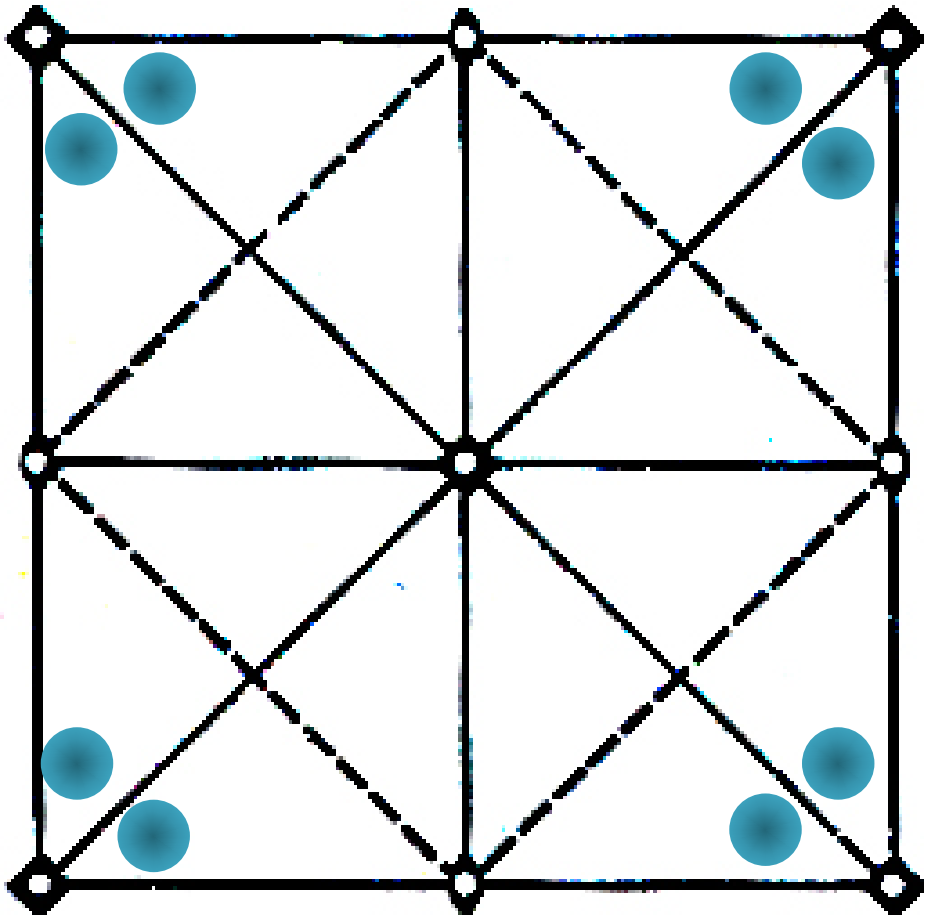


Rhombohedral

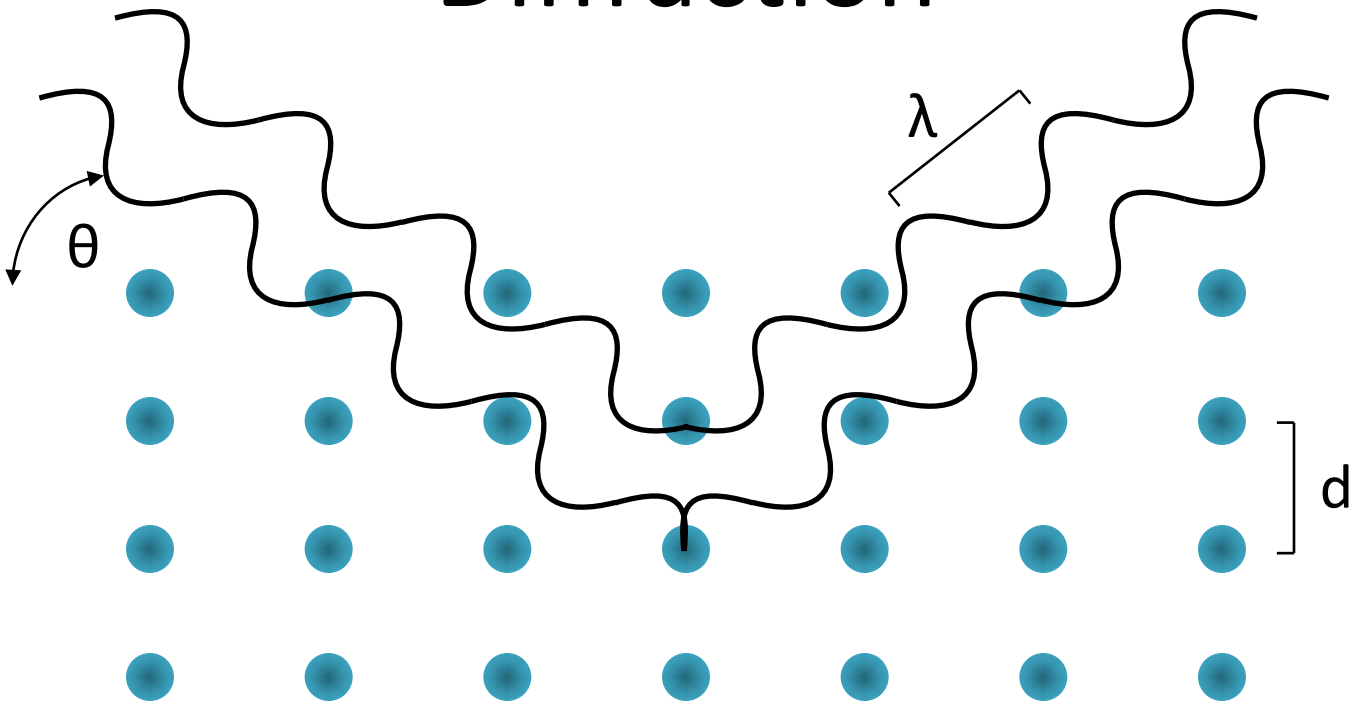
Images: allaboutgemstones.com

Image: organicsoul.com

Adding atoms

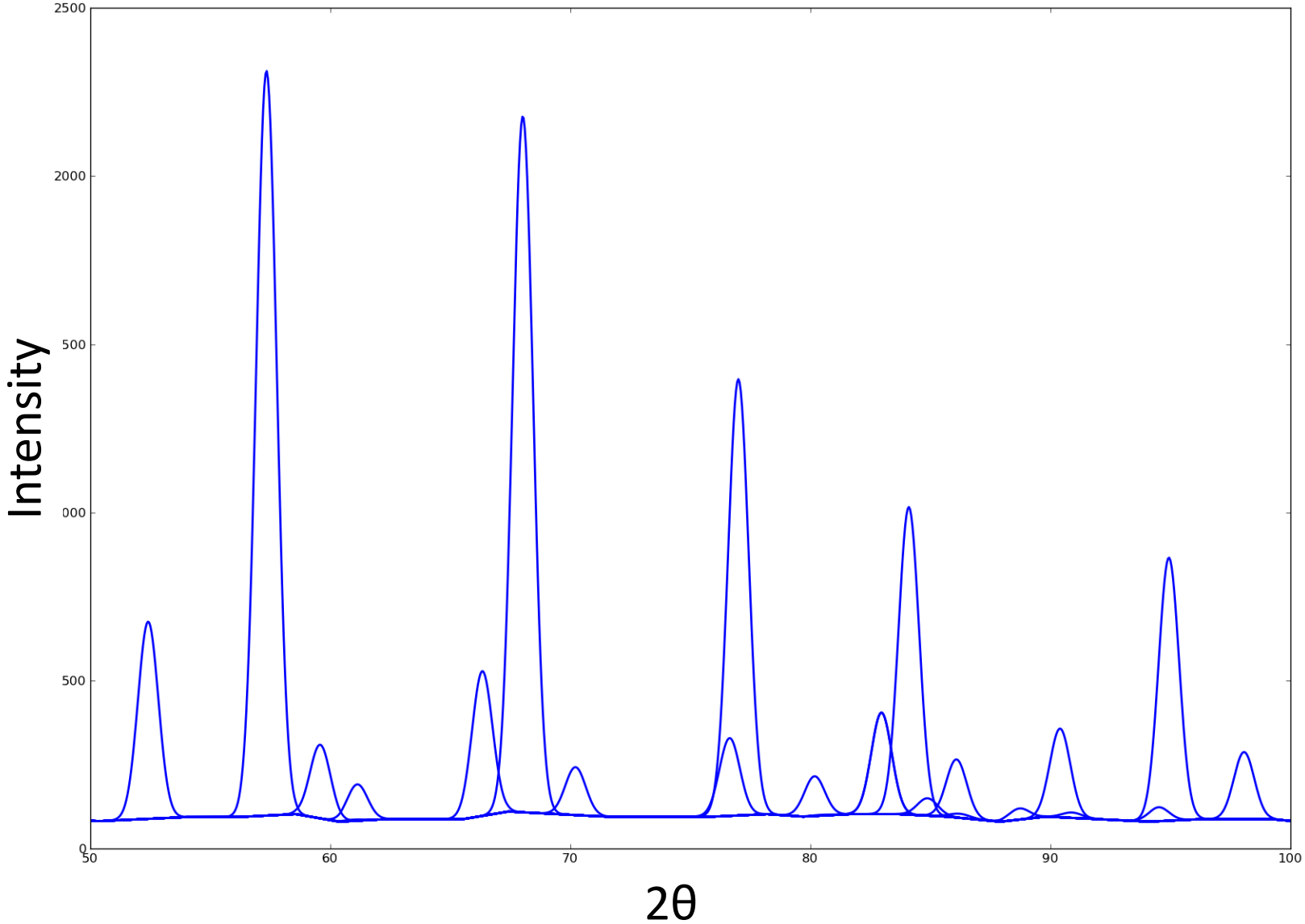


Diffraction

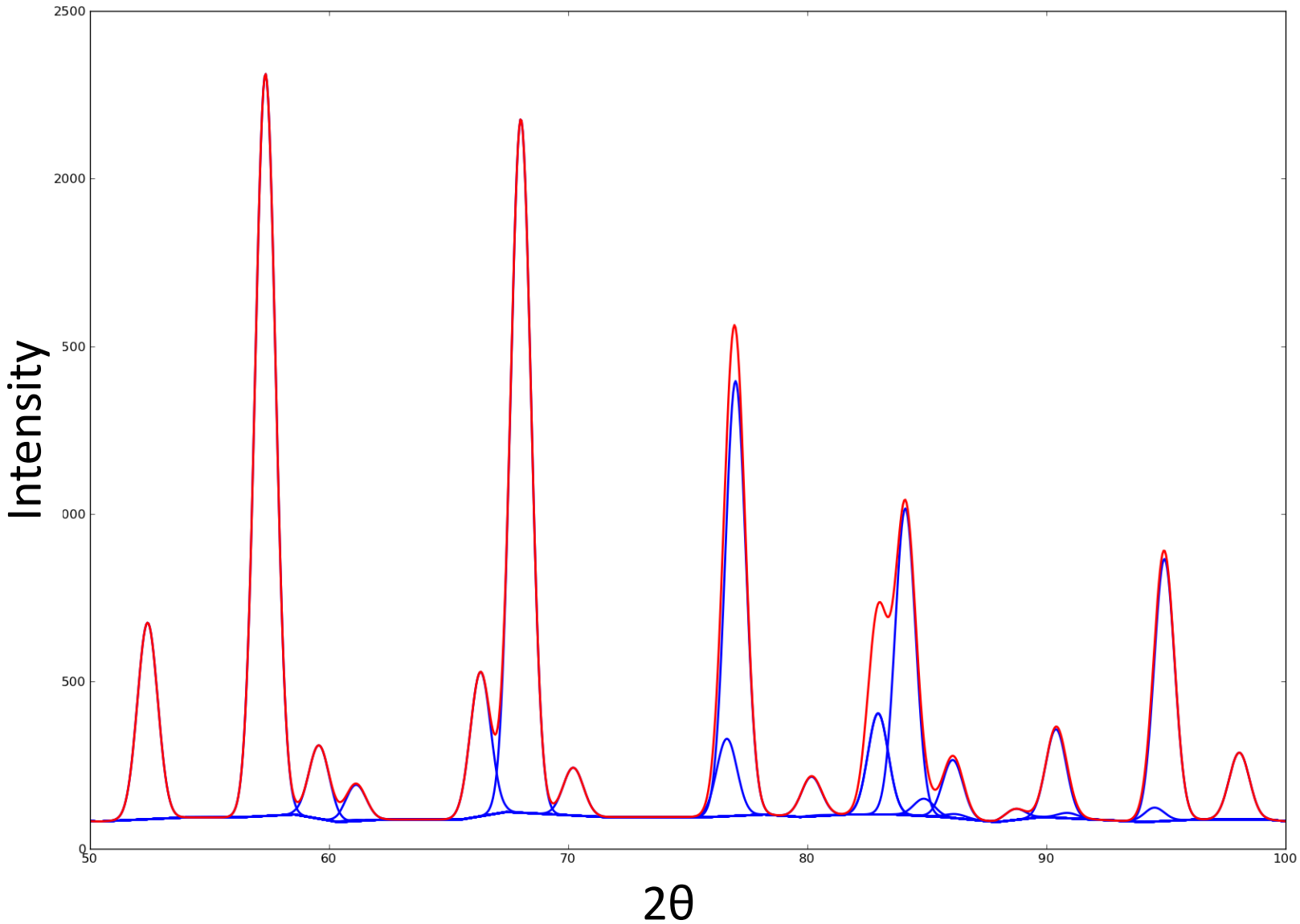


Bragg's Law: $2d \sin\theta = \lambda$

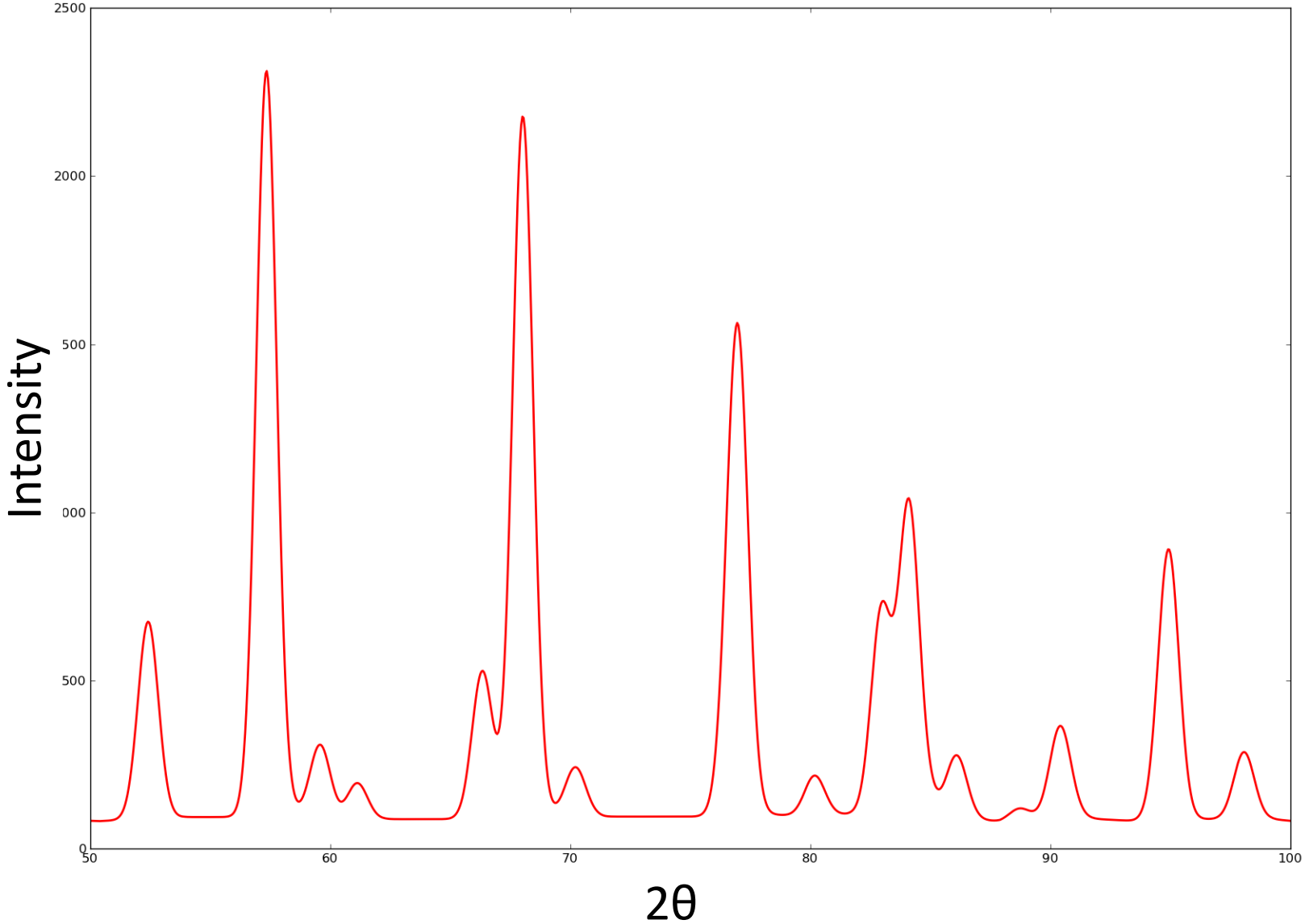
Peaks from Bragg Angles 2θ

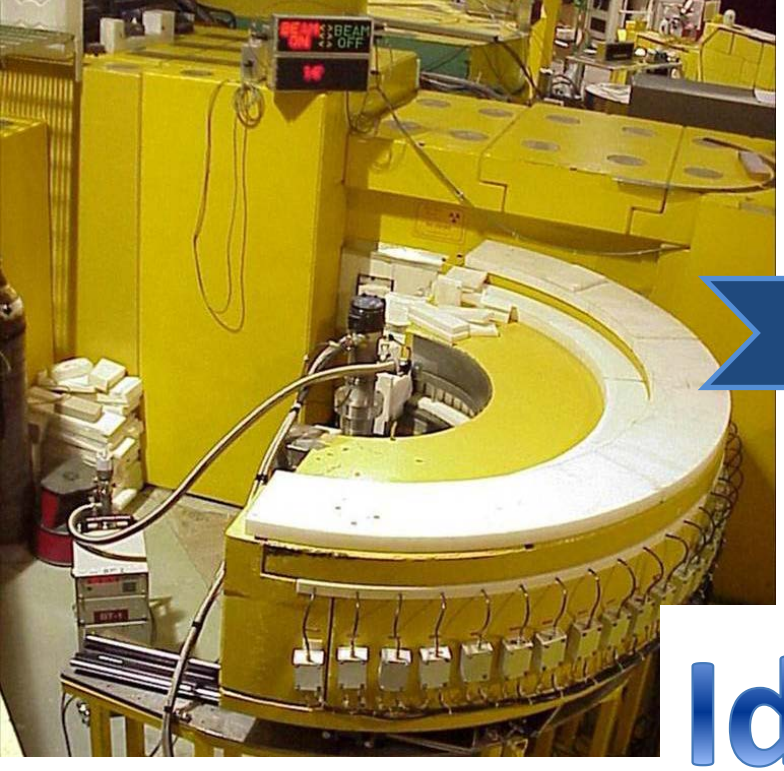


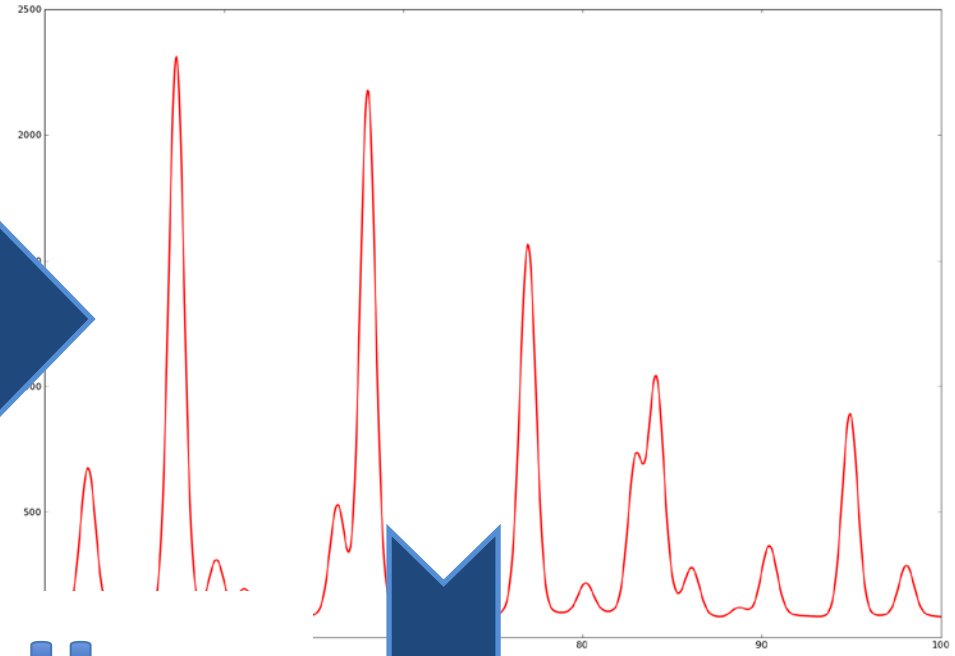
Superposition of Peaks



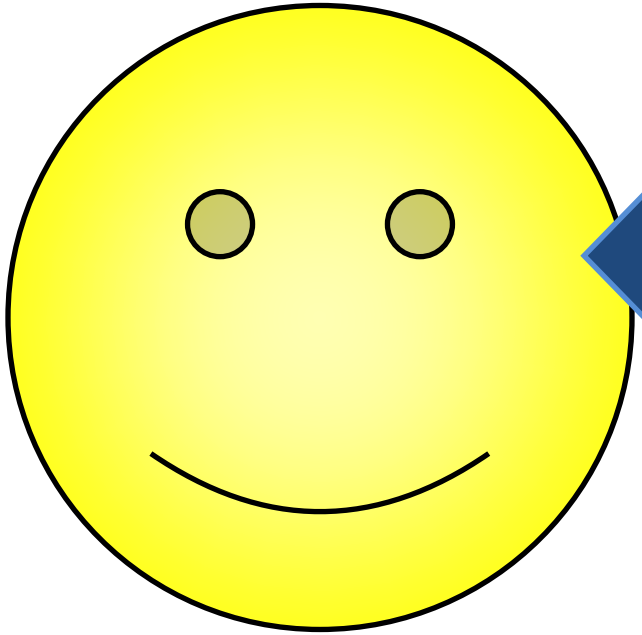
Diffraction Pattern

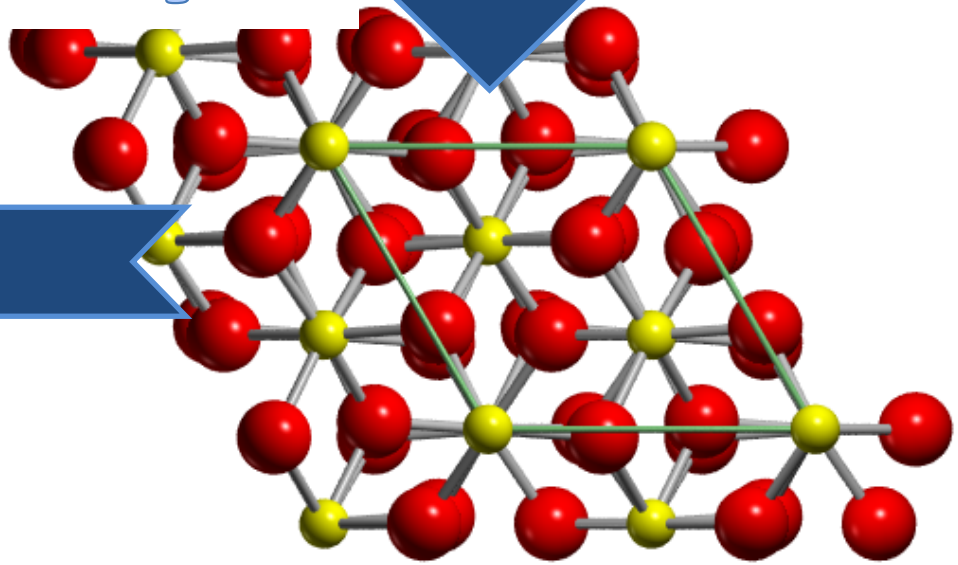




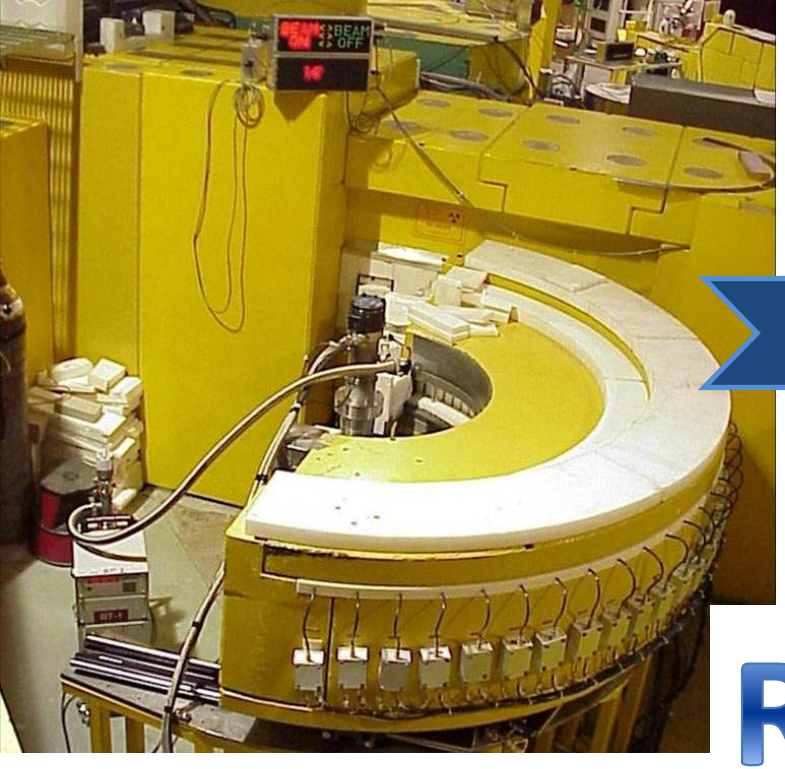


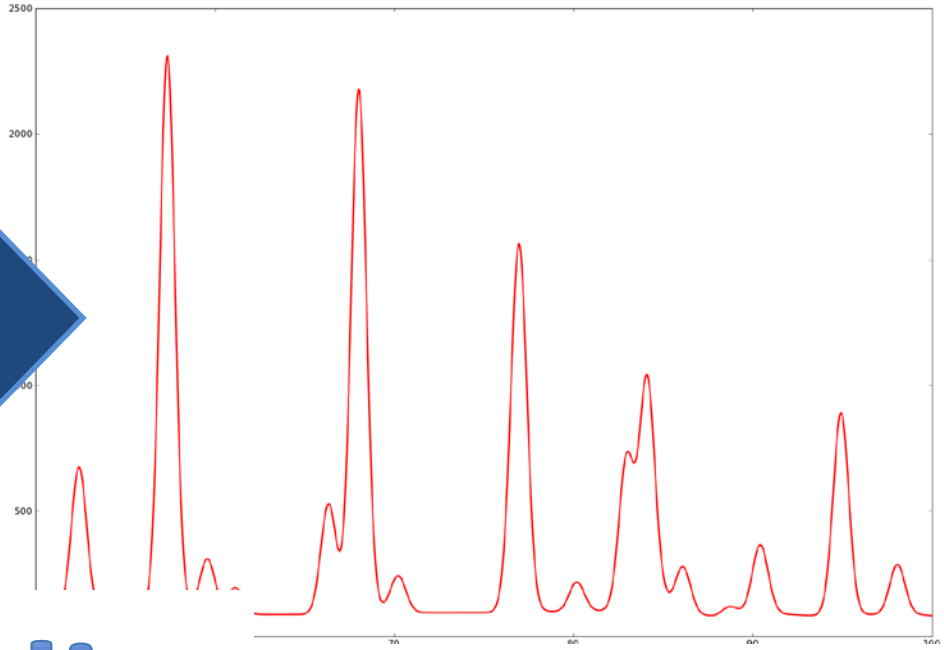
Ideally…



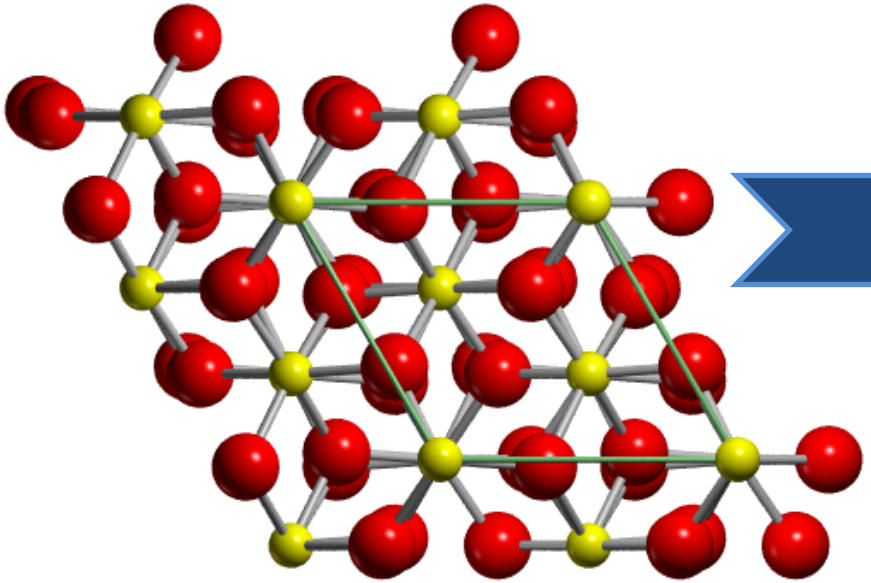


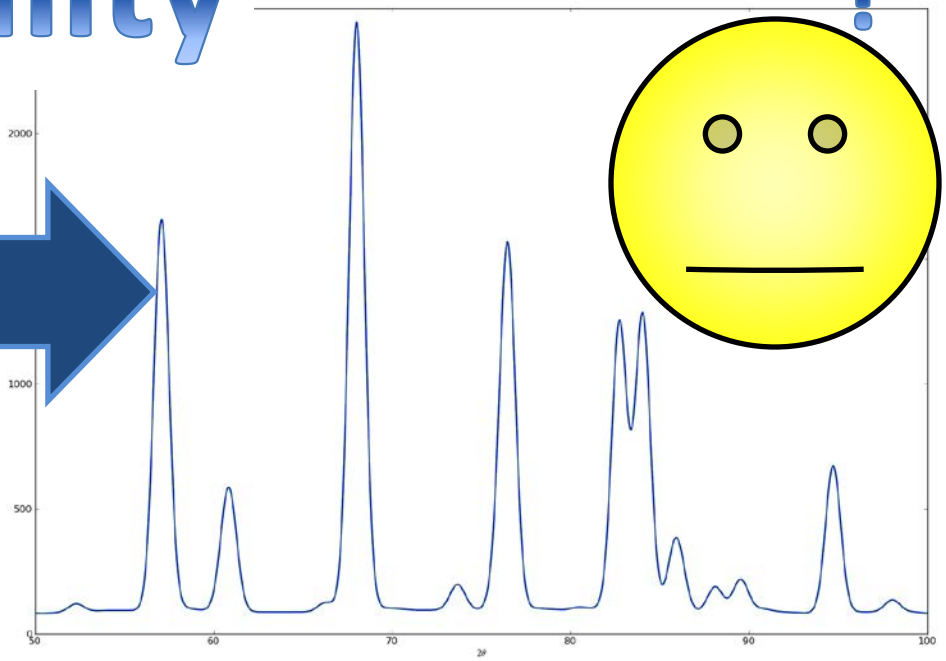
Images: ncnr.nist.gov, theochem.unito.it


BEAM ON
BEAM OFF

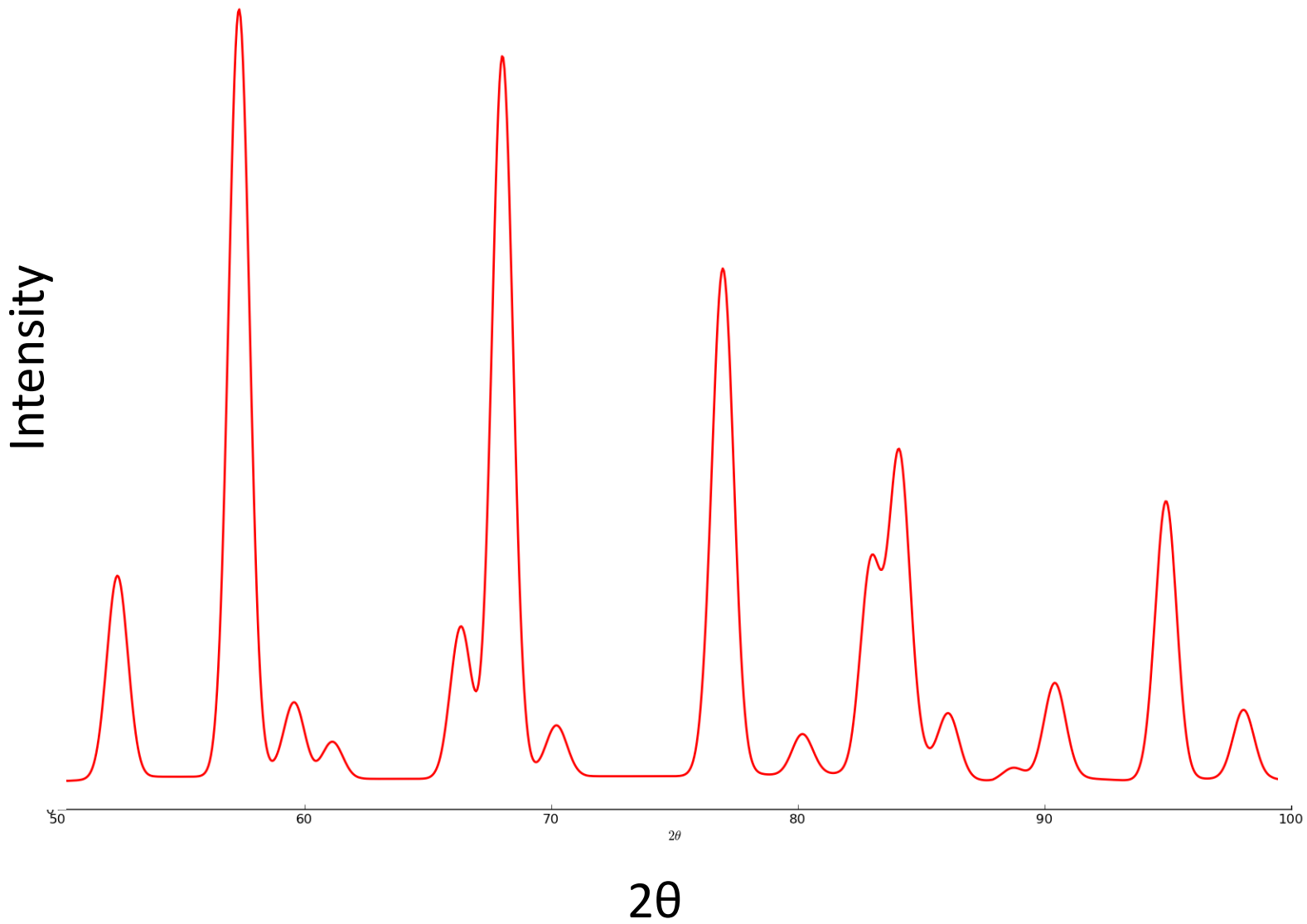

2500
2000
500

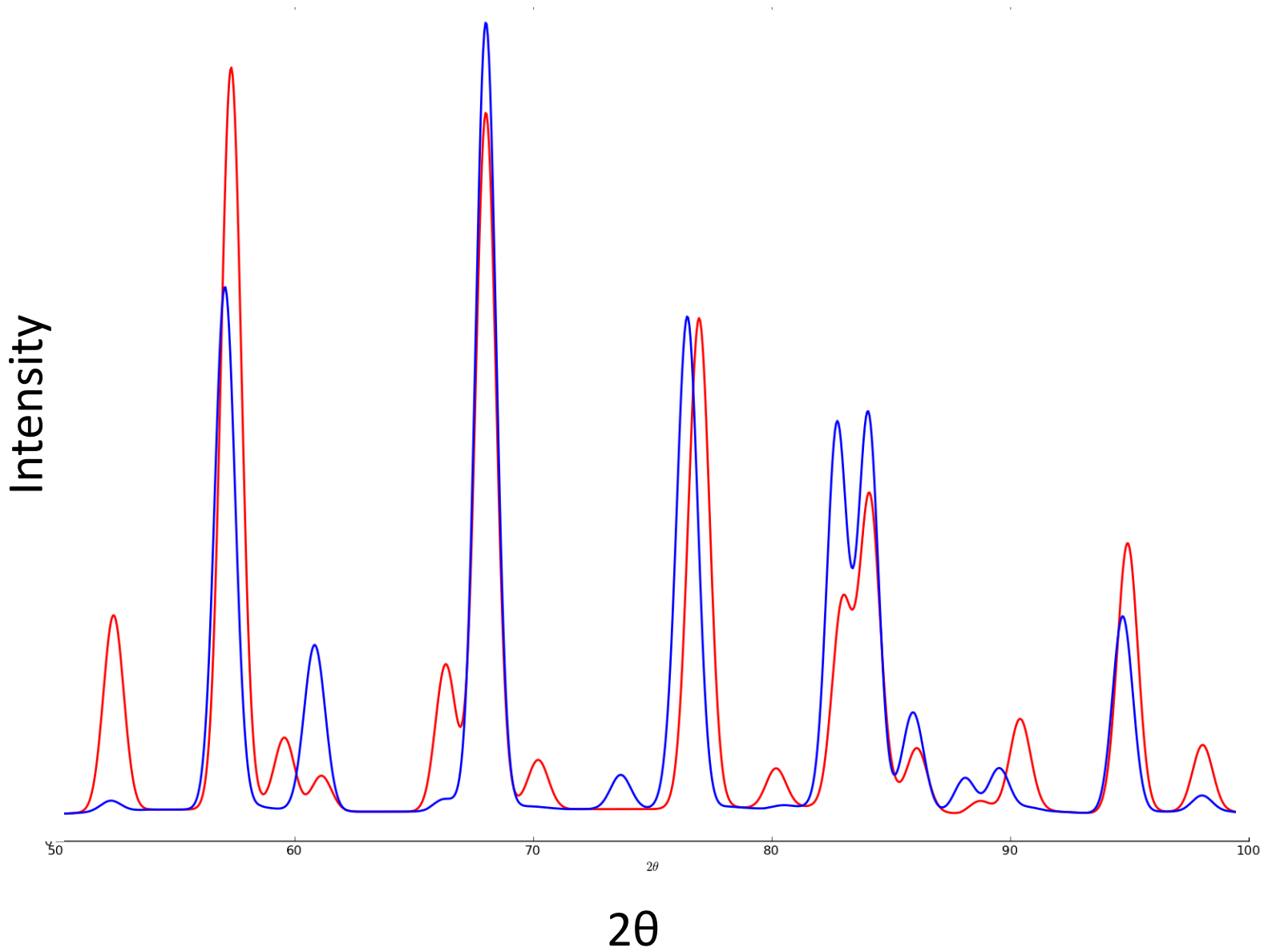
Reality

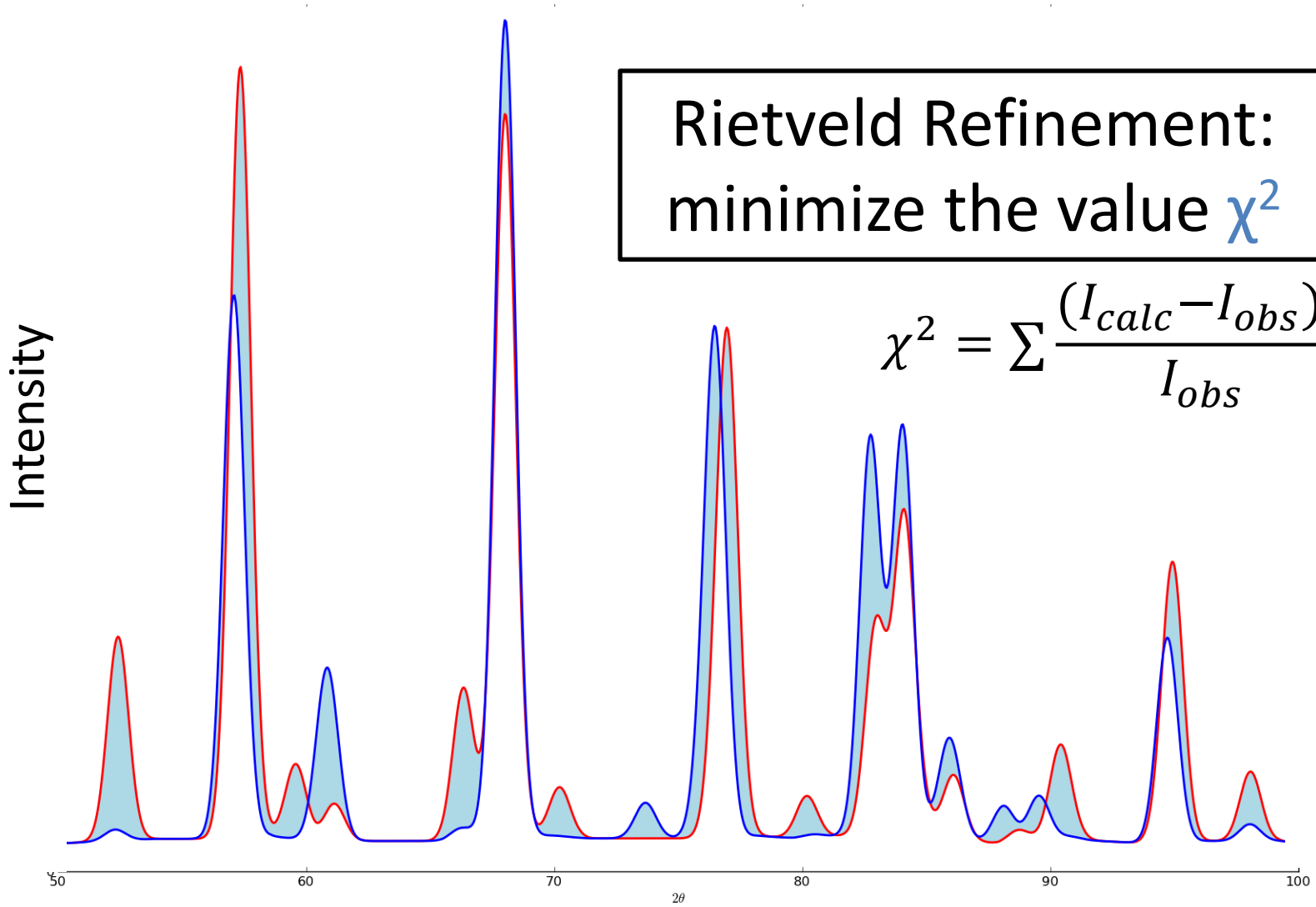



2000
1000
500
0
50
60
70
80
90
100
2θ

?


Intensity
50
60
70
80
90
100
2θ
2θ

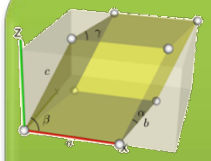

Intensity
50
60
70
80
90
100
2θ
2θ



Rietveld Refinement: minimize the value χ^2

$$\chi^2 = \sum \frac{(I_{calc} - I_{obs})^2}{I_{obs}}$$

2θ



Cell Parameters

a b c α β γ

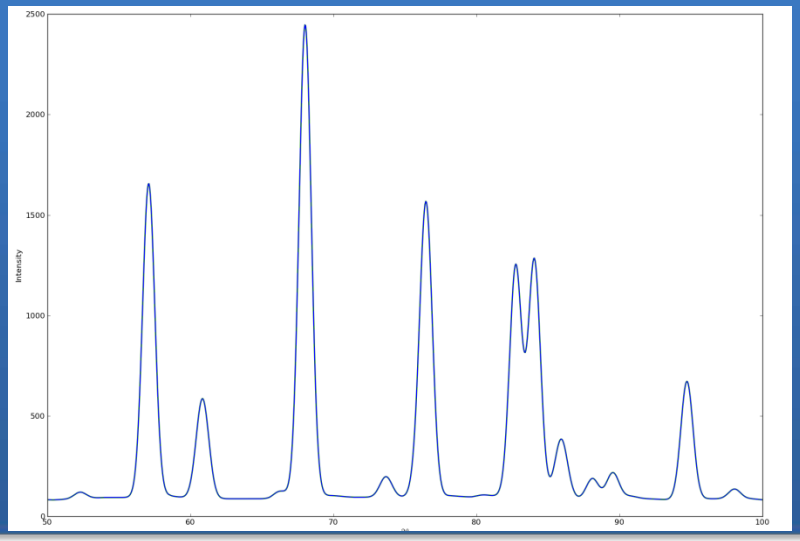
Atomic Parameters

x y z

Peak Parameters

u v w scale

Diffraction Pattern



FullProf Suite

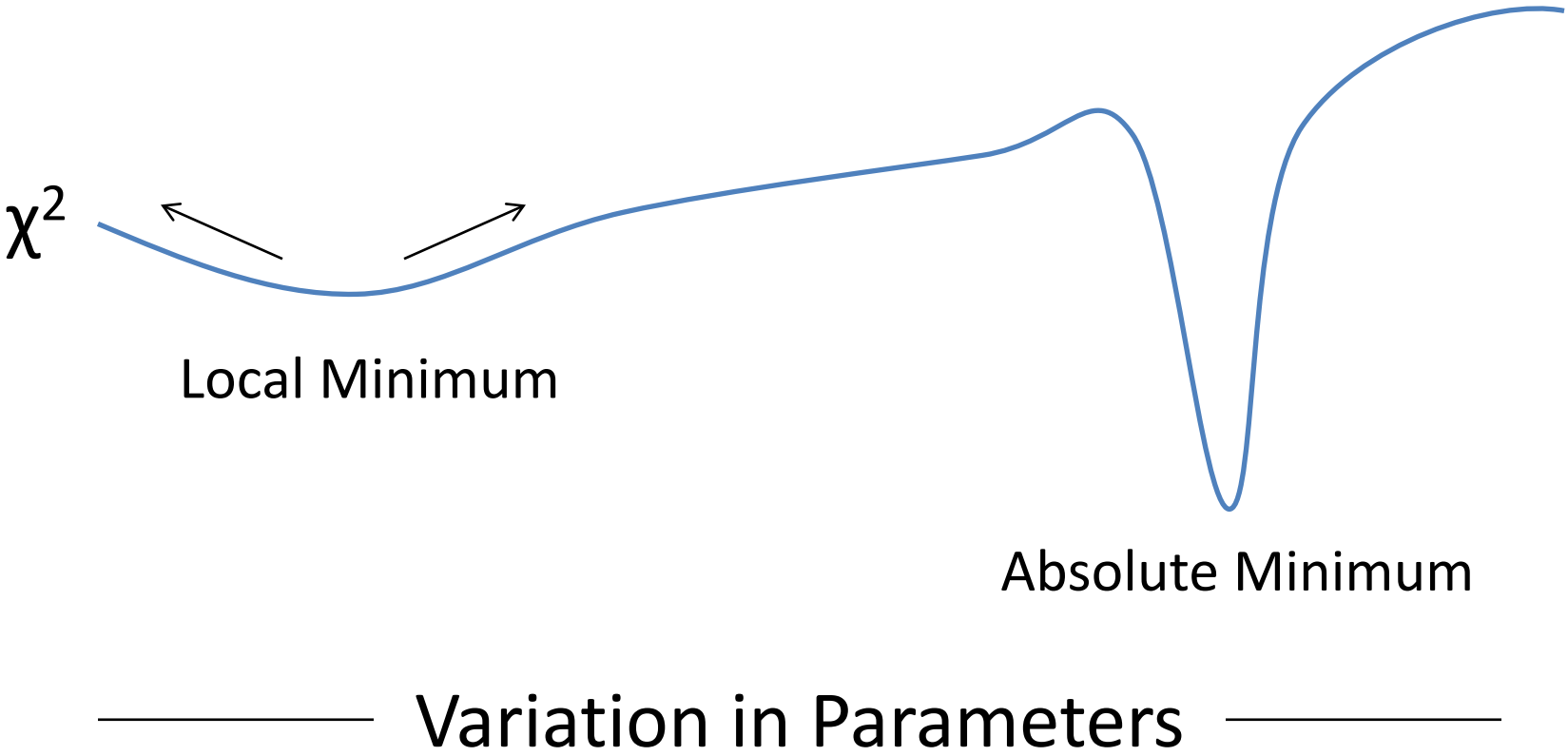
Crystallographic tools for Rietveld, profile matching & integrated intensity refinements of X-Ray and/or neutron data

(Juan Rodríguez-Carvajal)

Fitting algorithm: Gauss-Newton

See also: GSAS, TOPAS, etc.

Gauss-Newton Algorithm



```
COMM Ho2BaNiO5 D1B 1.5K  (Magnetic part: Basis Functions in numerical form)
! Current global Chi2 (Bragg contrib.) =      52.97
! Files => DAT-file: hobk.dat,  PCR-file: hobk_bas
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   5   2   0   2   0   0   0   0   0   0   0   0   0   0   0   0   0   1
!
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
   0   0   1   0   1   0   4   0   0   1   3   1   1   0   0   0   0
!
! Lambda1  Lambda2    Ratio    Bkpos    Wdt    Cthm     muR   AsyLim   Rpolarz  2nd-muR -> Patt# 1
 2.524000 2.524000  1.00000   30.000  5.0000  0.0000  0.0000    5.00    0.0000  0.0000
!
!NCY  Eps  R_at  R_an  R_pr  R_gl     Thmin       Step       Thmax    PSD    Sent0
  5  0.10  1.00  1.00  1.00  1.00     10.0100   0.200000    89.8100   0.000   0.000
!
! Excluded regions (LowT  HighT) for Pattern#  1
        0.00        8.00
       90.00      180.00
!
!
     20    !Number of refined parameters
!
!  Zero    Code    SyCos    Code   SySin    Code  Lambda     Code MORE ->Patt# 1
  0.08416  111.0  0.00000    0.0  0.00000    0.0 0.000000    0.00   0
!   Background coefficients/codes  for Pattern#  1  (Polynomial of 6th degree)
    7076.874    -154.577     458.319    -947.450     933.900    -293.350
       21.00       31.00       41.00        0.00        0.00        0.00
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     3.45
!-------------------------------------------------------------------------------
Ho2BaNiO5      magph2
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
   5   0   0 0.0 0.0 1.0   0   0   0   0   0       1211.800   0   5   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind   RMua    RMub    RMuc   Jtyp  Nsp_Ref Ph_Shift N_Domains
   3   0   0   0   0   0  1.0000  0.0000  0.0000  0.0000    1       0       0       0
```

Refinement for Lazy People

Dylan Quintana

Carnegie Mellon University / NIST Center for Neutron Research

Bumps

Bayesian Uncertainty Modeling of Parametric Systems

(Paul Kienzle)

Fitting algorithm: DREAM

DREAM Algorithm

- Markov Chain
- Monte Carlo
- Differential Evolution
- Bayesian Analysis

Image: lumick.buroncp.com

BLAND

Bumps Library for Analysis of Neutron Diffraction

Image: successfullivinginstitute.com

BLAND Goals

- ❑ Global fitting
- ❑ Eliminate need for intuition
- ❑ User-friendly interface
- ❑ Take over the world

Refinement at the push of a button!

Image: graphicsfuel.com

Fitting Example: Al_2O_3

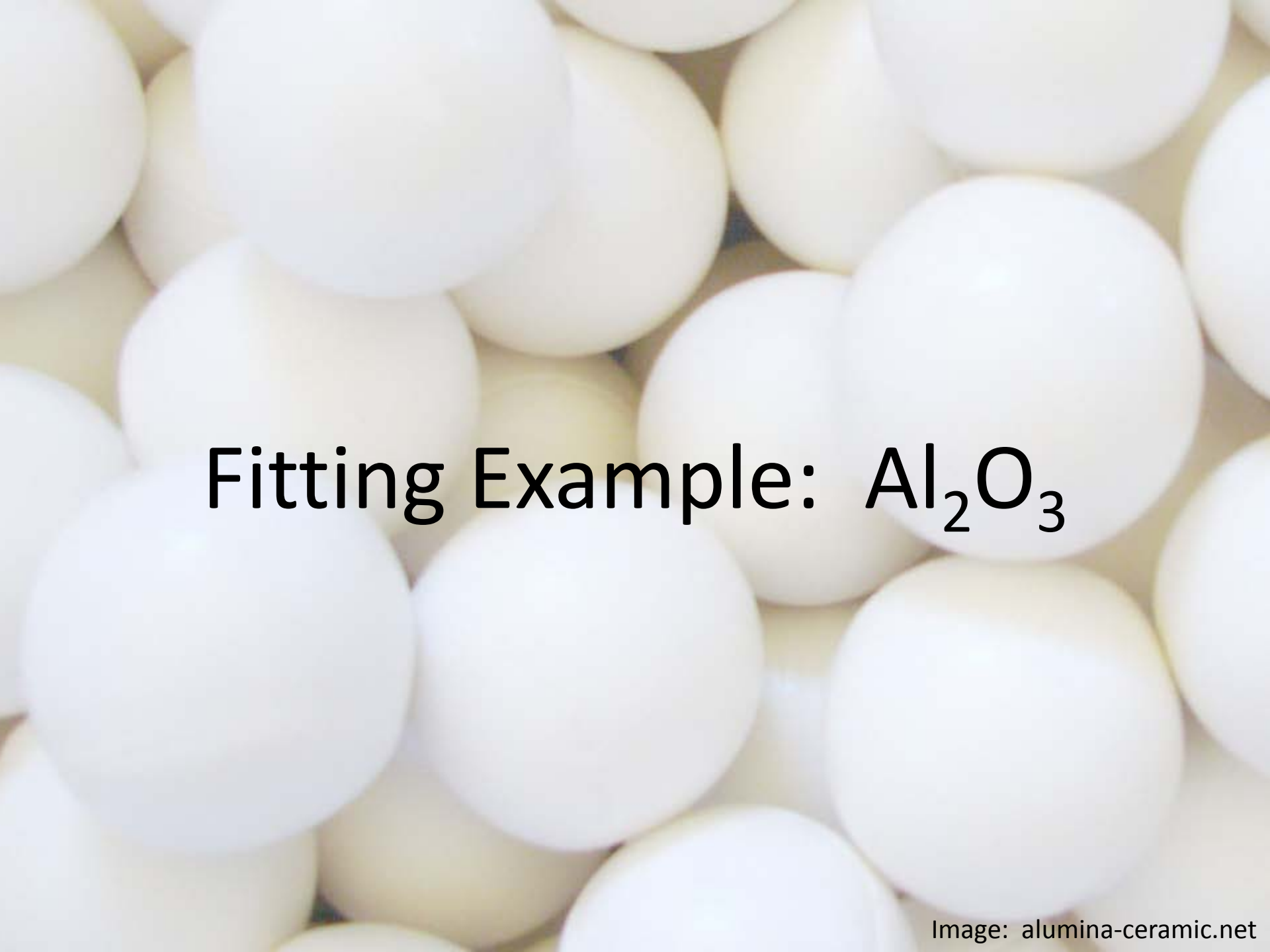
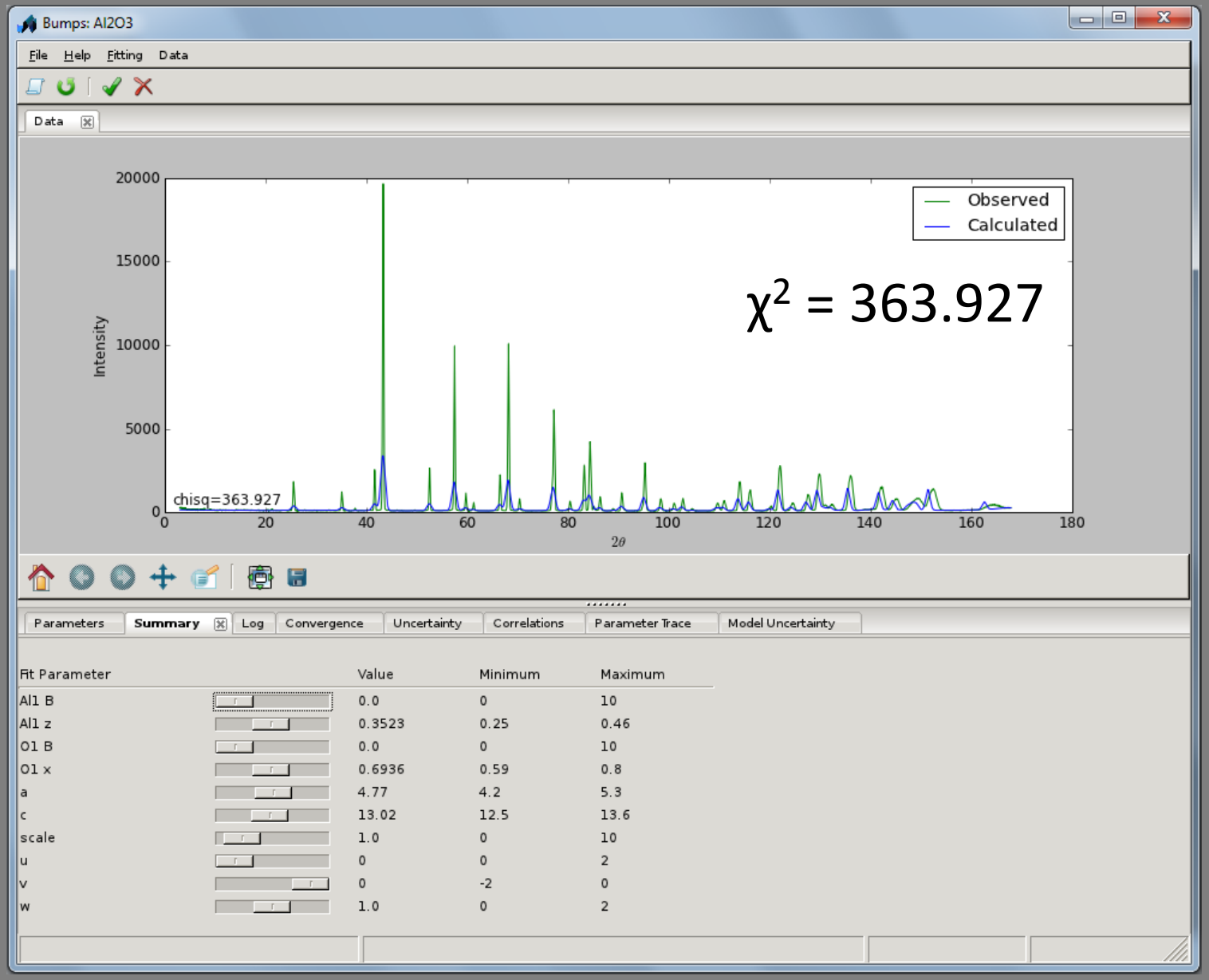


Image: alumina-ceramic.net

Pre-fit



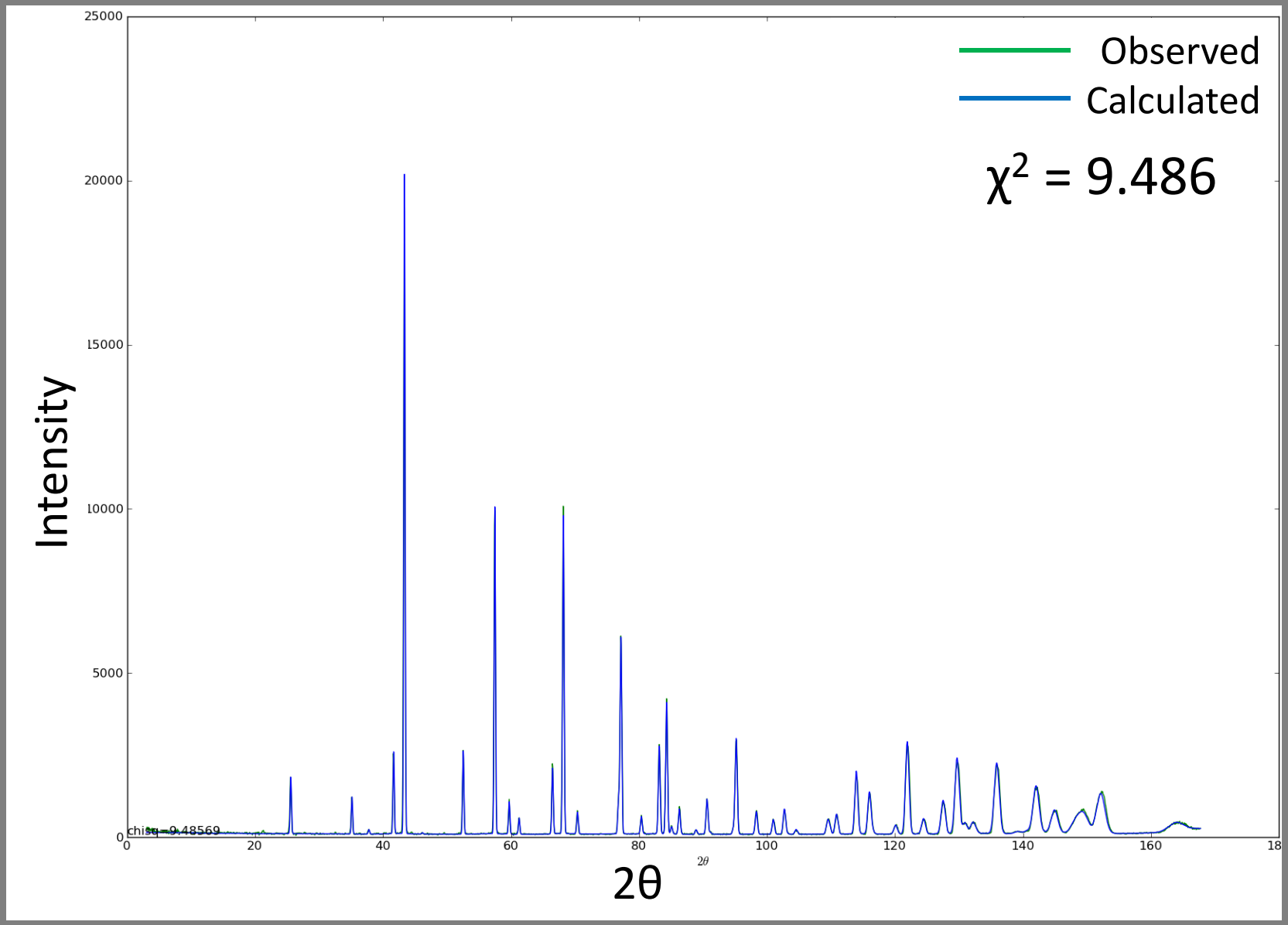
Fit Parameter	Value	Minimum	Maximum
Al1 B	0.0	0	10
Al1 z	0.3523	0.25	0.46
O1 B	0.0	0	10
O1 x	0.6936	0.59	0.8
a	4.77	4.2	5.3
c	13.02	12.5	13.6
scale	1.0	0	10
u	0	0	2
v	0	-2	0
w	1.0	0	2

THREE HOURS LATER...

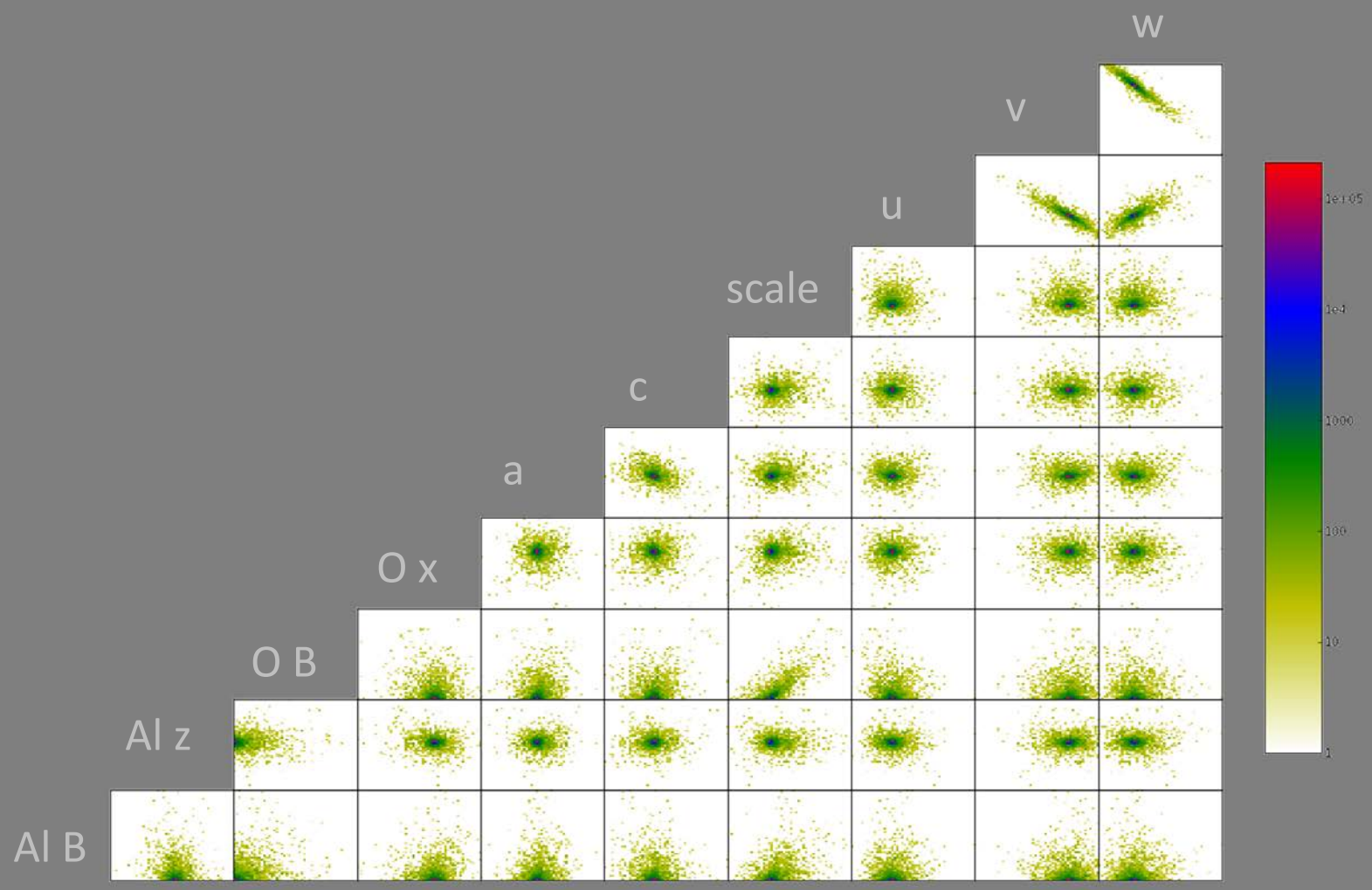
Post-fit: Parameters

Parameter	Value	95% Interval
Al1 B	0	[0, 0.063]
Al1 z	0.352282	[0.35188, 0.35279]
O1 B	0.0001	[0, 0.064]
O1 x	0.69347	[0.6929, 0.6941]
a	4.760787	[4.76068, 4.76100]
c	13.00072	[13.0000, 13.0015]
scale	1.4711	[1.457, 1.519]
u	0.1721	[0.161, 0.185]
v	-0.1188	[-0.139, -0.092]
w	0.0772	[0.069, 0.086]

Post-fit: Diffraction Pattern



Post-fit: Correlation Plot



BLAND Goals

- ☑ Global fitting
- ☑ Eliminate need for intuition
- ☐ User-friendly interface
- ☐ Extensive testing
- ☐ Feature completeness
- ☐ Take over the world

Summary

Crystal structures and diffraction

The refinement process

The old ways (FullProf)

The new ways (BLAND)

Special Thanks

NIST

CHRNS Center for High Resolution Neutron Scattering NIST

William Ratcliff

Paul Kienzle

Alex Zhang

Julie Borchers

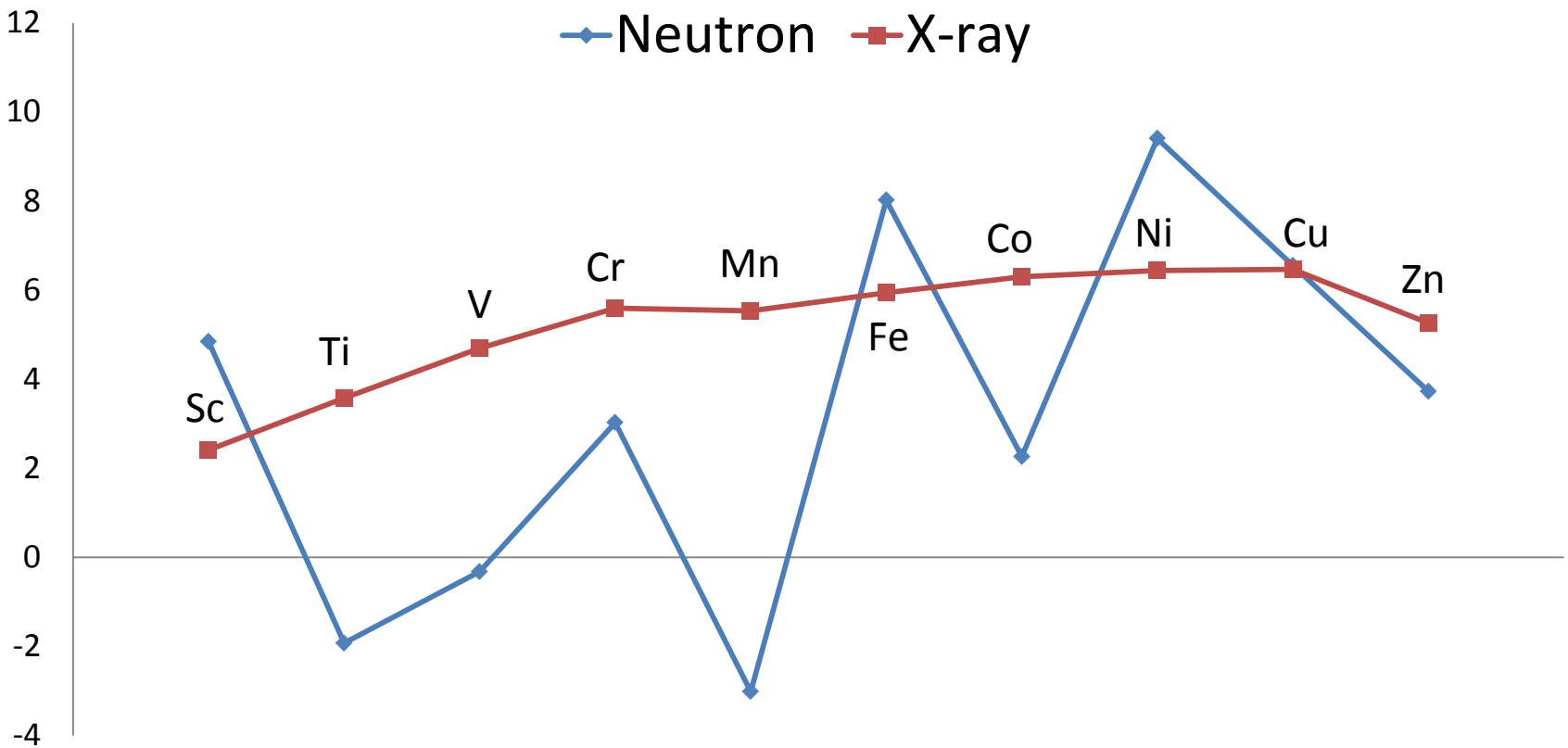
SURF directors

?

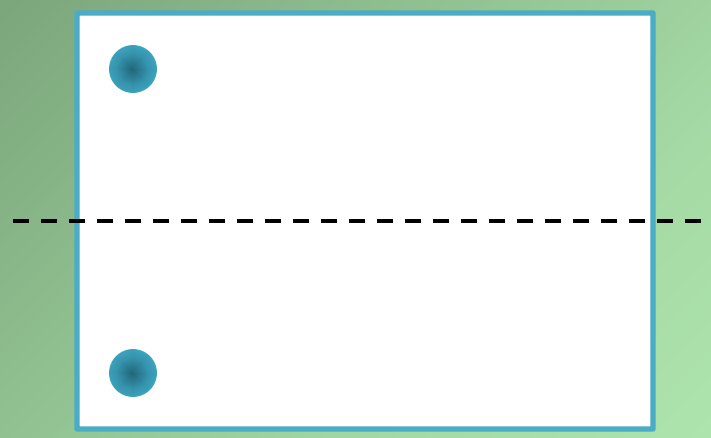
Appendix

Why use neutrons?

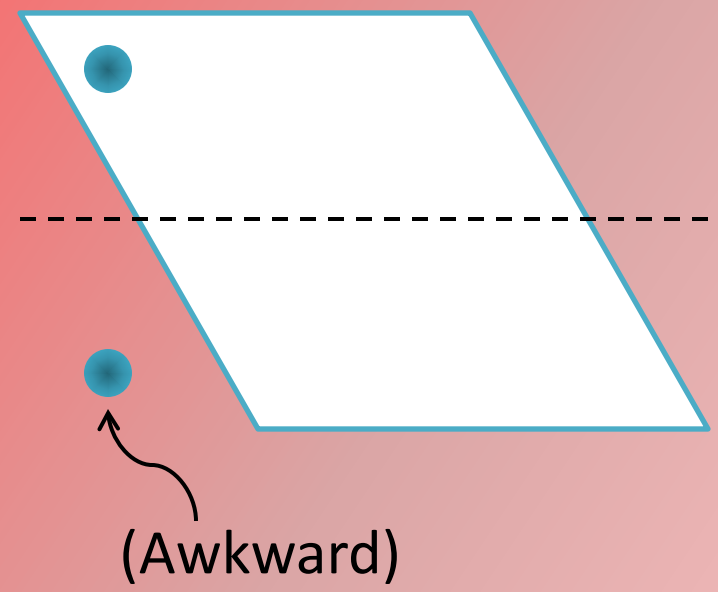
Scaled scattering length densities:



Neutrons can differentiate between **similar elements**, and even **isotopes of the same element**

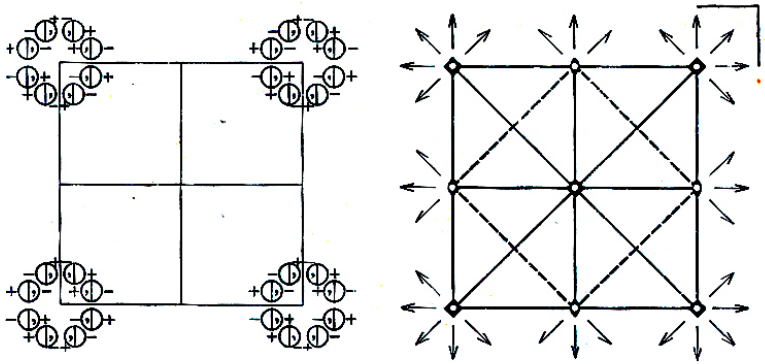


COMPATIBLE



INCOMPATIBLE

Tetragonal $4/m\,m\,m$ $P\,4/m\,2/m\,2/m$ No. 123 $P4/mmm$ D_{4h}^{1}

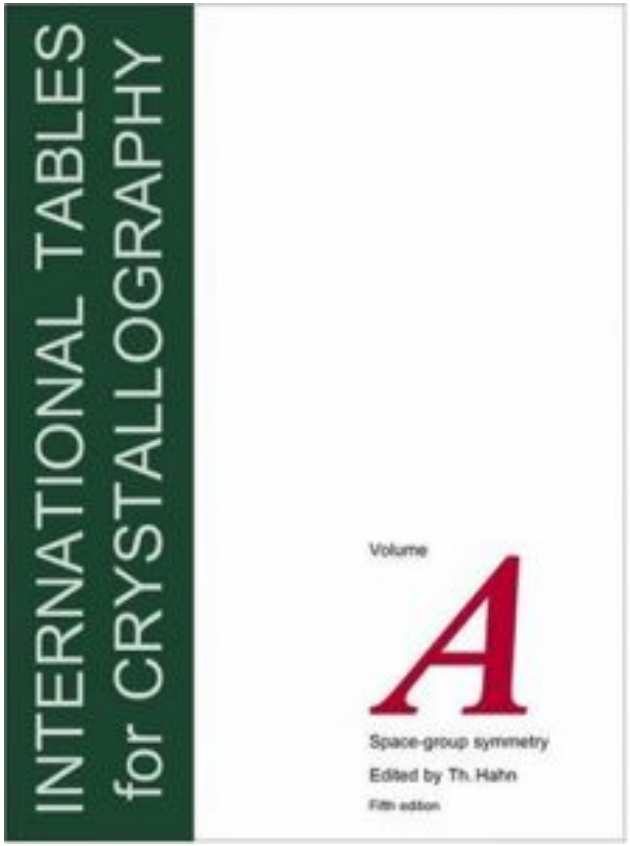


Origin at centre ($4/mmm$)

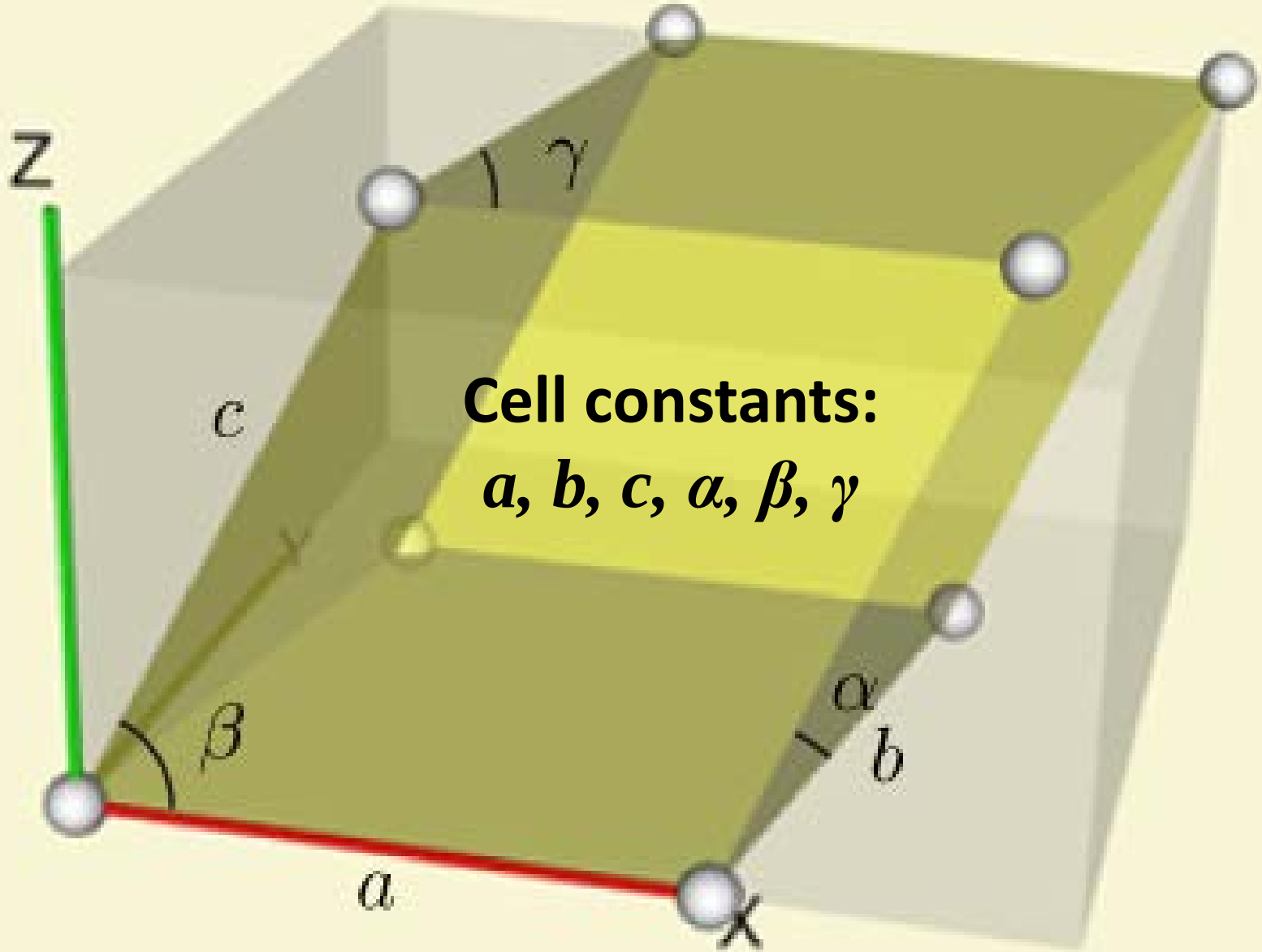
Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions				Conditions limiting possible reflections
16	u	1	x,y,z;	$\bar{x},\bar{y},z$;	$x,y,\bar{z}$;	$\bar{x},\bar{y},\bar{z}$;	General:
			$\bar{x},y,z$;	$x,\bar{y},z$;	$\bar{x},y,\bar{z}$;	$x,\bar{y},\bar{z}$;	No conditions
			$\bar{y},x,z$;	$y,\bar{x},z$;	$\bar{y},x,\bar{z}$;	$y,\bar{x},\bar{z}$;	
			y,x,z;	$\bar{y},\bar{x},z$;	$y,x,\bar{z}$;	$\bar{y},\bar{x},\bar{z}$.	

Space Group

× 230 =



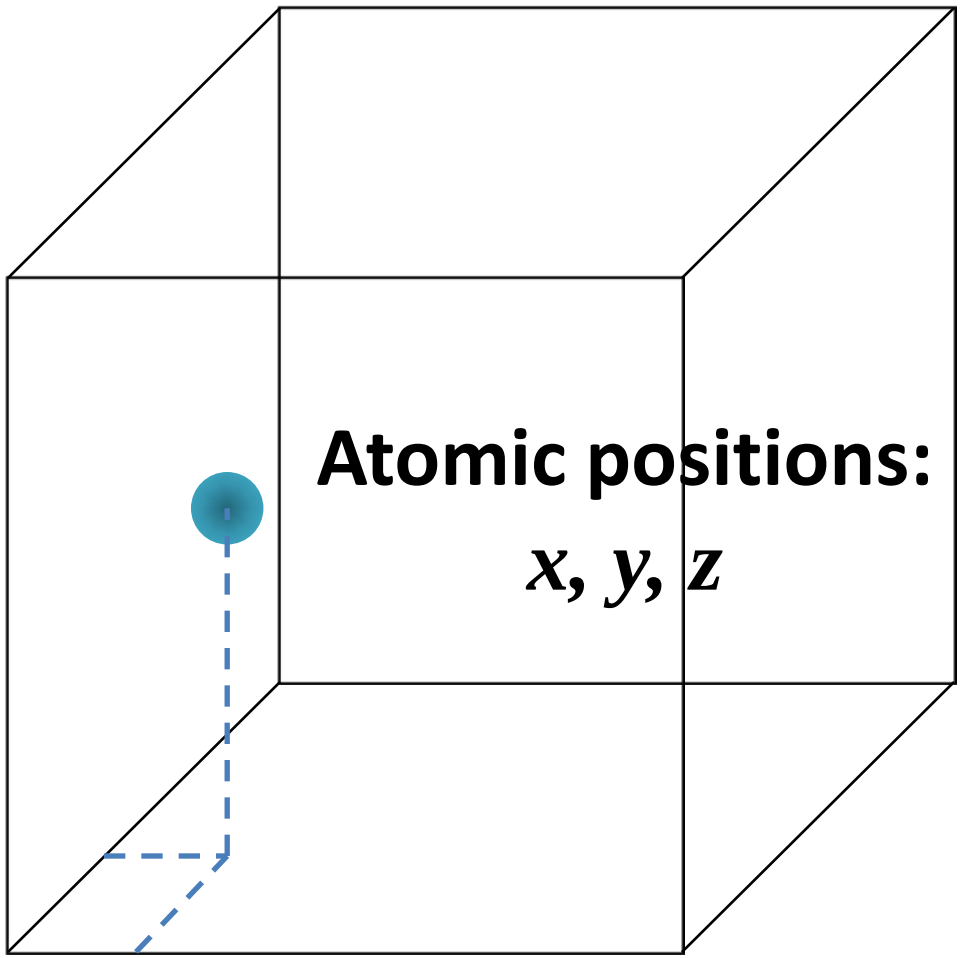
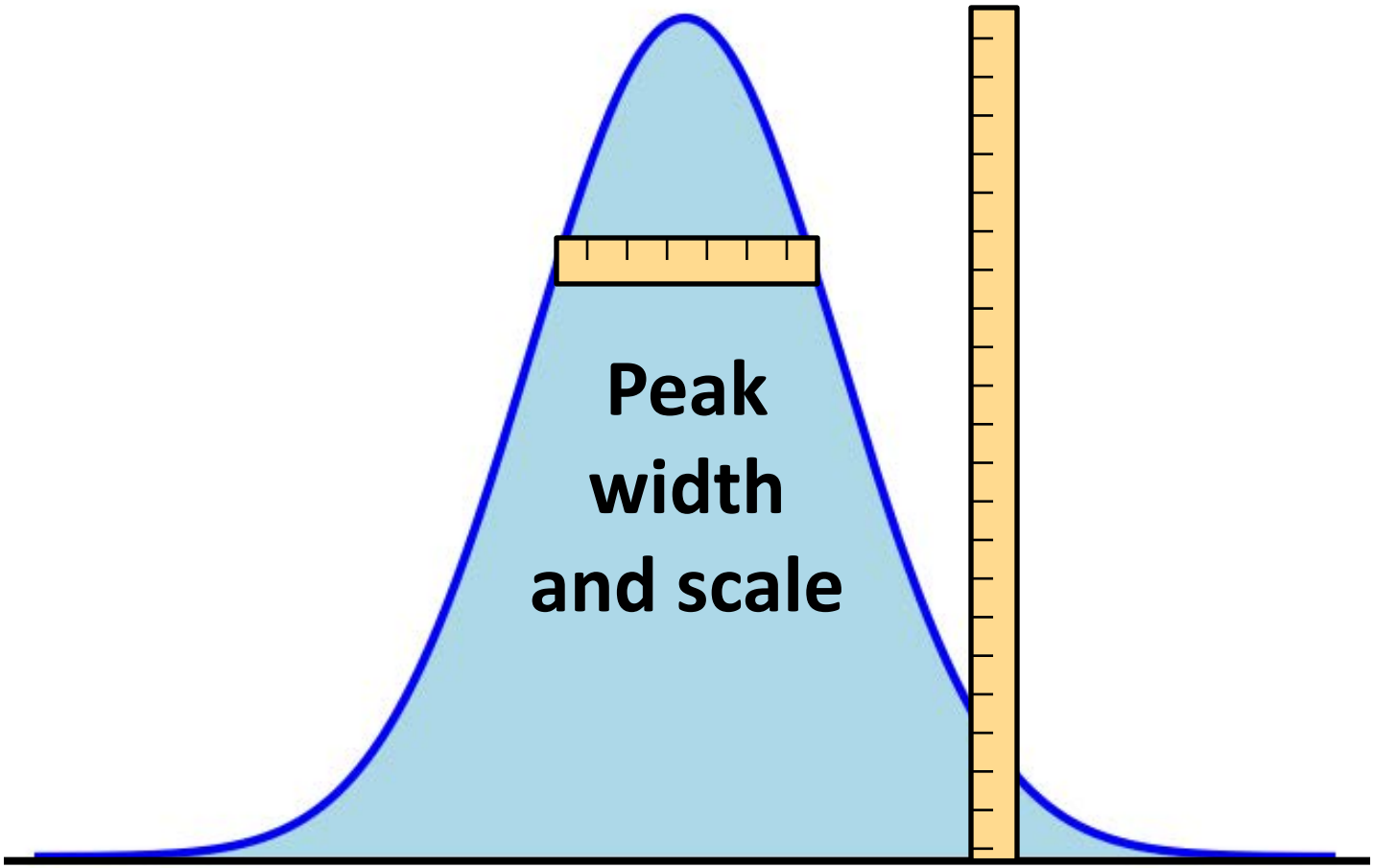
Refinement Parameters



Cell constants:

a, b, c, α, β, γ

Refinement Parameters



Refinement Parameters