Single Crystal Diffraction at a Synchrotron

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24th National School on Neutron & X-ray Scattering

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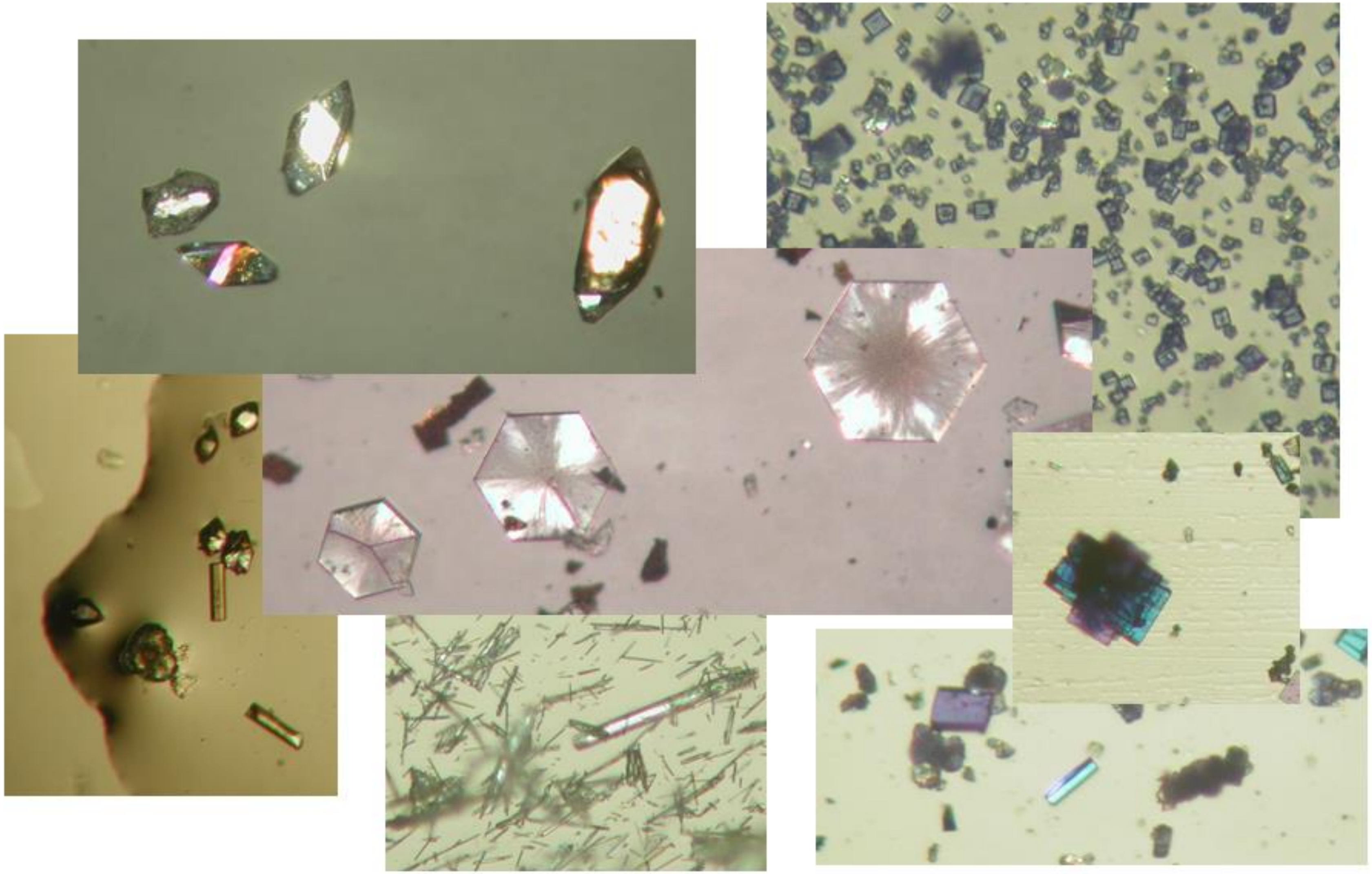
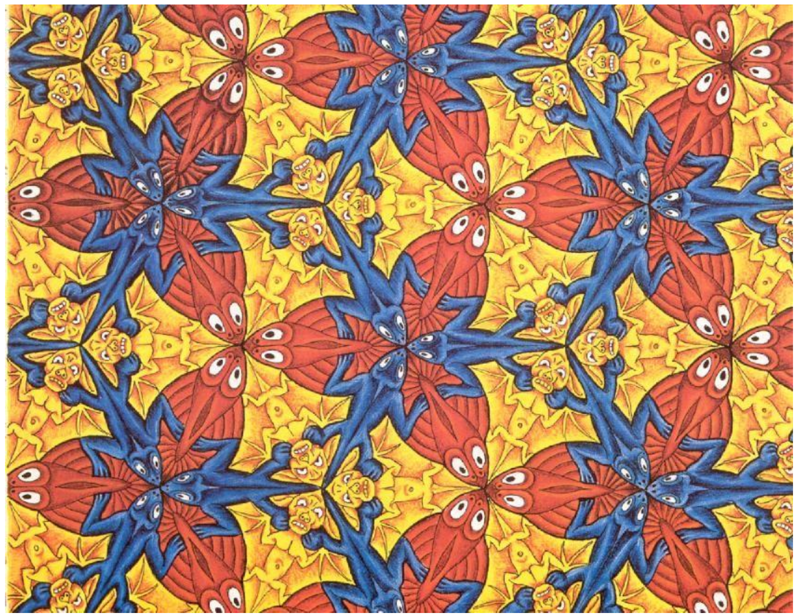
crys·tal·log·ra·phy

the branch of science dealing with the formation and properties of crystals

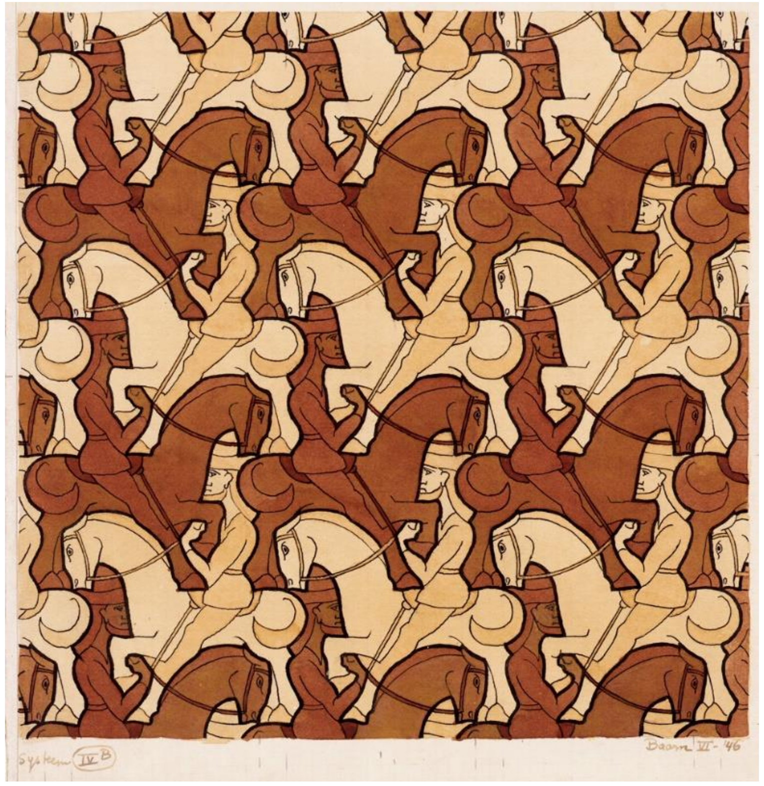


What is a Crystal?

- A crystal is a periodic arrangement of matter

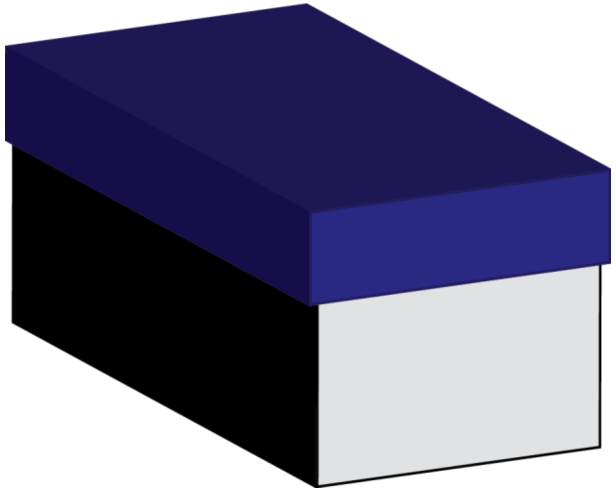


Search Escher tessellations for more

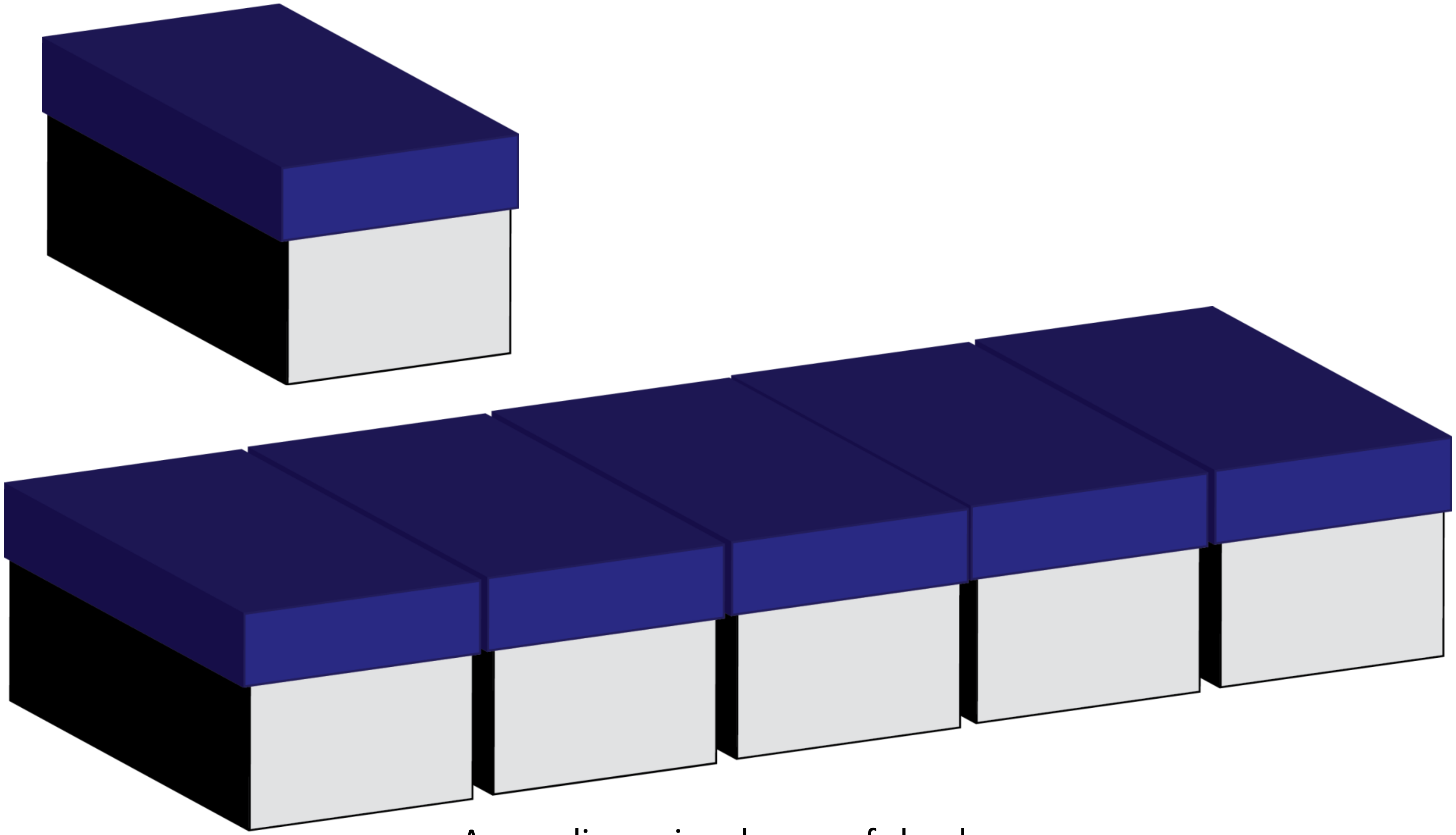


What is a Crystal?

- A Crystal is a three-dimensional repeating array of atoms or molecules.
- In this example, our molecule is going to be in a shoebox, for simplicity.

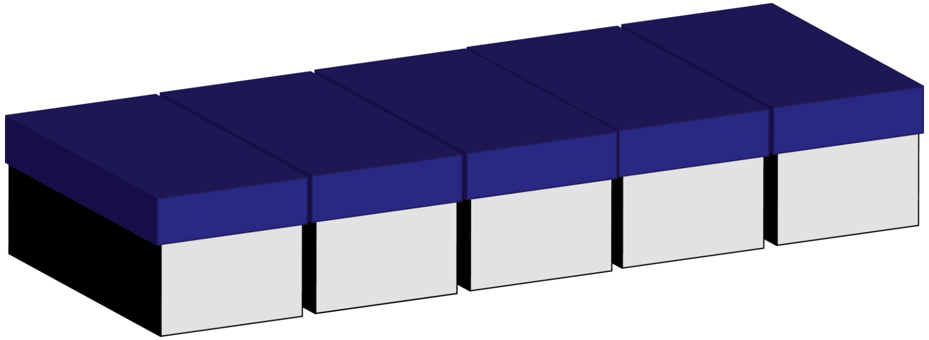


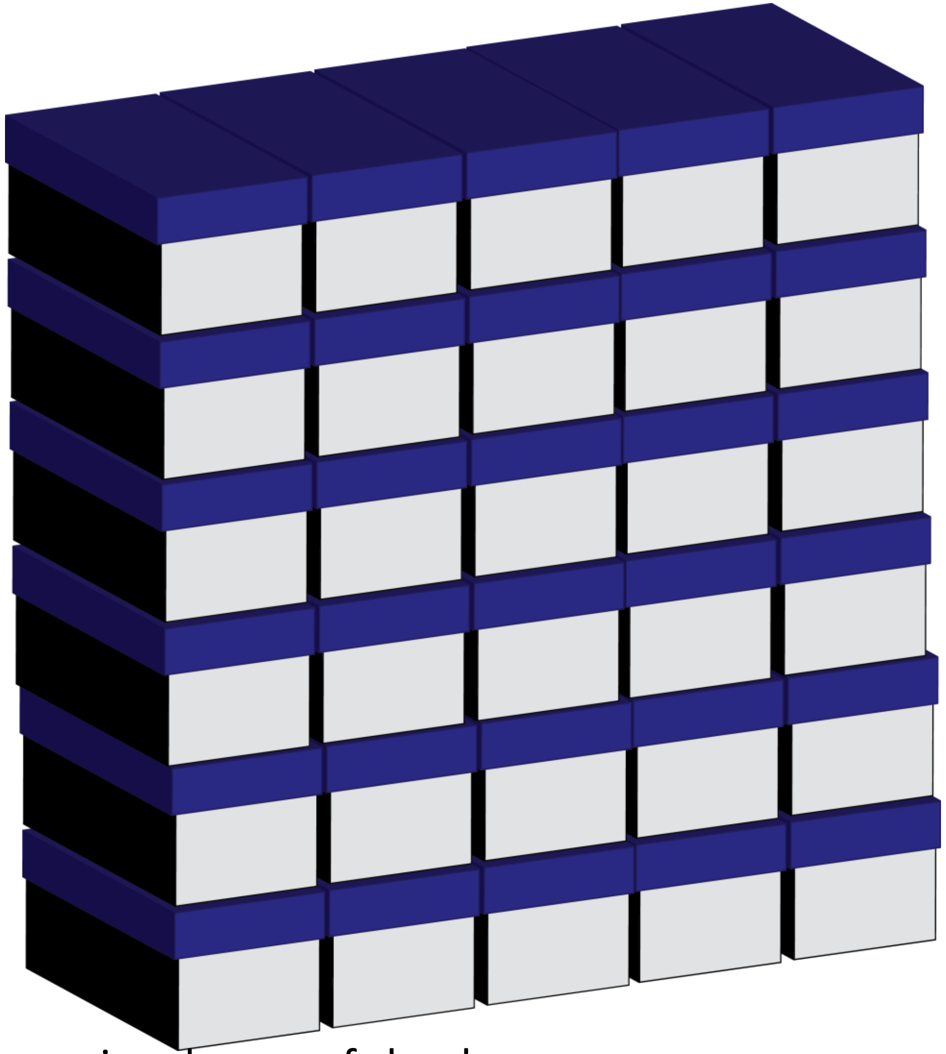
Dimensionality



A one-dimensional array of shoeboxes

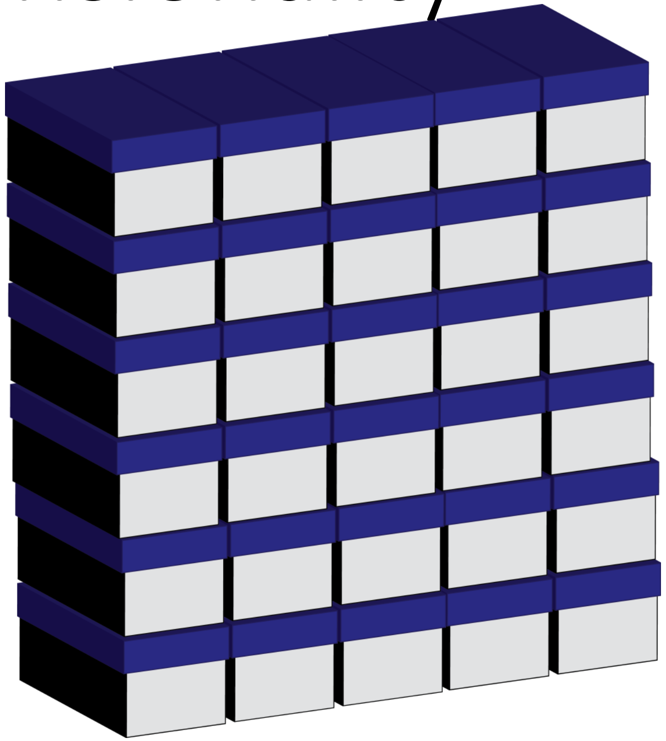
Dimensionality

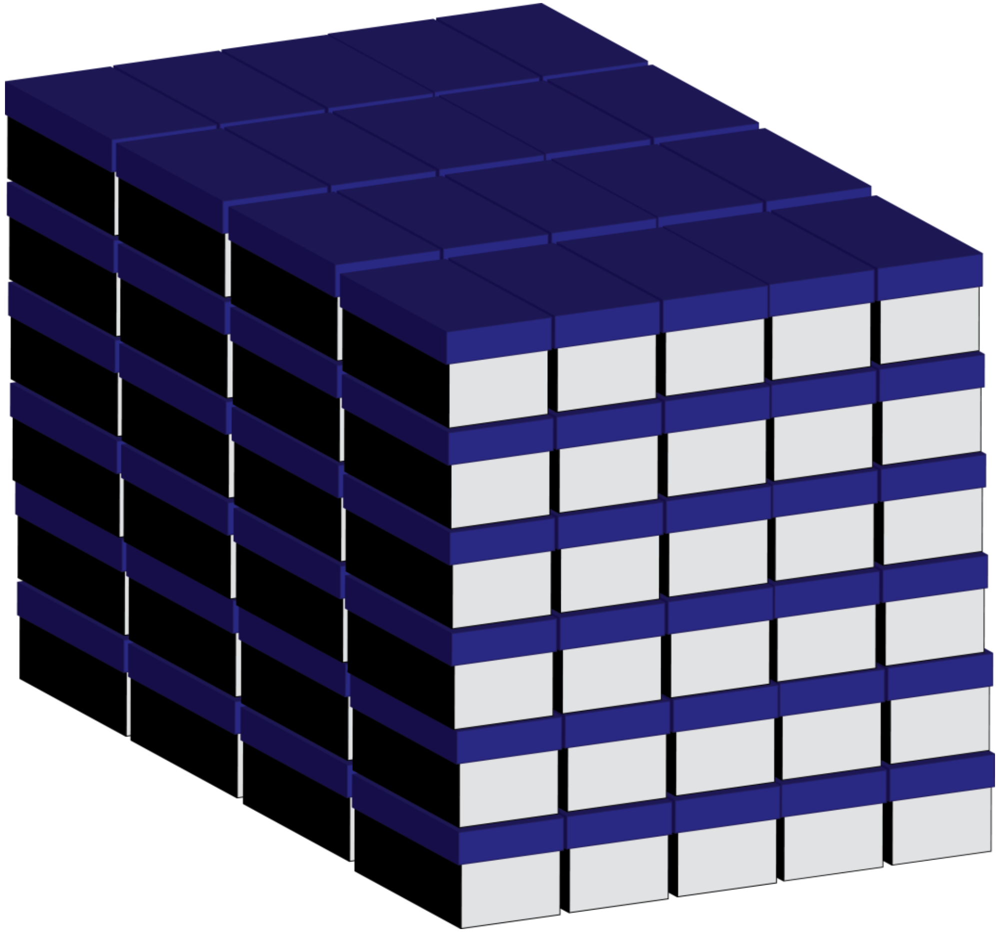




A two-dimensional array of shoeboxes

Dimensionality

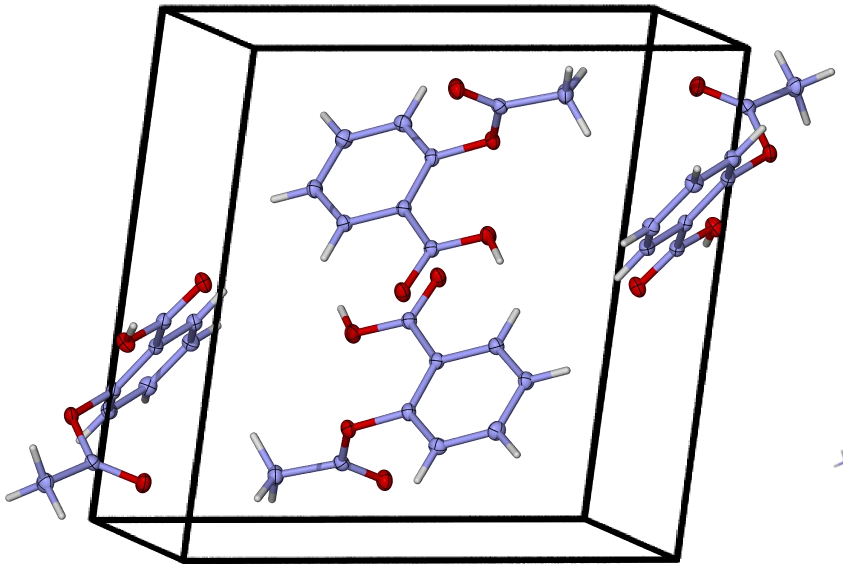


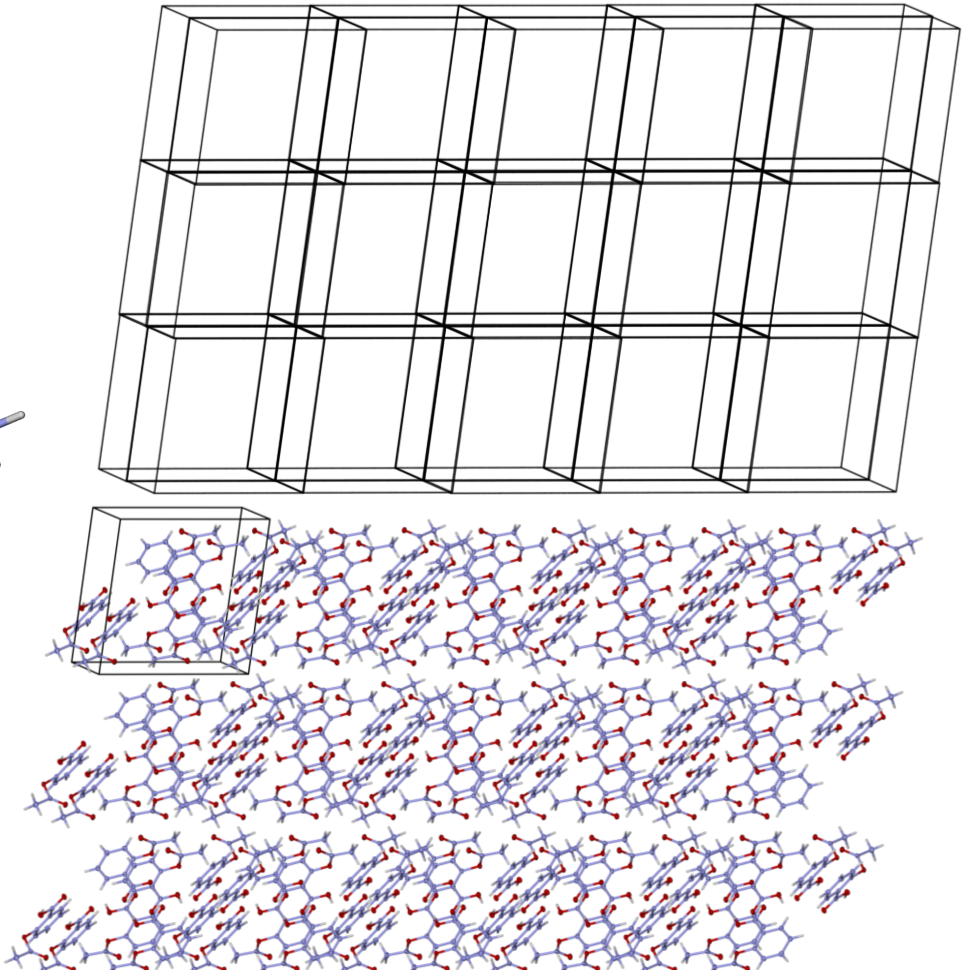


A three-dimensional array of shoeboxes

From Shoeboxes to Unit Cells

Unit Cell Definition:
Smallest volume unit of highest symmetry which, when translated in 3D will generate the crystal

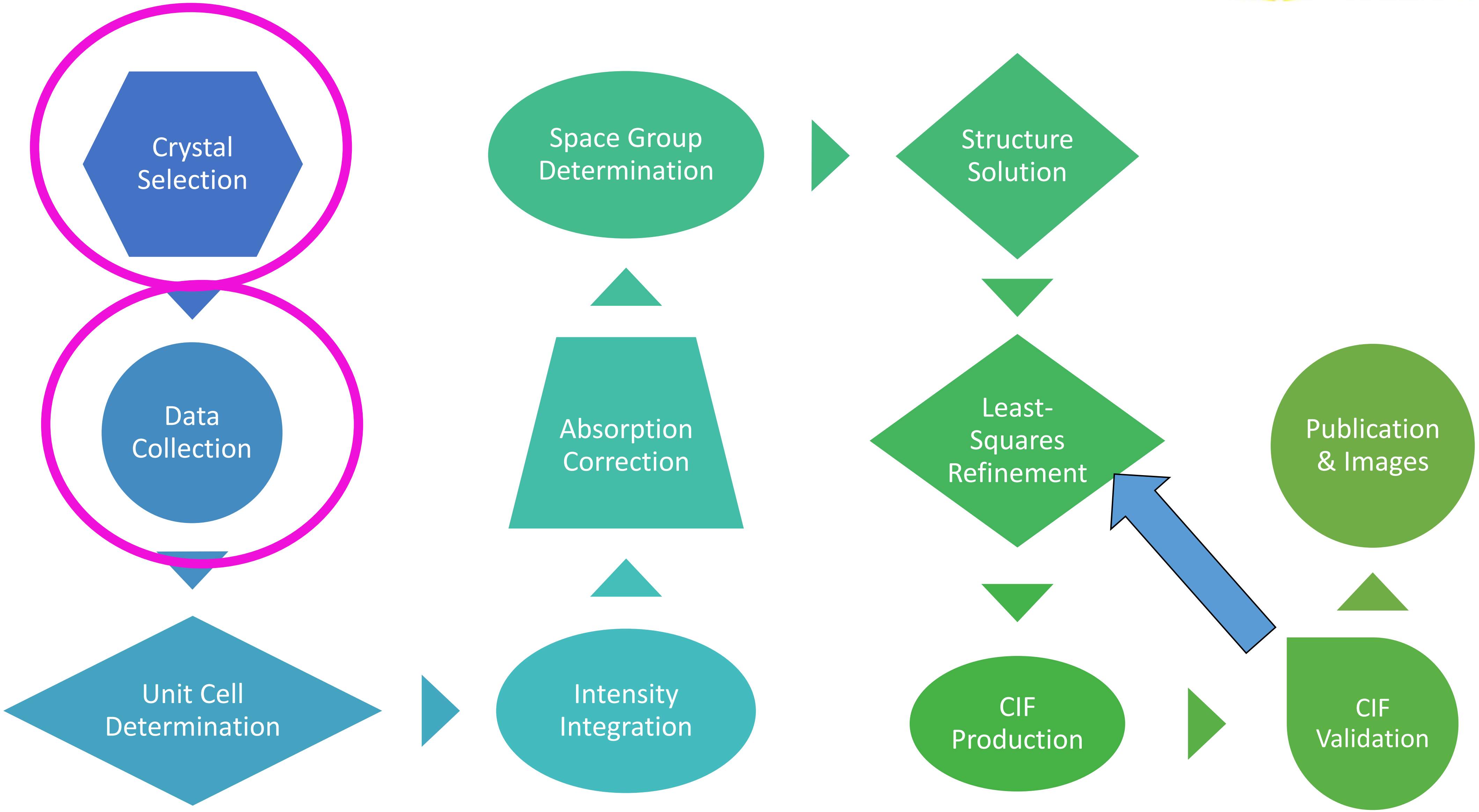




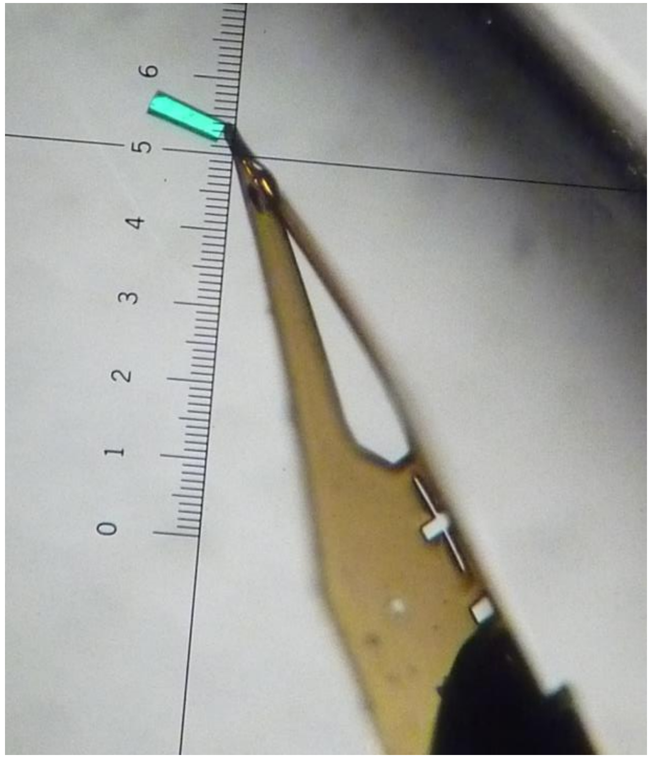
The dimensions of the Unit Cell are an identifying feature for a specific crystal!

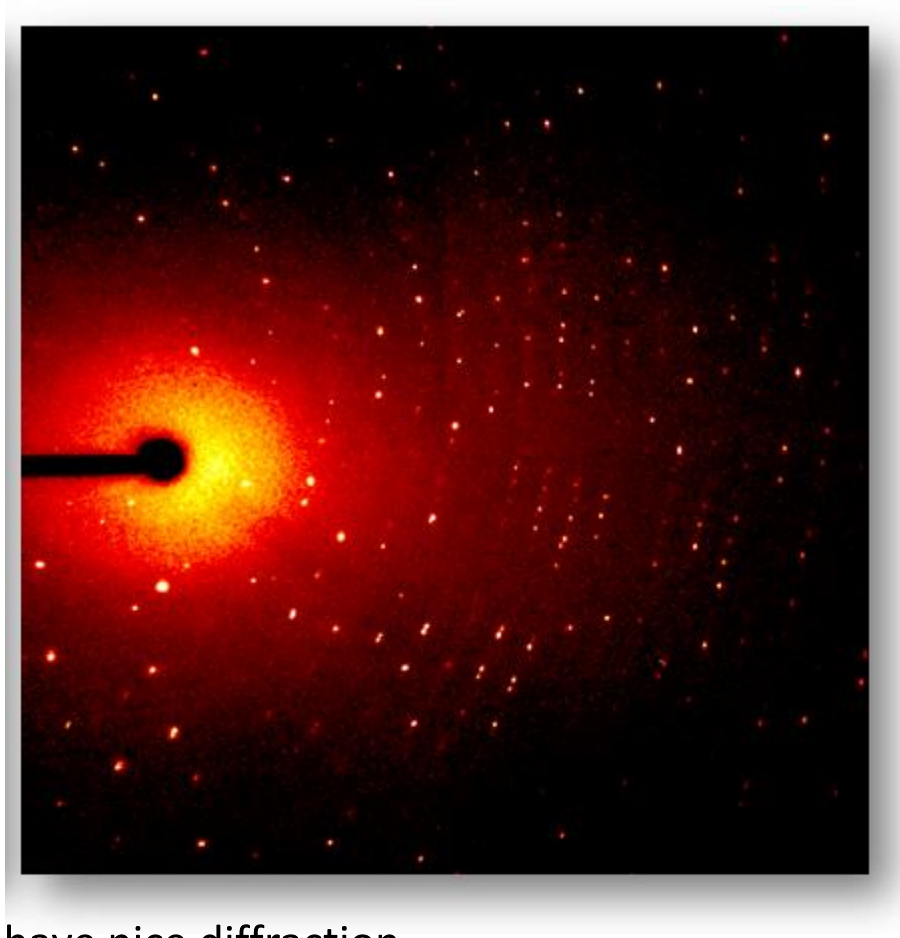
This slide courtesy of Mark Warren, Diamond Light Source

Crystal to Structure



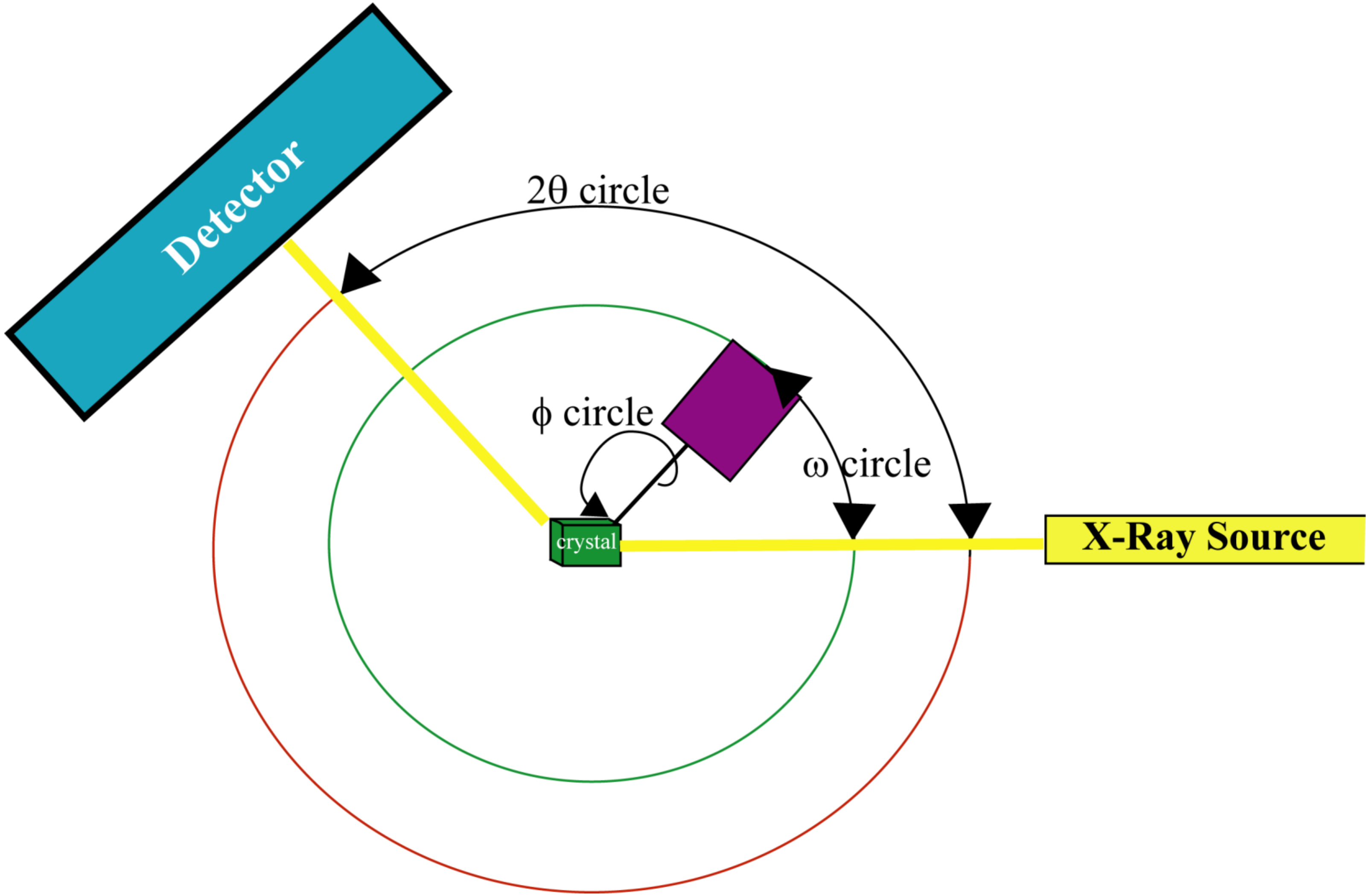
Crystal Selection #LifeGoals



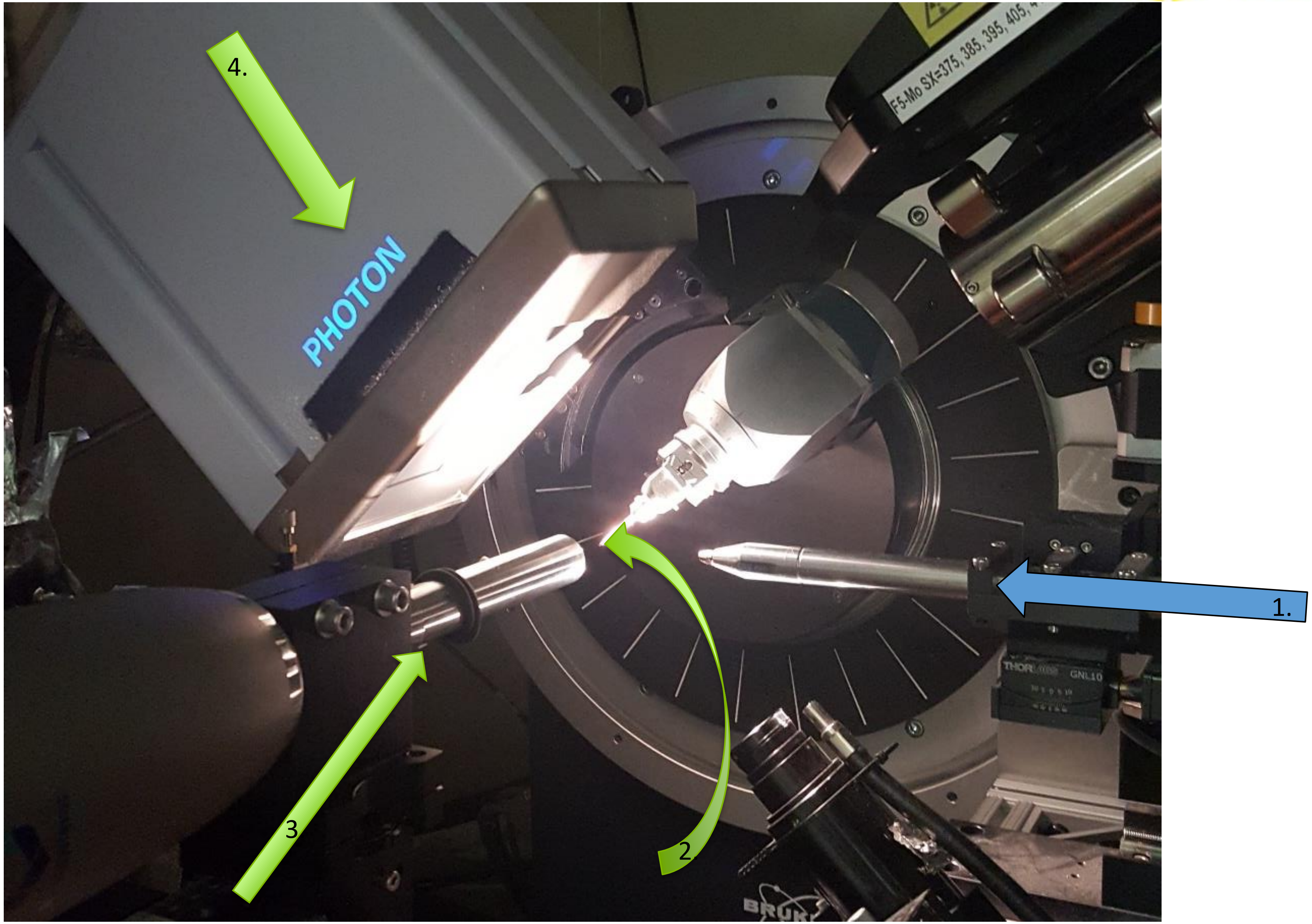


Nice crystals are more likely to have nice diffraction

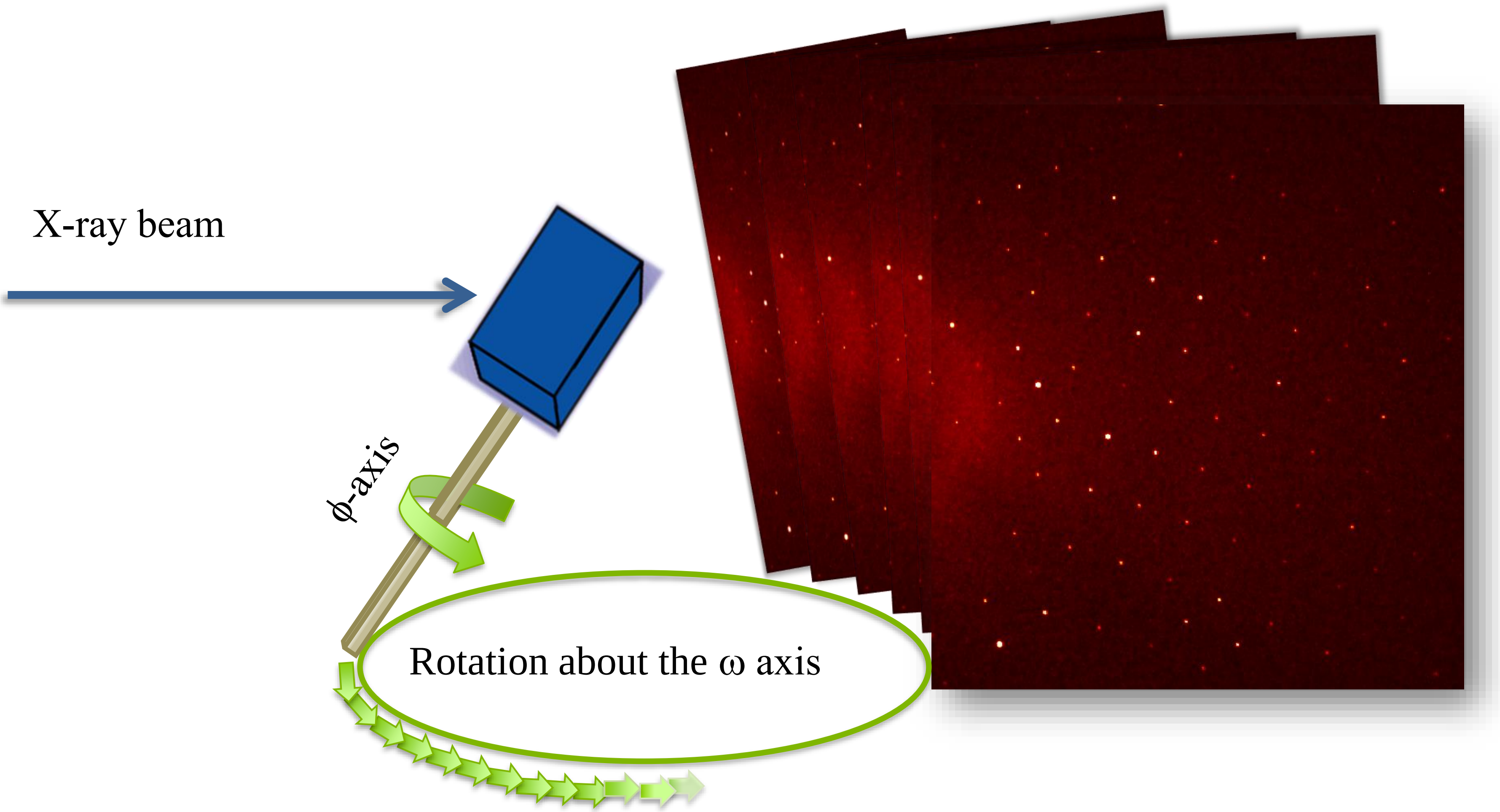
Diffractometer Schematic



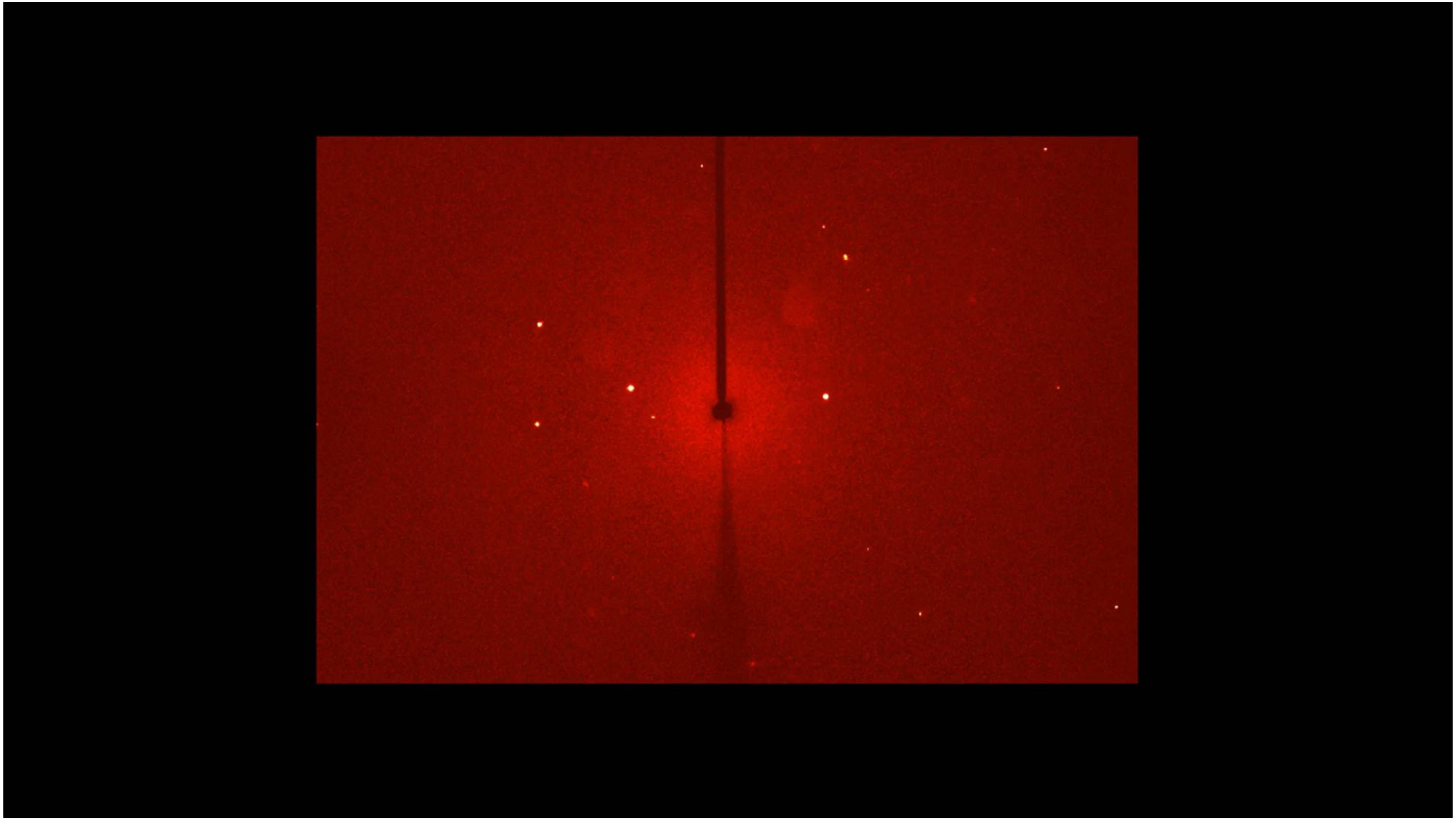
SXD Diffractometer



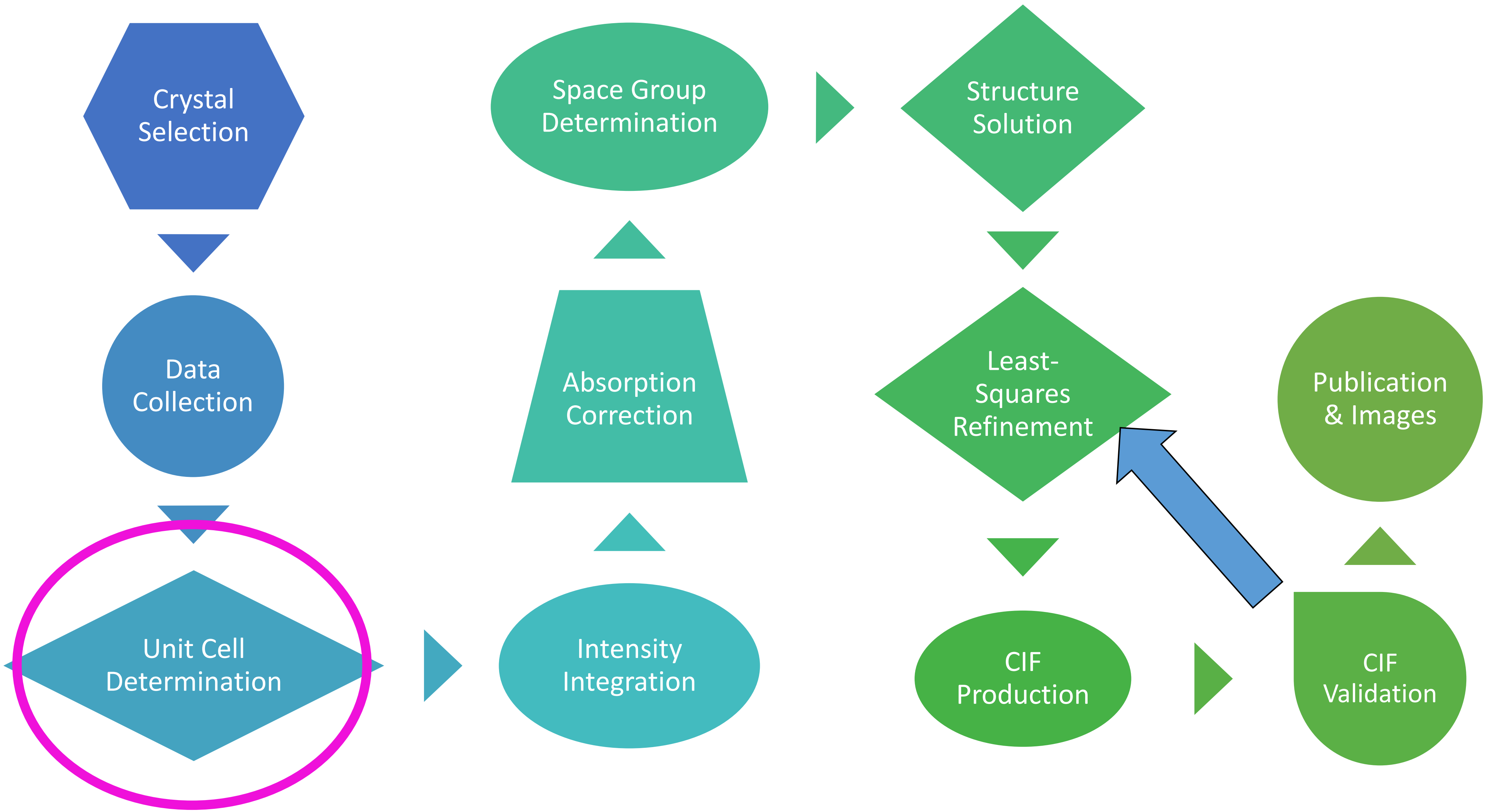
Data Collection Schematic



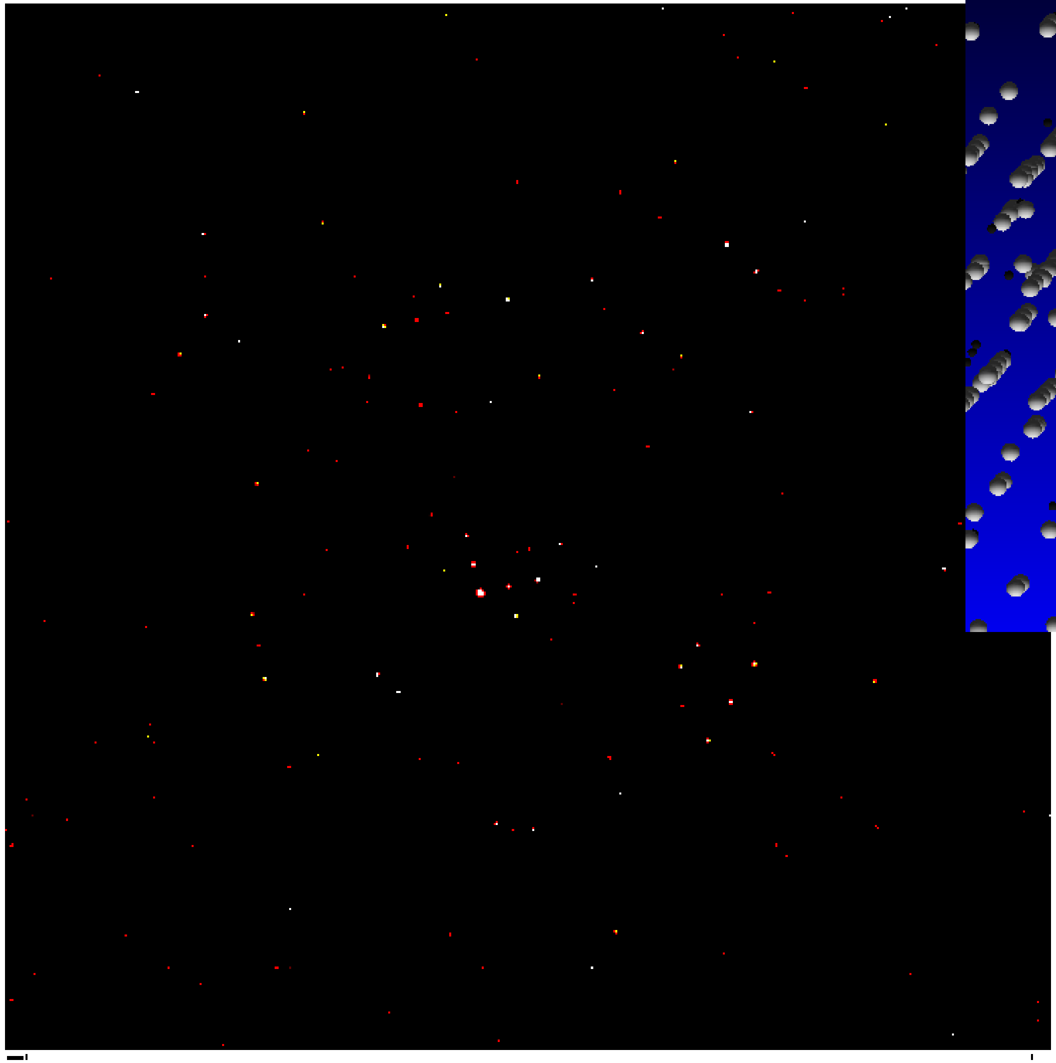
Data Collection

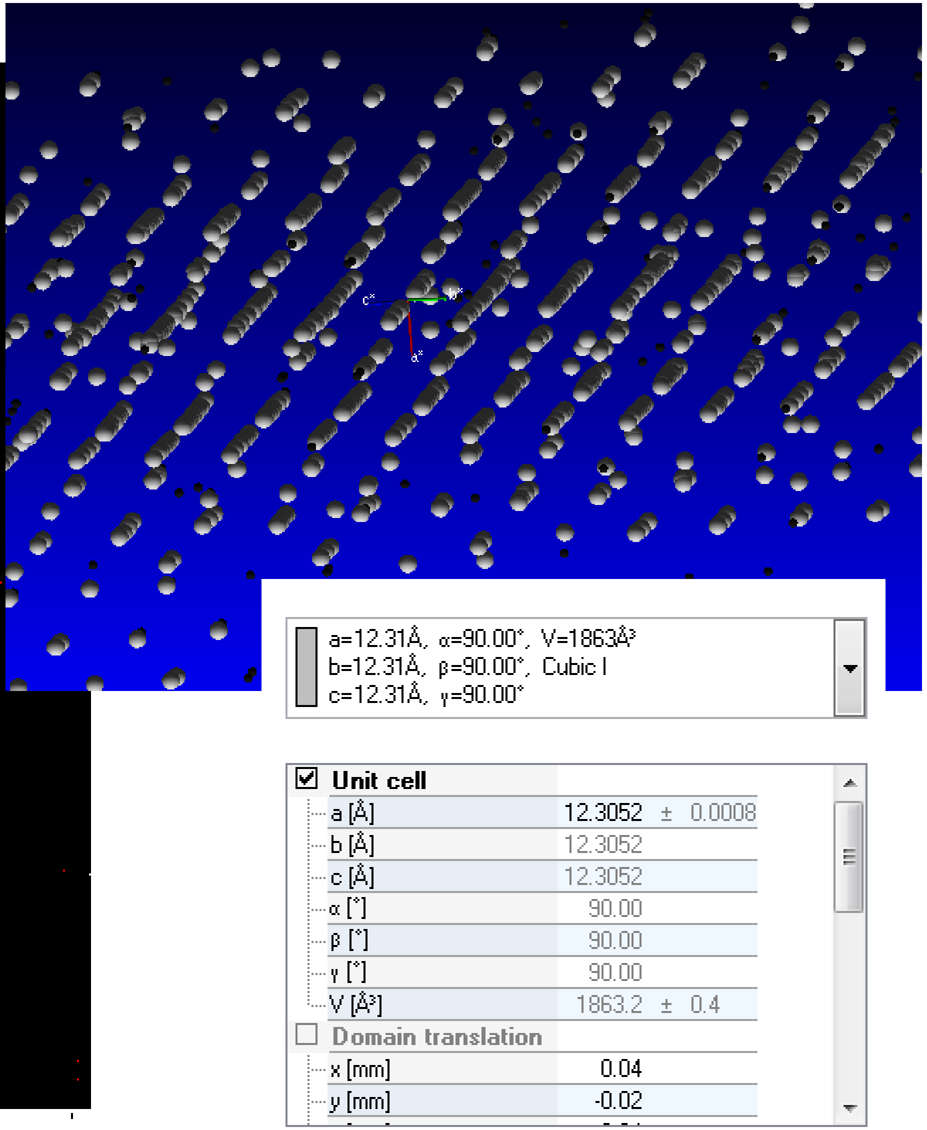


Crystal to Structure

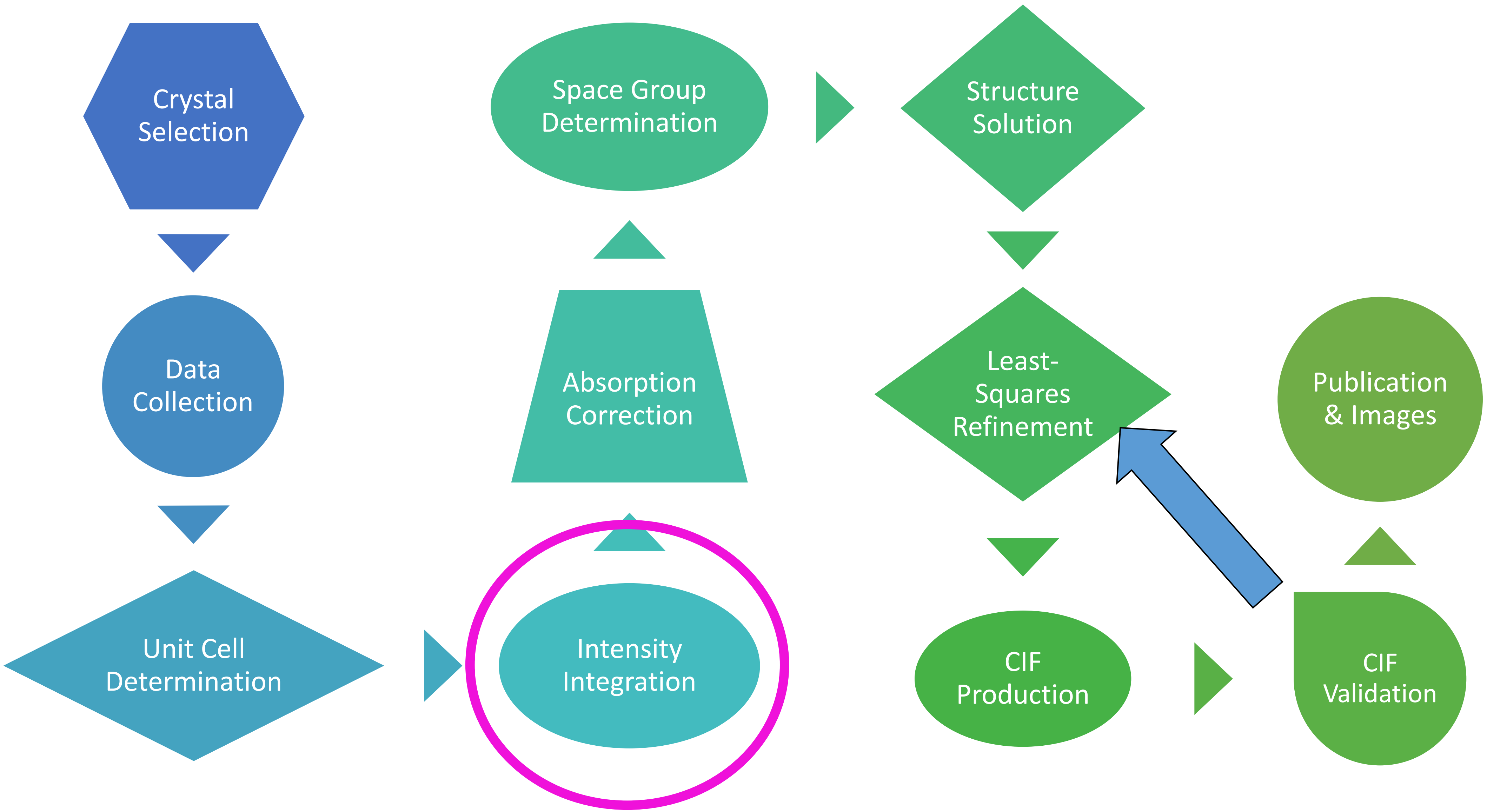


Indexing

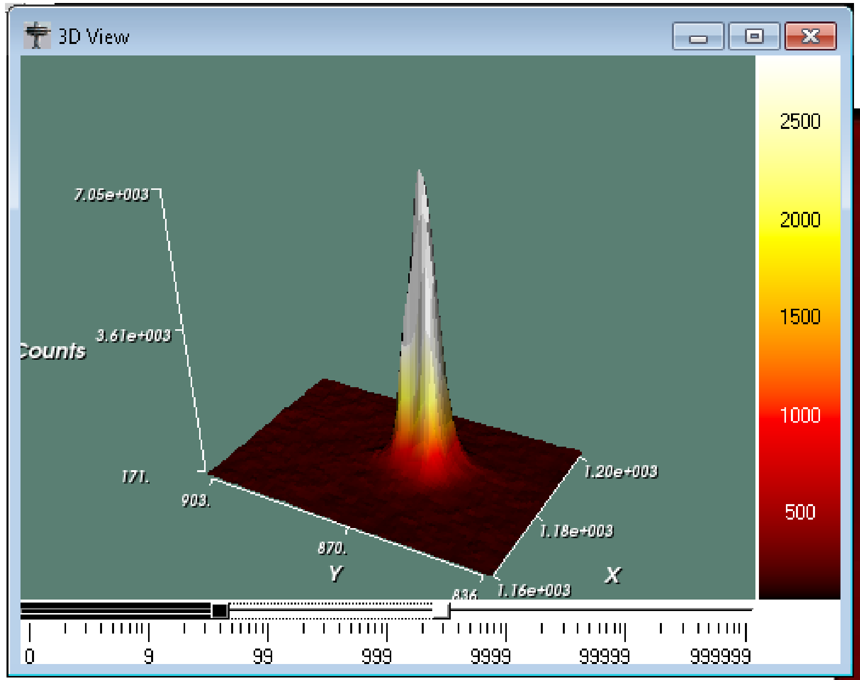


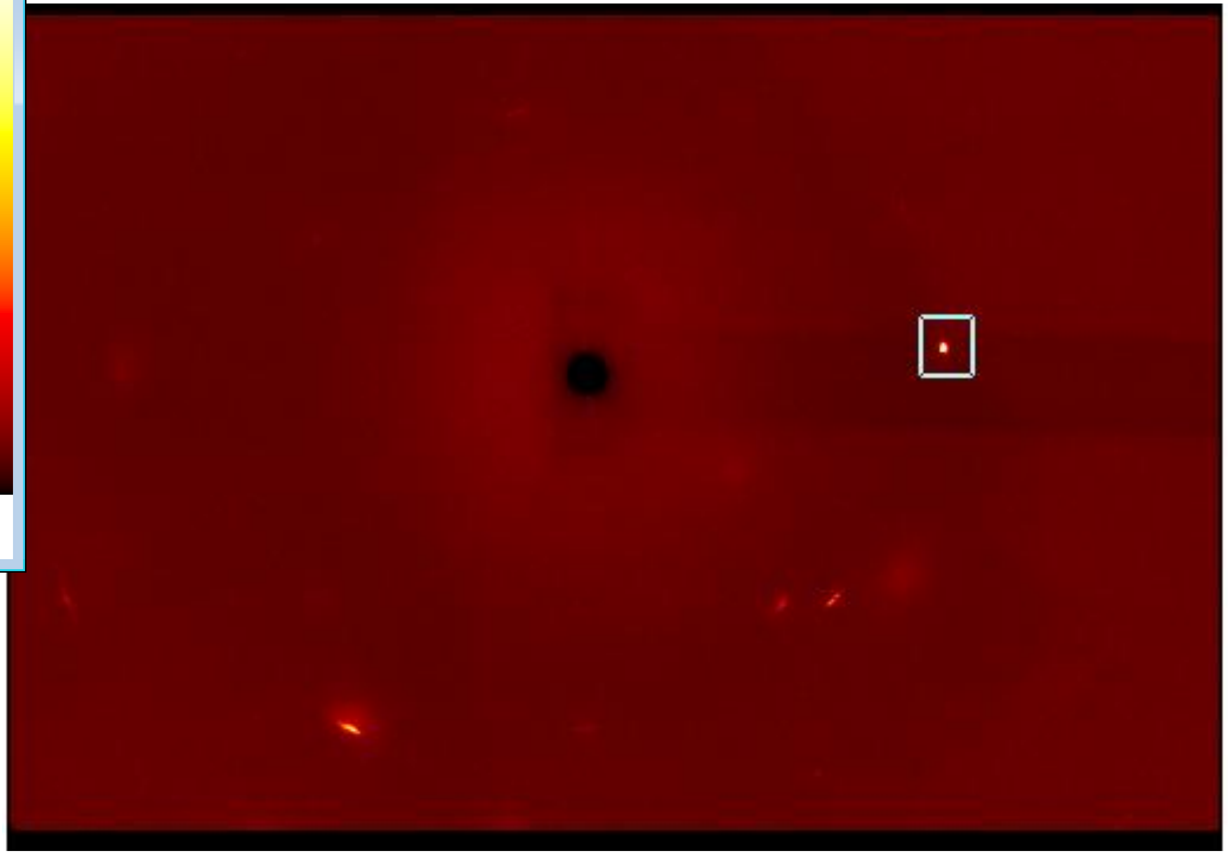

a=12.31Å, α=90.00°, V=1863Å³
b=12.31Å, β=90.00°, Cubic I
c=12.31Å, γ=90.00°
Unit cell
a [Å] 12.3052 ± 0.0008
b [Å] 12.3052
c [Å] 12.3052
α [°] 90.00
β [°] 90.00
γ [°] 90.00
V [Å³] 1863.2 ± 0.4
Domain translation
x [mm] 0.04
y [mm] -0.02

Crystal to Structure

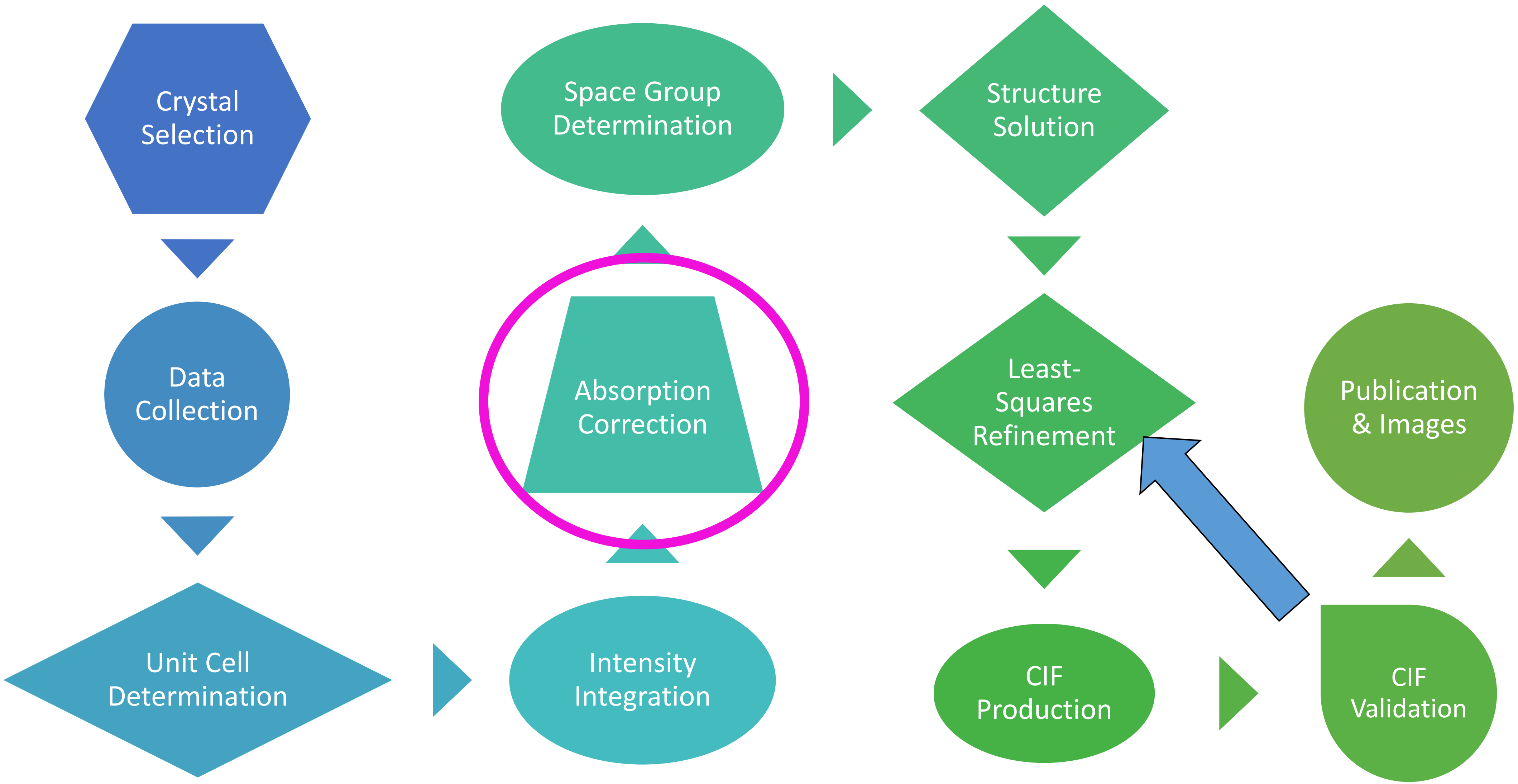


Data Integration

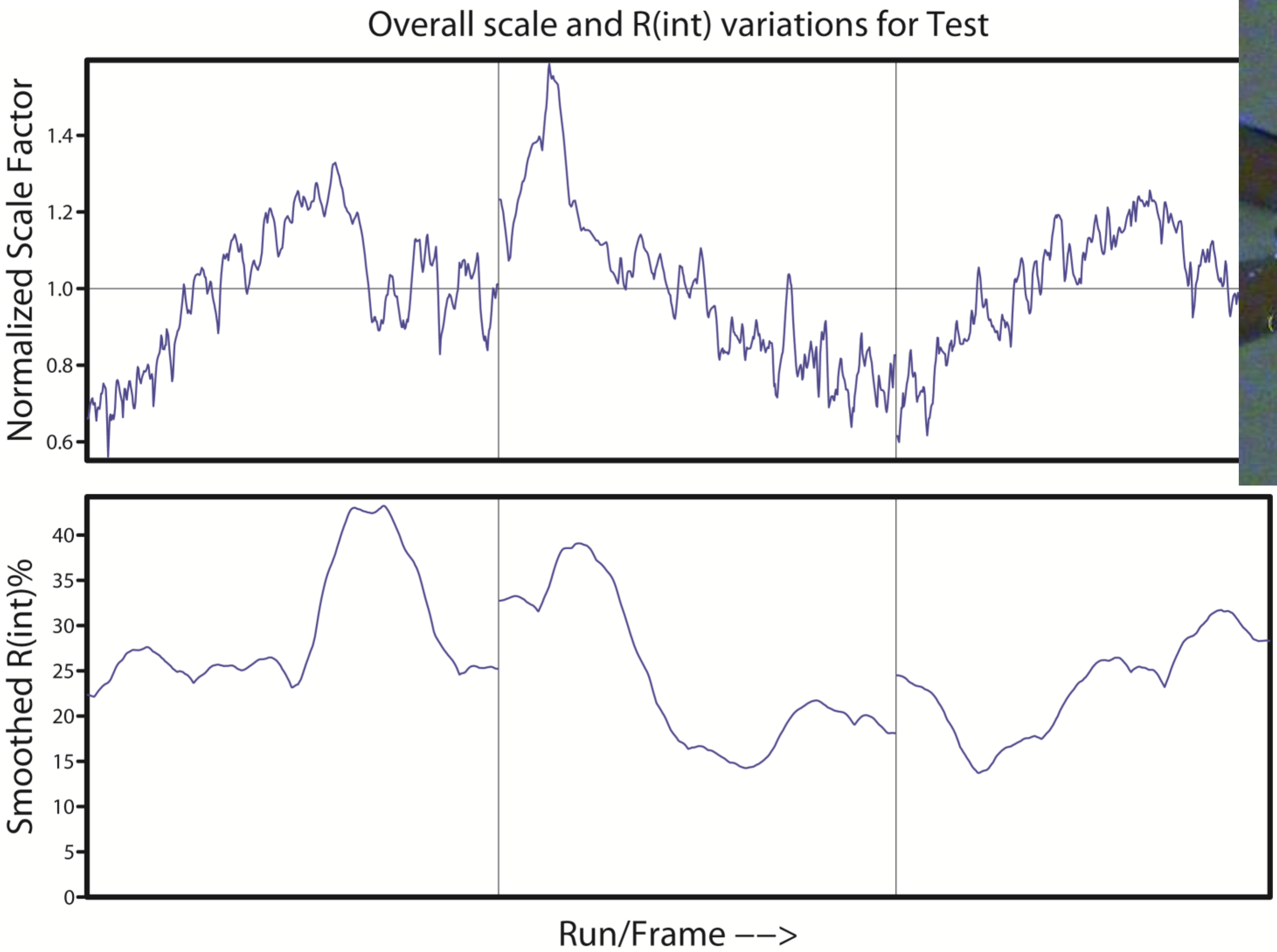


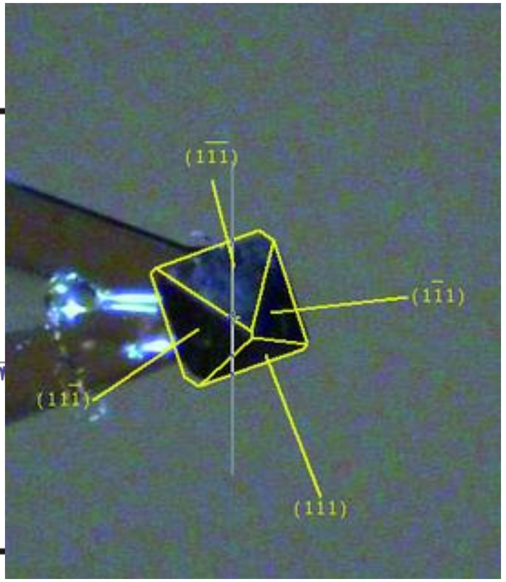


Crystal to Structure

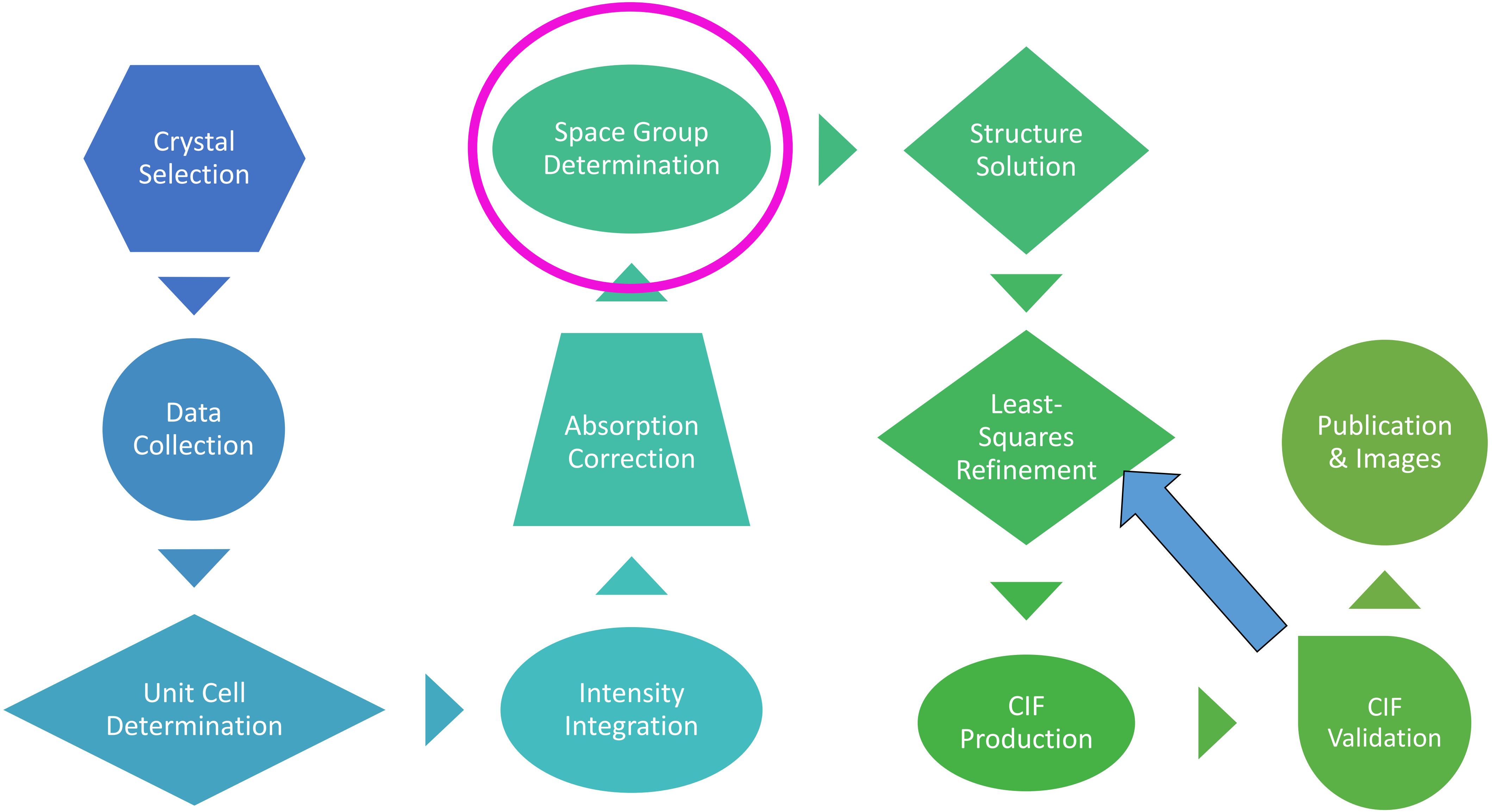


Absorption Correction

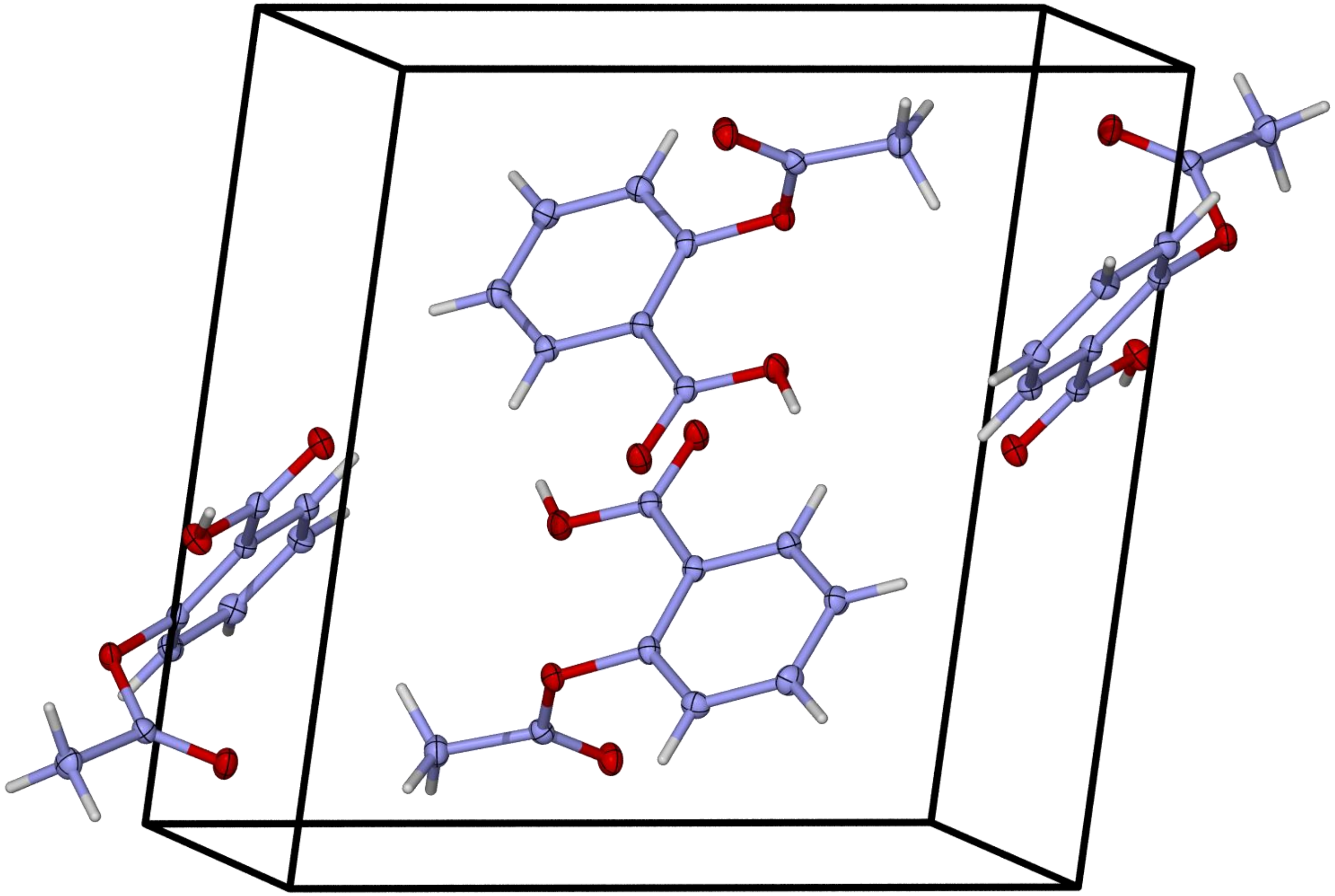




Crystal to Structure

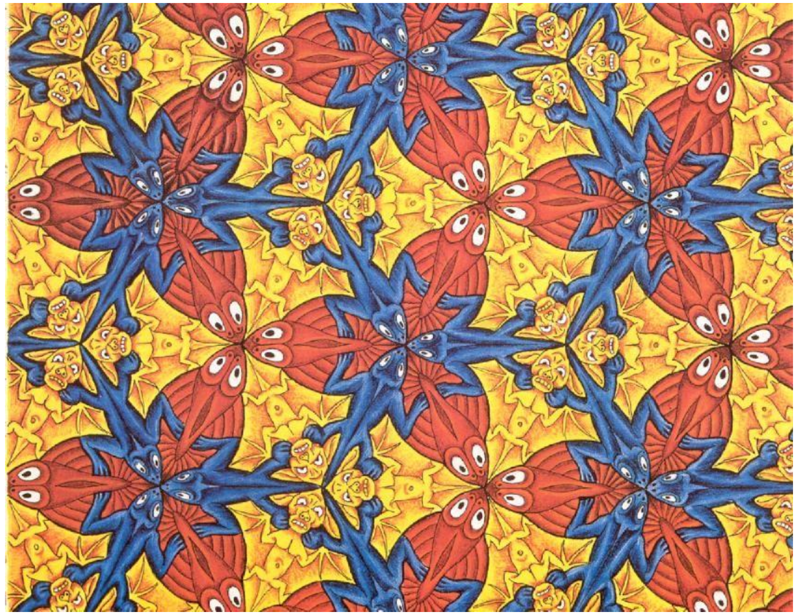


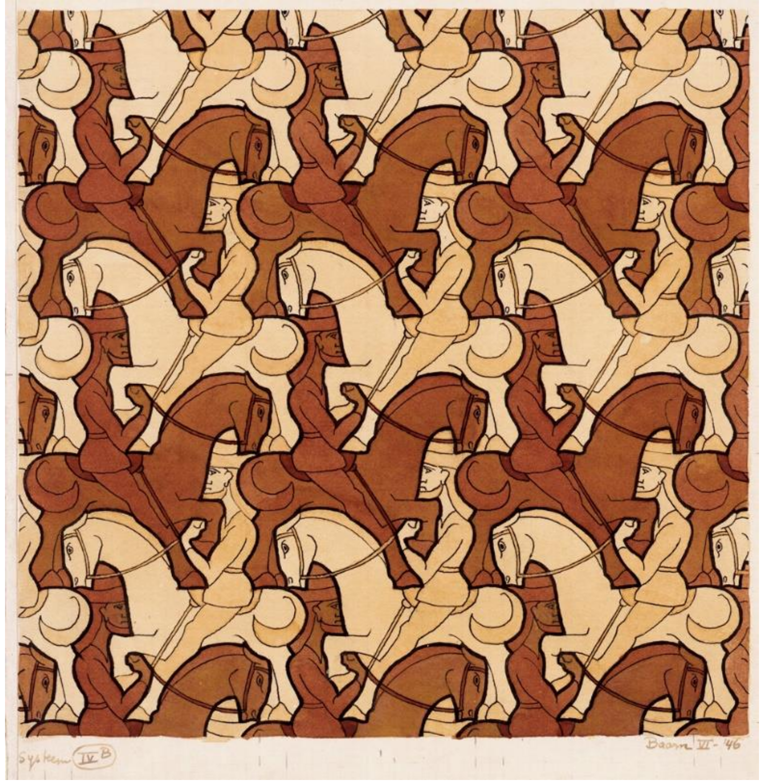
Why do I need a space group?



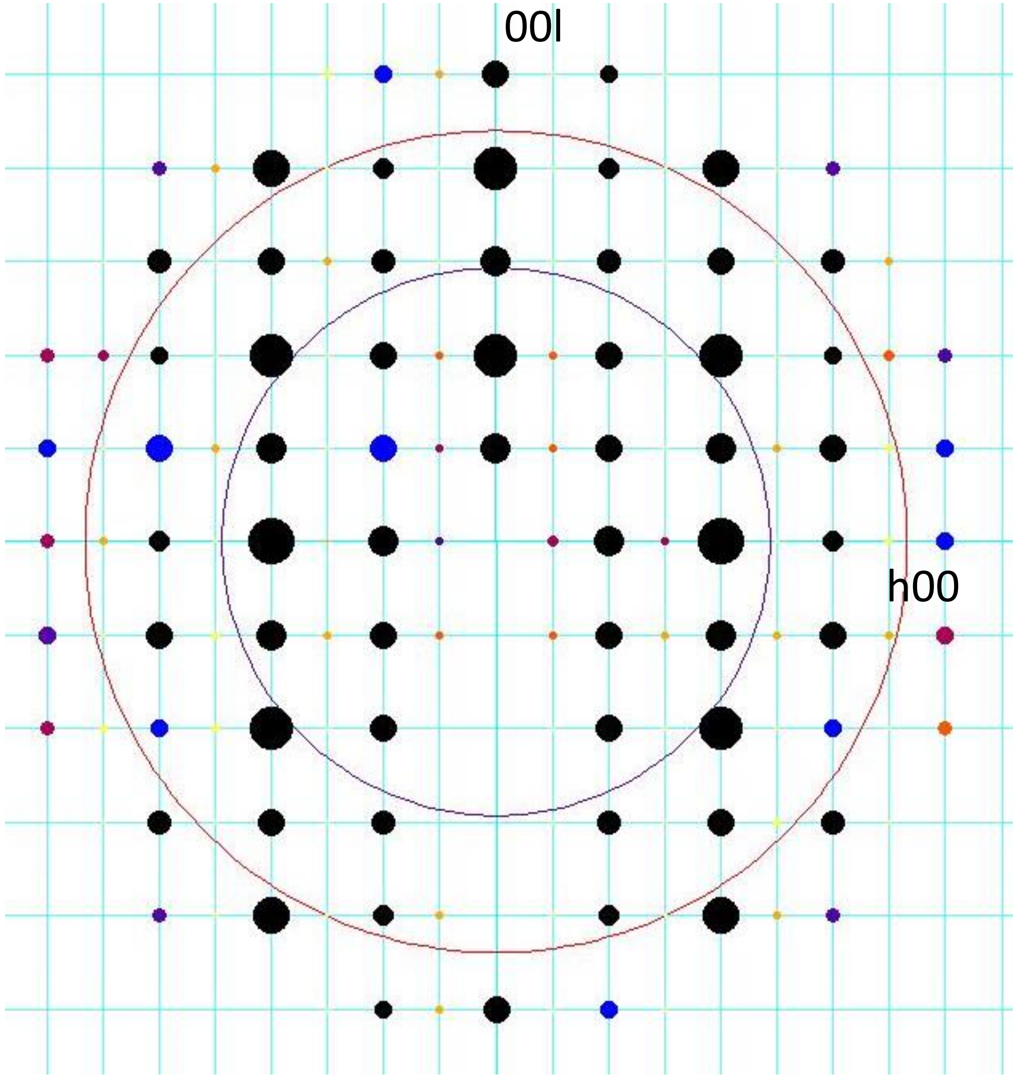
Escher loved his symmetry

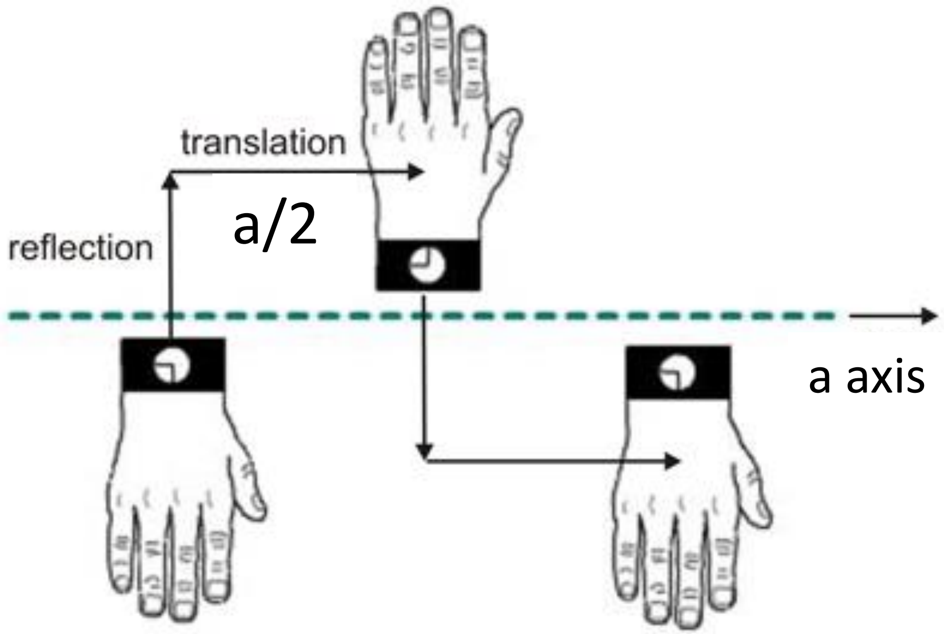
- Tessellations are made using symmetry operations





Space Group Determination





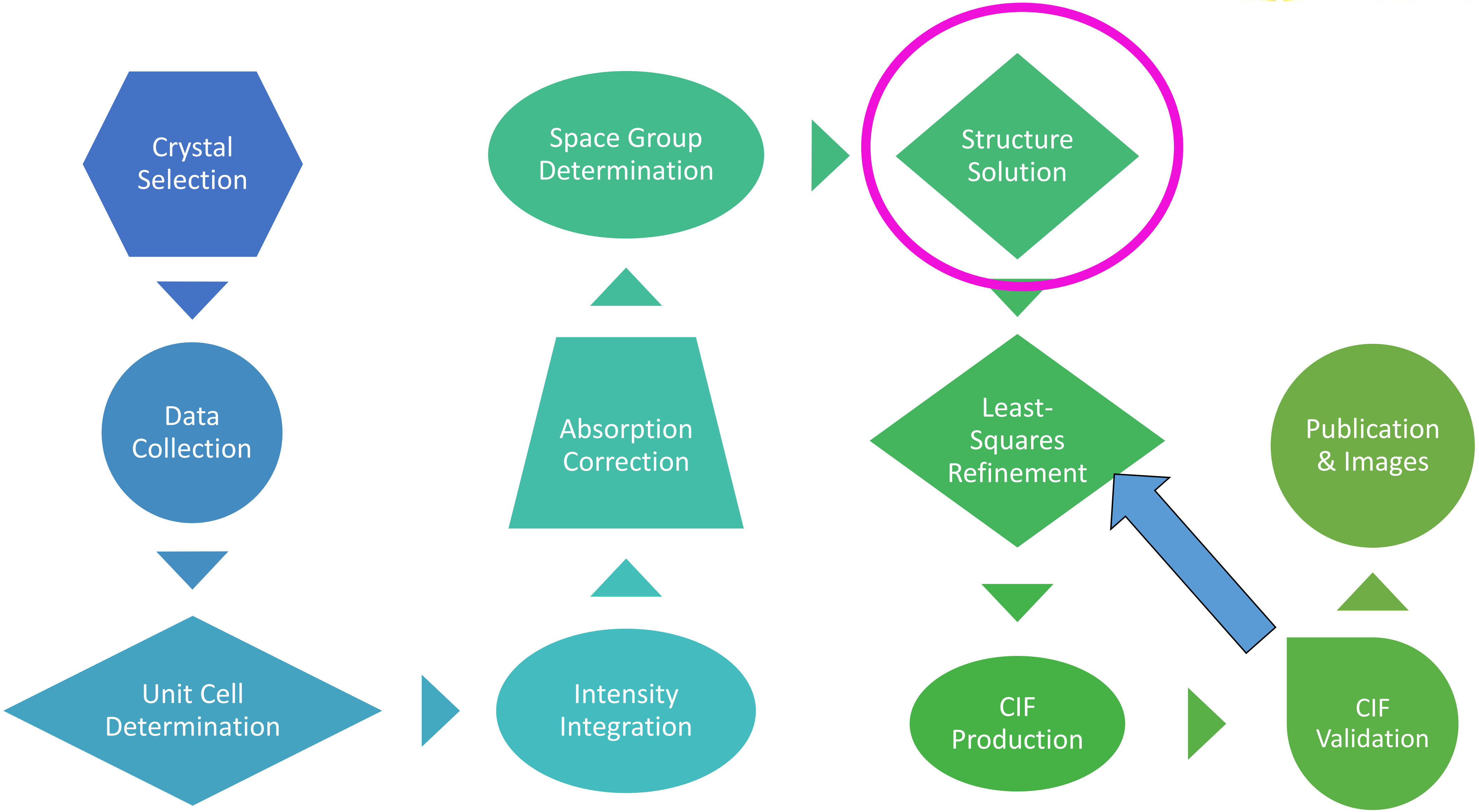
Space Group Determination

Table 3.1.4.1. *Reflection conditions, diffraction symbols and possible space groups* (*cont.*)

ORTHORHOMBIC, Laue class *mmm* (2/*m* 2/*m* 2/*m*) (*cont.*)

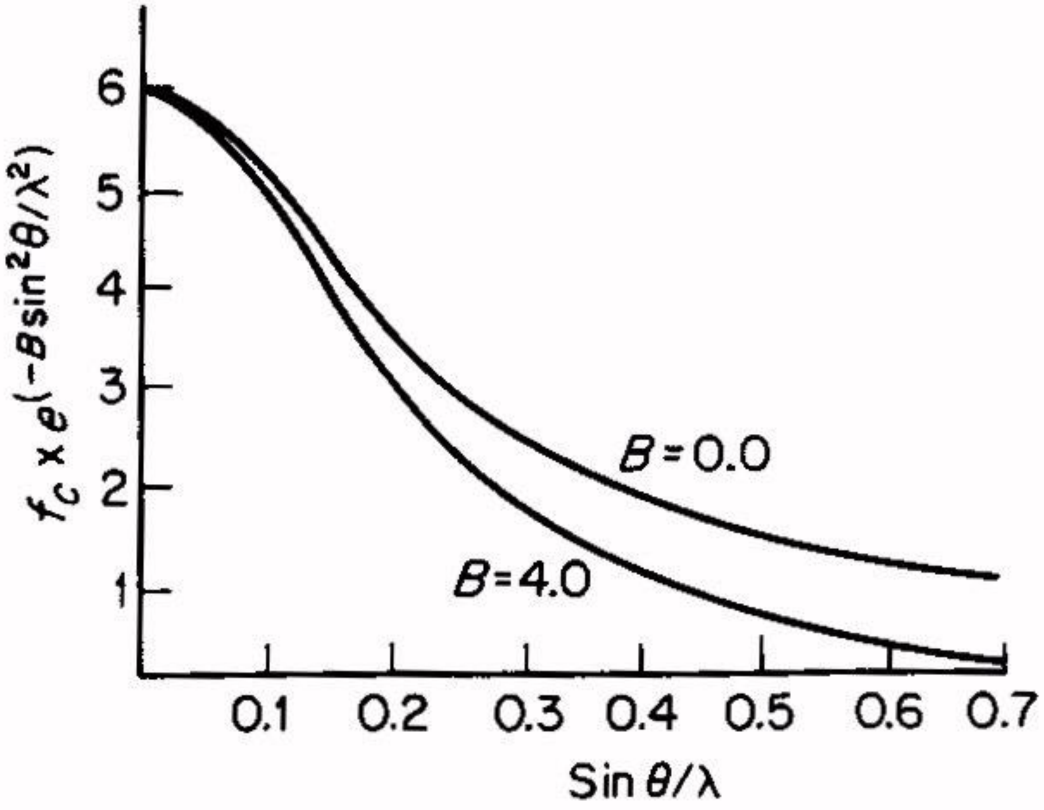
Reflection conditions								Laue class *mmm* (2/*m* 2/*m* 2/*m*)		
								Point group		
hkl	0*kl*	*h*0*l*	*hk*0	*h*00	0*k*0	00*l*	Extinction symbol	222	*mm*2 *m*2*m* 2*mm*	*mmm*
	$k+l$	l	k		k	l	*Pncb*			*Pncb* (50)
	$k+l$	l	$h+k$	h	k	l	*Pncn*			*Pncn* (52)
	$k+l$	$h+l$		h	k	l	*Pnn* –		***Pnn*2** (34)	***Pnnm*** (58)
	$k+l$	$h+l$	h	h	k	l	*Pnna*			***Pnna*** (52)
	$k+l$	$h+l$	k	h	k	l	*Pnnb*			*Pnnb* (52)
	$k+l$	$h+l$	$h+k$	h	k	l	*Pnnn*			***Pnnn*** (48)
$h+k$	k	h	$h+k$	h	k		*C* – – –	***C*222** (21)	***Cmm*2** (35) *Cm*2*m* (38) *C*2*mm* (38)	***Cmmm*** (65)
$h+k$	k	h	$h+k$	h	k	l	*C*– –2_1	***C*222$_1$** (20)		
$h+k$	k	h	h, k	h	k		*C*– –(*ab*)		*Cm*2*e* (39) *C*2*me* (39)	***Cmme*** (67)
$h+k$	k	h, l	$h+k$	h	k	l	*C*–*c* –		***Cmc*2$_1$** (36) *C*2*cm* (40)	***Cmcm*** (63
$h+k$	k	h, l	h, k	h	k	l	*C*–*c*(*ab*)		*C*2*ce* (41)	***Cmce*** (64

Crystal to Structure



Electron Density from Diffraction

$$\rho_{xyz} = \frac{1}{V}\sum_{hkl} \bar{F}_{hkl}\, e^{-i2\pi(hx+ky+lz)}$$



Structure Solution

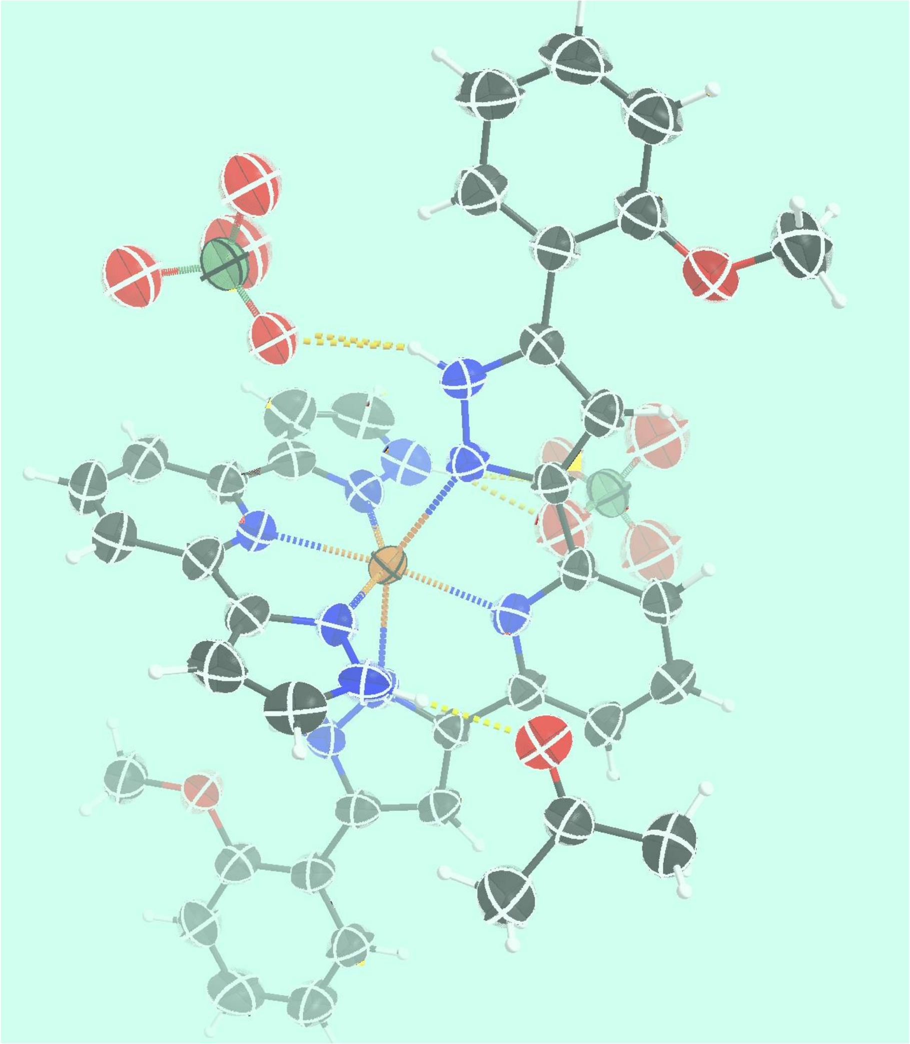
$$\rho_{xyz} = \frac{1}{V}\sum_{hkl} \boxed{\bar{F}_{hkl}}\, e^{-i2\pi(hx+ky+lz)}$$

-5	10	-3	0.01	0.45
-6	10	-3	-0.28	0.49
-7	10	-3	-0.28	0.52
-8	10	-3	1.63	0.56
12	9	-3	1.15	0.68
-12	-9	3	0.64	0.66
11	9	-3	5.65	0.82
-11	-9	3	6.17	0.77
10	9	-3	-0.14	0.65
-10	-9	3	-0.17	0.48
9	9	-3	2.01	0.72
-9	-9	3	2.11	0.51
8	9	-3	4.10	0.72
8	9	-3	6.25	0.82
-8	-9	3	5.89	0.63
7	9	-3	9.05	0.95
-7	-9	3	9.79	0.79
6	9	-3	4.40	0.72
-6	-9	3	7.25	0.65
5	9	-3	8.03	0.84
-5	-9	3	7.17	0.73
4	9	-3	5.66	0.71
-4	-9	3	4.98	0.65
3	9	-3	1.28	0.51
-3	-9	3	1.40	0.46
2	9	-3	18.66	1.23
-2	-9	3	16.45	1.18
1	9	-3	8.06	0.84
-1	-9	3	7.75	0.75
0	9	-3	17.88	1.22

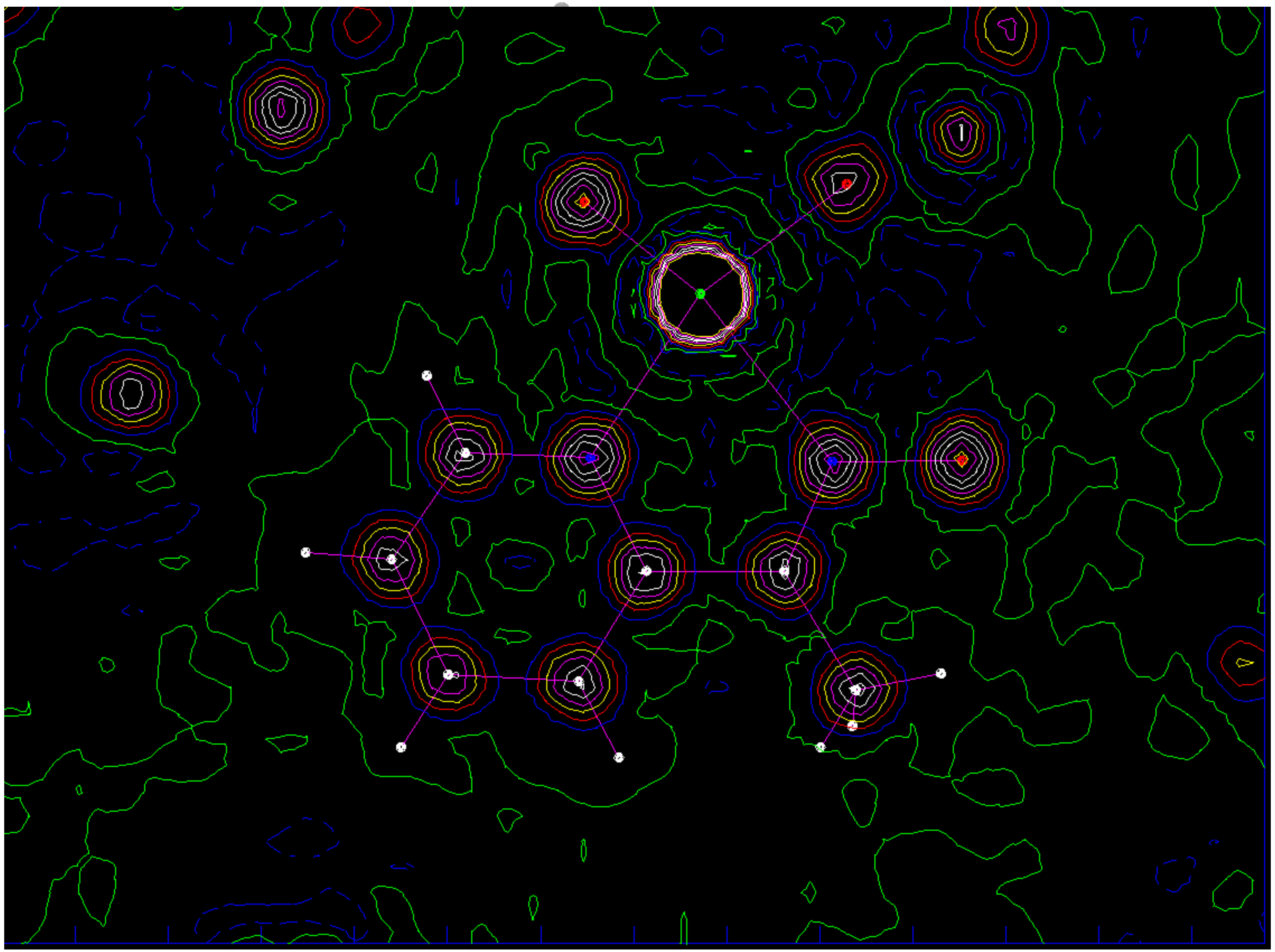
$$\boxed{\bar{F}_{hkl} = |F_{hkl}|\, e^{i\varphi_{hkl}}}$$

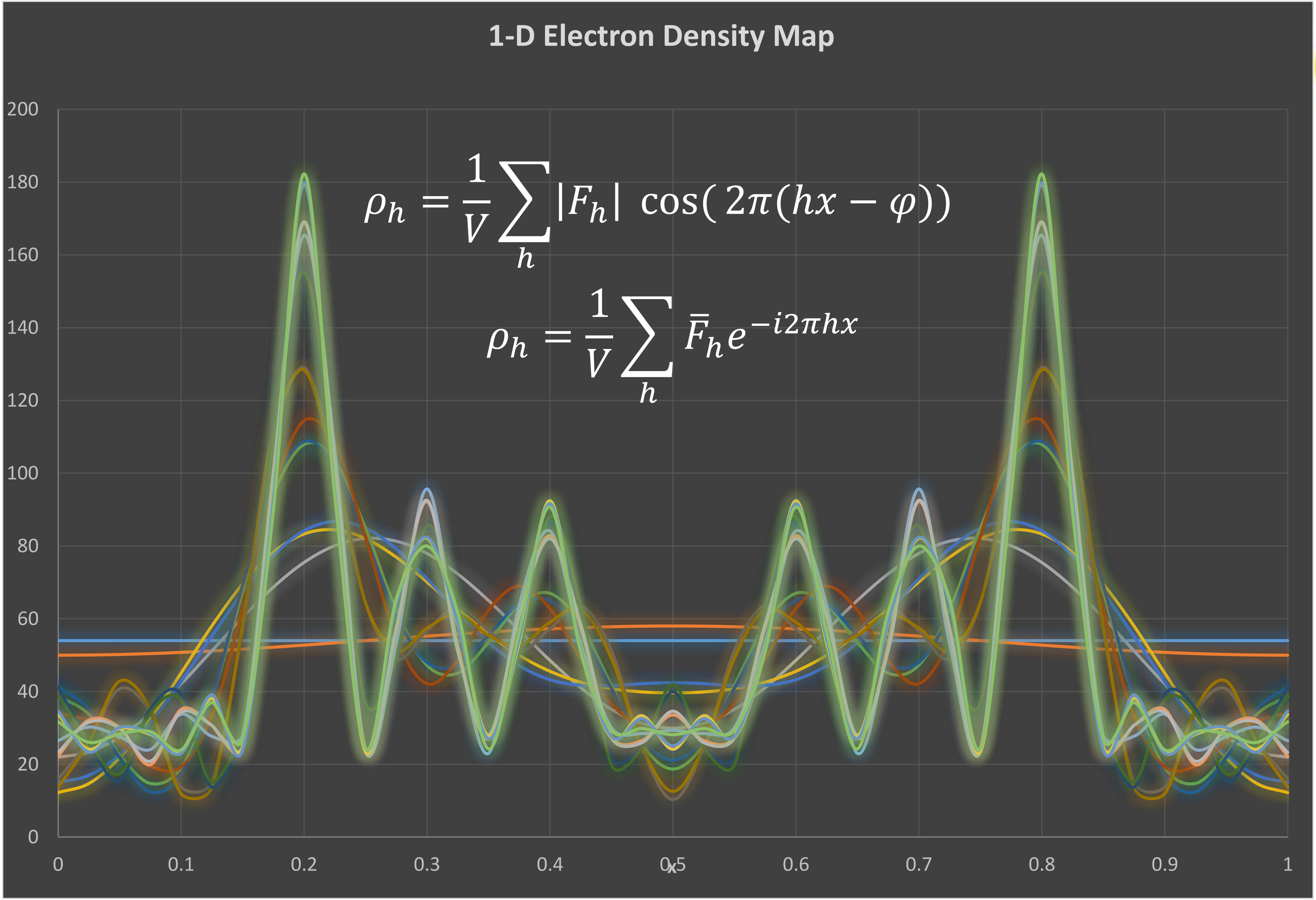
????

SHELXT
SHELXS
SIR2011+
SUPERFLIP



What is a Structure?

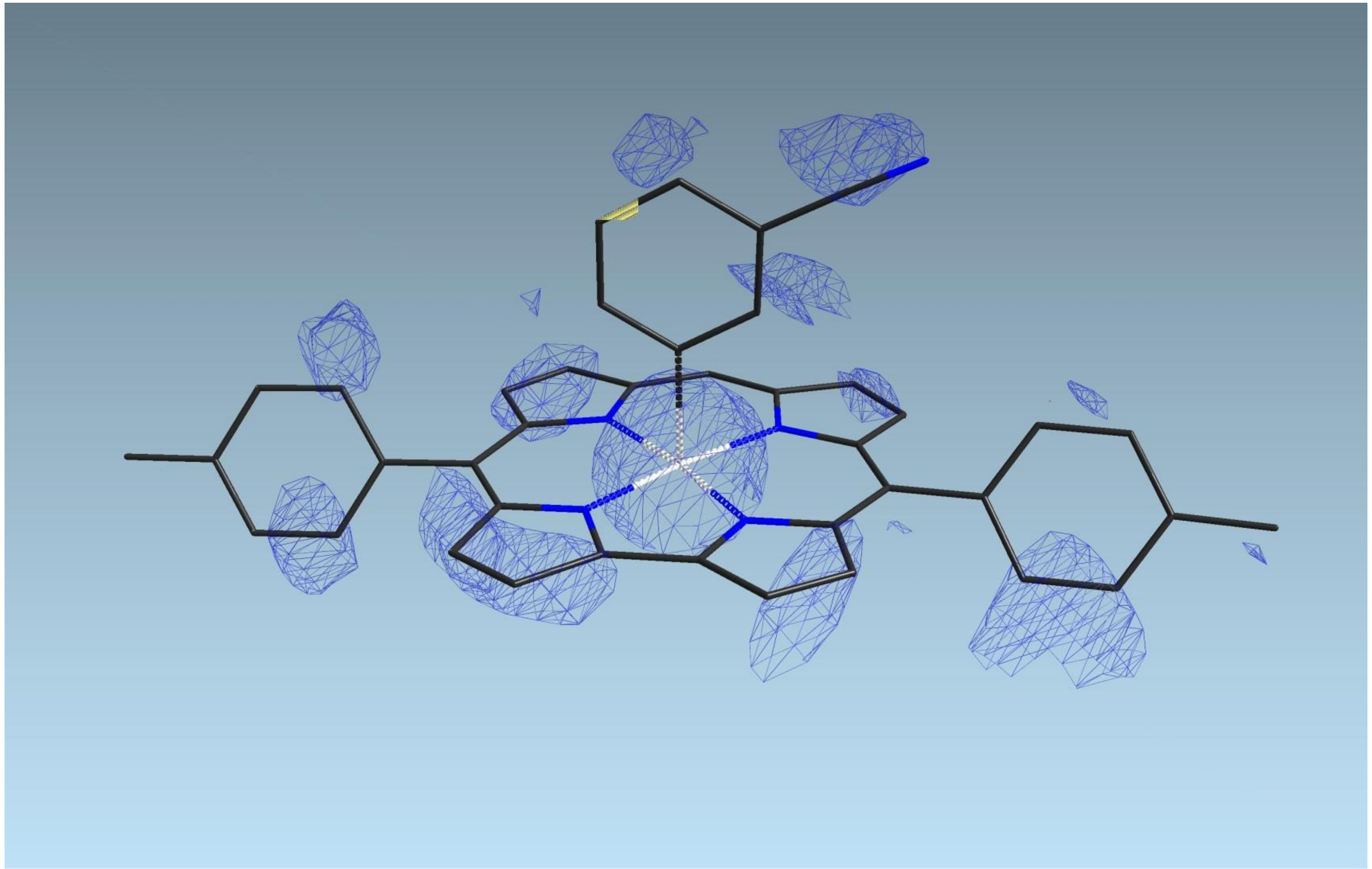




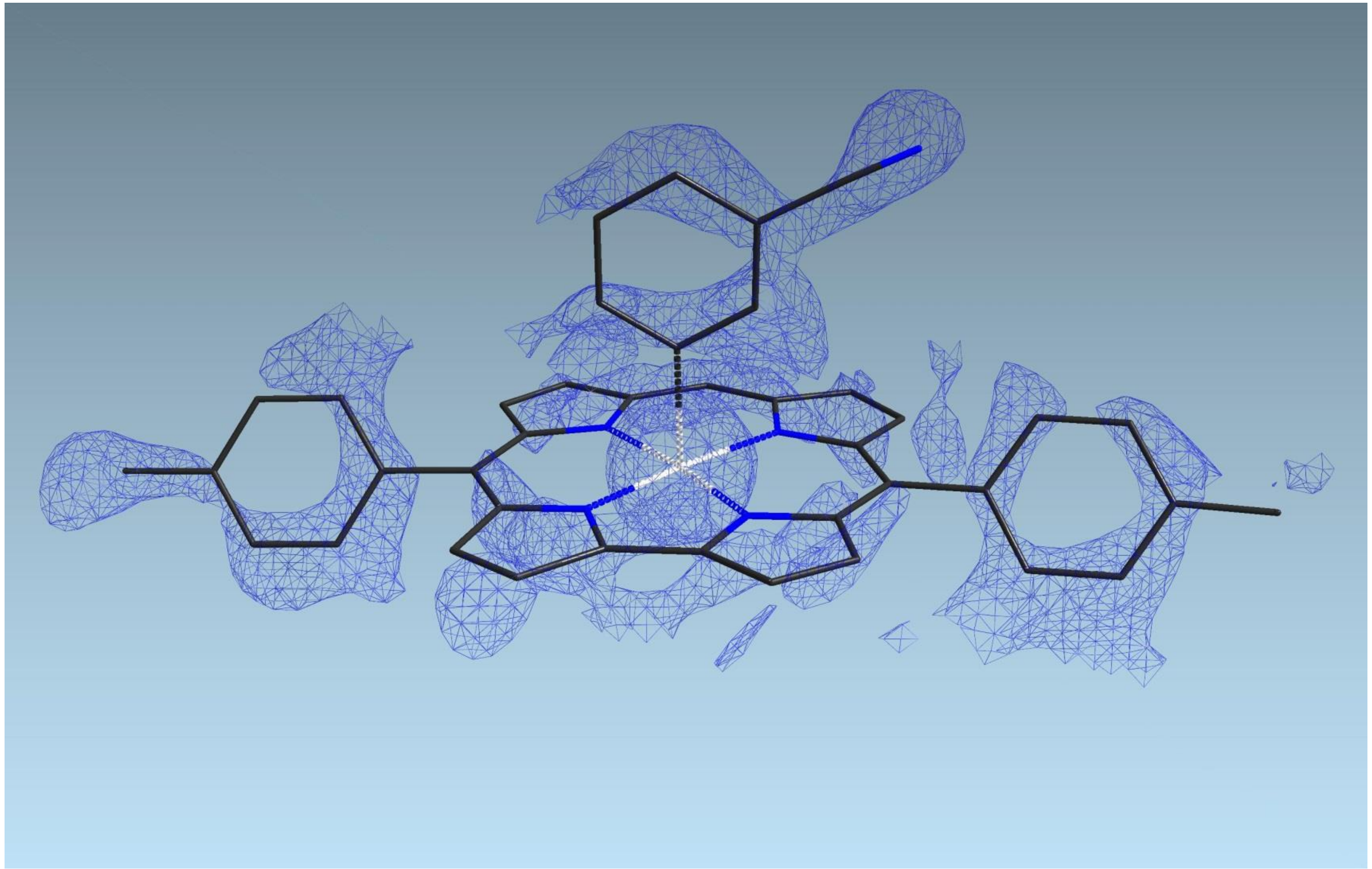
$$\rho_h = \frac{1}{V}\sum_h |F_h| \cos(2\pi(hx - \varphi))$$

$$\rho_h = \frac{1}{V}\sum_h \bar{F}_h e^{-i2\pi hx}$$

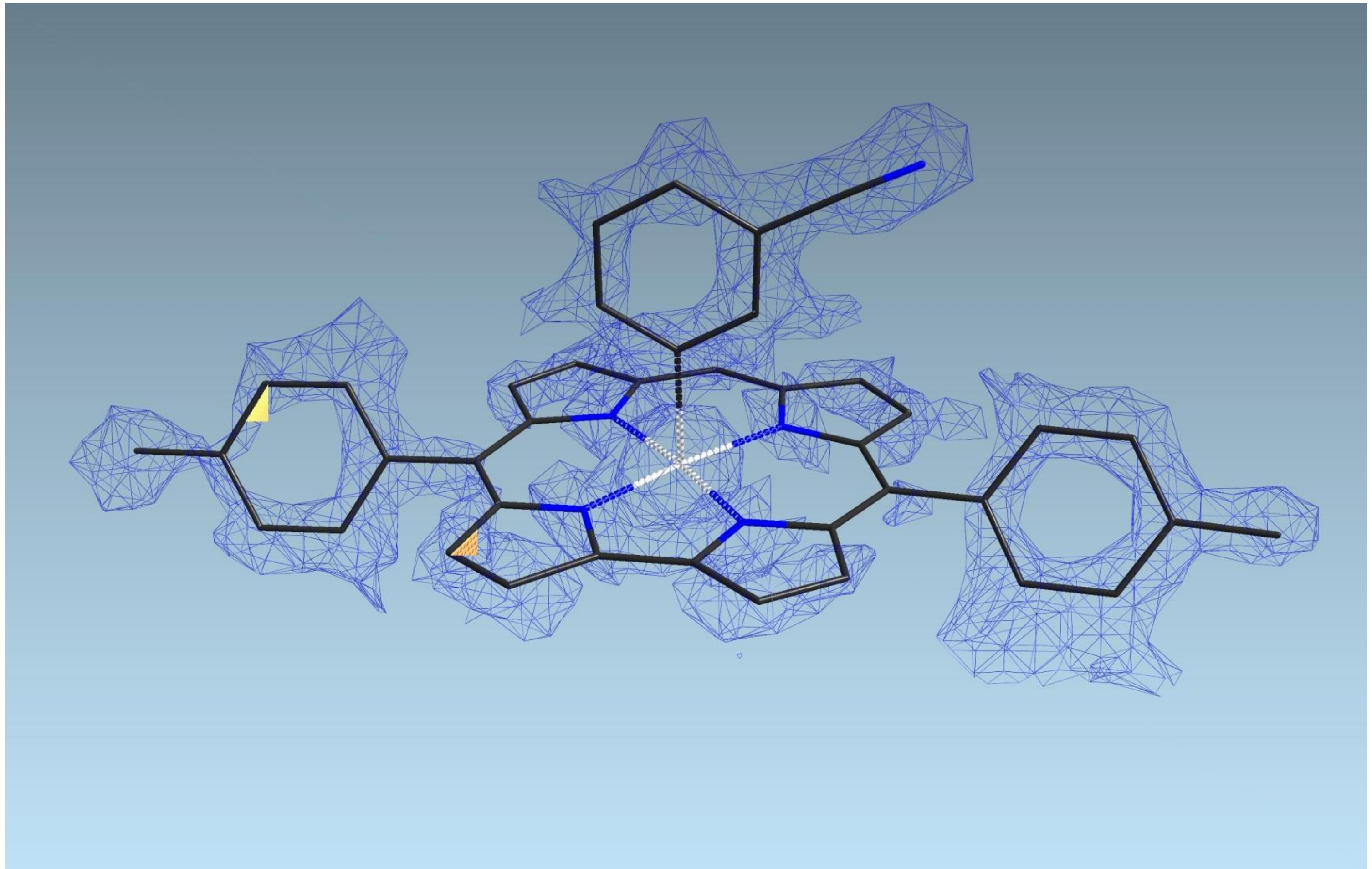
F_{obs} Map at 2.50Å



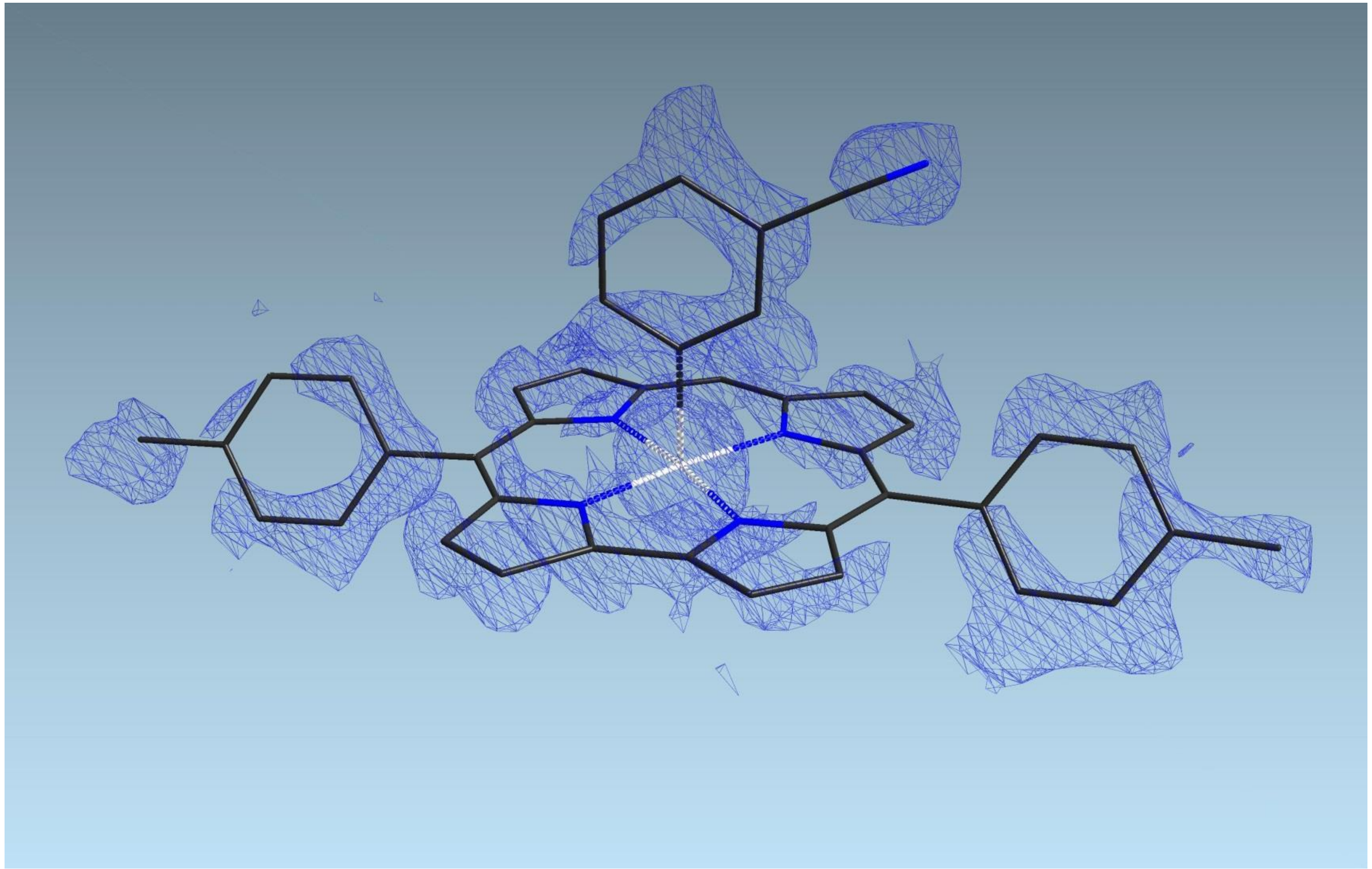
F_{obs} Map at 2.0Å



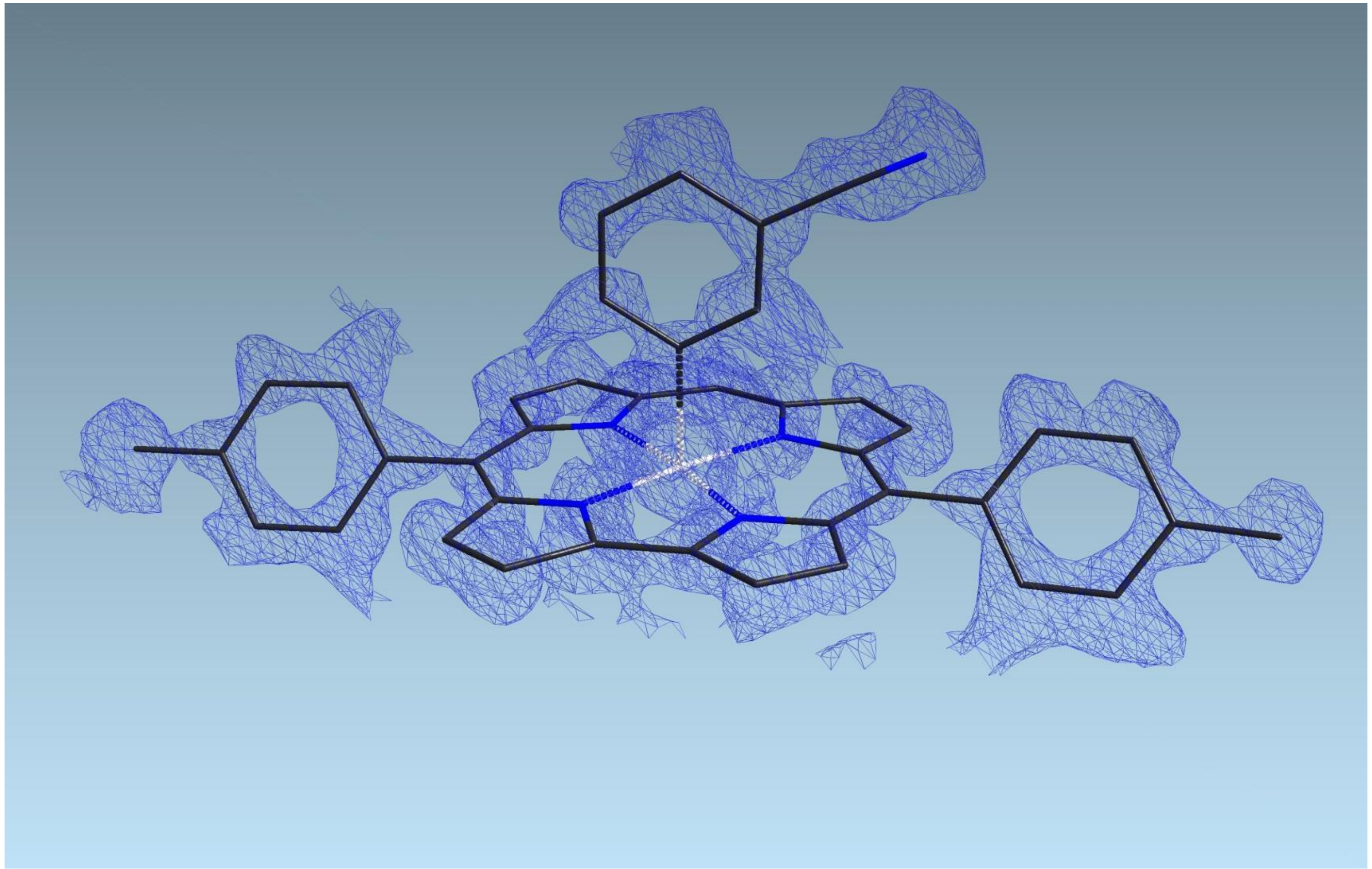
F_{obs} Map at 1.75Å



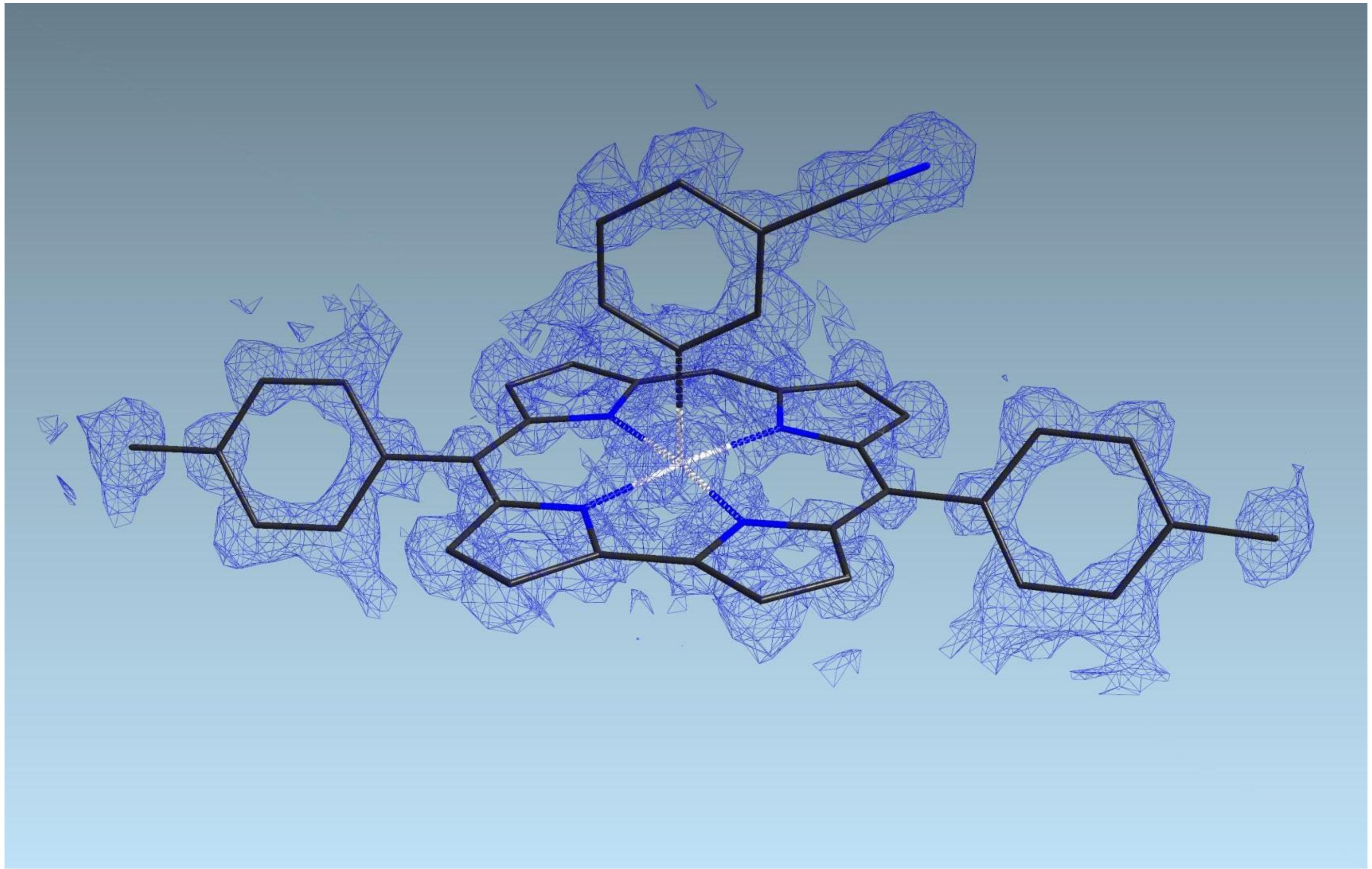
F_{obs} Map at 1.50Å



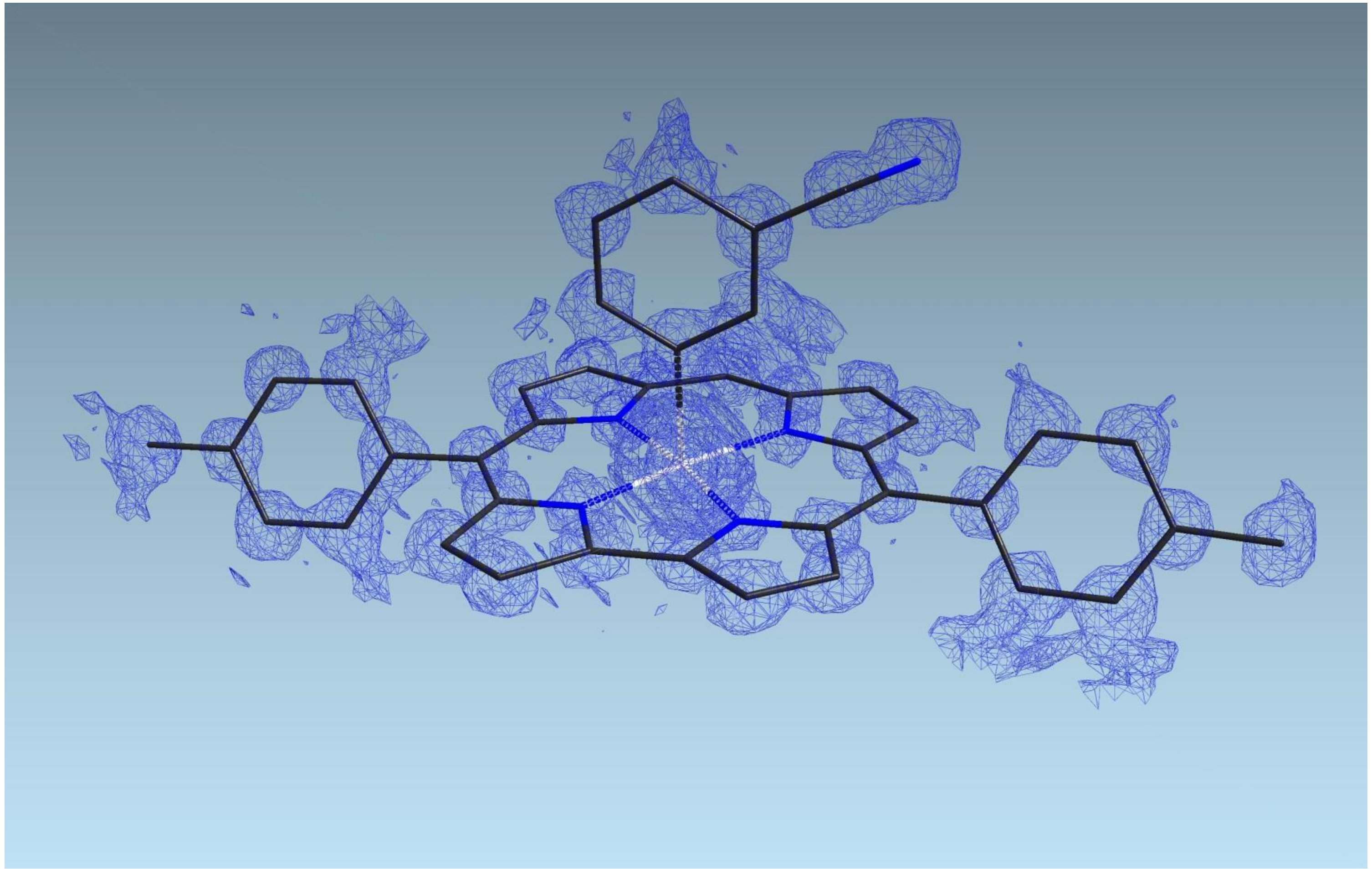
F_{obs} Map at 1.25Å



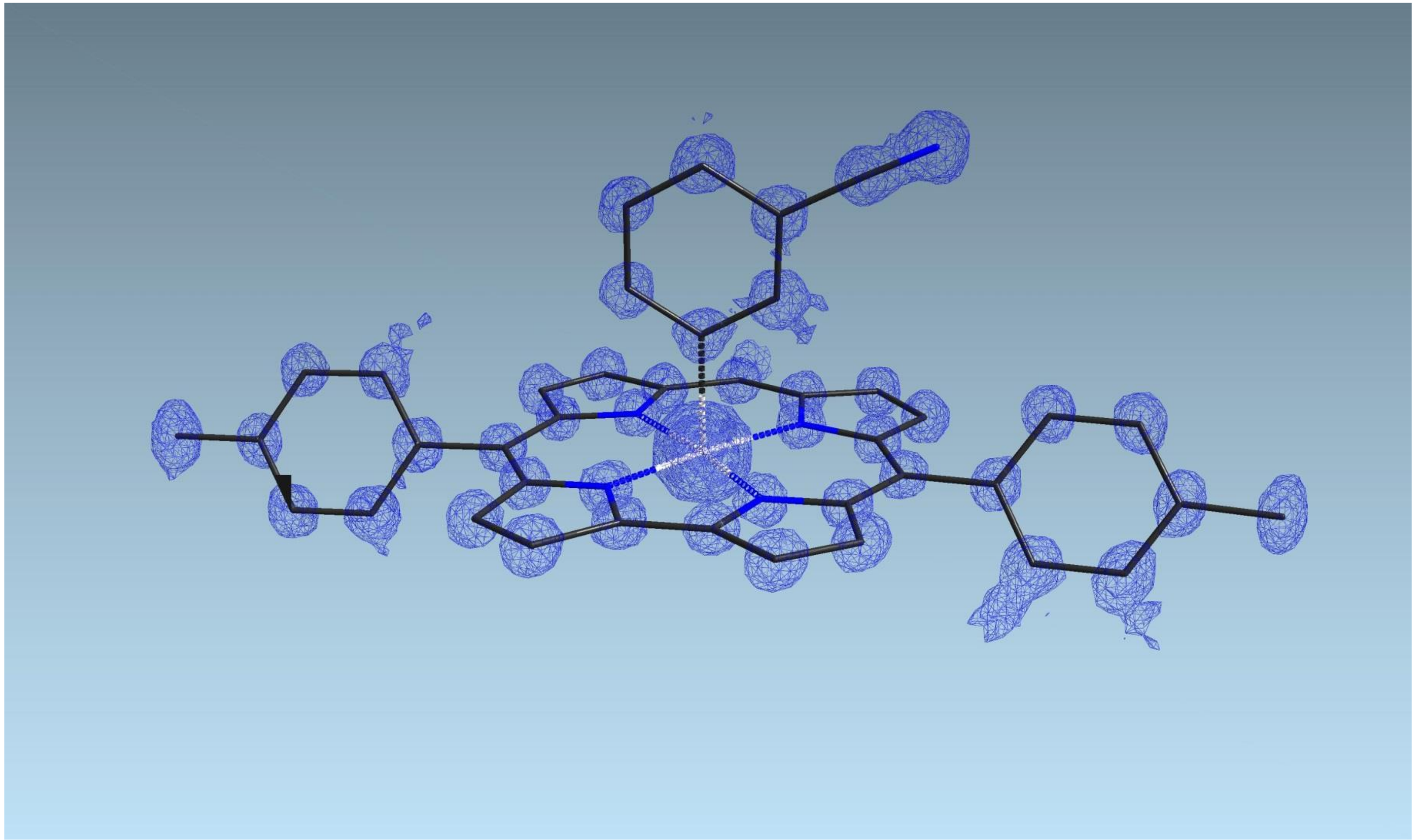
F_{obs} Map at 1.00Å



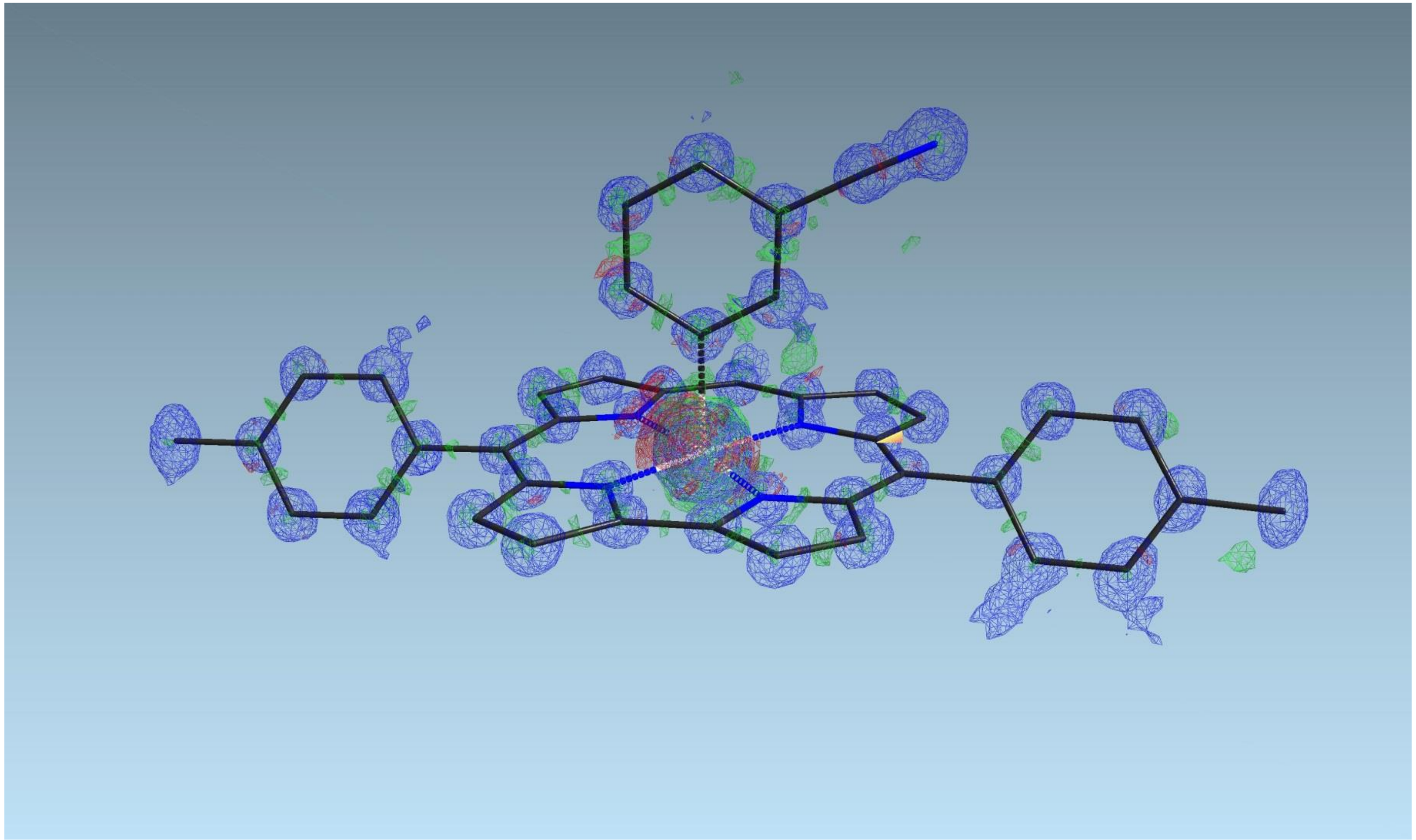
Fobs Map at 0.75Å



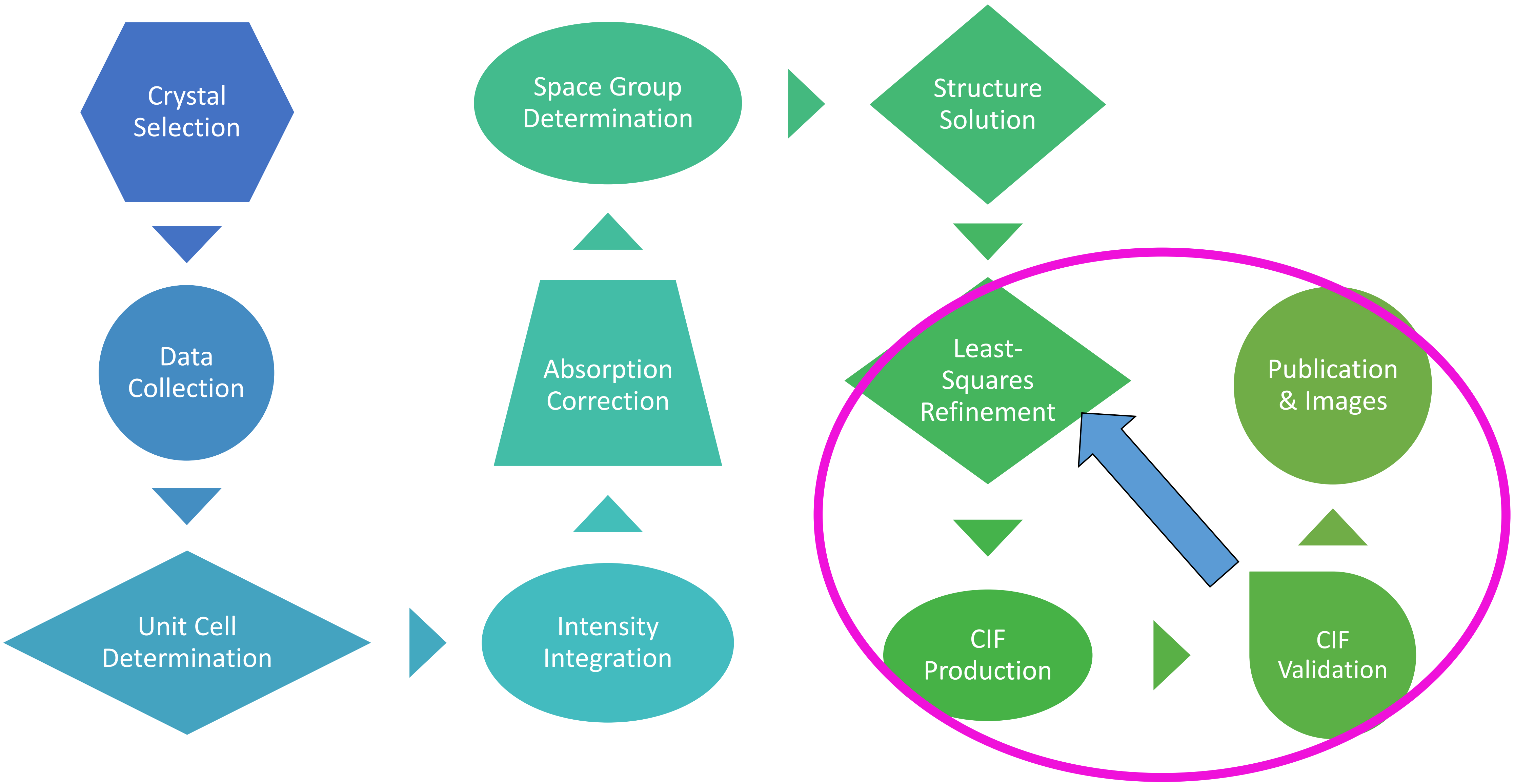
F_{obs} Map at 0.50Å



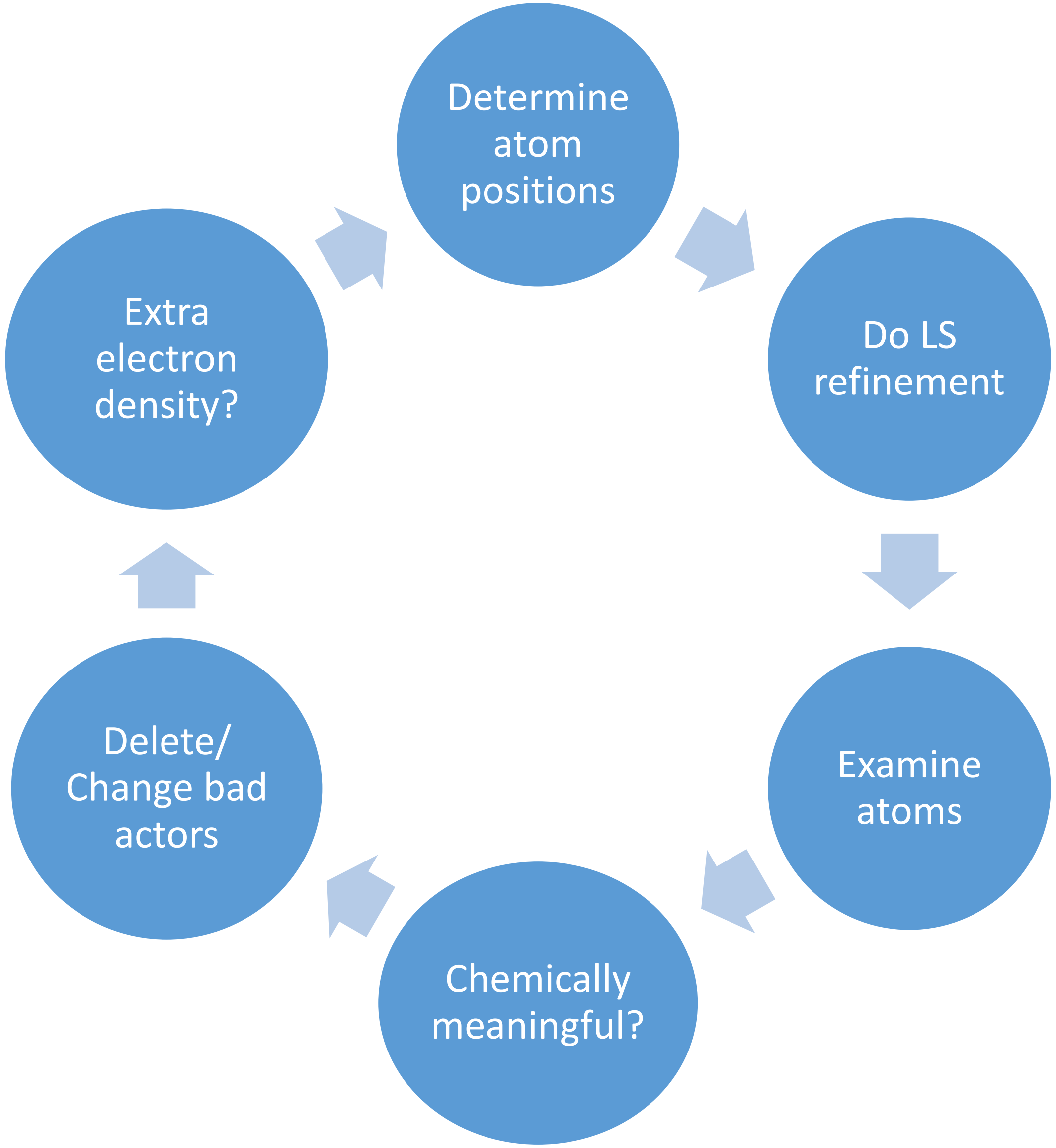
Fobs and Difference Map 0.5Å

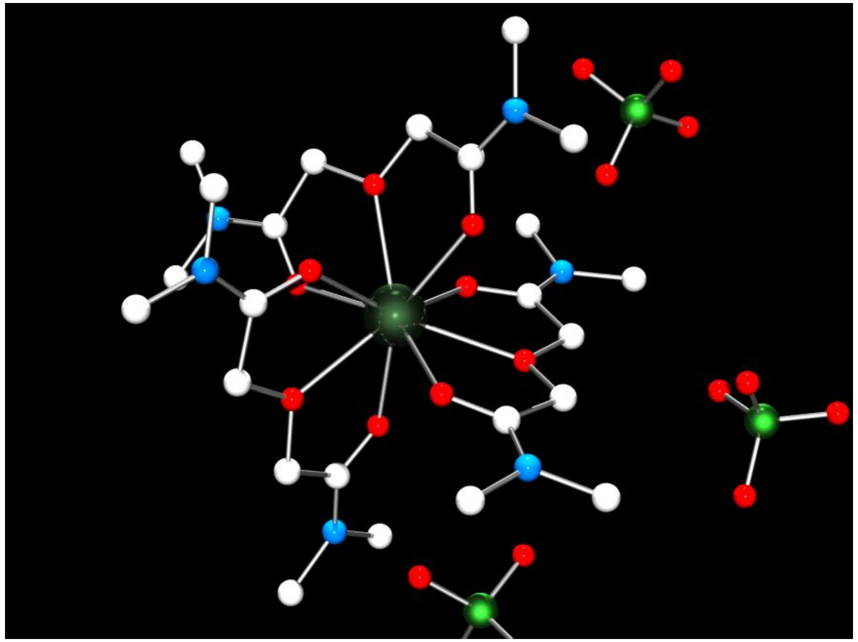


Crystal to Structure



Refinement & Validation

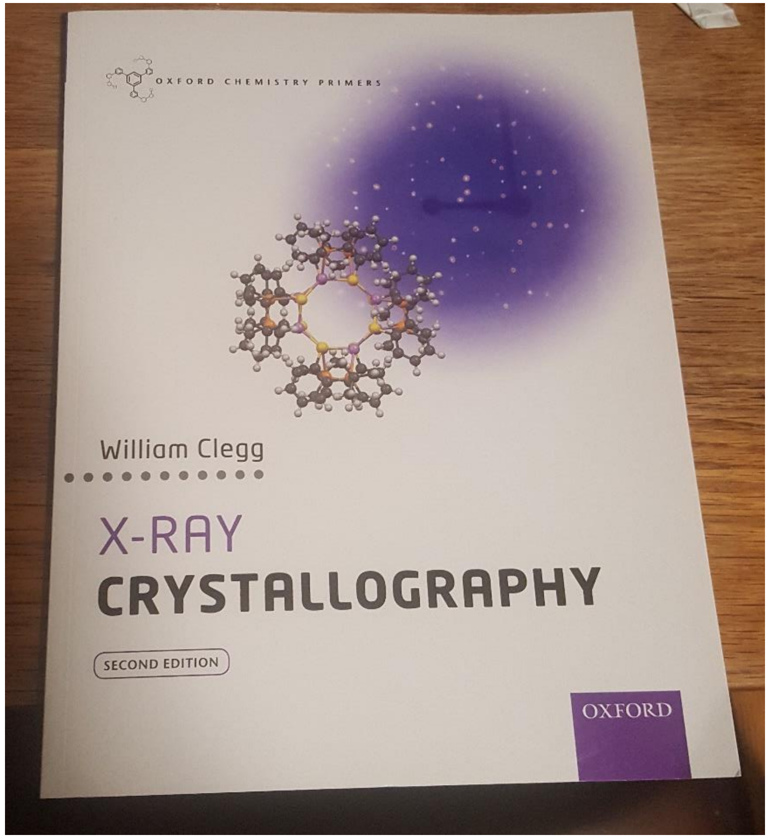


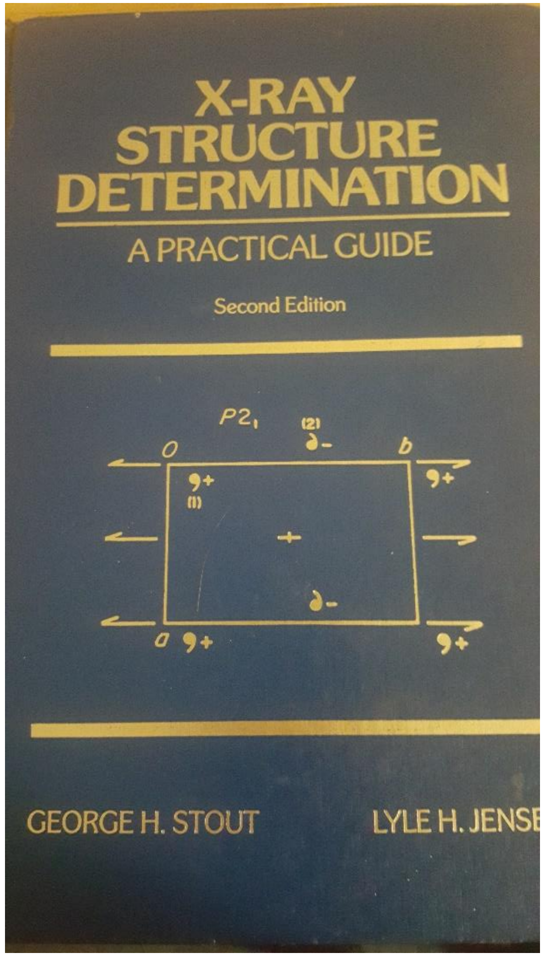


$$R_1 = \frac{\sum_{hkl} ||F_{obs}| - |F_{calc}||}{\sum_{hkl} ||F_{obs}||}$$

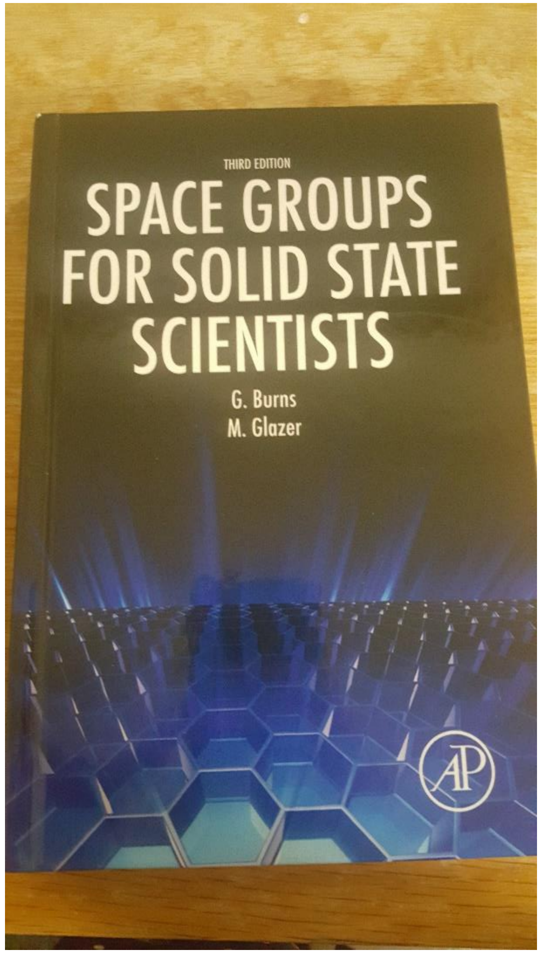
$$wR_2 = \sqrt{\frac{\sum_{hkl} w(F_{obs}^2 - F_{calc}^2)^2}{\sum_{hkl} w(F_{obs}^2)^2}}$$

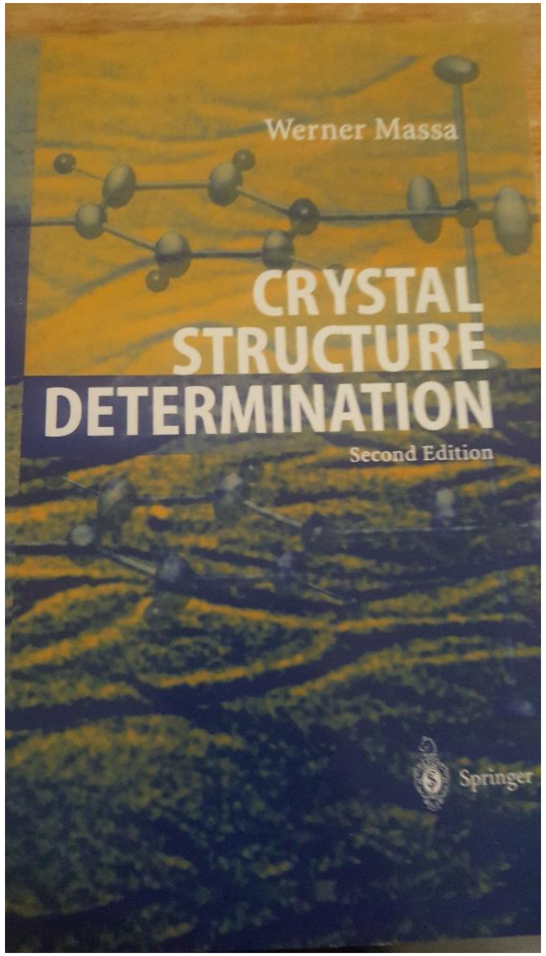
For More Information





Even More Information





More Resources!!!

Internet

- X-ray Forum
  - www.xray**forum**.co.uk/
- IUCr Forum
  - forums.iucr.org
- CCP4
  - http://www.ccp4.ac.uk

Single Crystal Diffraction at a Synchrotron

or

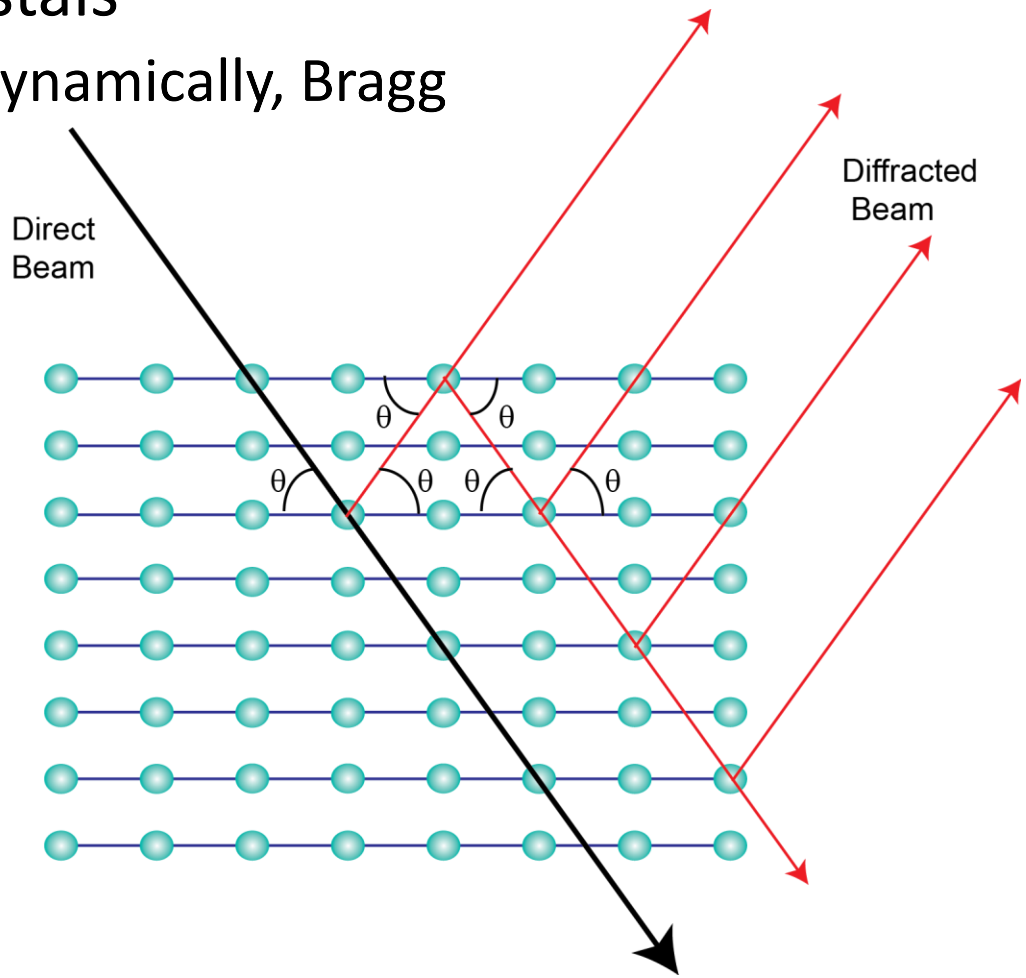
What can you do with more flux?

Contents

- Why do crystals diffract poorly?
- What can we do to them to make them diffract poorly?
- What can we learn from poorly diffracting crystals?
- What do synchrotrons have to do with all this?

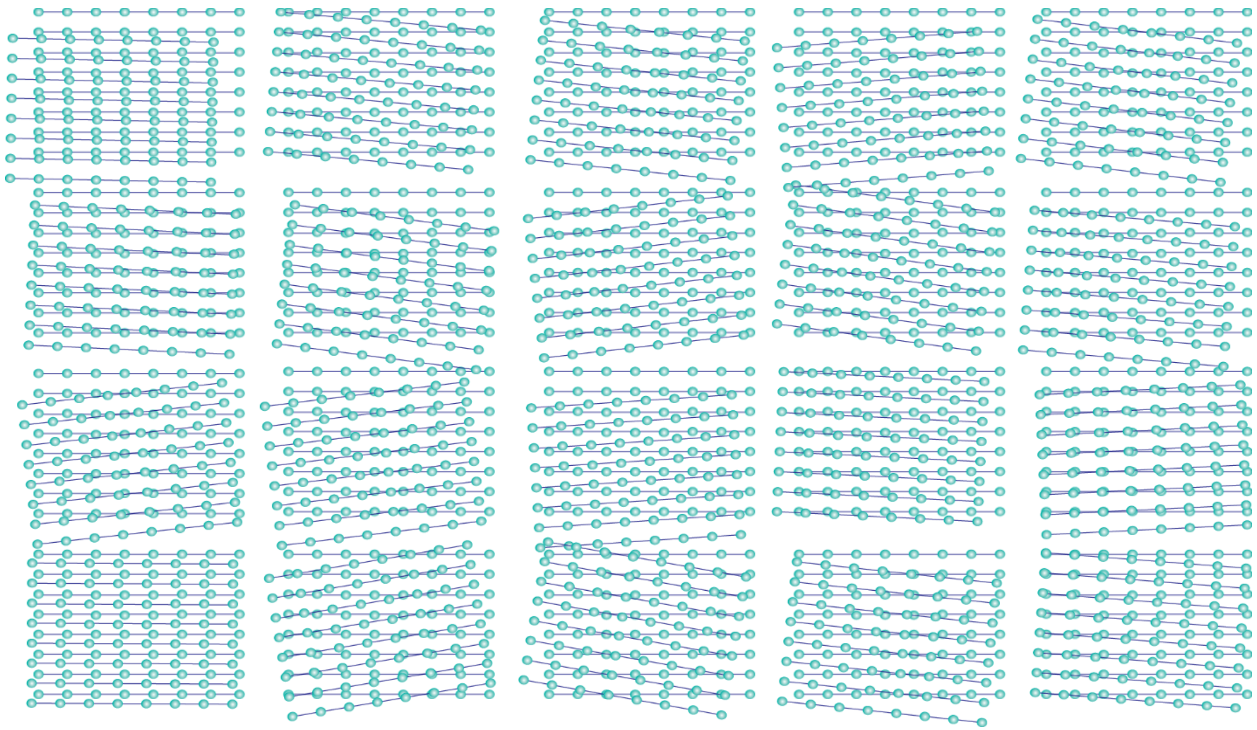
The Spectrum of Crystallinity

- Perfect crystals
  - Diffract dynamically, Bragg



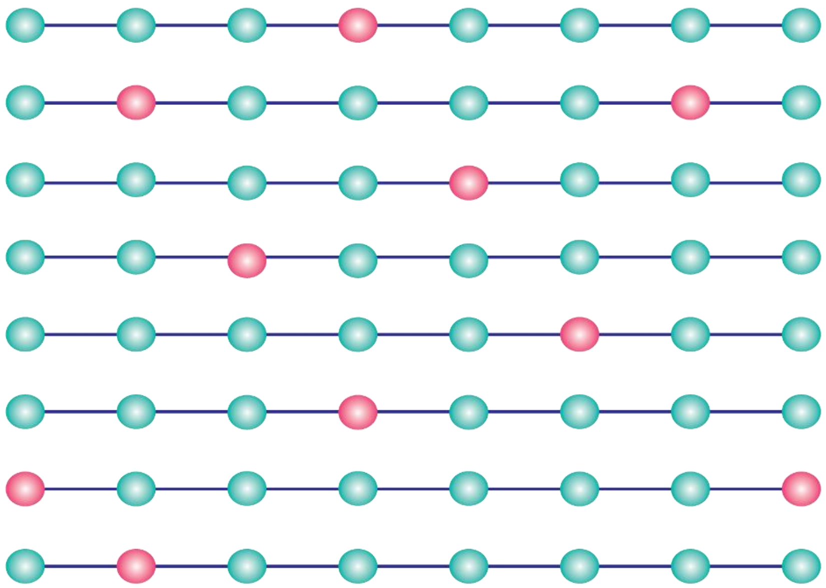
The Spectrum of Crystallinity

- Good Crystals
  - Diffract kinematically(Bragg), due to mosaicity, but still have good long range order

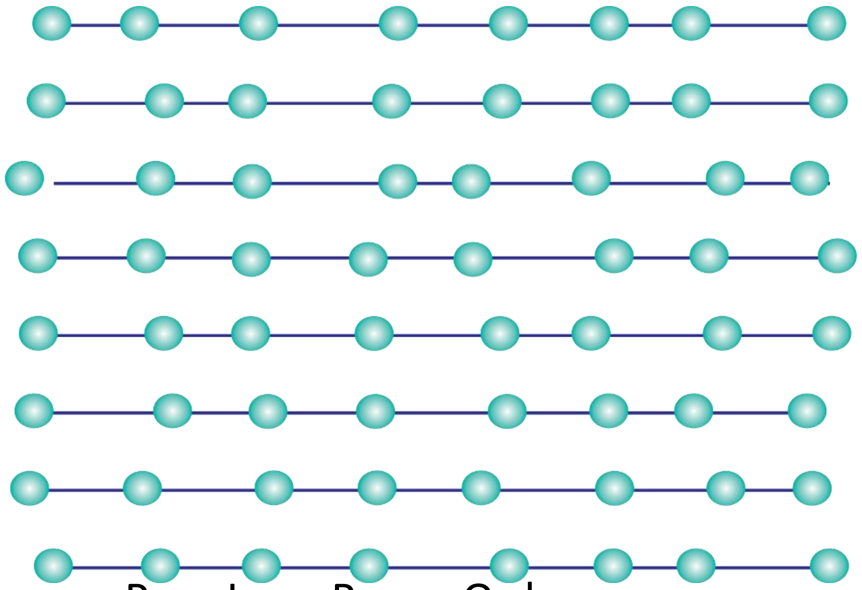


The Spectrum of Crystallinity

- Poor crystals
  - Diffract kinematically(Bragg), but diffraction limited due to poor long range order.
  - Can show powder Laue rings/spot smearing due to mosiaicity becoming microcrystallinity
  - Can also display non-Bragg scatter due to TDS



Positional Disorder



Poor Long Range Order

Scattering Efficiency

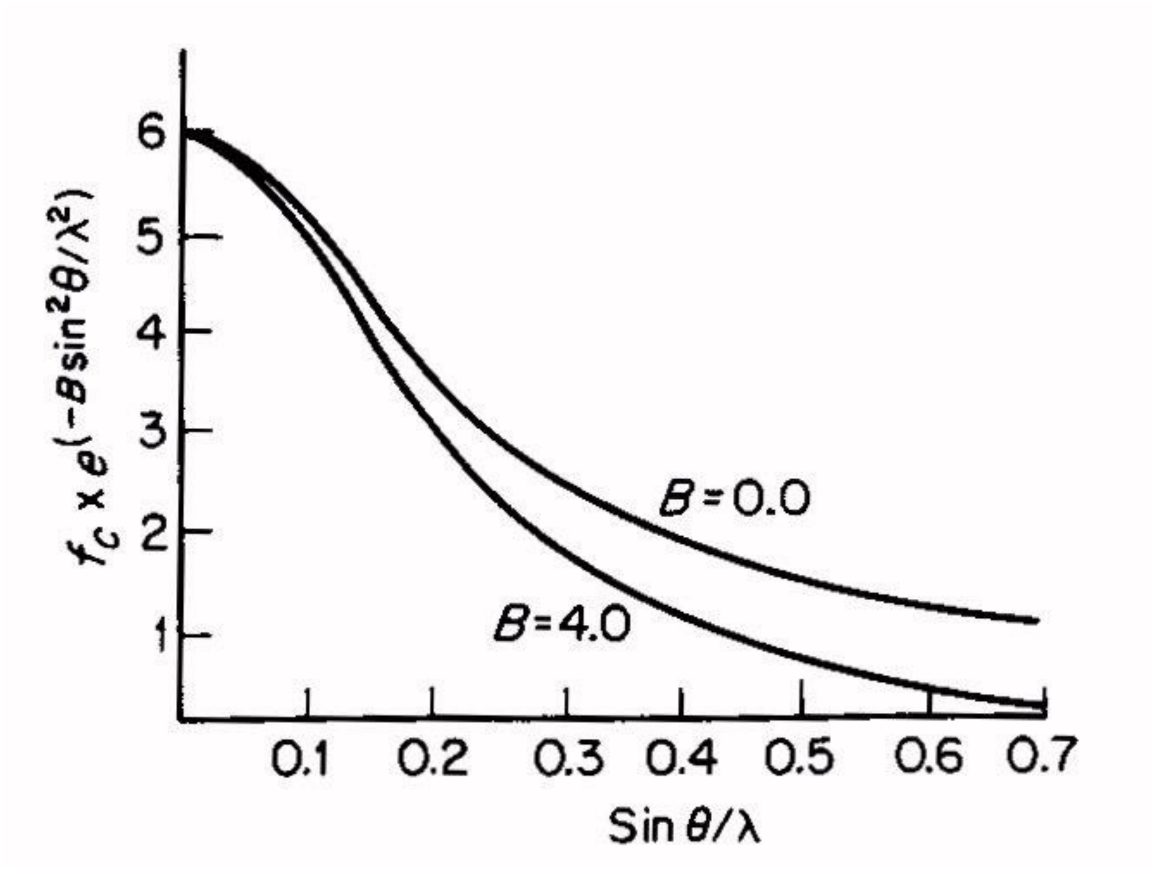
$$Intensity\ of\ Diffraction \approx \lambda^3 = \frac{LI_{incident}\langle|F_{hkl}^2|\rangle V_{crystal}}{V_{cell}^2}$$

Where:

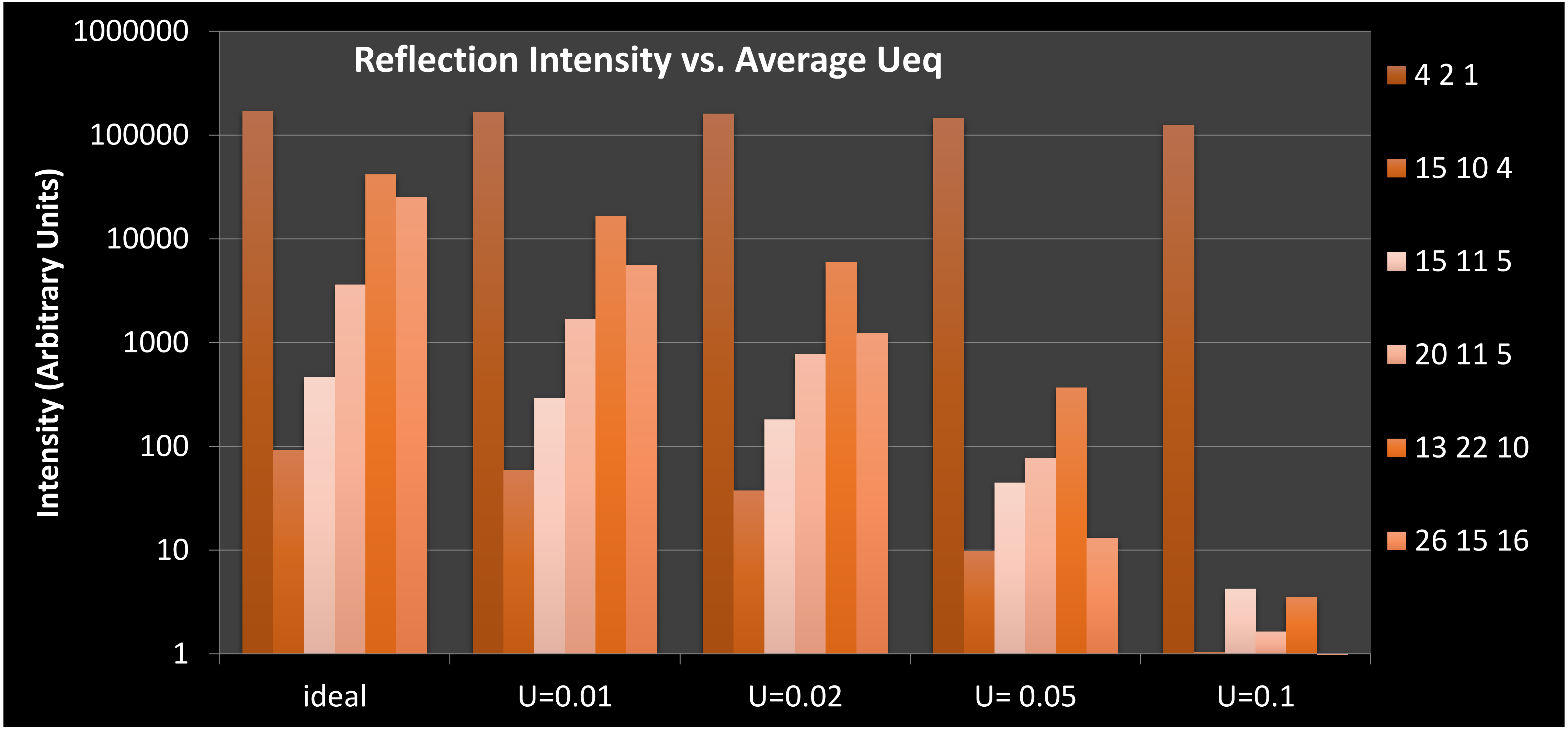
- F = number of electrons per atom
- $V_{crystal}$ = volume of the crystal
- V_{cell} = volume of the unit cell

M.M.Harding *J. Synchrotron Radiation, 250-259 1996*

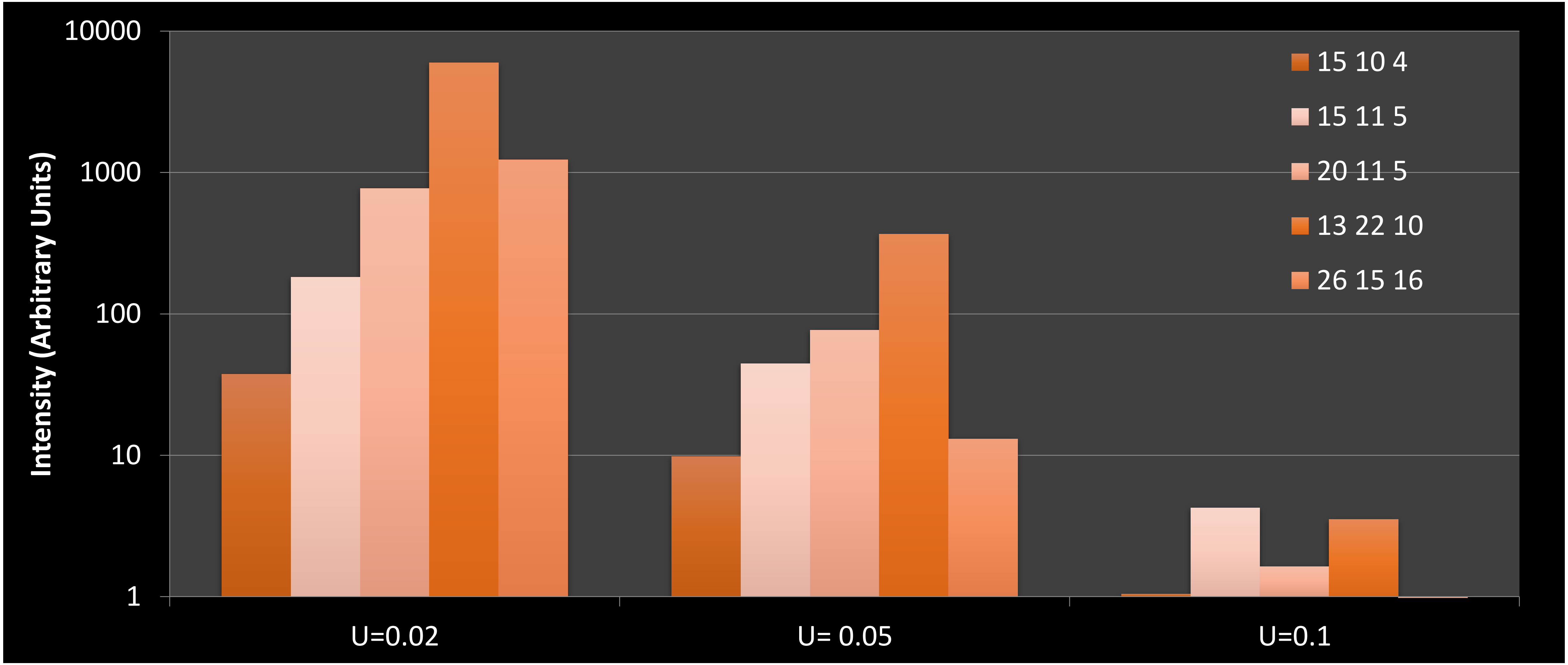
Effect of disorder



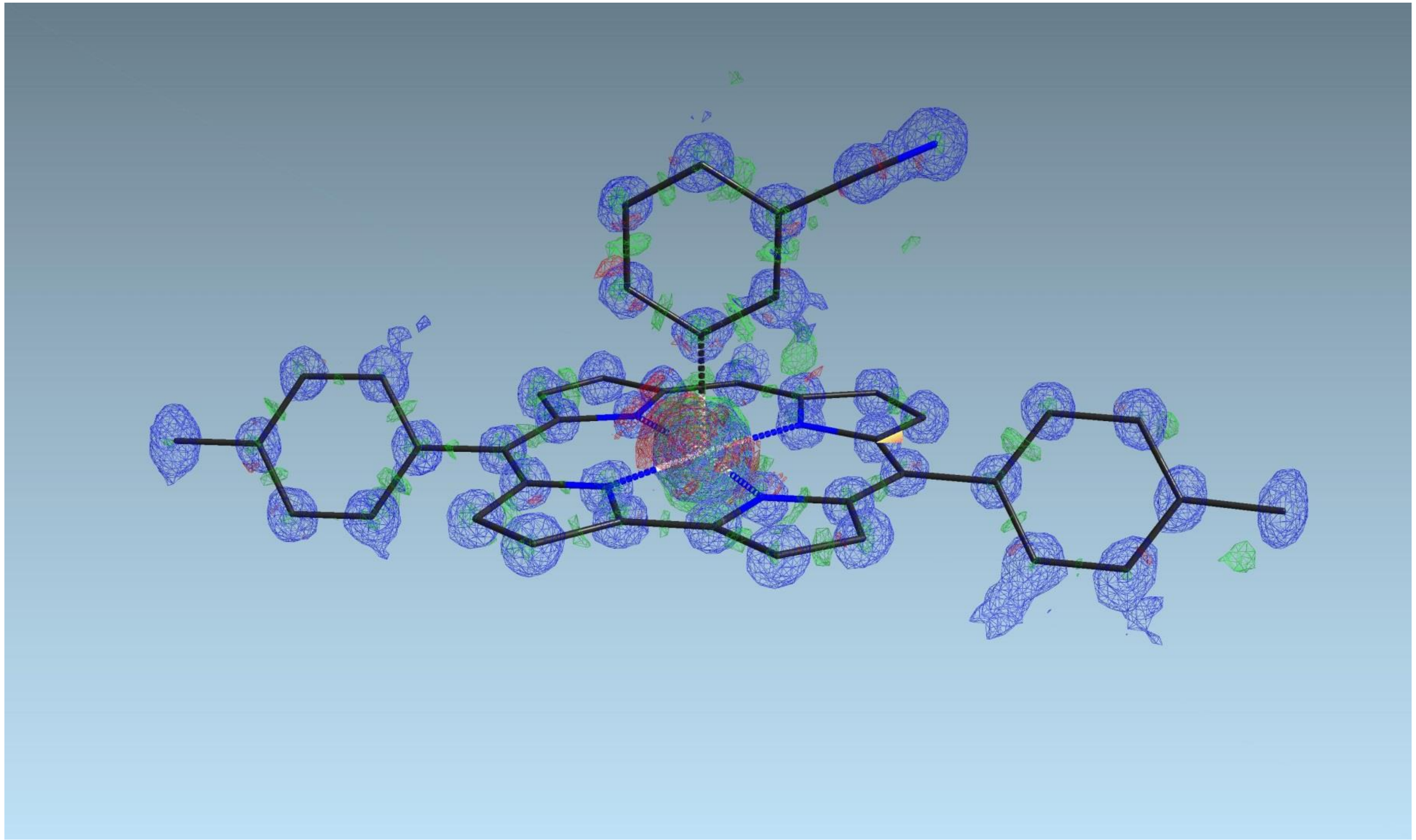
Intensity vs. Displacement



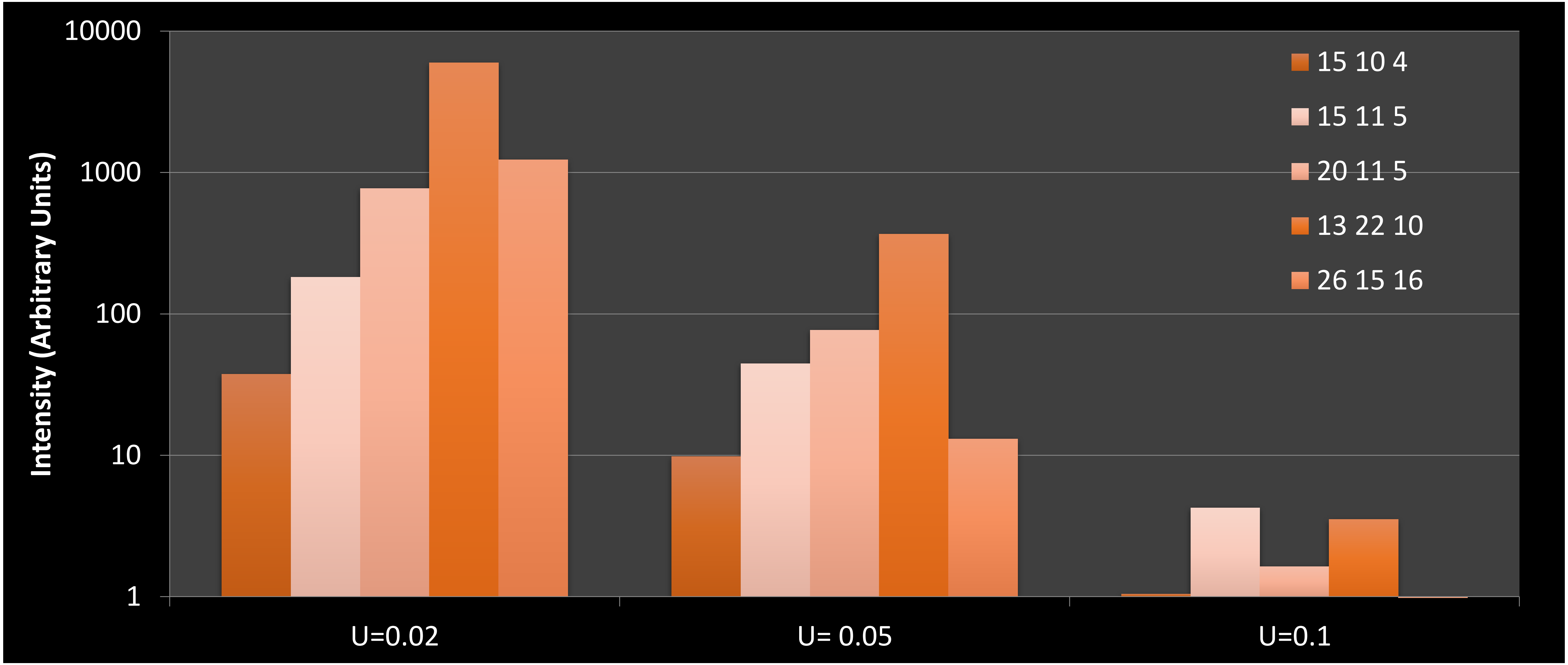
Higher Angle Reflections Affected by Larger ADPs



F_{obs} and Difference Map 0.5Å



Higher Angle Reflections Affected by Larger ADPs



Wavelength

- The material and the wavelength need to be compatible
  - Short wavelengths better for heavy absorbers, samples that need high resolution, and sample environments with limited angular access
  - Long wavelengths better for light atoms (weakly diffracting elements)
  - Be aware of absorption edges and potential fluorescence from sample

Bigger isn't always better

- Large crystals aren't guaranteed to diffract better
- Crystal should match beam size
  - But if there is a choice, smaller than the beam is usually better
- Rocking width can be worse with large crystals due to poor mosaicity

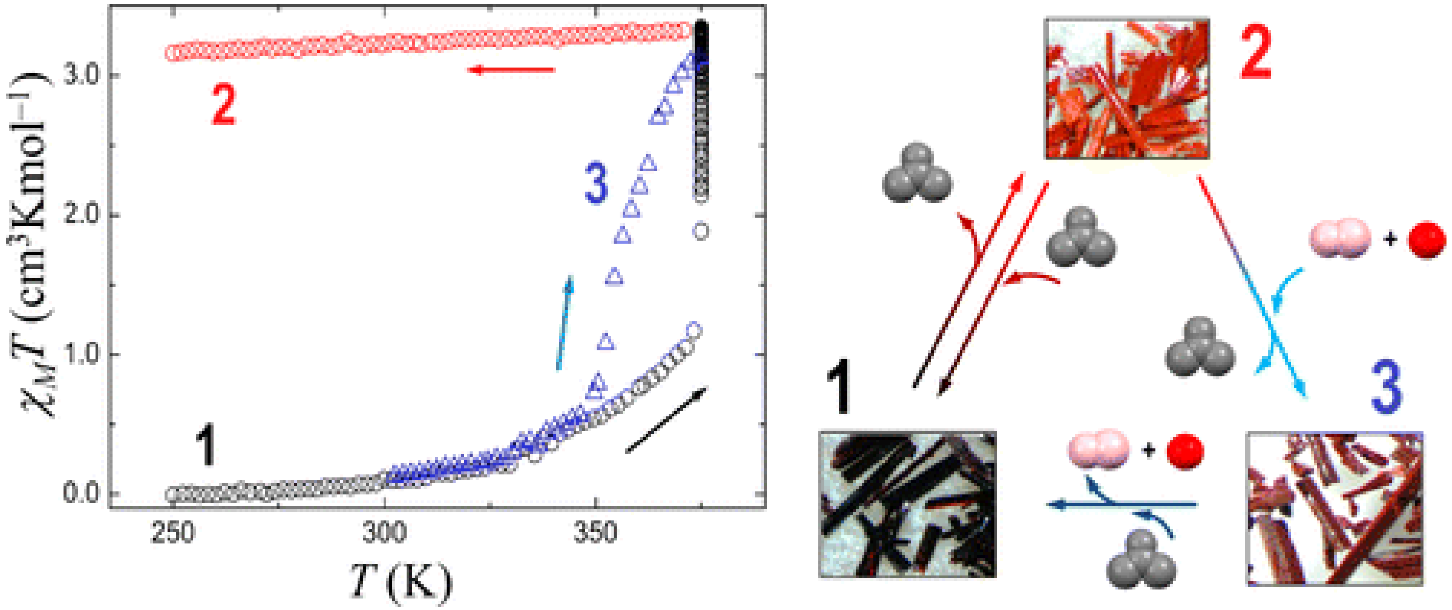
In situ experiments

Structures from change.

In-situ Crystallography

- The application of a stimuli to produce structural change
  - Temperature
  - Pressure
  - Gas or Vacuum
  - Light
  - Electric or Magnetic Fields

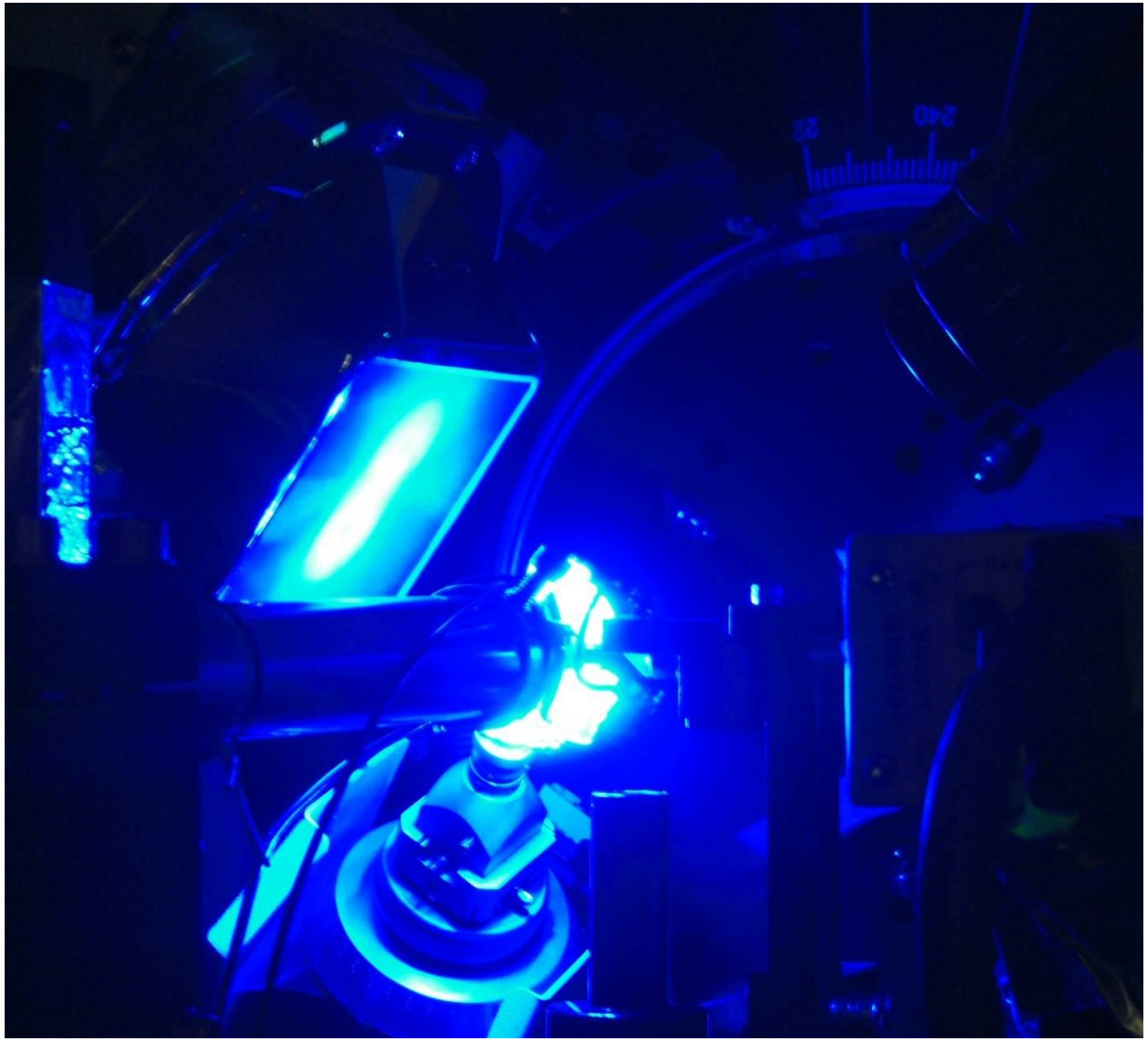
Desolvation



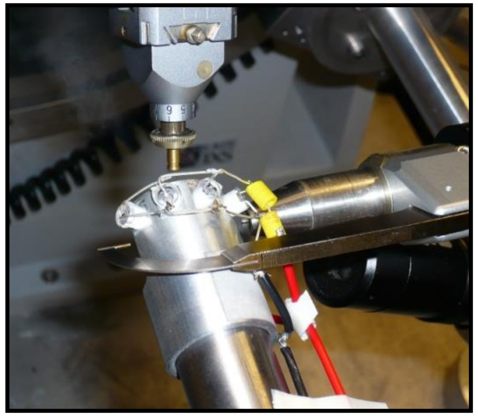
Three-Way Crystal-to-Crystal Reversible Transformation and Controlled Spin Switching by a Nonporous Molecular Material

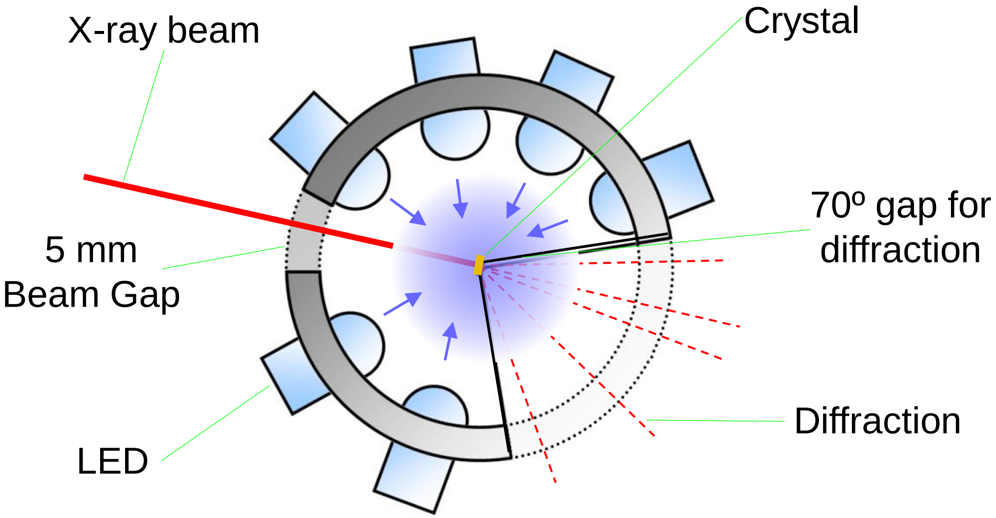
Sanchez Costa et al.,*J. Am. Chem. Soc.*, **2014**, *136* (10), pp 3869–3874
DOI: 10.1021/ja411595y

Photocrystallography



Experimental Procedure





Procedure

- High quality ground state data collection
- Irradiation (LEDs) - LED ring
- Metastable state data collection
- Inspection of the density map
- Temperature variation experiments

***N*-bound**

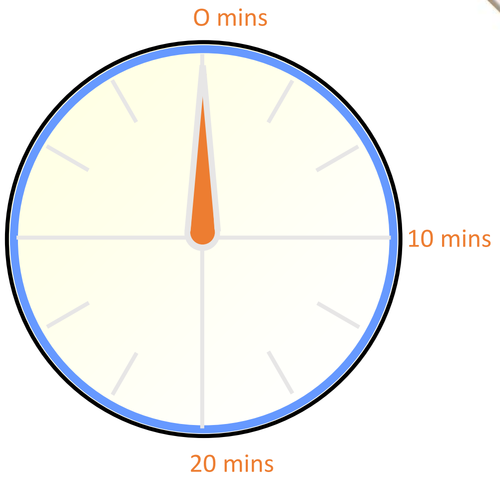
nitro

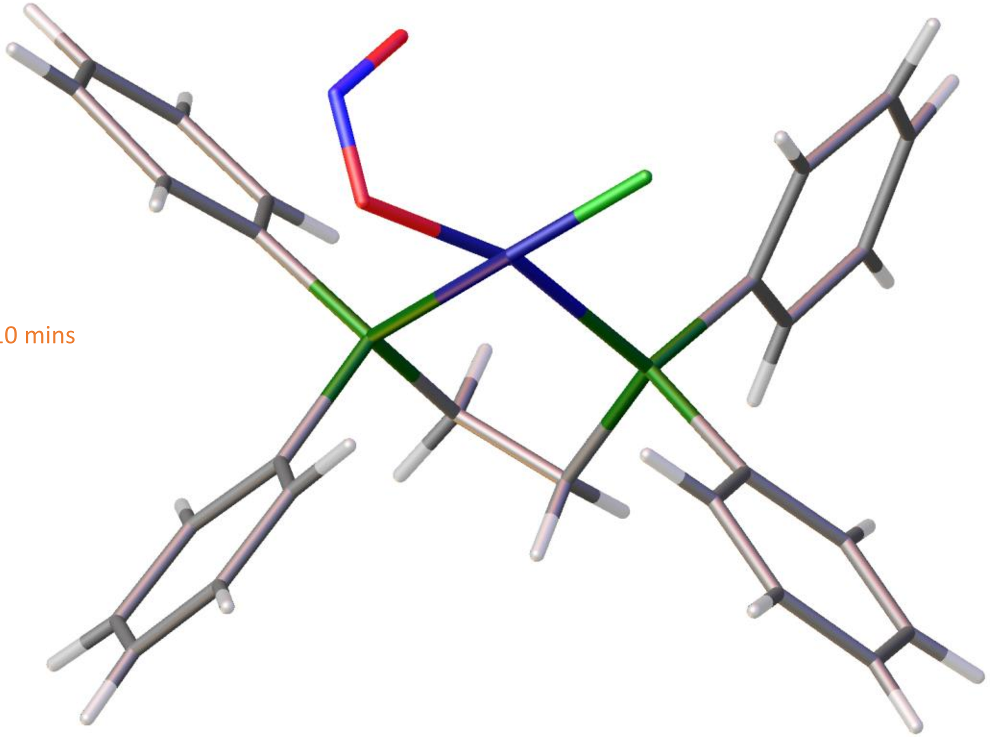
0 % | 50 % | 100 %

No irradiation | 10 minutes irradation | 20 minutes irradiation

***O*-bound**

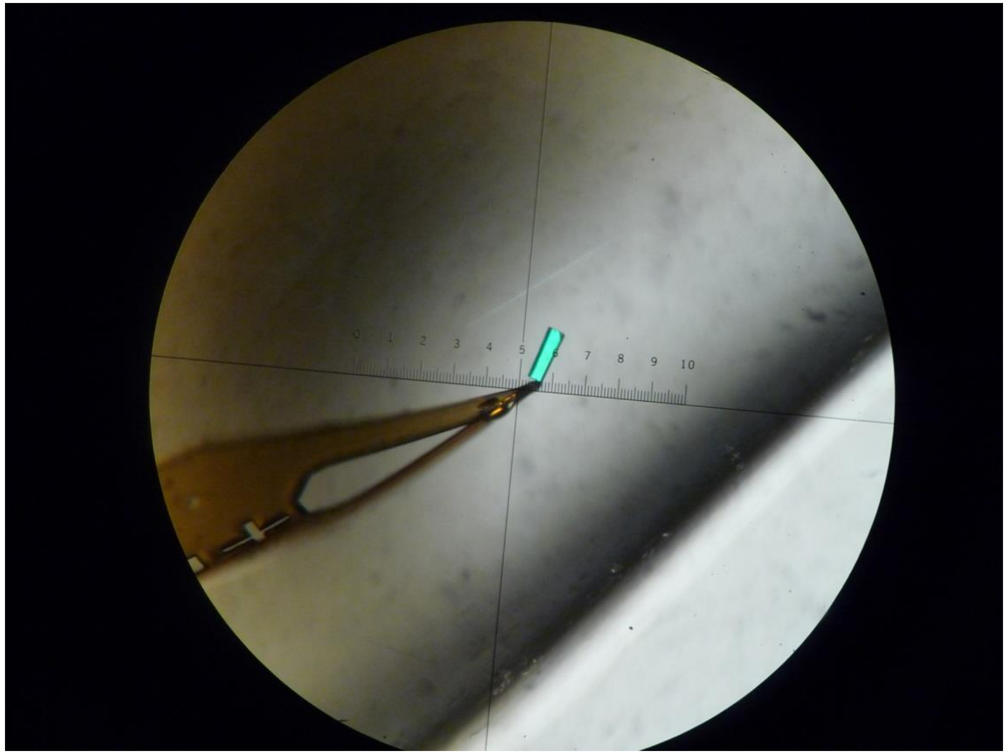
nitrito



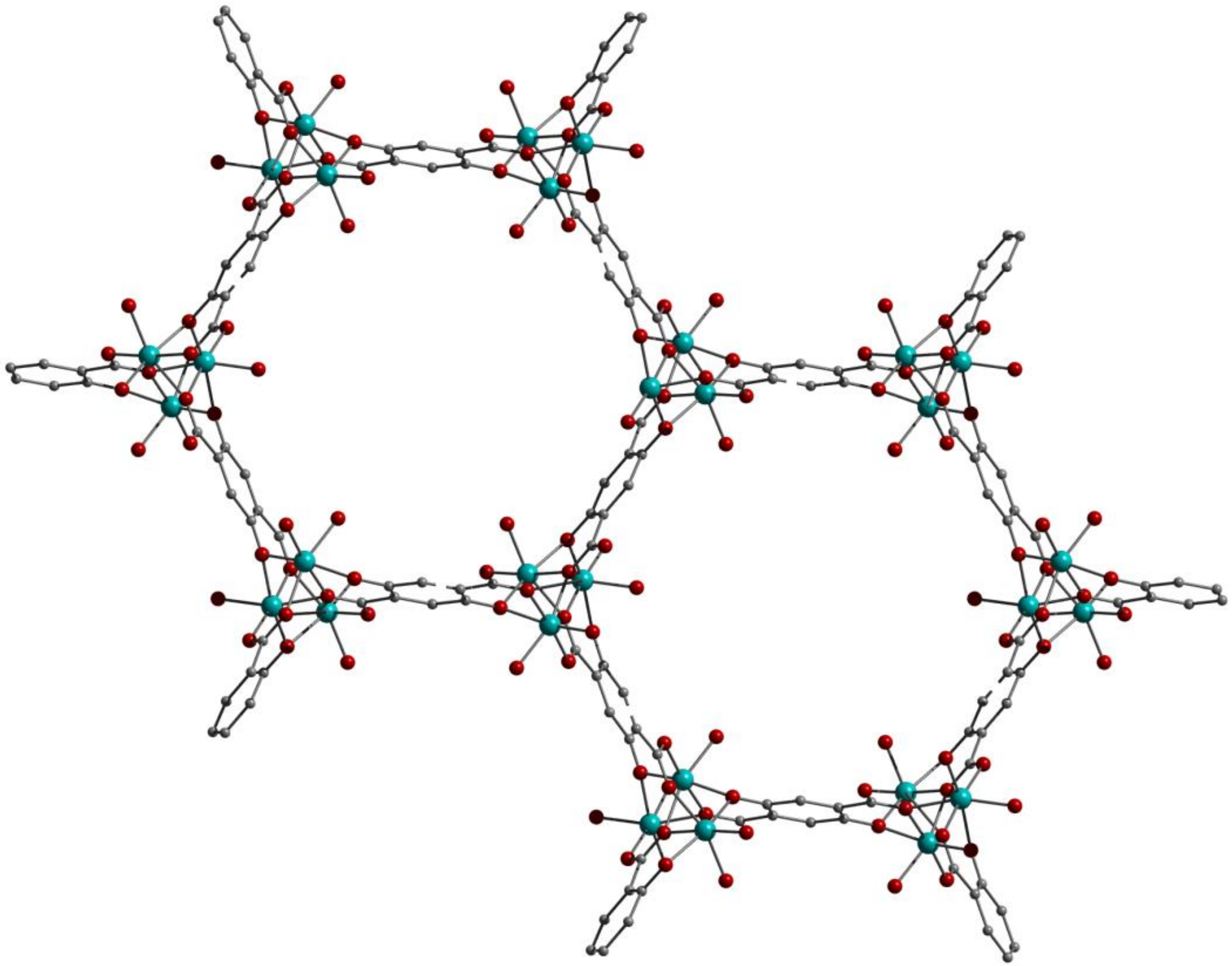


J. Appl. Cryst. 2010, **43**, 337-340

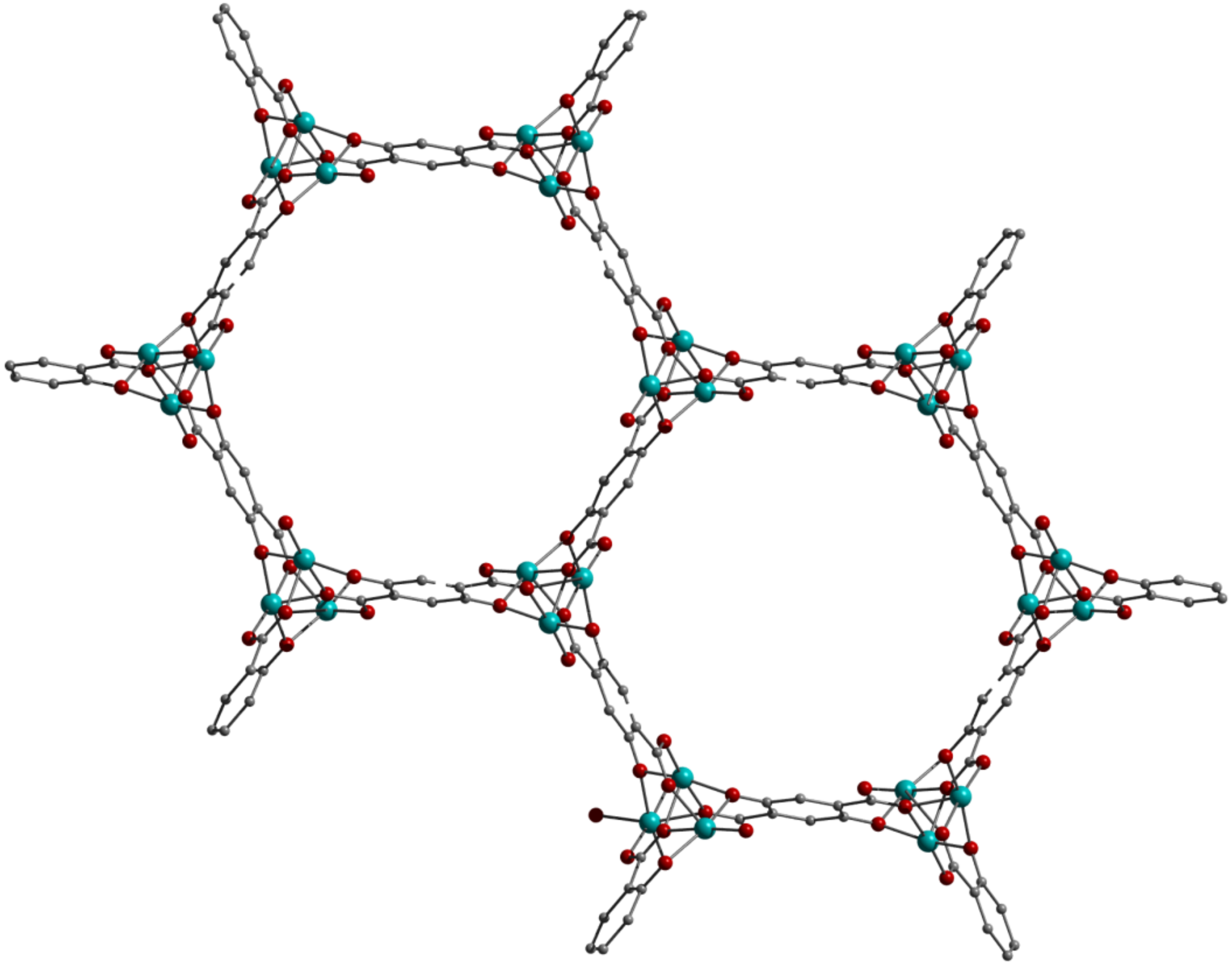
Gas Cell



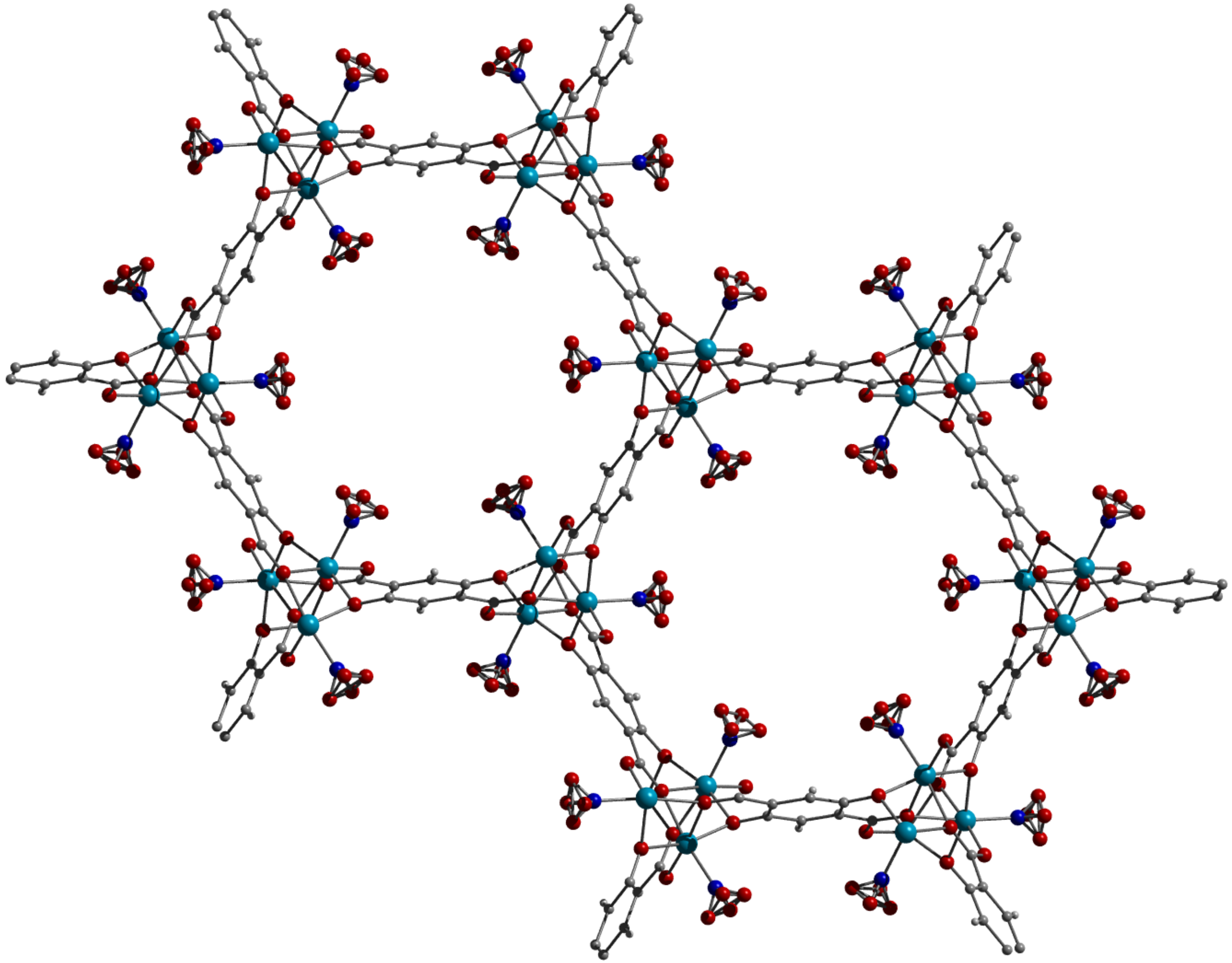
Hydrated MOF



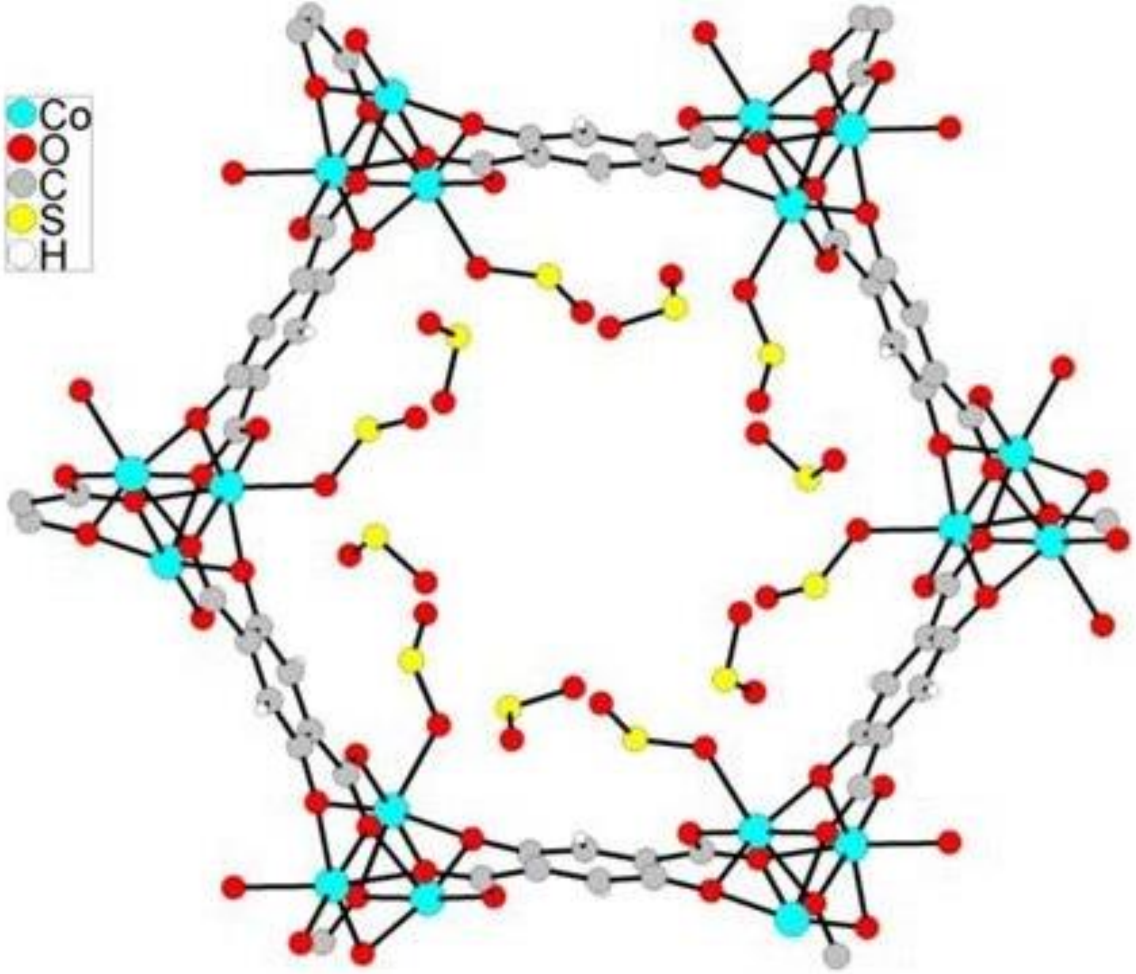
Dehydrated



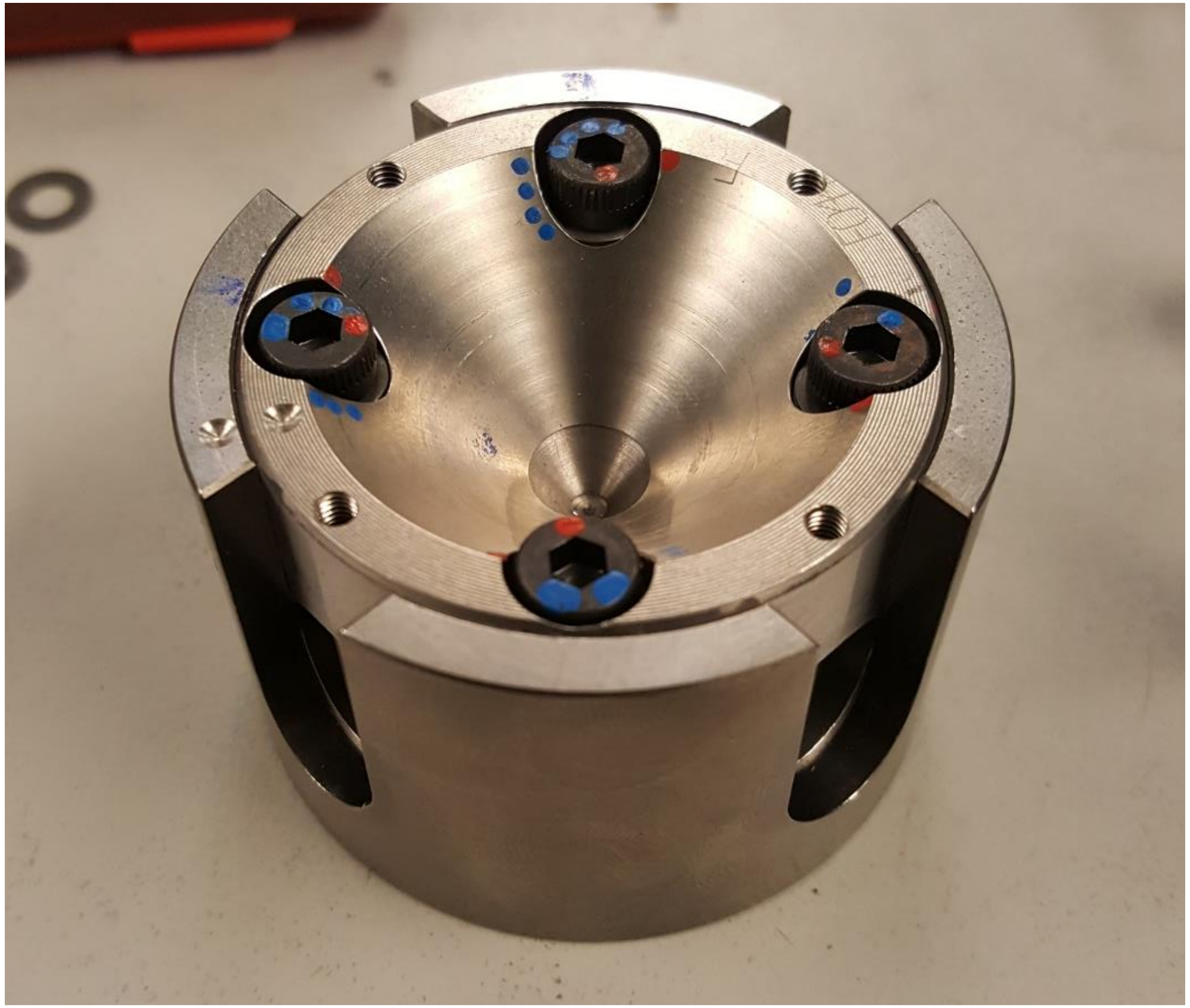
NO absorbed

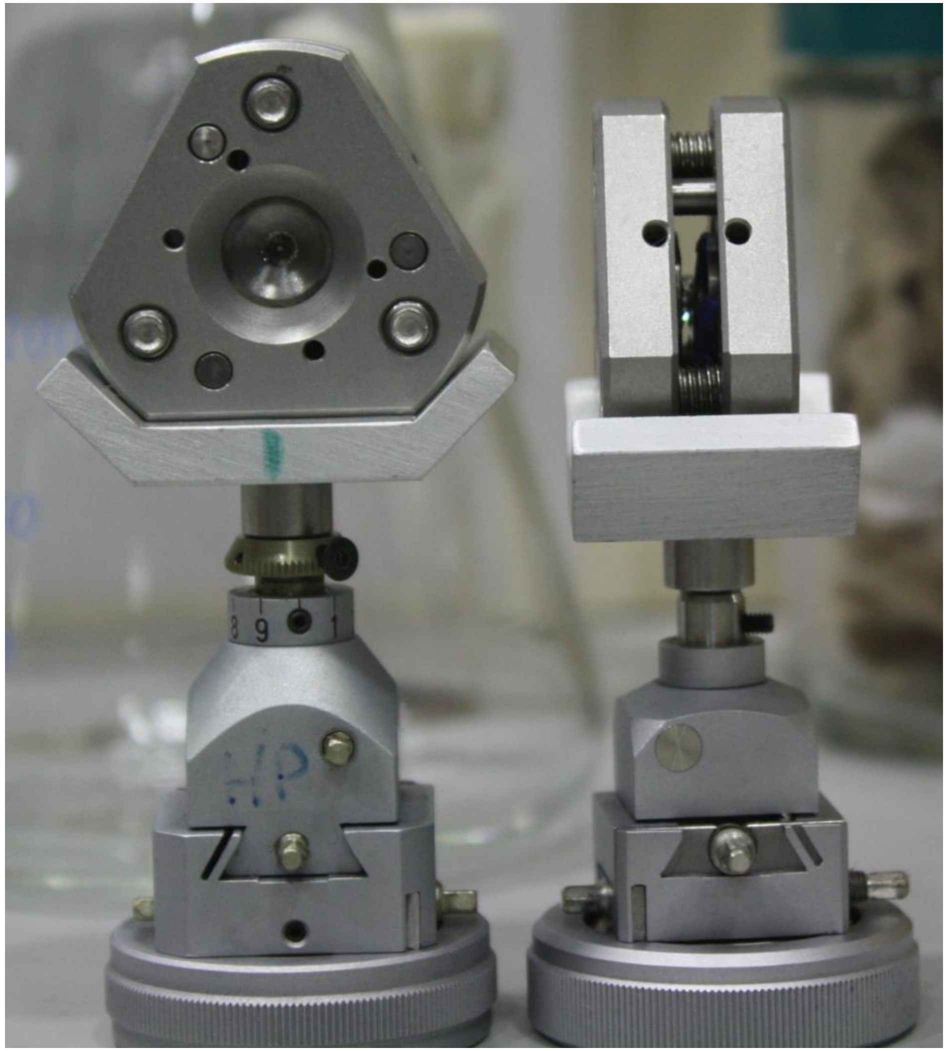


SO_2 absorbed



High Pressure with Diamond Anvil Cells



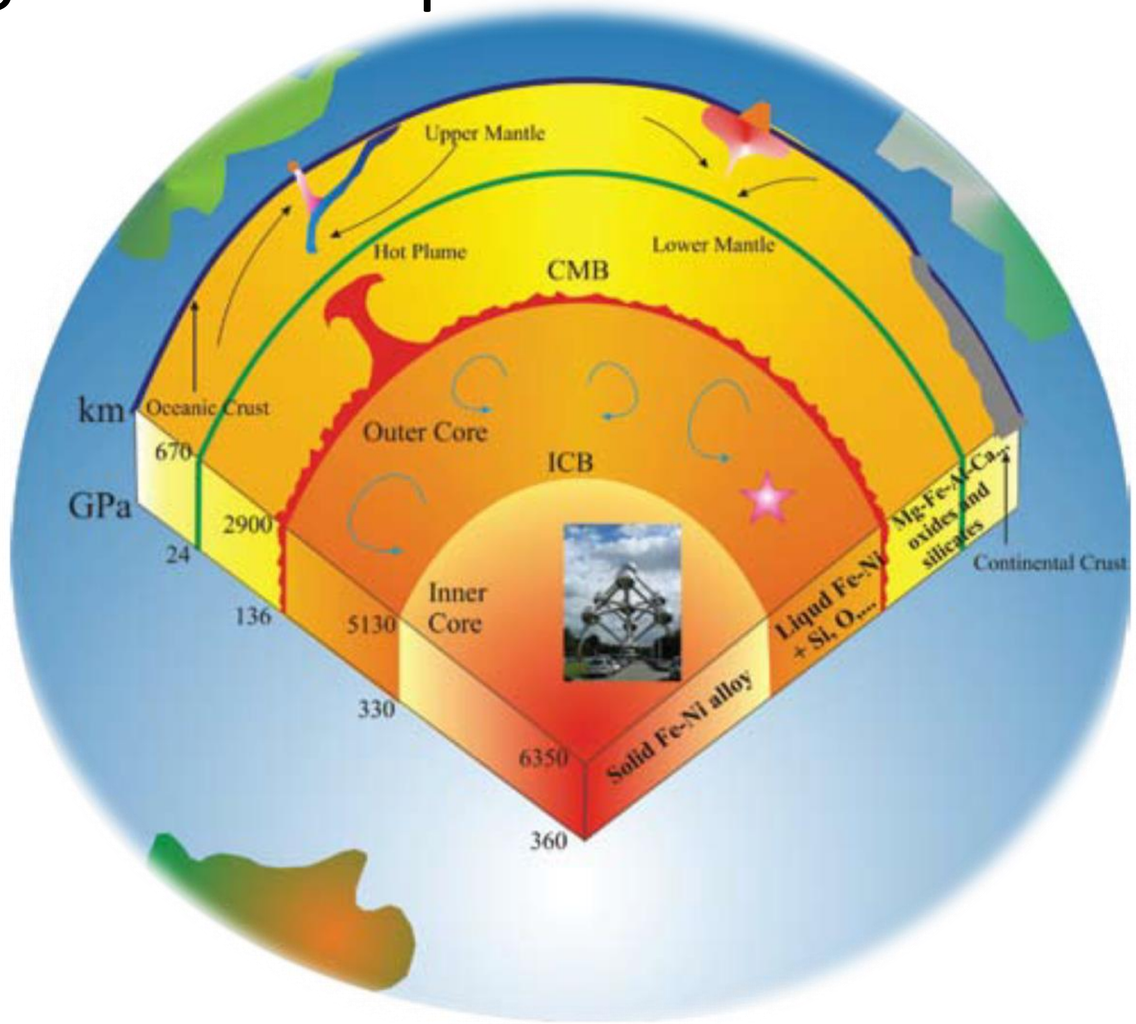


Why High Pressure?

"Pressure is highly efficient for
generating phase transitions and new phases,
for triggering new chemical reactions,
conformational and structural transformations of molecules,
polymerization,
polymorphism
and determining structure–property relations
which are of interest to chemists and physicists."

Katrusiak, A. *Acta Cryst., Sect. A,* **2007**, *64*, 135-148.

Exploring the Deep Earth…



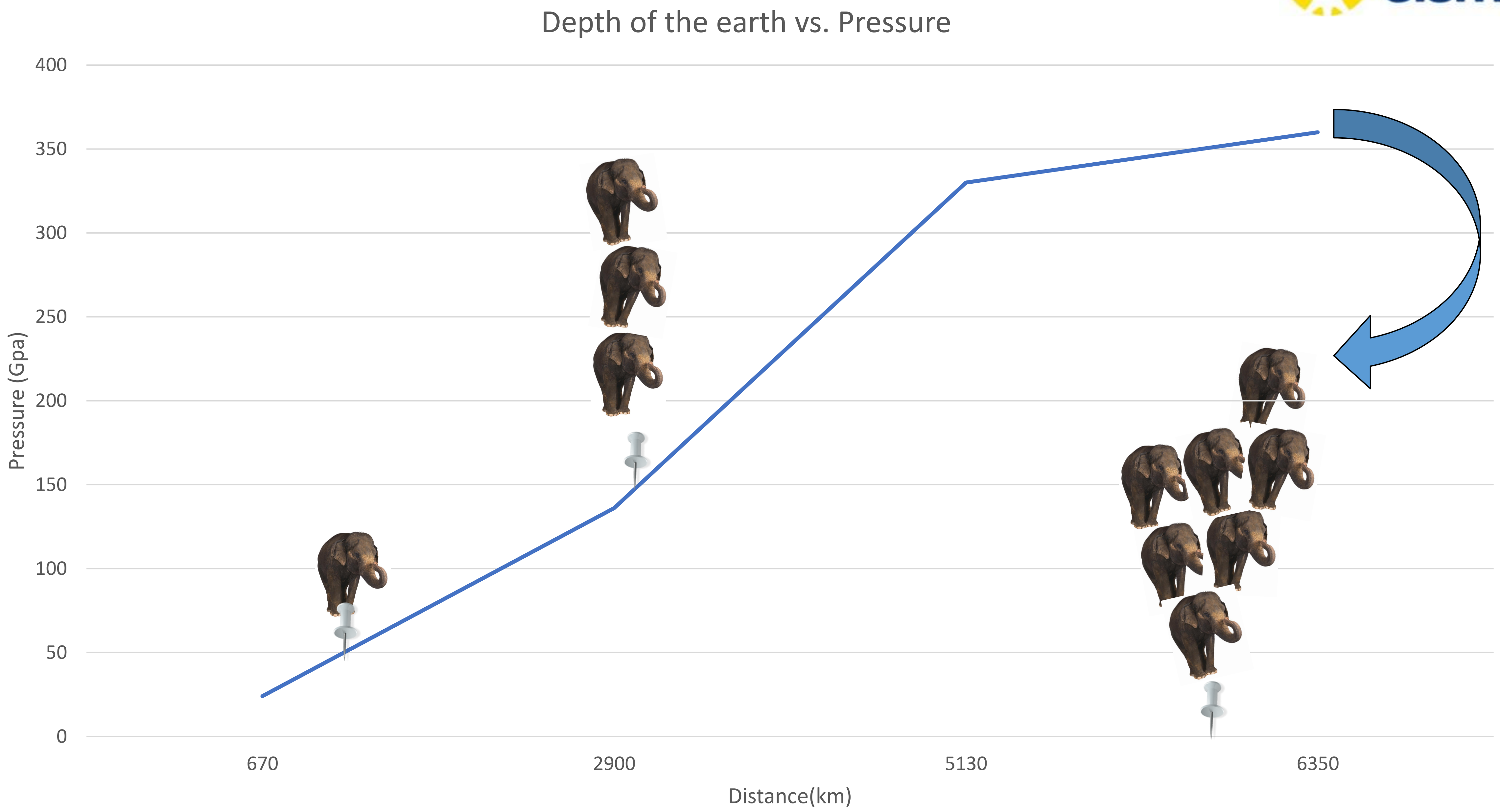
…Without Any Digging

Deep Earth Pressures!

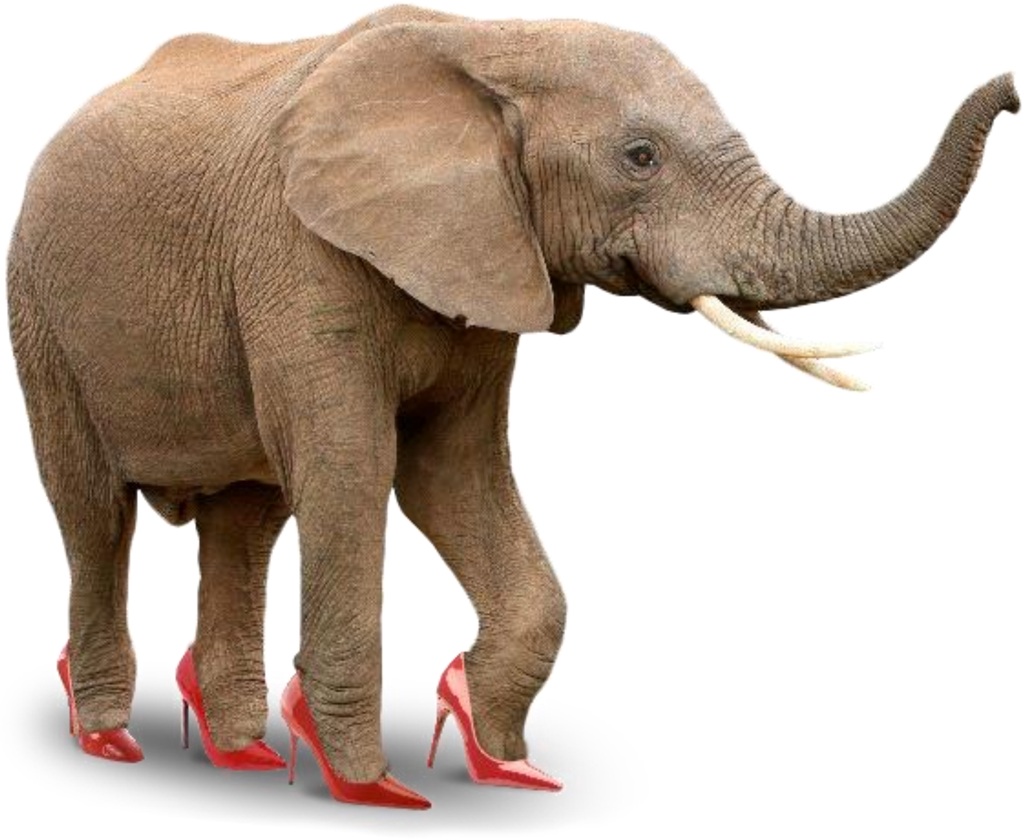
1 gigapascal (Gpa) = 145038 psi

One Elephant on a pushpin = 50GPa

Deep Earth Pressures!



Luckily I'm usually doing chemistry…



Thanks to Helen Maynard-Casely(ANSTO) for this image!

A Diamond Anvil Cell

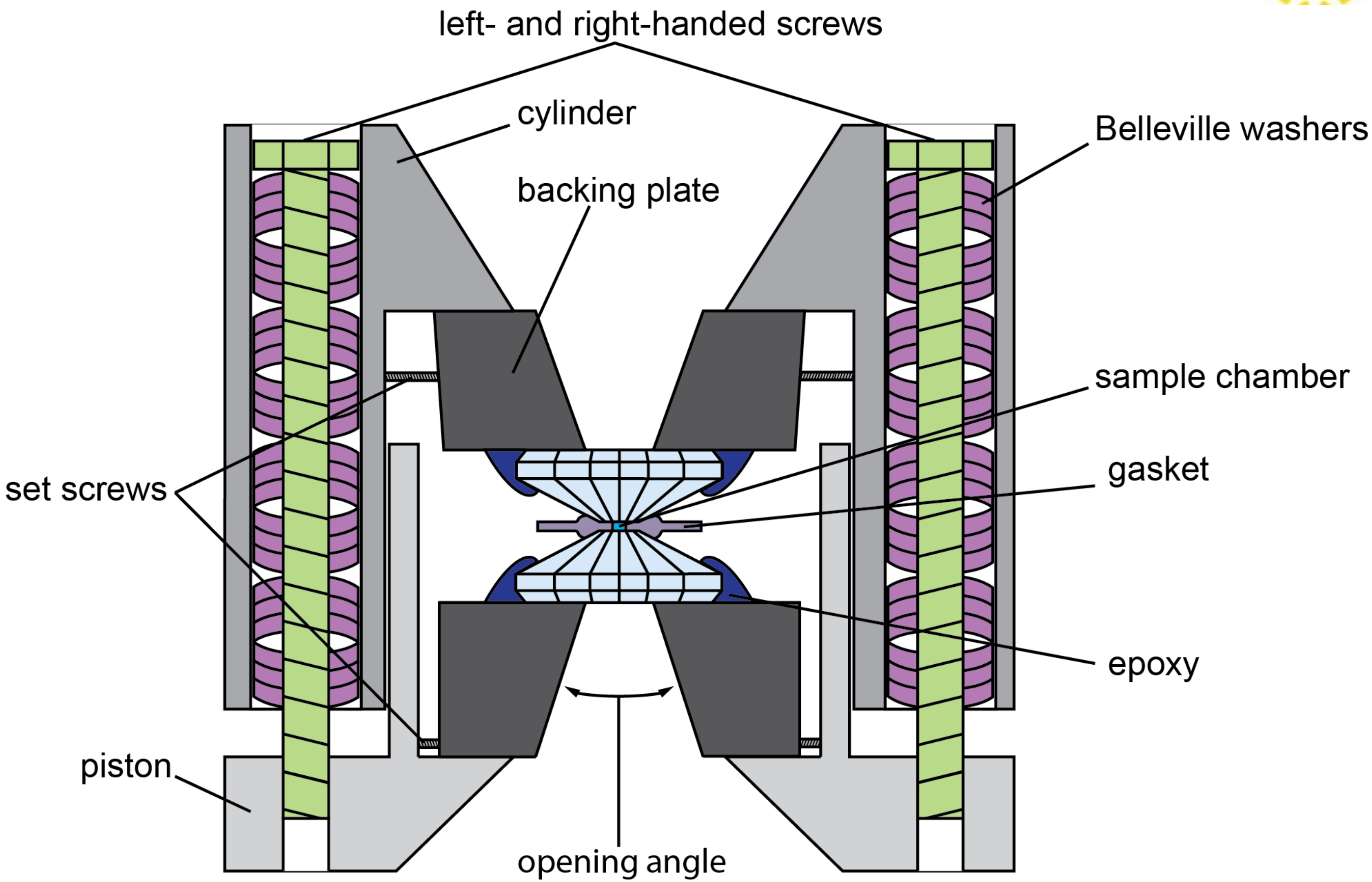
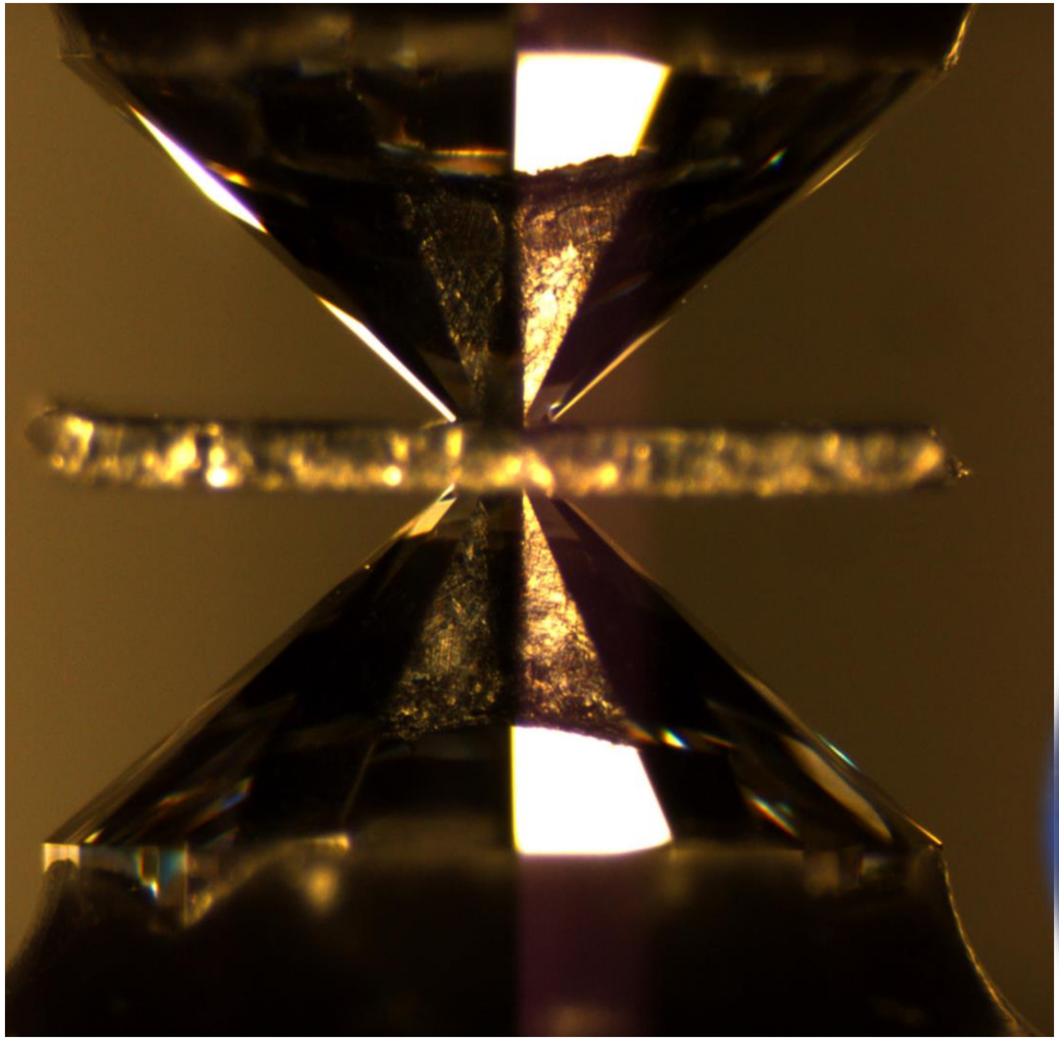
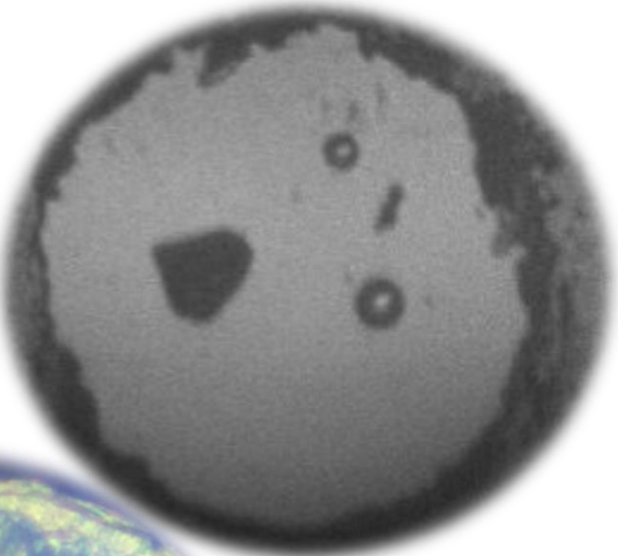
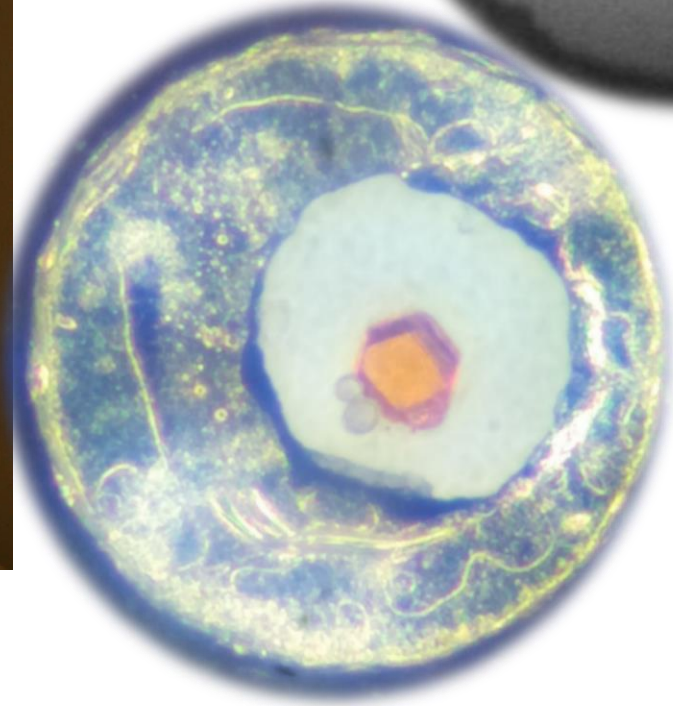


Image by Camelia Stan, LLNL

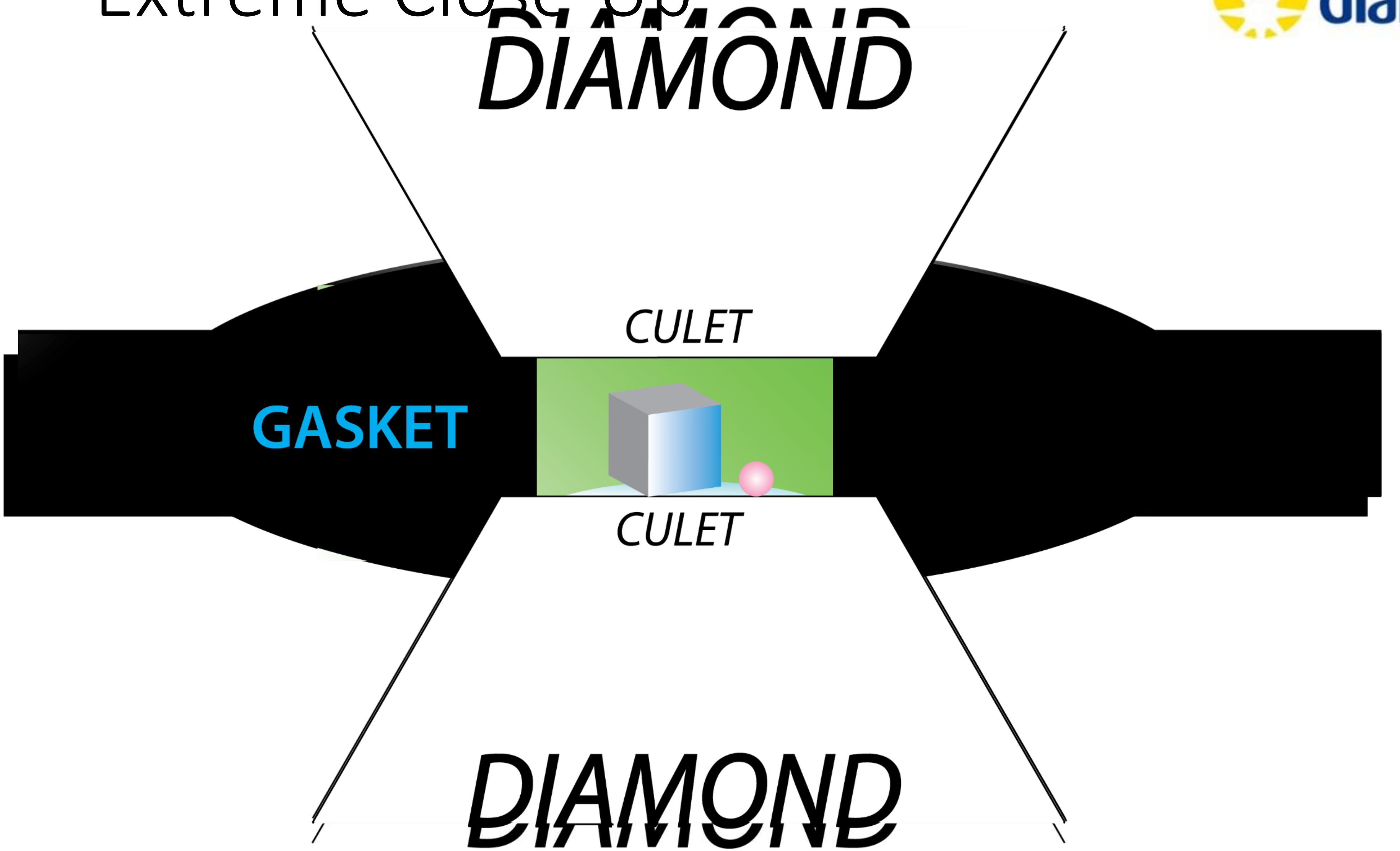
Diamond Anvil Cell (DAC)



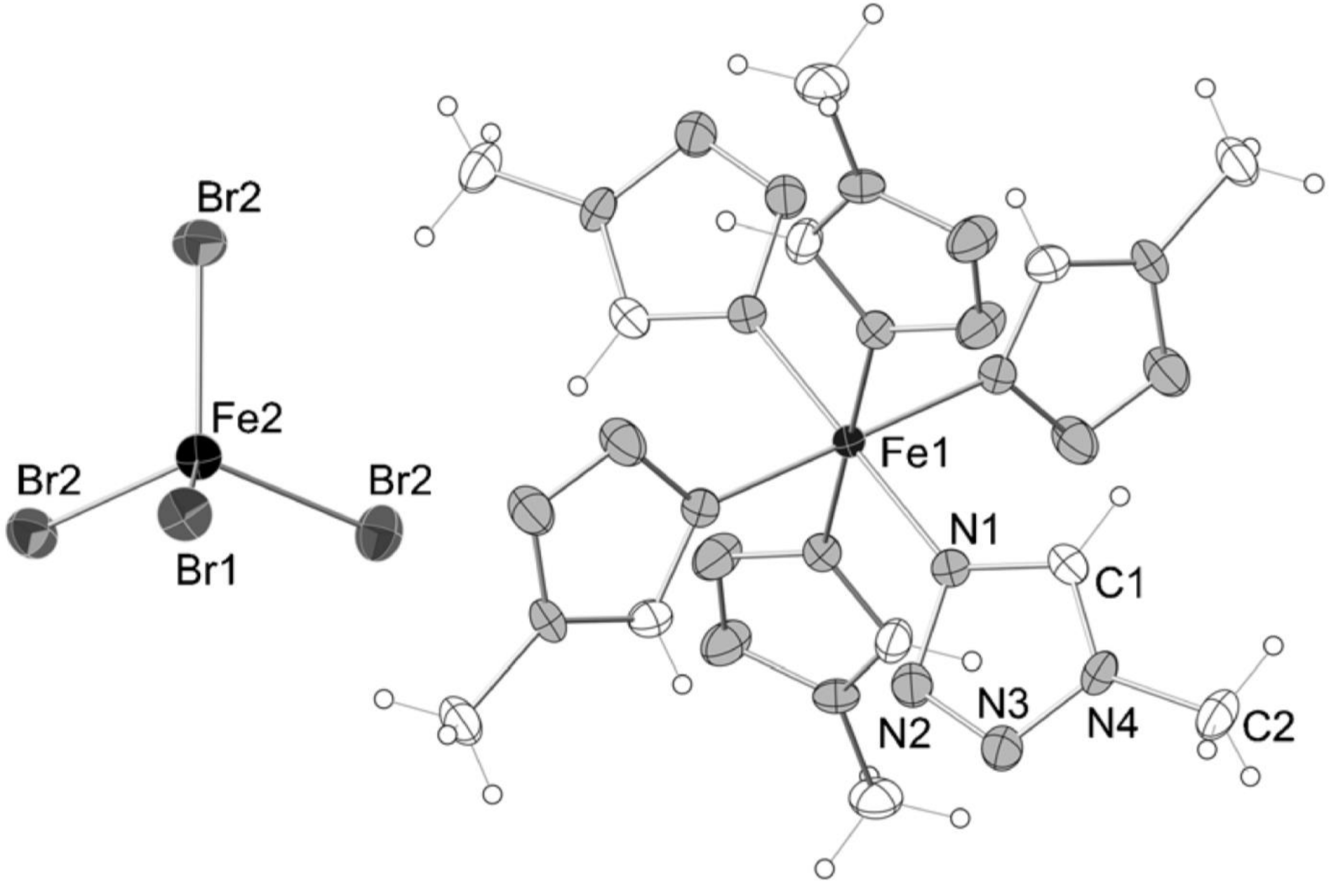




Extreme Close-Up

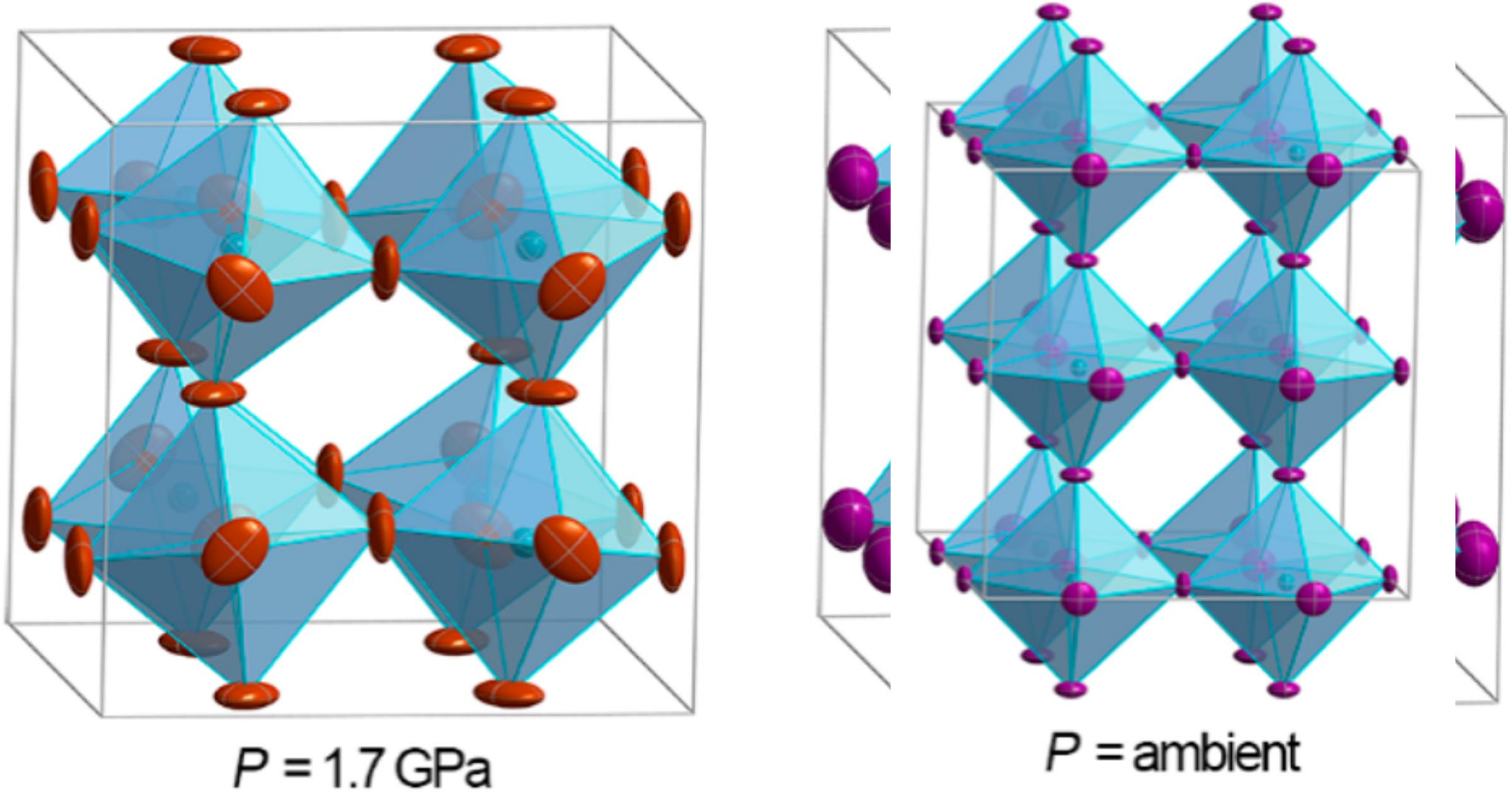


Spin Crossover at Pressure



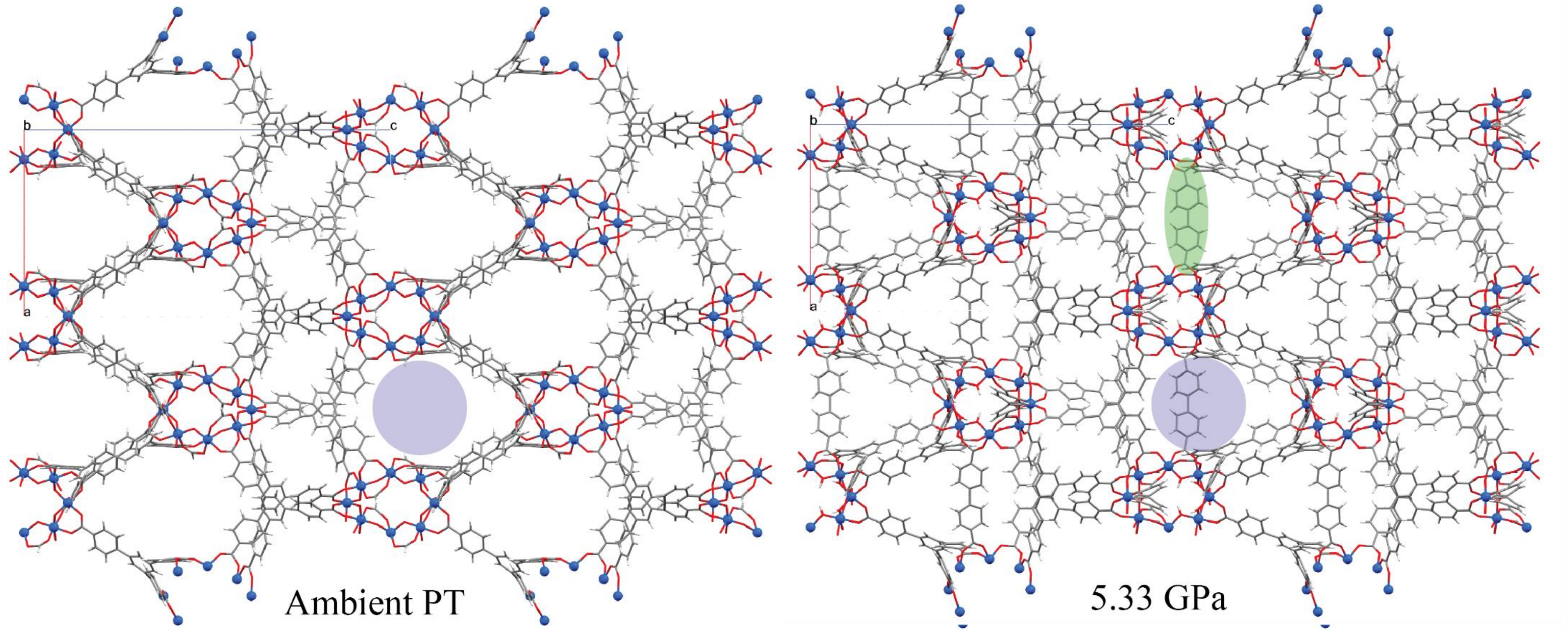
Alberto Rodriguez-Velamazan, J. *et al*; A Multifunctional Magnetic Material under Pressure. *Chemistry-a European Journal* **2014,** *20* (26), 7956-7961

Pb Halide Perovskites at Pressure



Jaffe, A. *et al*; High-Pressure Single-Crystal Structures of 3D Lead-Halide Hybrid Perovskites and Pressure Effects on their Electronic and Optical Properties. *ACS Central Science* **2016,** *2* (4), 201-209.

Retrofitting a MOF



Kapustin, E. A. *et al;* Molecular Retrofitting Adapts a Metal–Organic Framework to Extreme Pressure. *ACS Central Science* **2017,** *3* (6), 662-667.

Why Synchrotrons?

- In situ experiments usually produce the degradation of a crystal, and most are more successful with small crystals.
- Poorly diffracting crystals need as much intensity as they can take.

- In both cases, a synchrotron offers orders of magnitude more flux, which means a better chance of success.

wellcome trust

Science & Technology
Facilities Council

diamond

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231

COMPRES, the Consortium for Material Properties Research in Earth Sciences, is supported under NSF Cooperative Agreement EAR 11-57758.

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