Single Crystal Diffraction:
The Definitive Structural Technique

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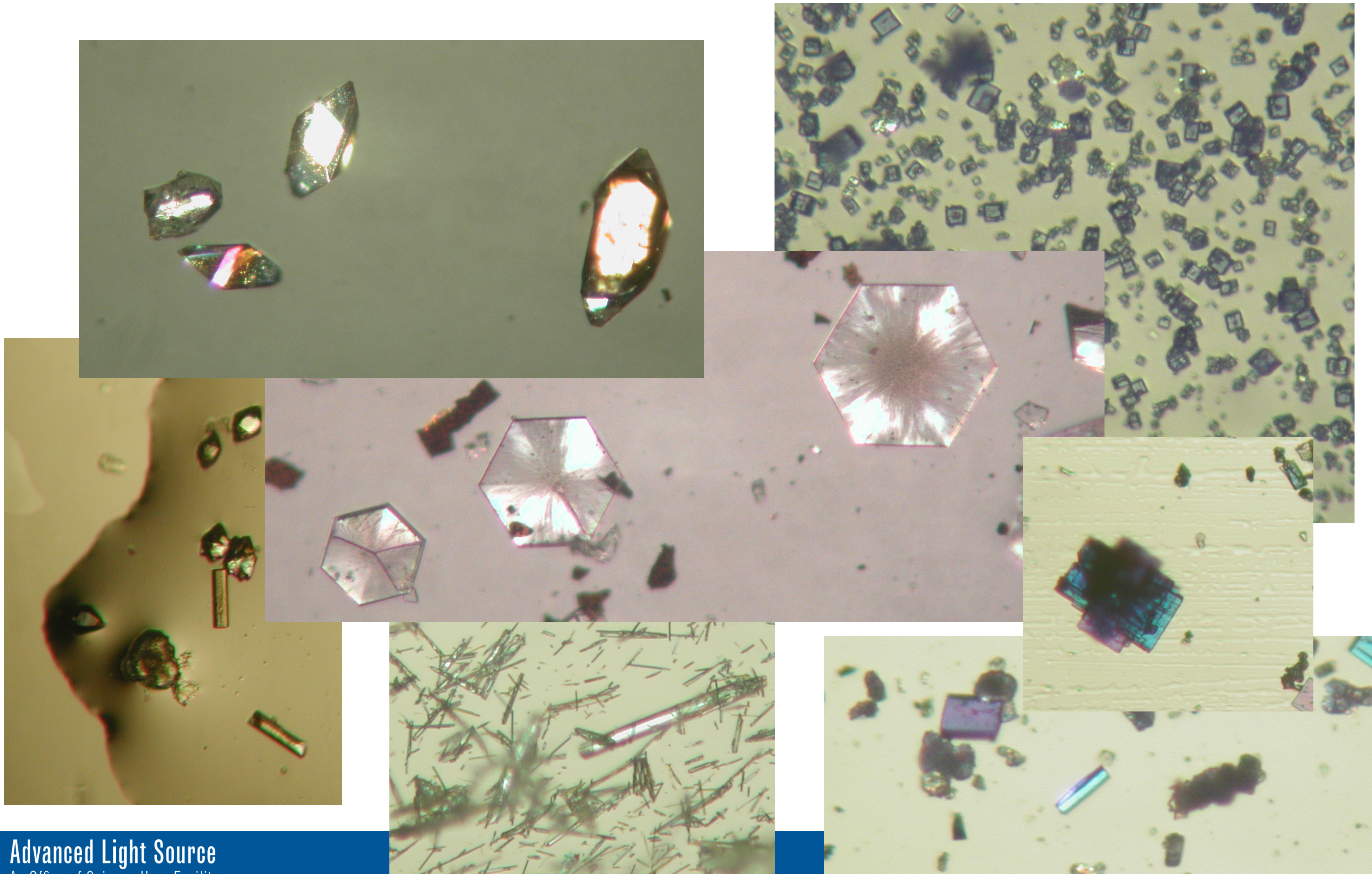
18th National School on Neutron & X-ray Scattering

August 2nd, 2016

crys·tal·log·ra·phy

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

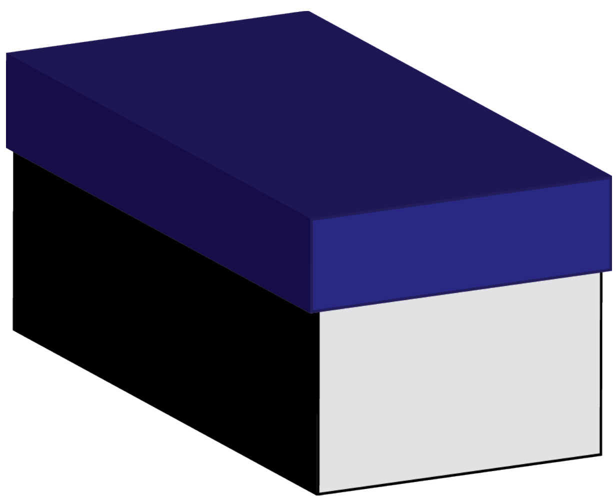


What is a Crystal?

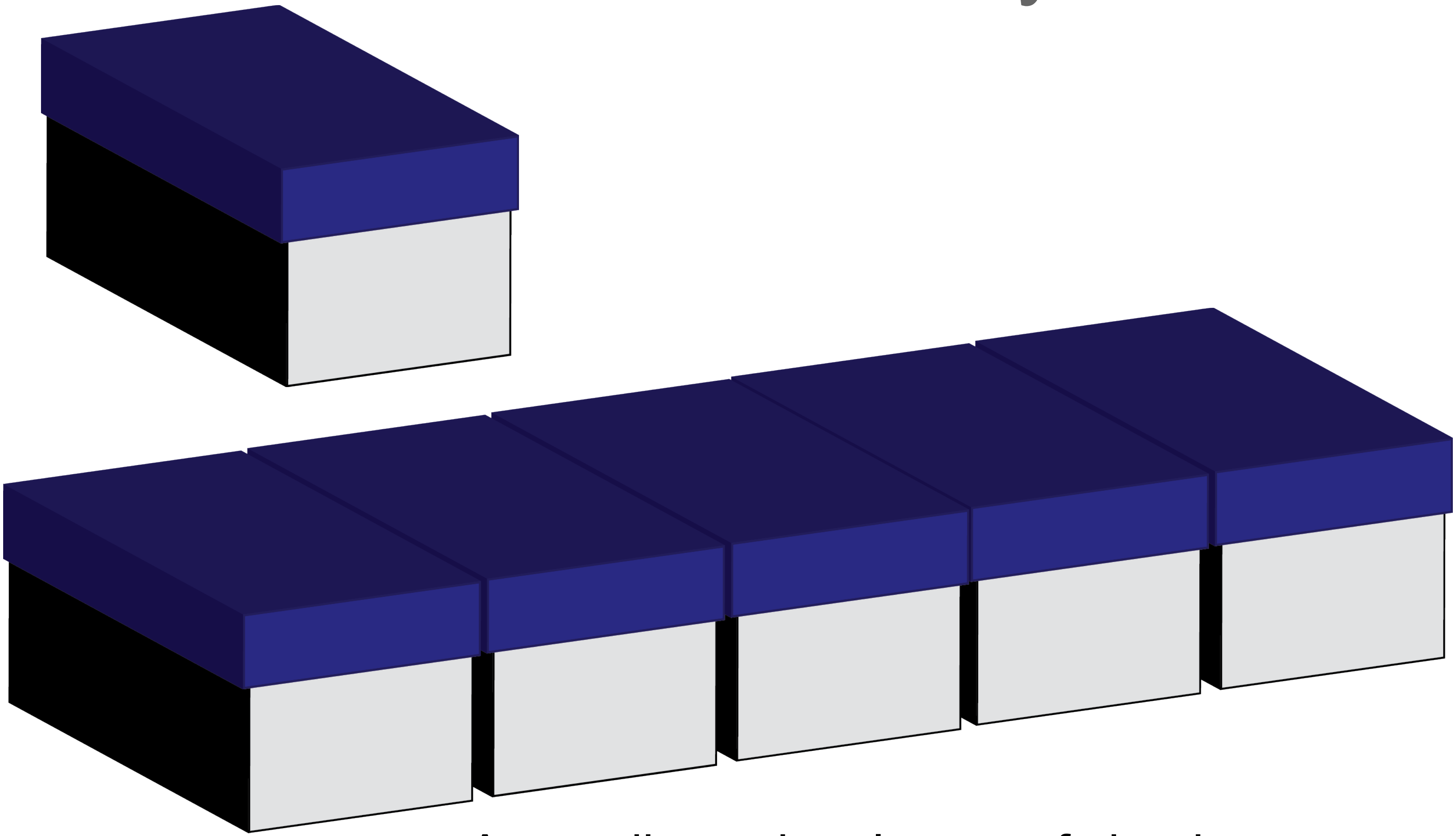
- A crystal is a periodic arrangement of matter

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.

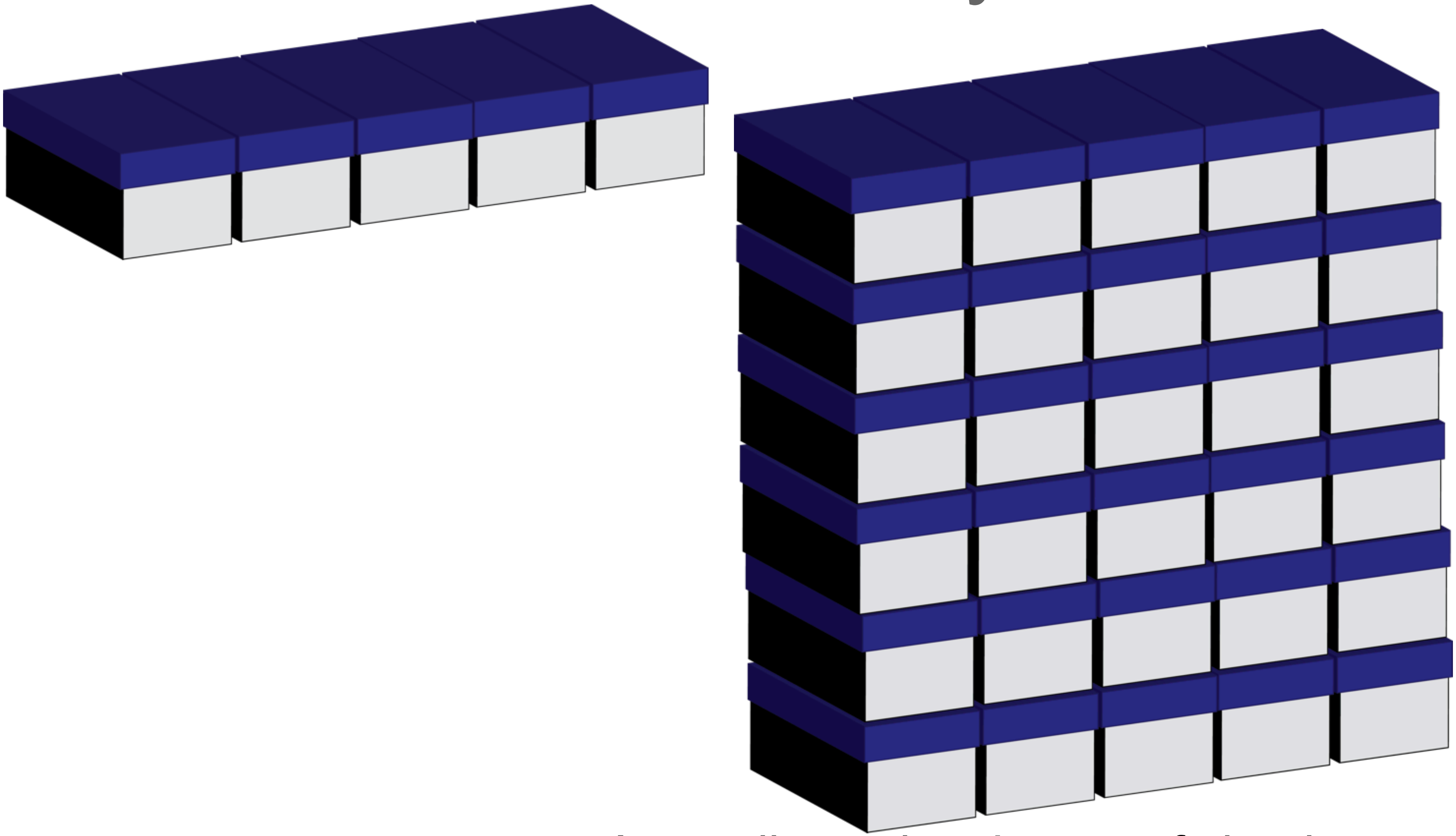


Dimensionality



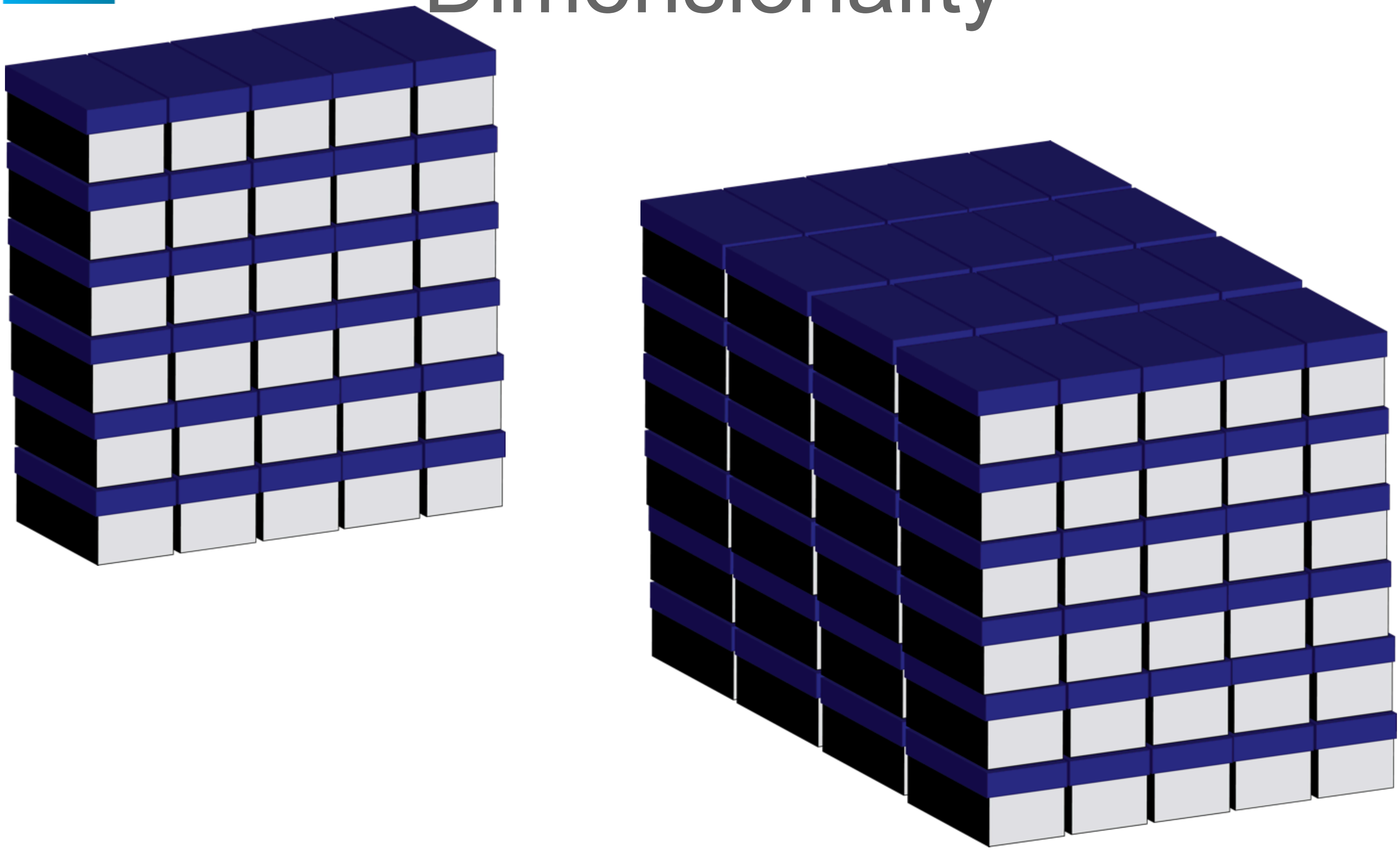
A one-dimensional array of shoeboxes

Dimensionality



A two-dimensional array of shoeboxes

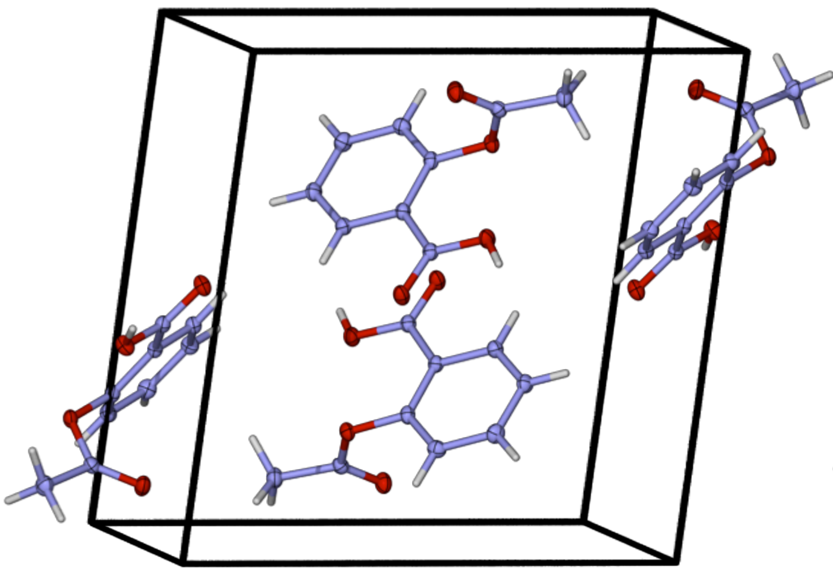
Dimensionality

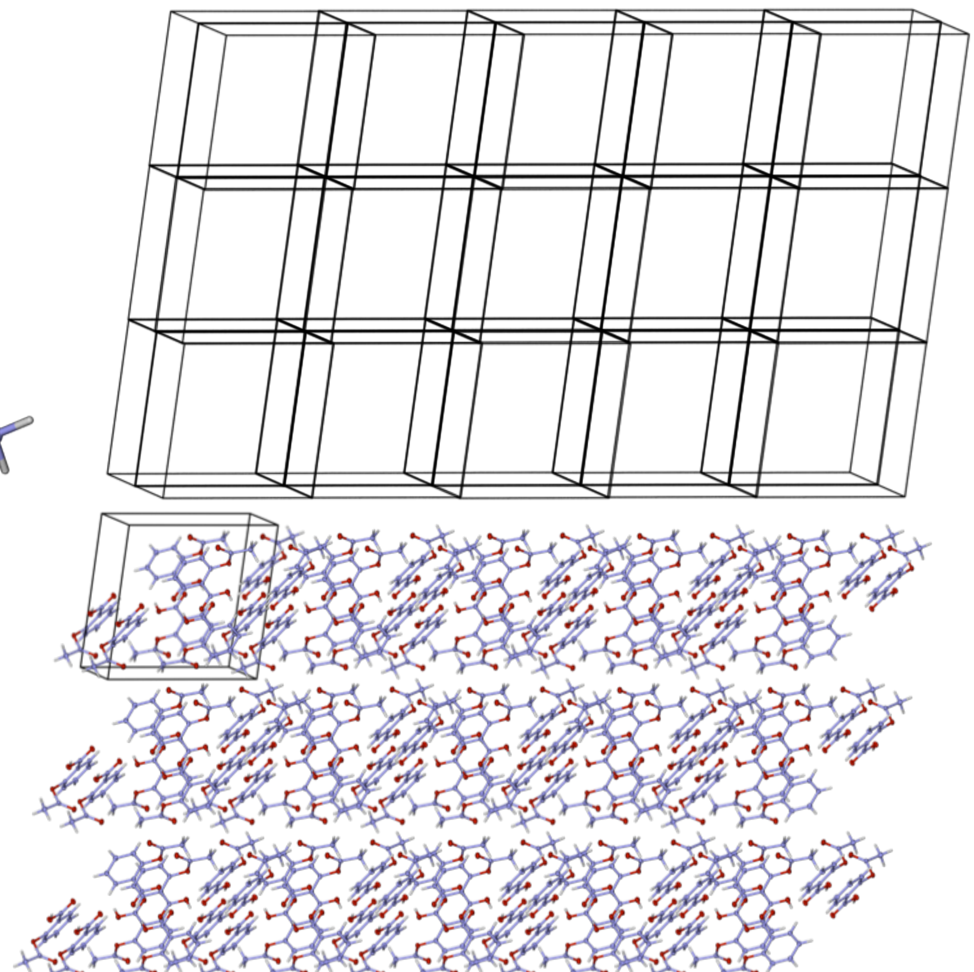


A three-dimensional array of shoeboxes

From Shoeboxes to Unit Cells

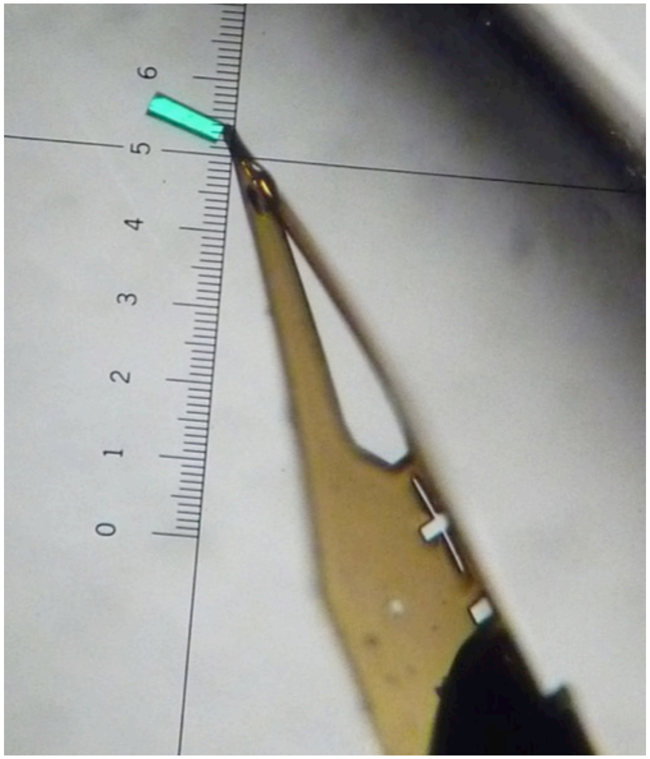
Unit Cell Definition:
Smallest volume unit of highest symmetry which, when translated in 3D will generate the crystal

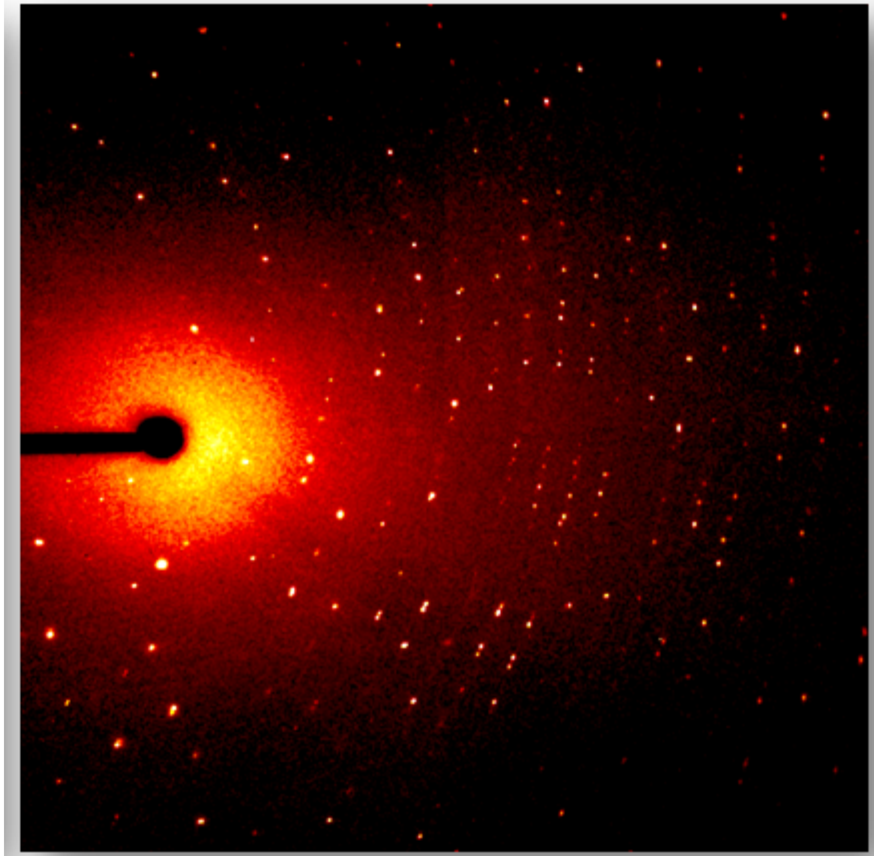




The dimensions of the Unit Cell are an identifying feature for a specific crystal!

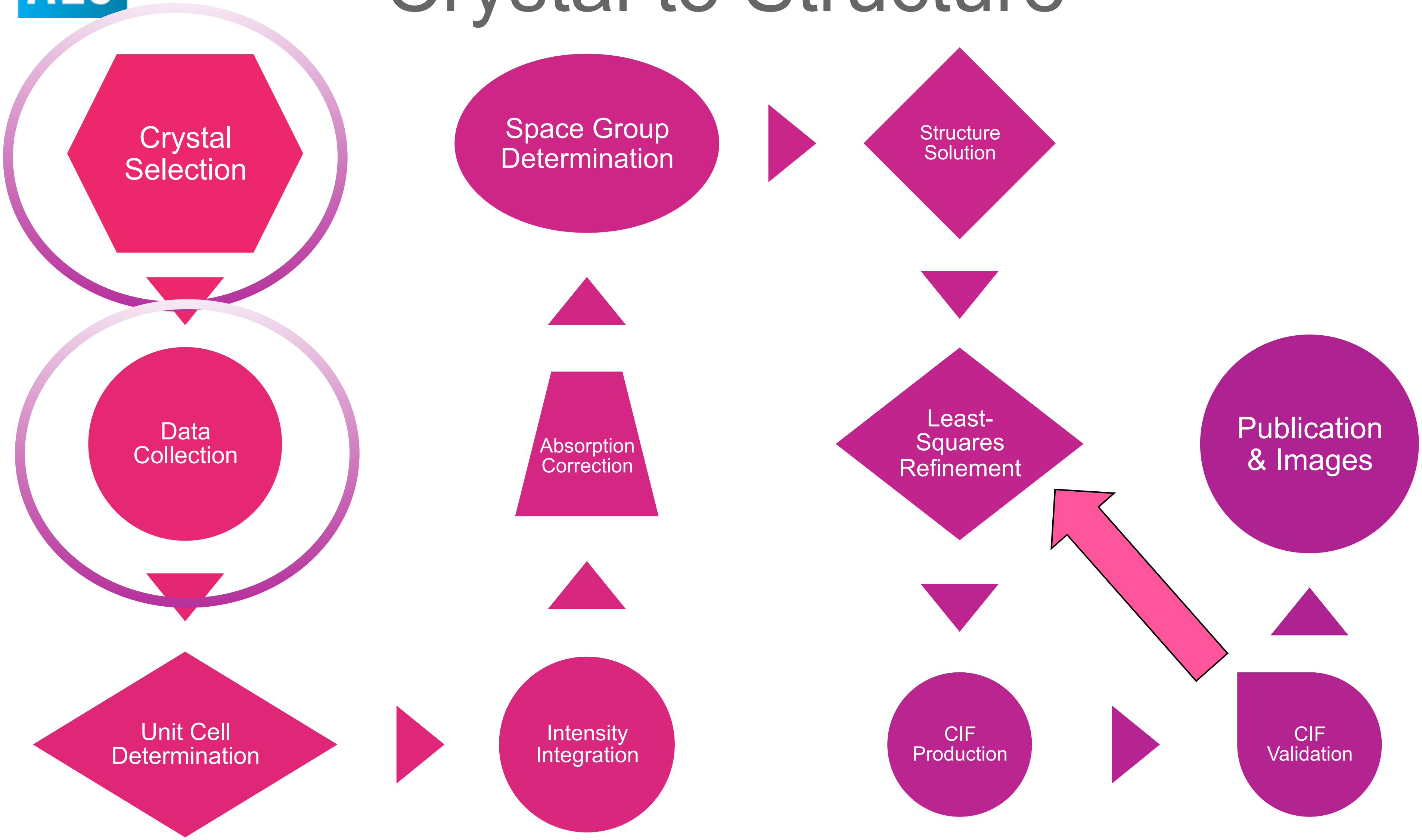
Crystal Selection #LifeGoals



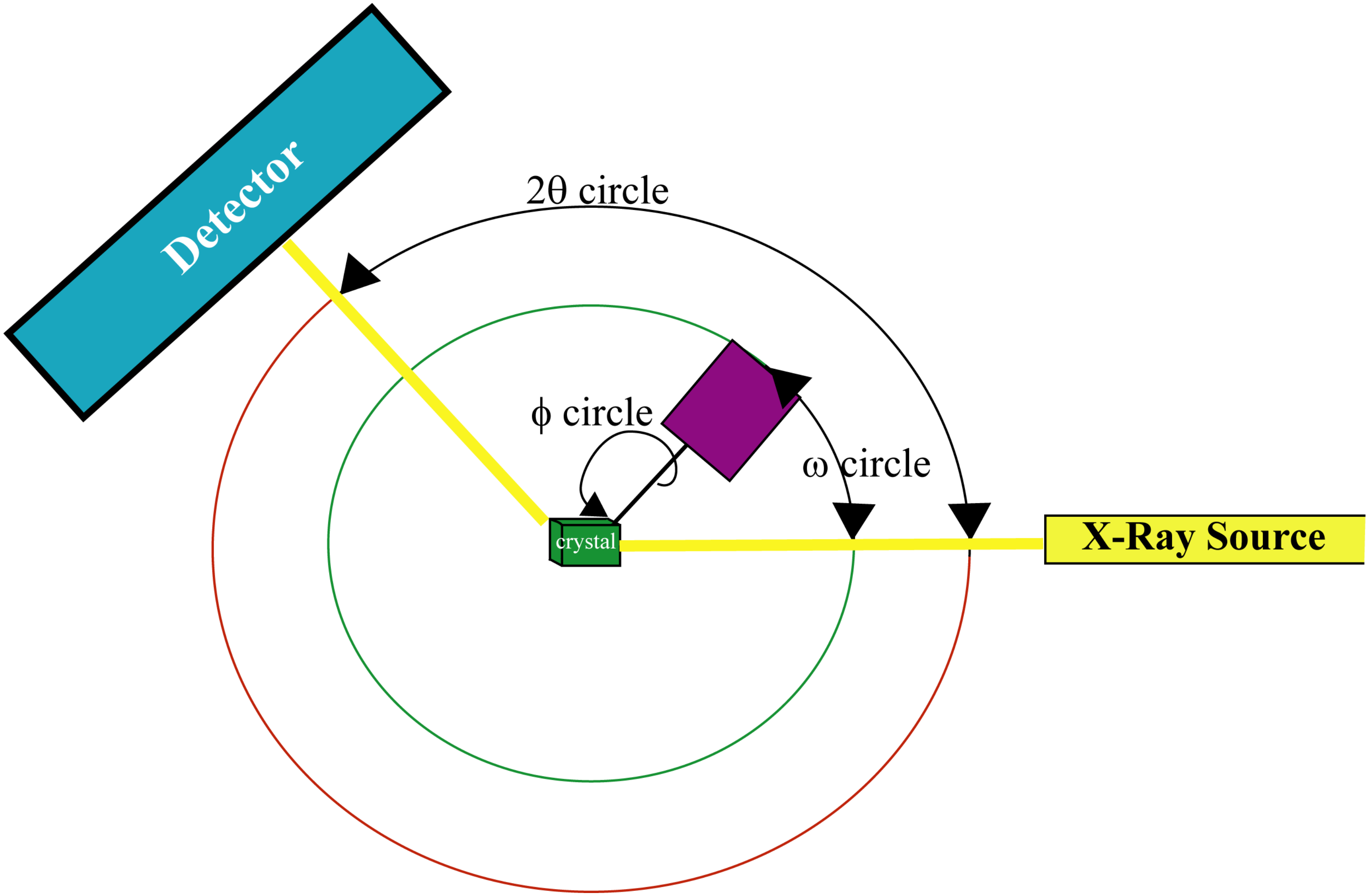


Nice crystals are more likely to have nice diffraction

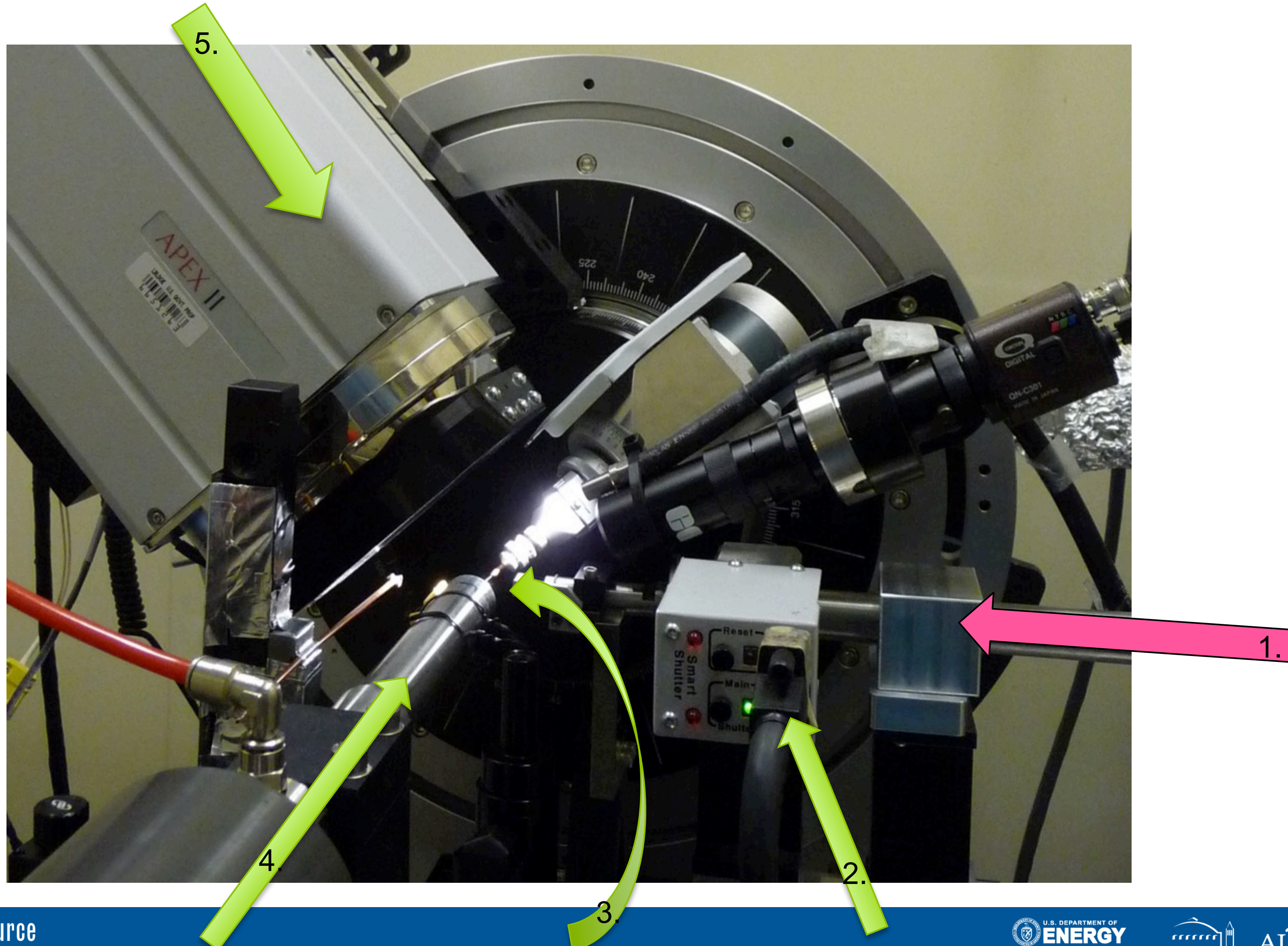
Crystal to Structure



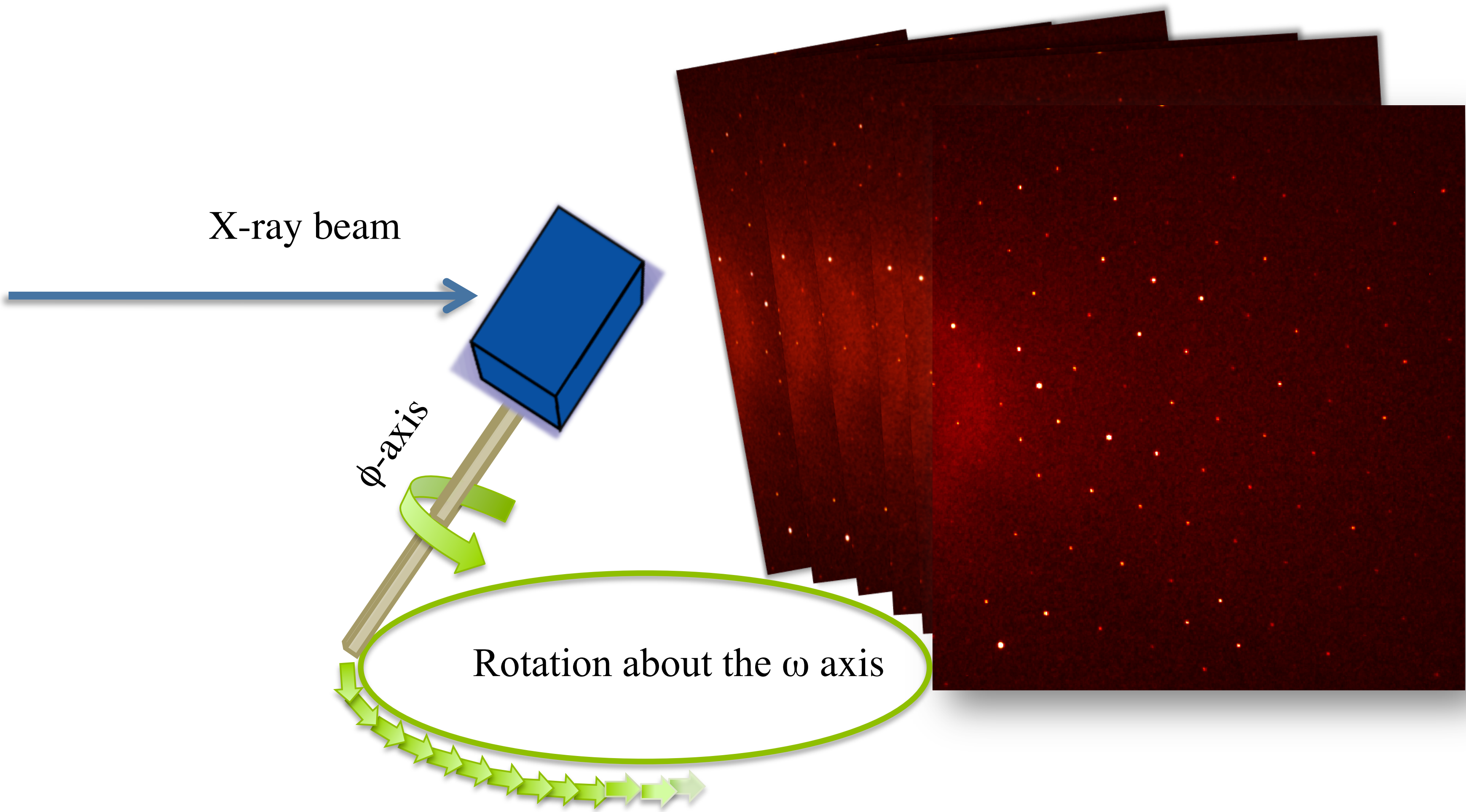
Diffractometer Schematic



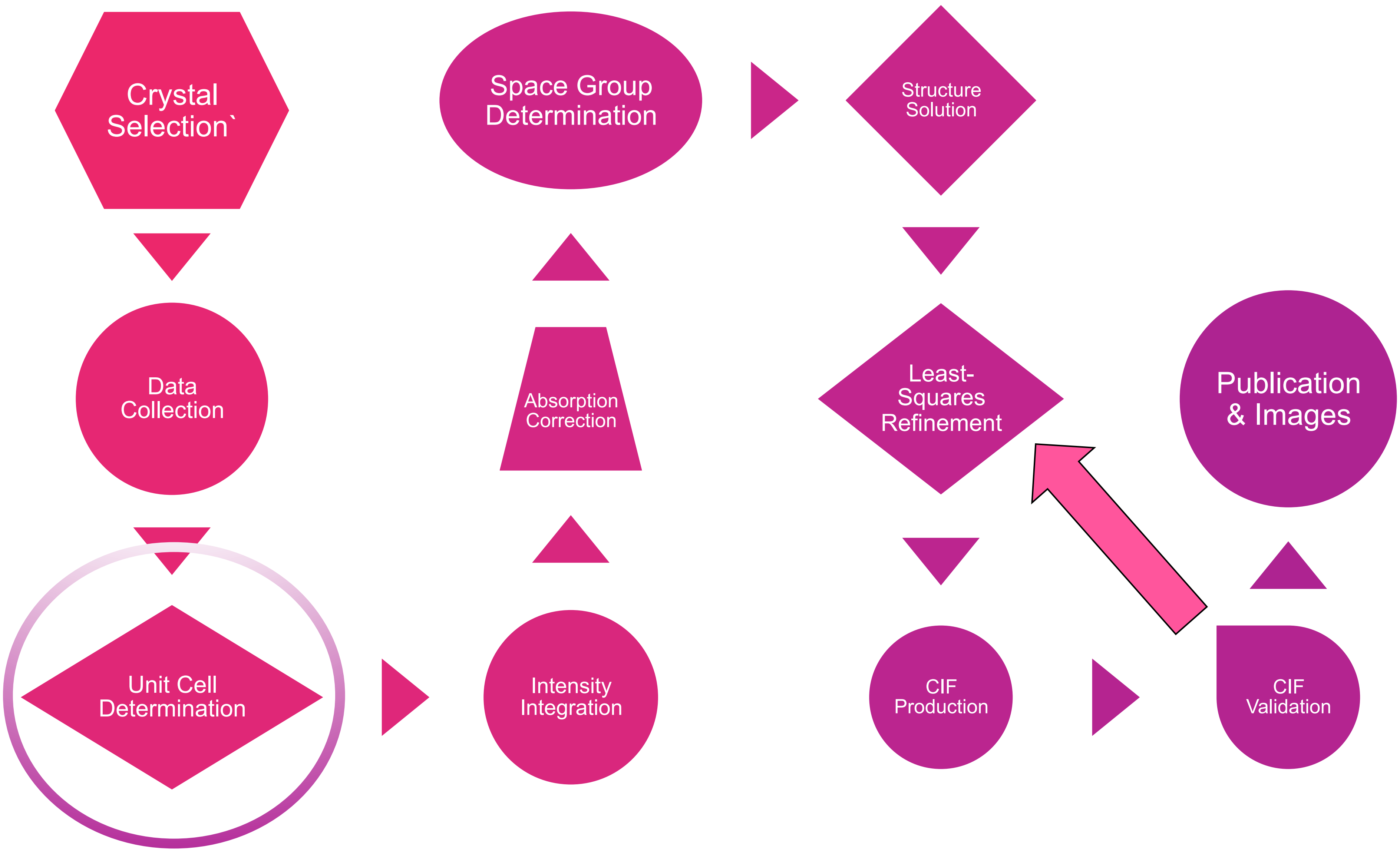
SXD Diffractometer



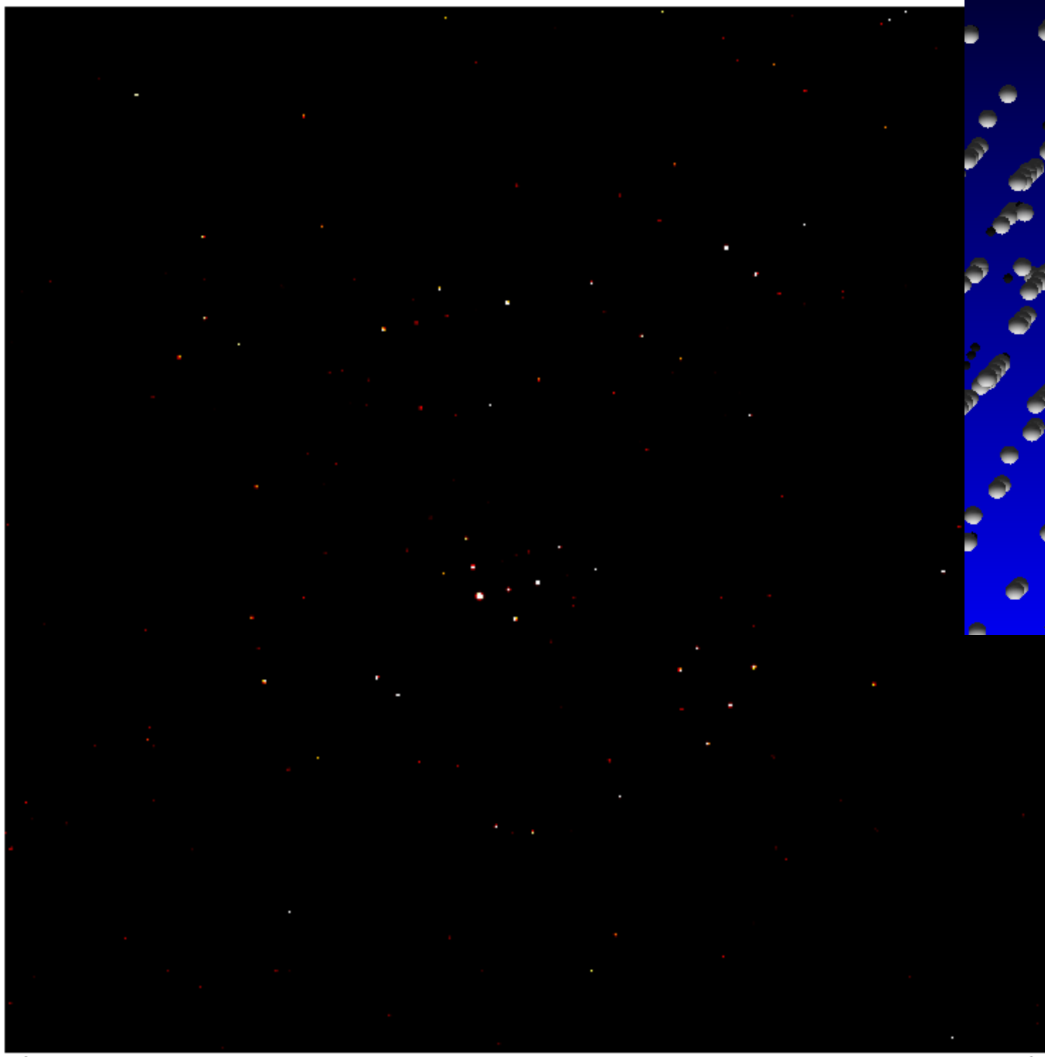
Data Collection Schematic

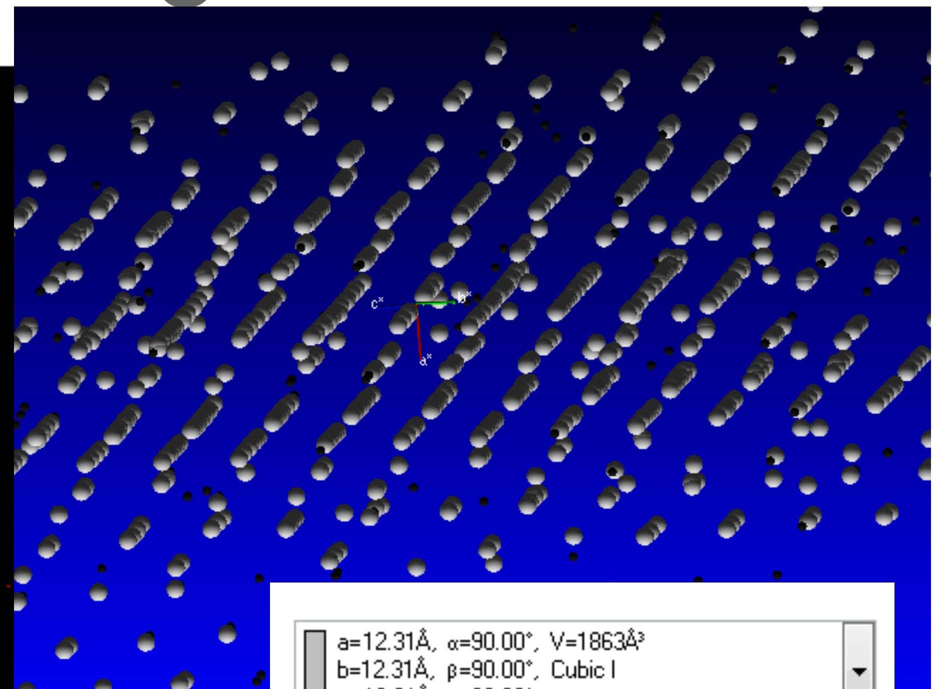


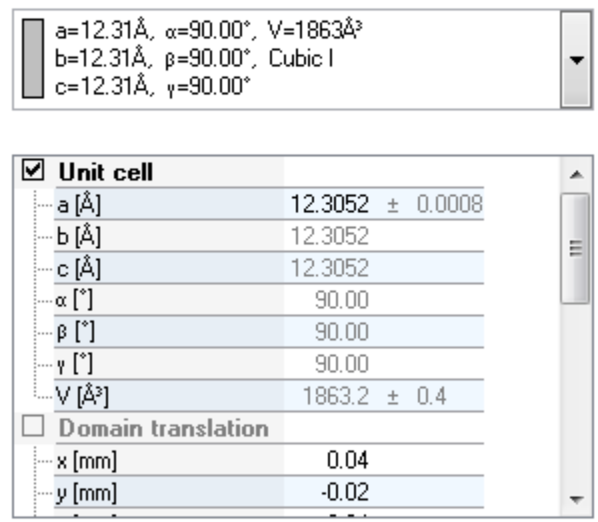
Crystal to Structure



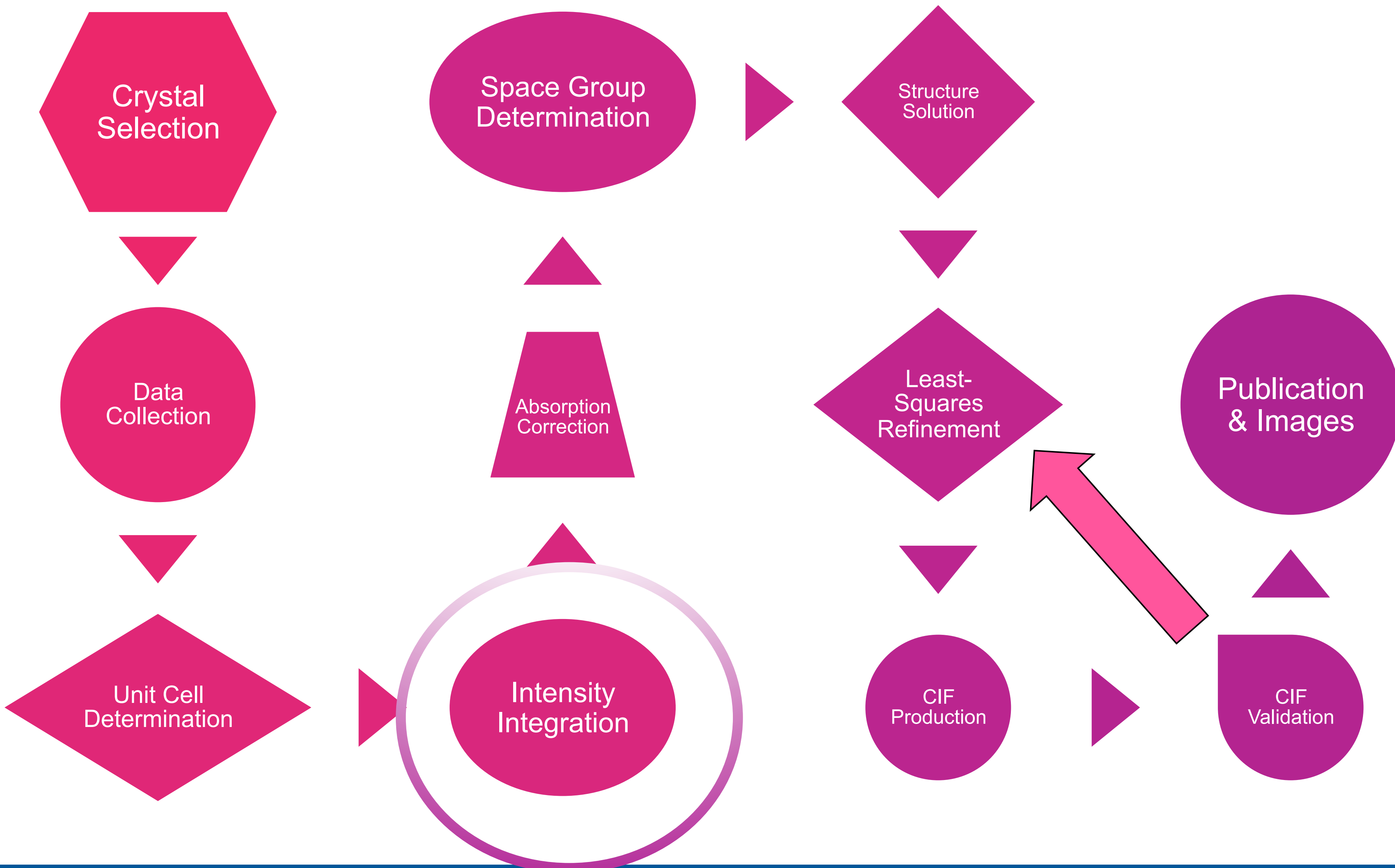
Indexing



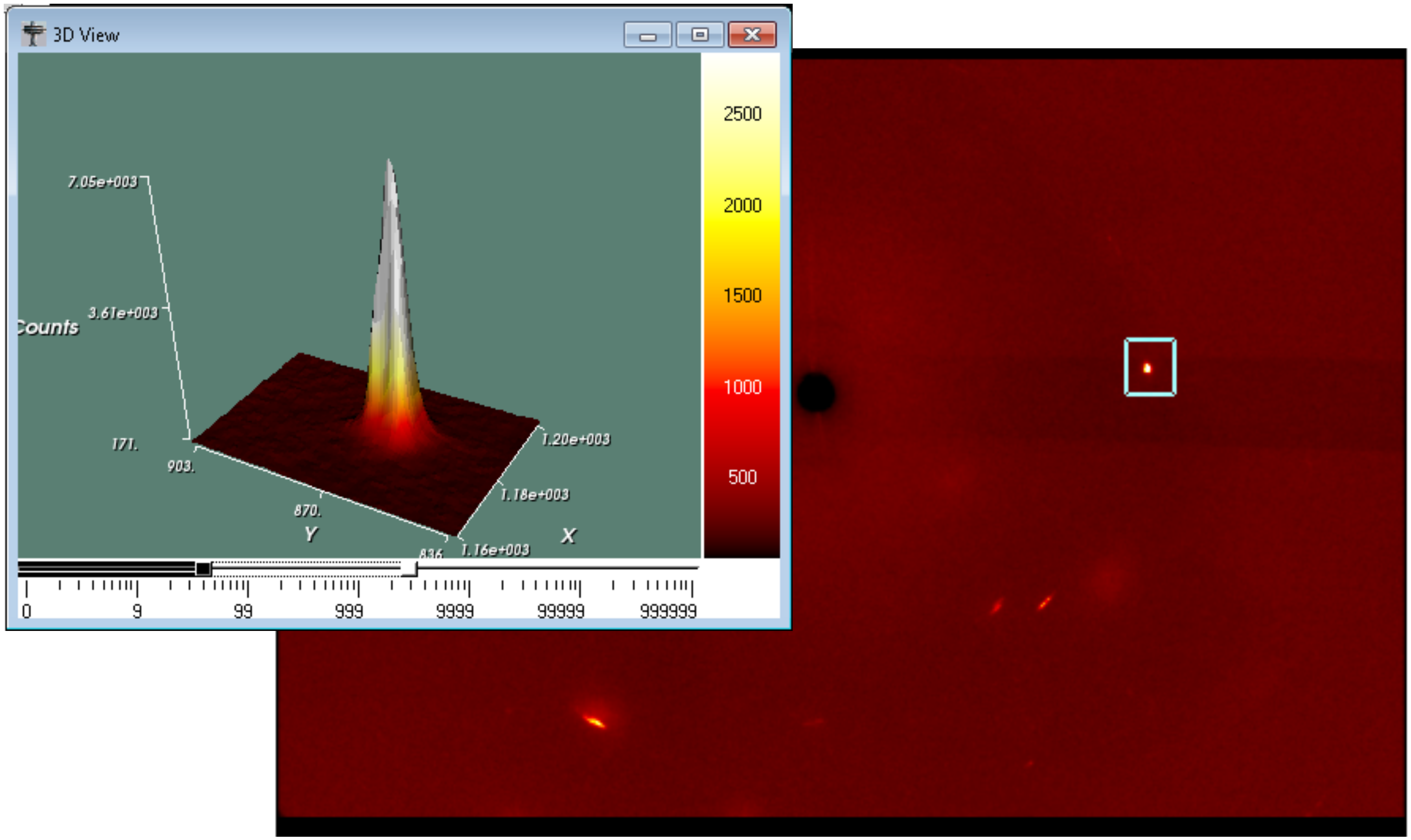

c*
b*
a*


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

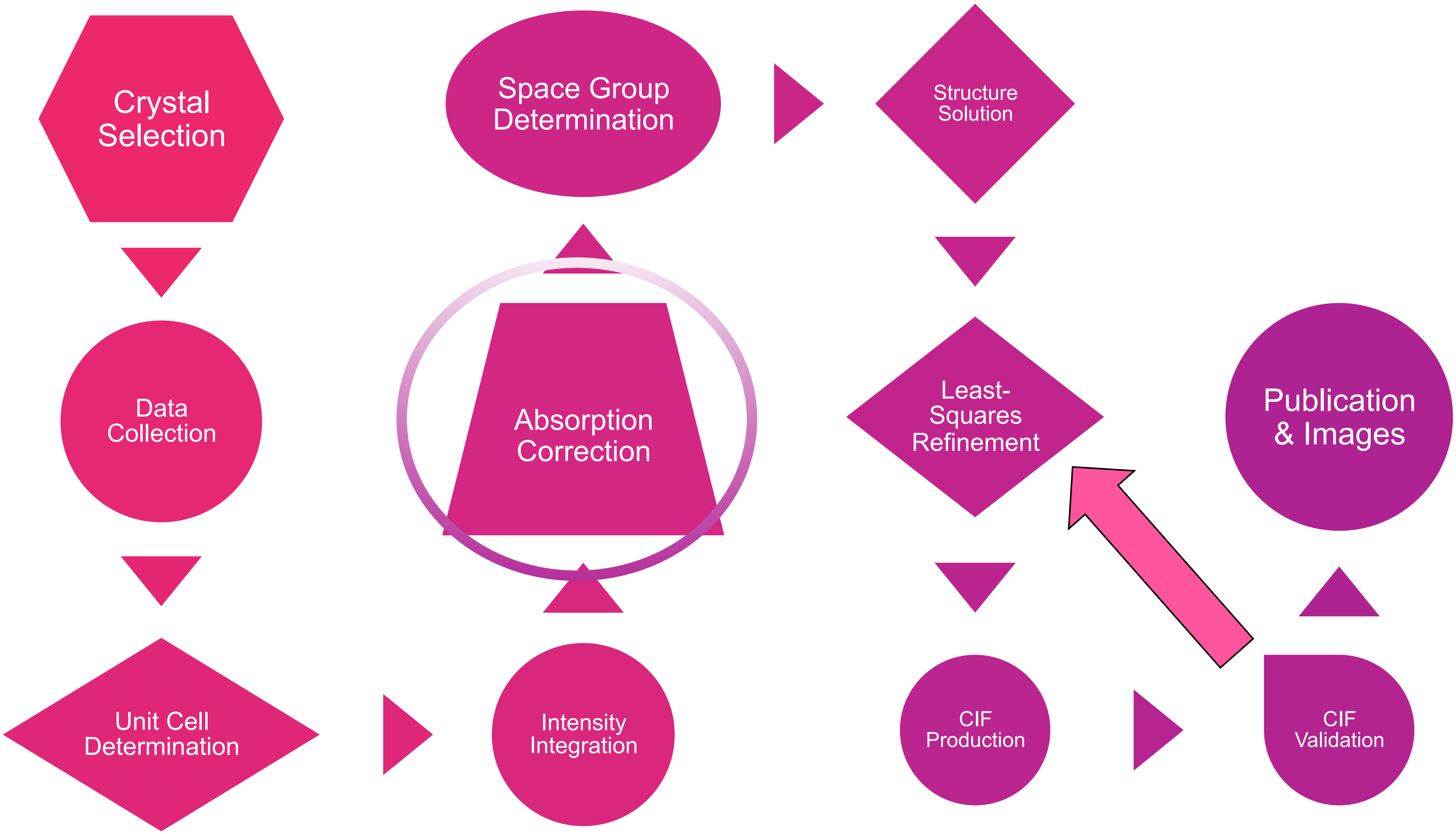
Crystal to Structure



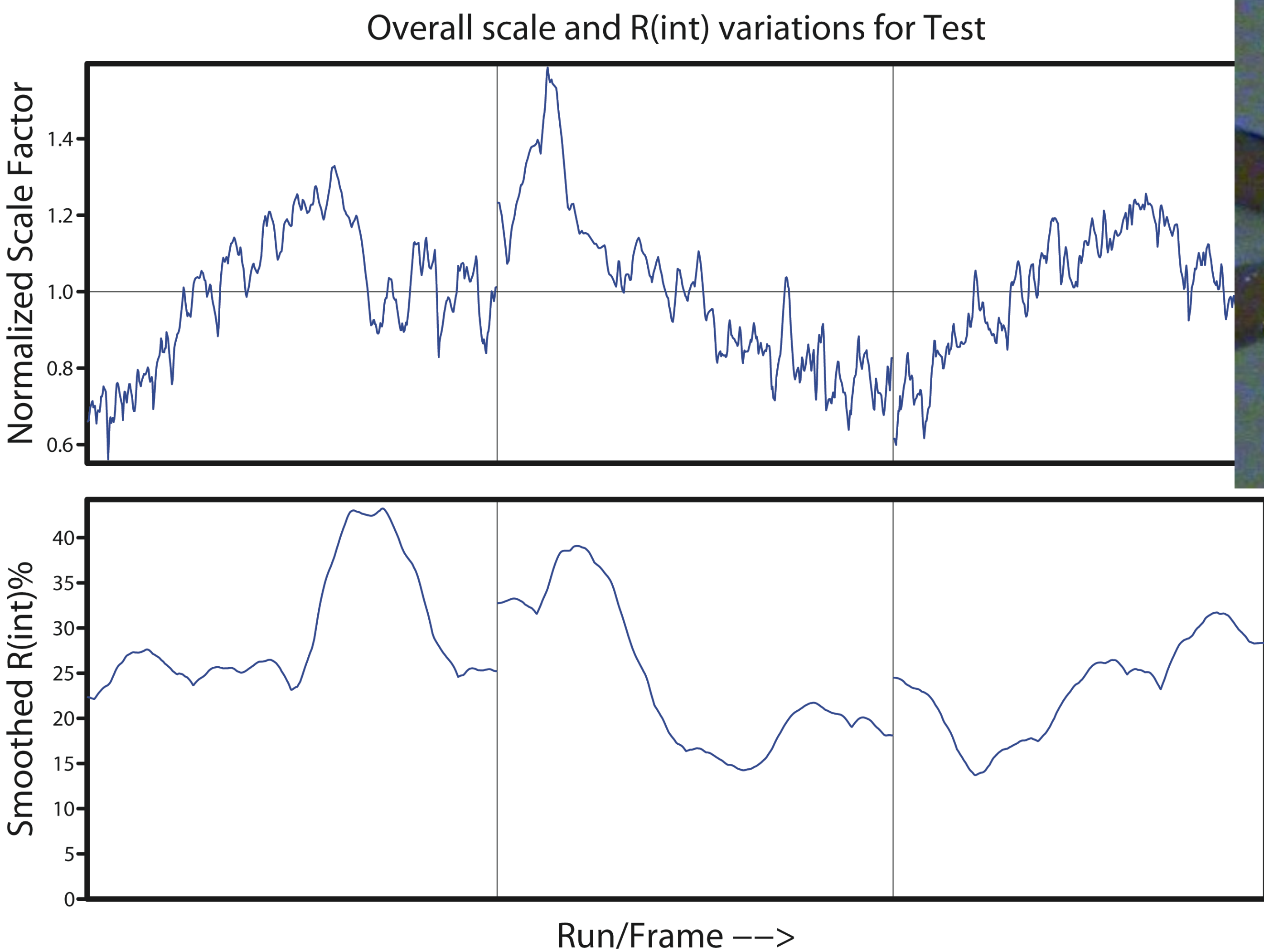
Data Integration

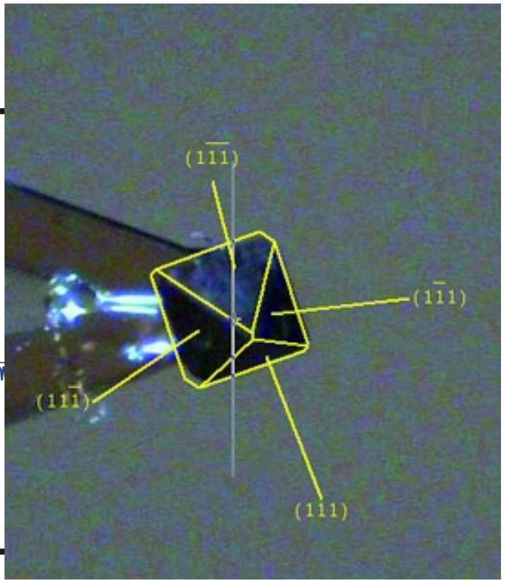


Crystal to Structure

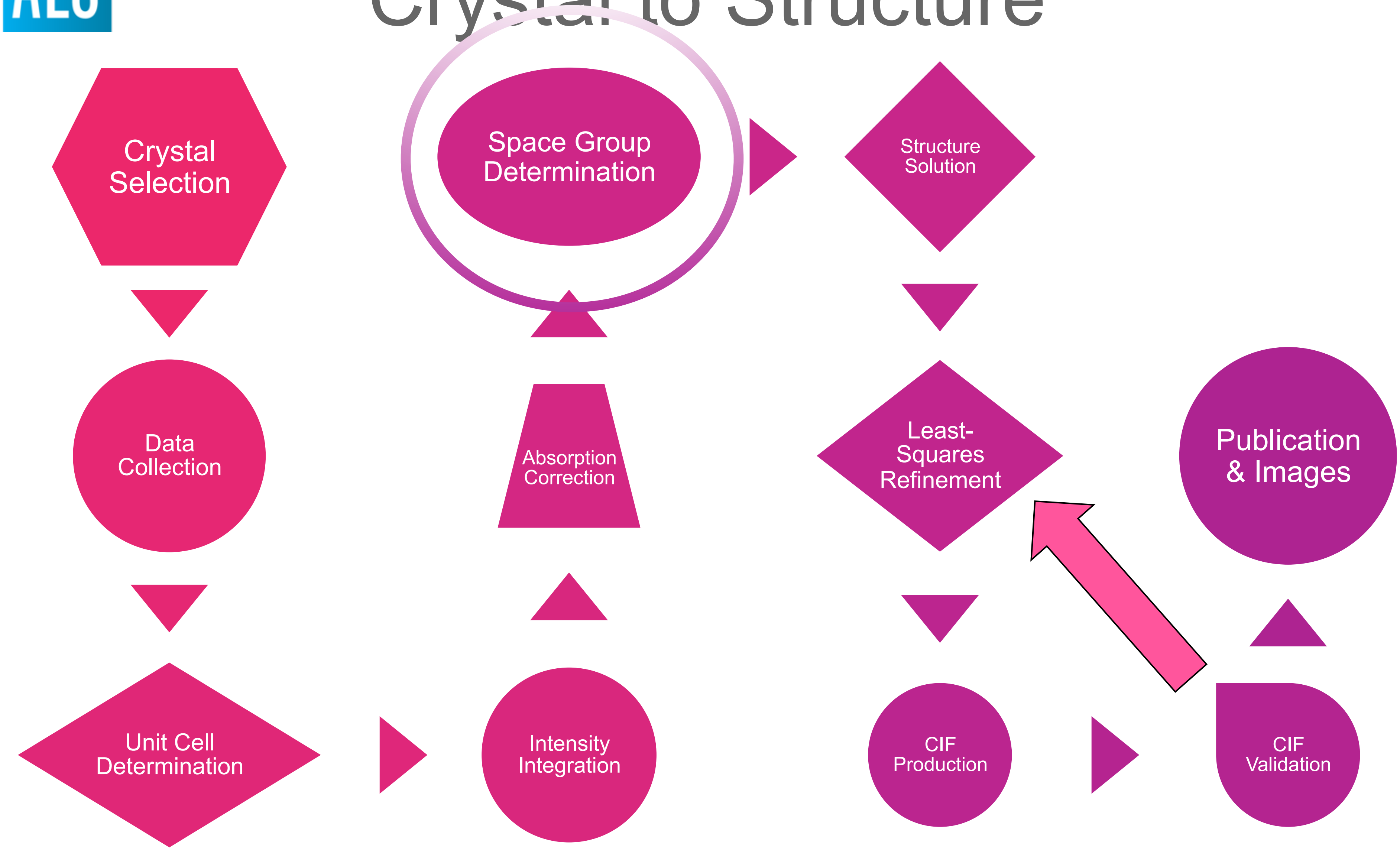


Absorption Correction

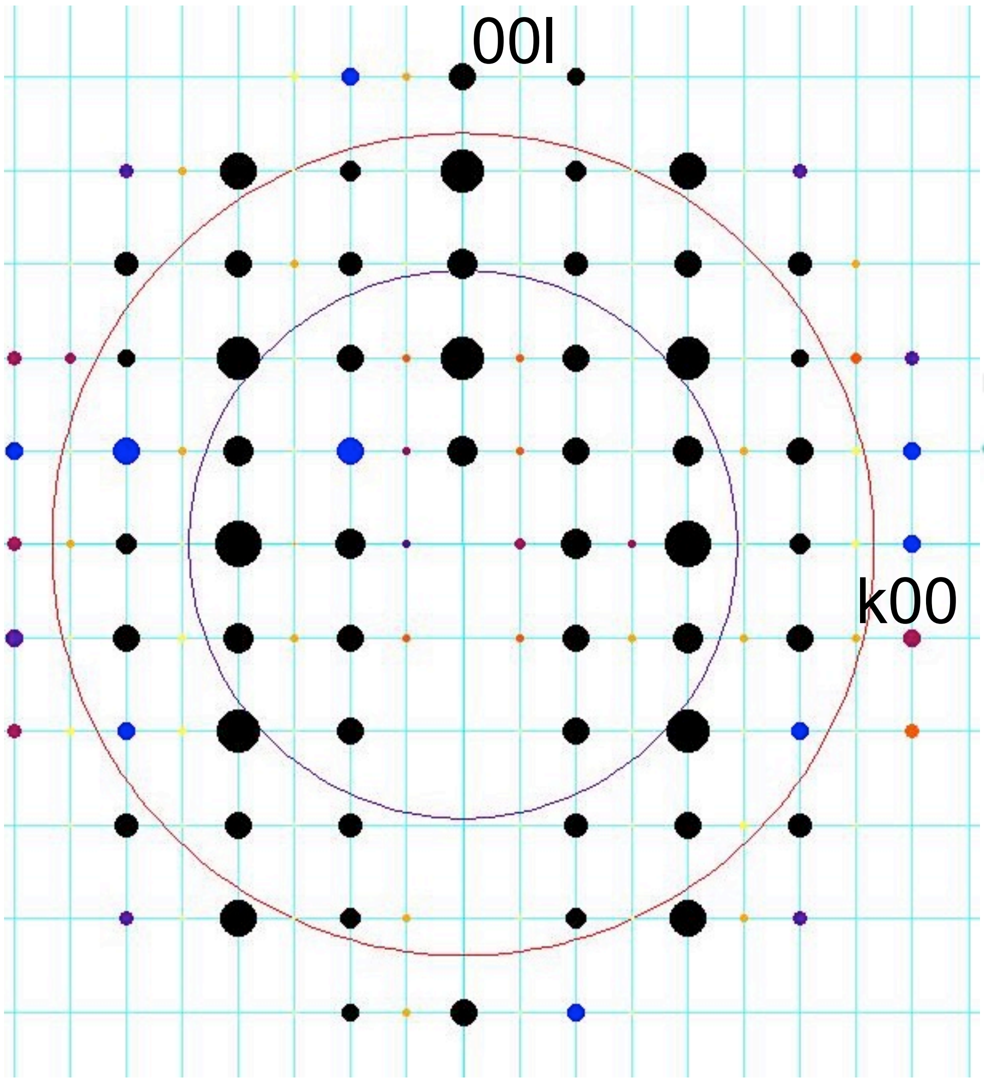


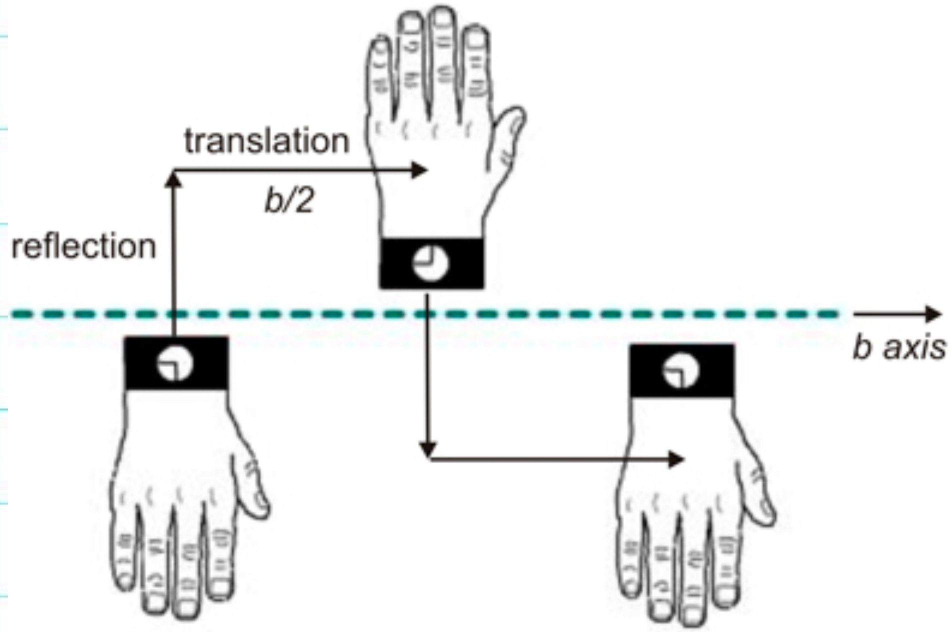


Crystal to Structure

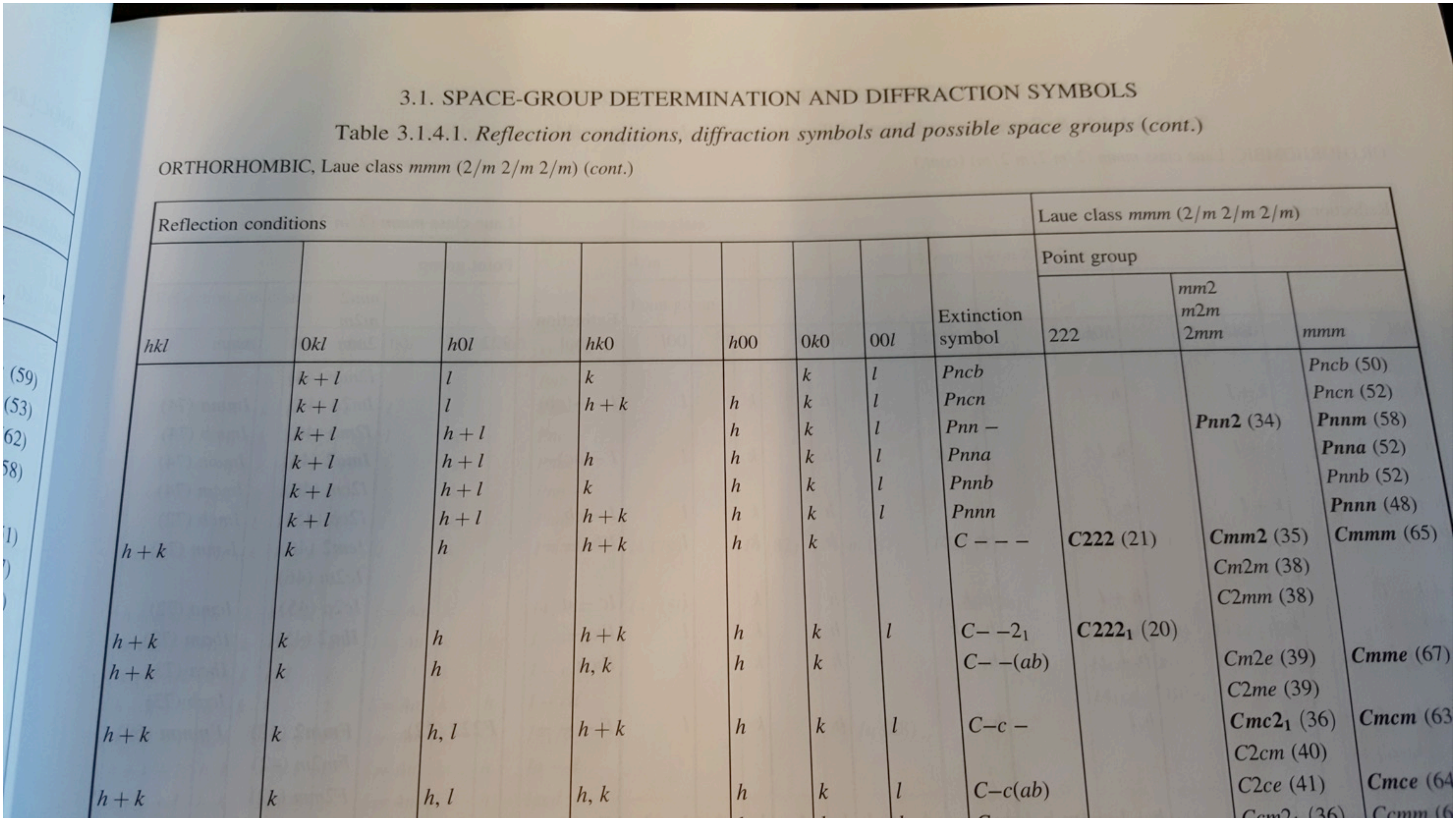


Space Group Determination





Space Group Determination



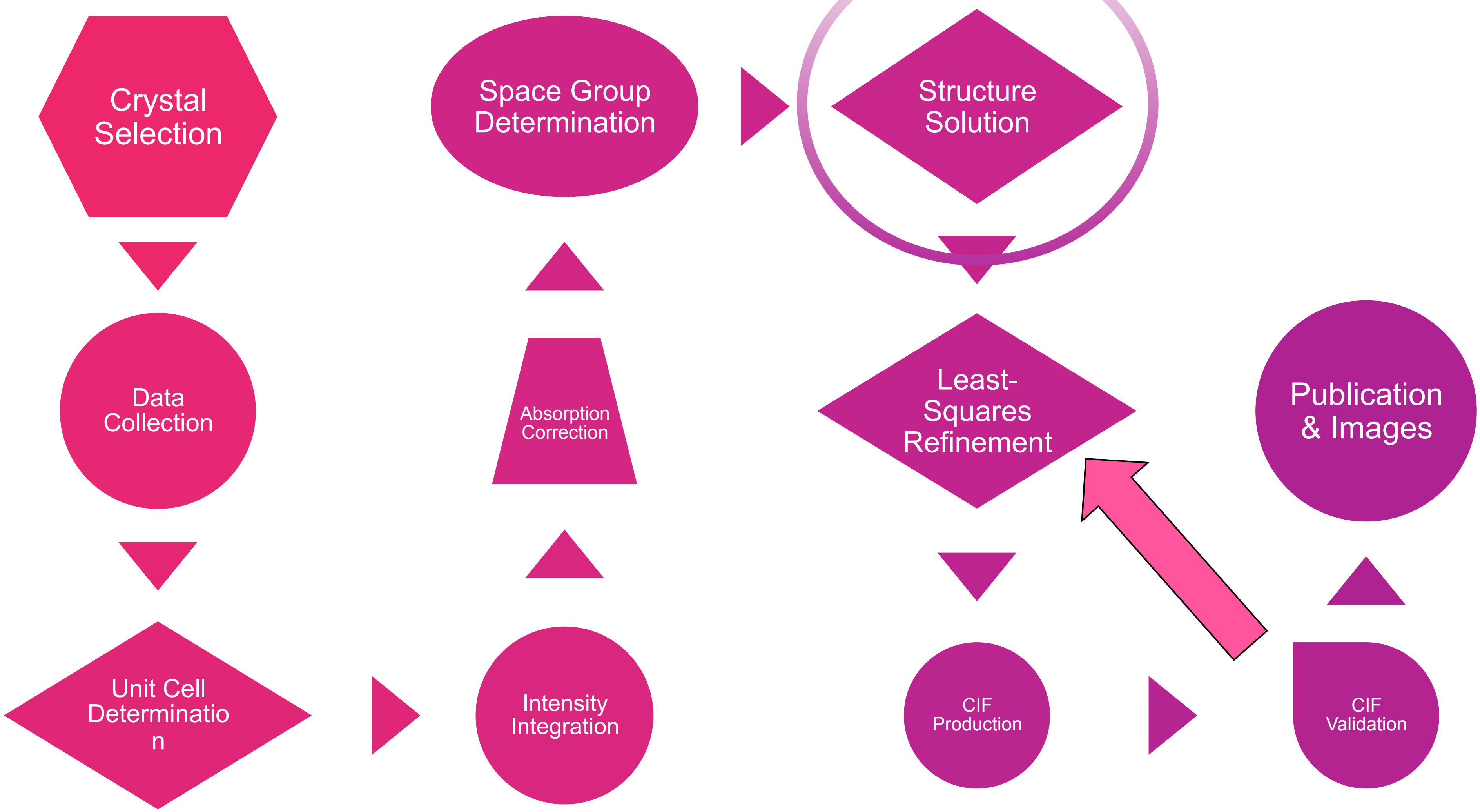
3.1. SPACE-GROUP DETERMINATION AND DIFFRACTION SYMBOLS

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.*)

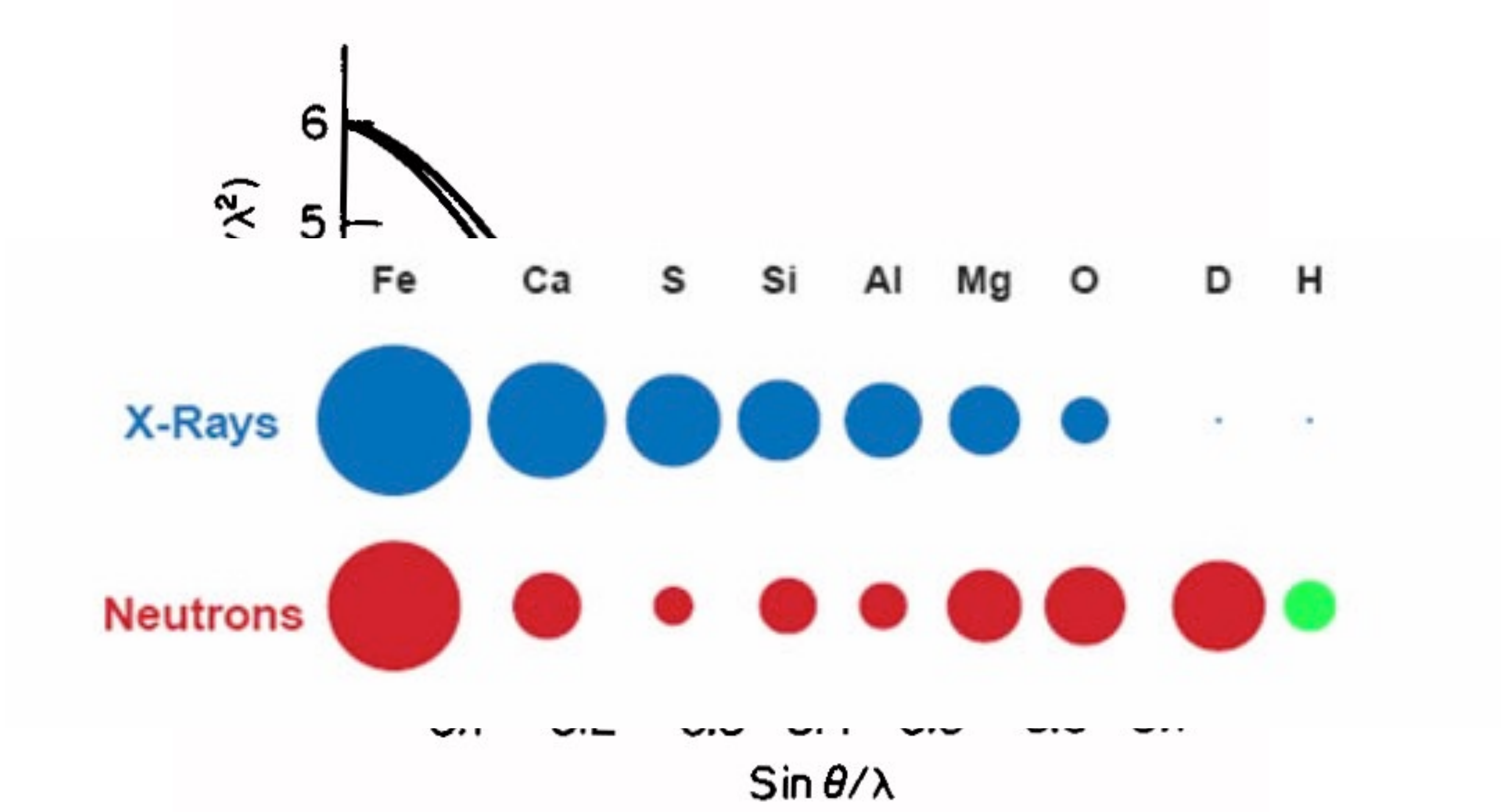
Reflection conditions								Laue class *mmm* (2/*m* 2/*m* 2/*m*)		
								Point group		
hkl	*0kl*	*h0l*	*hk0*	*h00*	*0k0*	*00l*	Extinction symbol	222	*mm2* *m2m* *2mm*	*mmm*
	$k+l$	l	k		k	l	*Pncb*			*Pncb* (50)
	$k+l$	l	$h+k$	h	k	l	*Pncn*			*Pncn* (52)
	$k+l$	$h+l$		h	k	l	*Pnn*–		***Pnn2*** (34)	***Pnnm*** (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*–––	***C222*** (21)	***Cmm2*** (35) *Cm2m* (38) *C2mm* (38)	***Cmmm*** (65)
$h+k$	k	h	$h+k$	h	k	l	*C*––2_1	***C222$_1$*** (20)		
$h+k$	k	h	h, k	h	k		*C*––(*ab*)		*Cm2e* (39) *C2me* (39)	***Cmme*** (67)
$h+k$	k	h, l	$h+k$	h	k	l	*C*–*c*–		***Cmc2$_1$*** (36) *C2cm* (40)	***Cmcm*** (63
$h+k$	k	h, l	h, k	h	k	l	*C*–*c*(*ab*)		*C2ce* (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

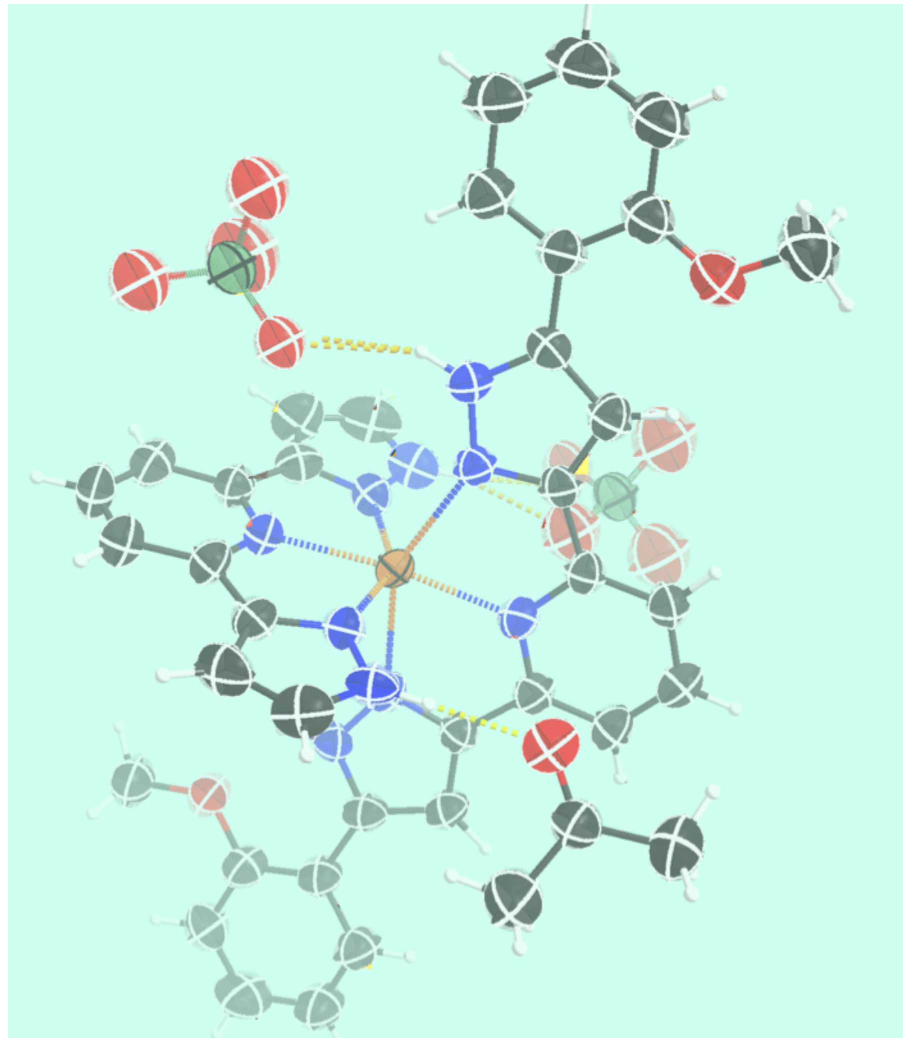
$$\rho_{xyz} = \frac{1}{V} \sum_{hkl} \bar{F}_{hkl} e^{-i2\pi(hx+ky+lz)}$$

-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

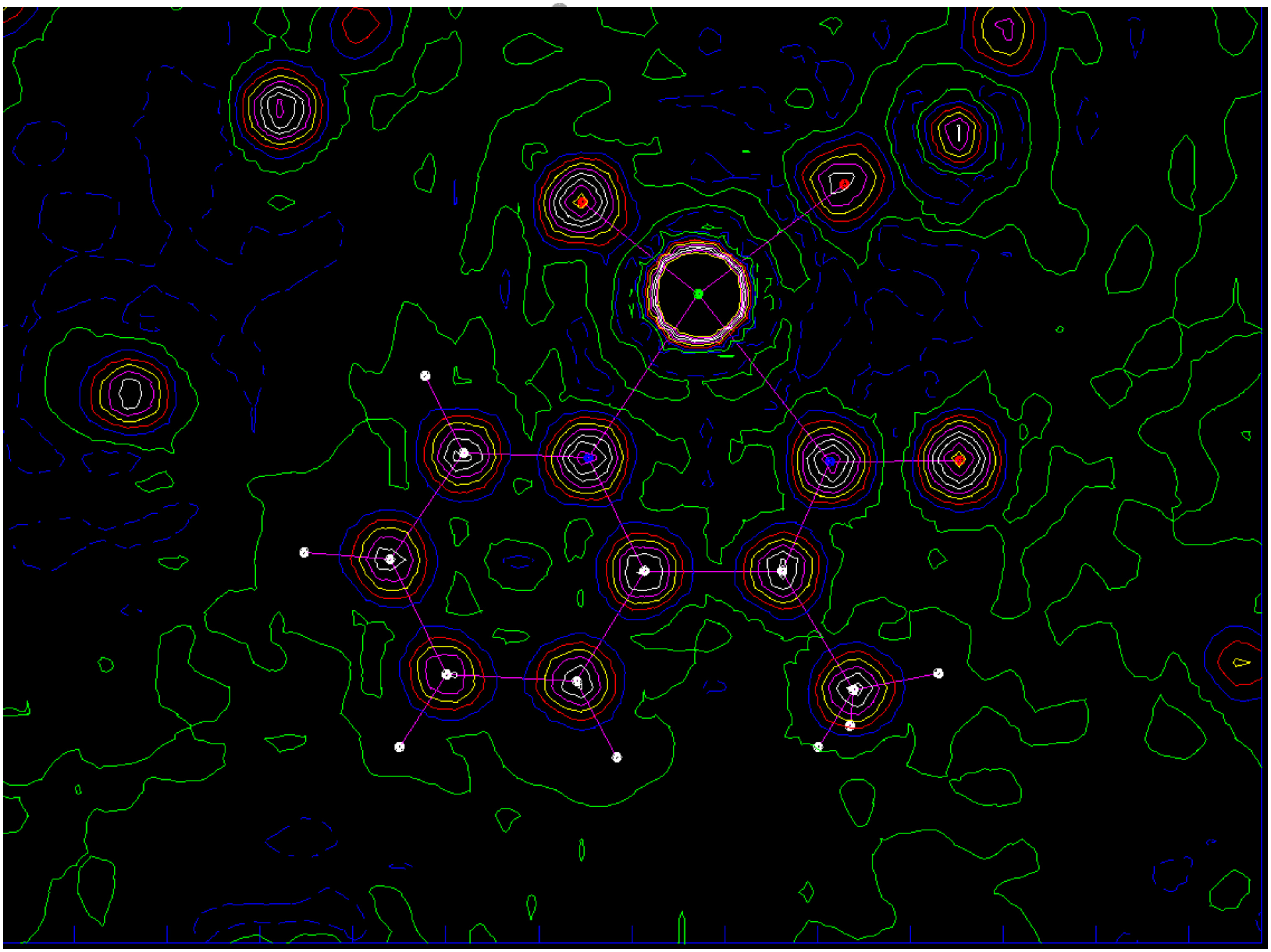
$$F_{hkl} = |F_{hkl}| e^{i\varphi_{hkl}}$$

????

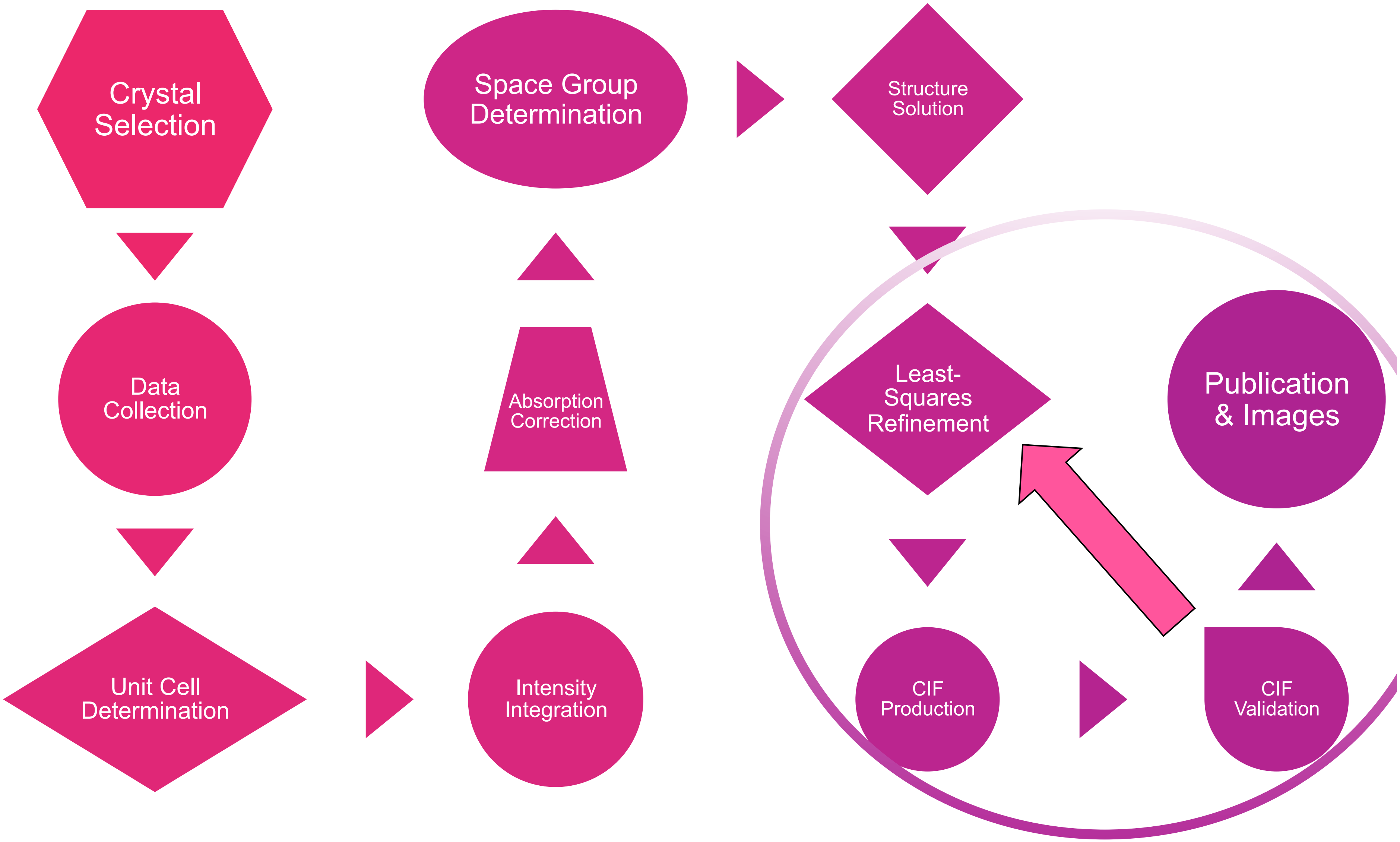
SHELXT
SHELXS
SIR2011+
SUPERFLIP



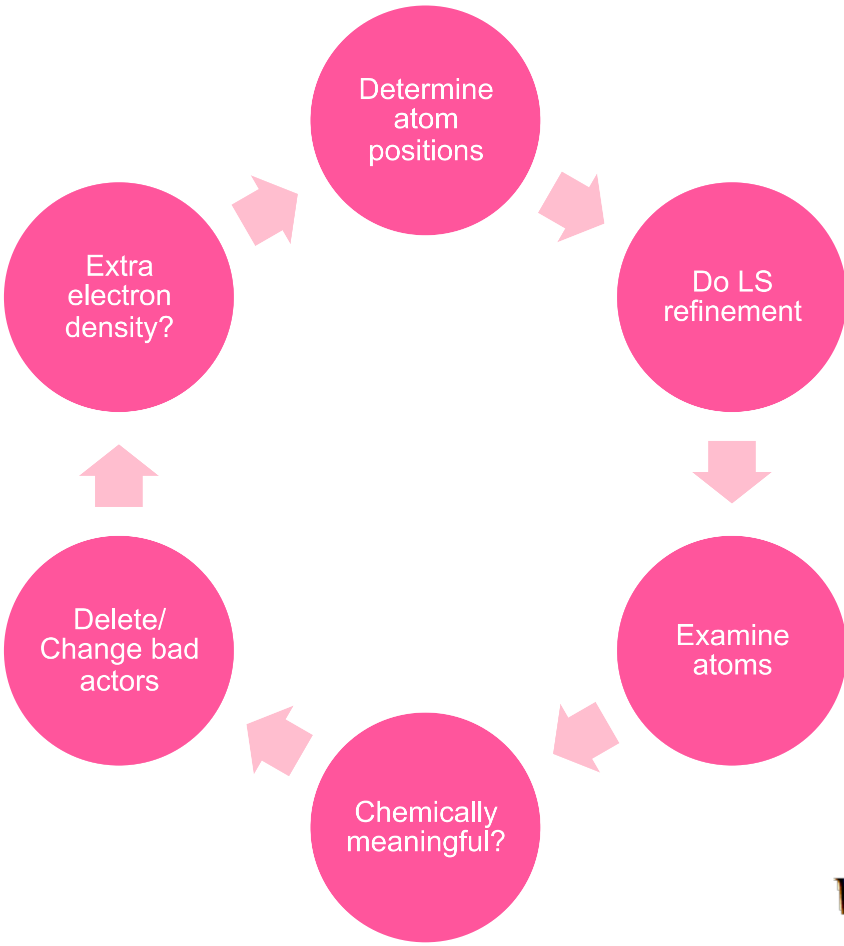
What is a Structure?

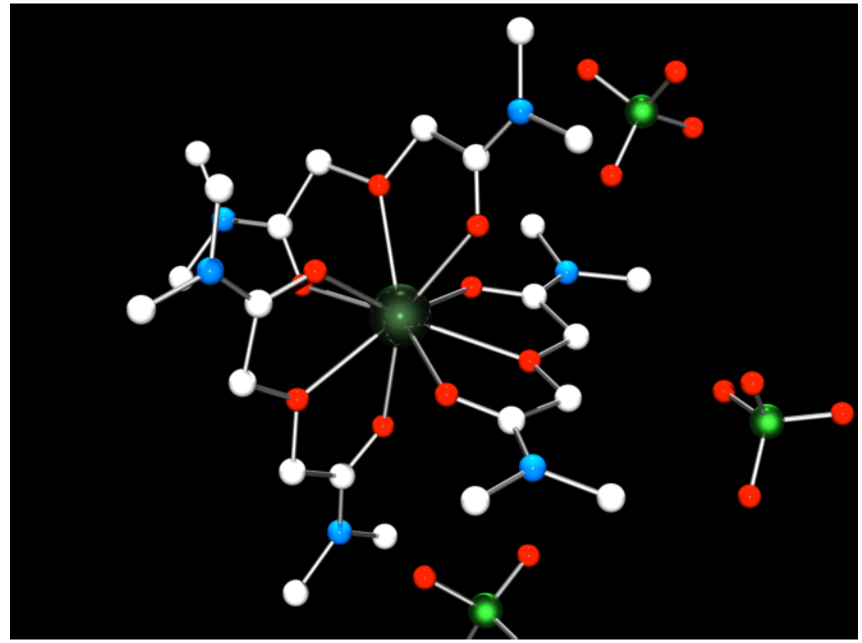


Crystal to Structure



Refinement & Validation





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

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

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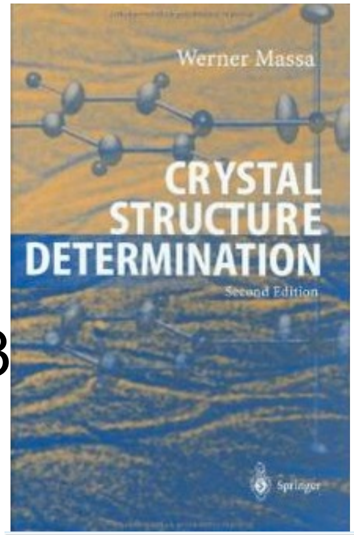
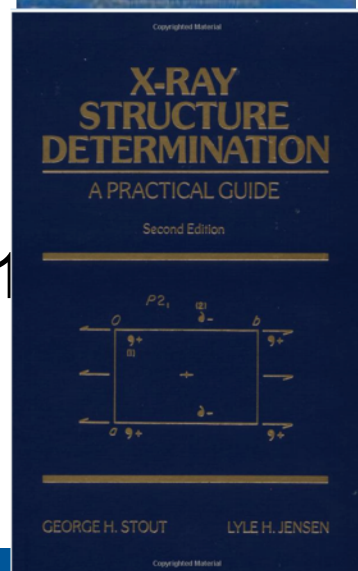
More Resources!!!

Books

- Werner Massa
  - ISBN-13: 978-3 540206446



- Stout & Jensen
  - ISBN-13: 978-047160711 3



Internet

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

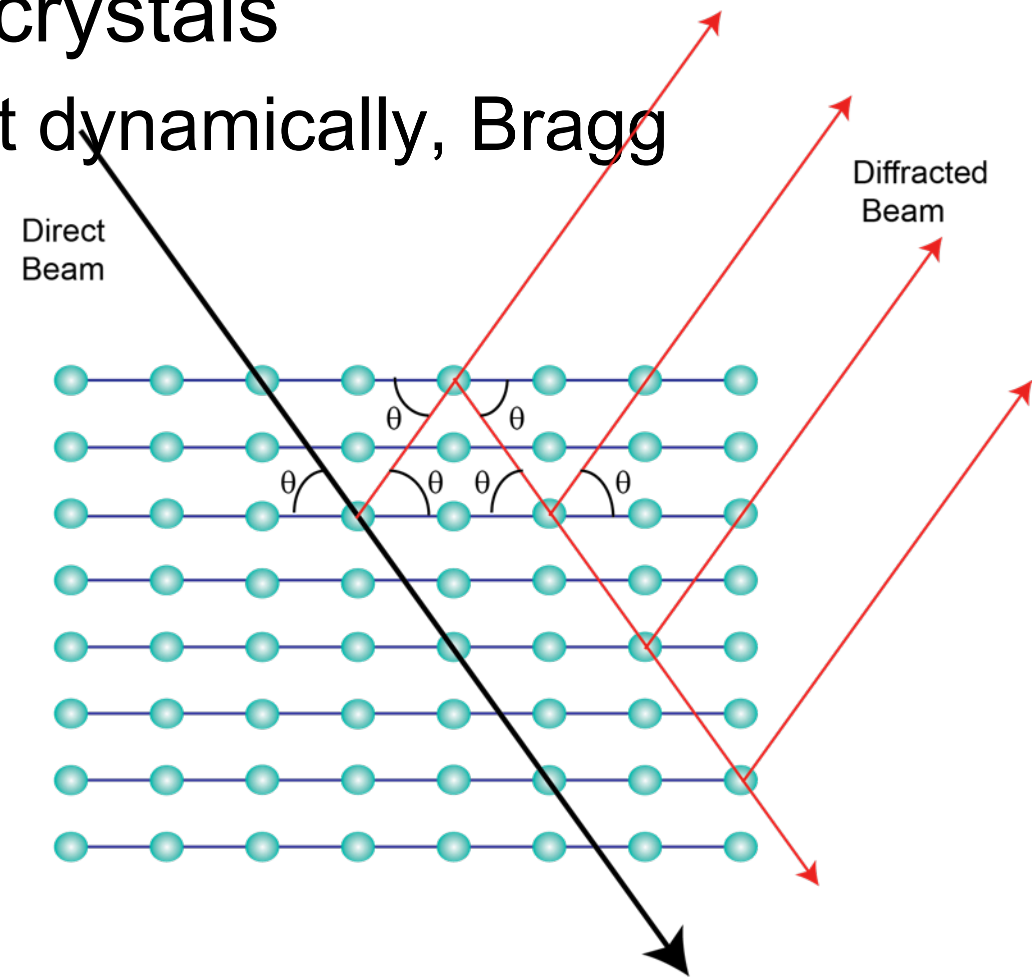
Small Molecule Crystallography at a Synchrotron
or
What can you do with more flux?

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?

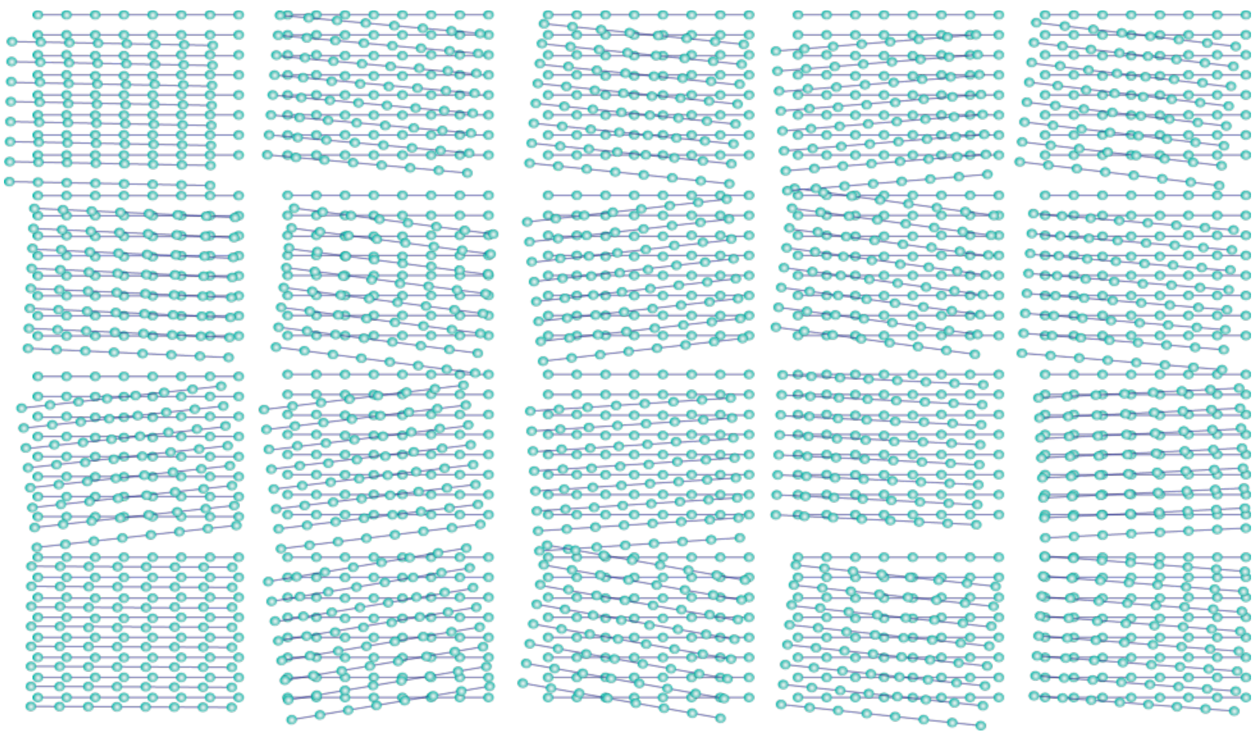
The Spectrum of Crystallinity

- Perfect crystals
  - Diffract dynamically, Bragg



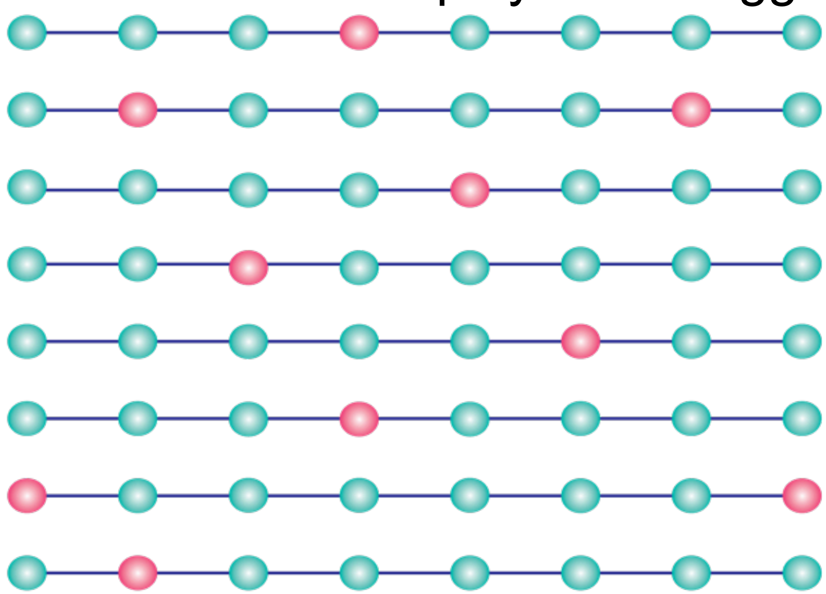
The Spectrum of Crystallinity

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

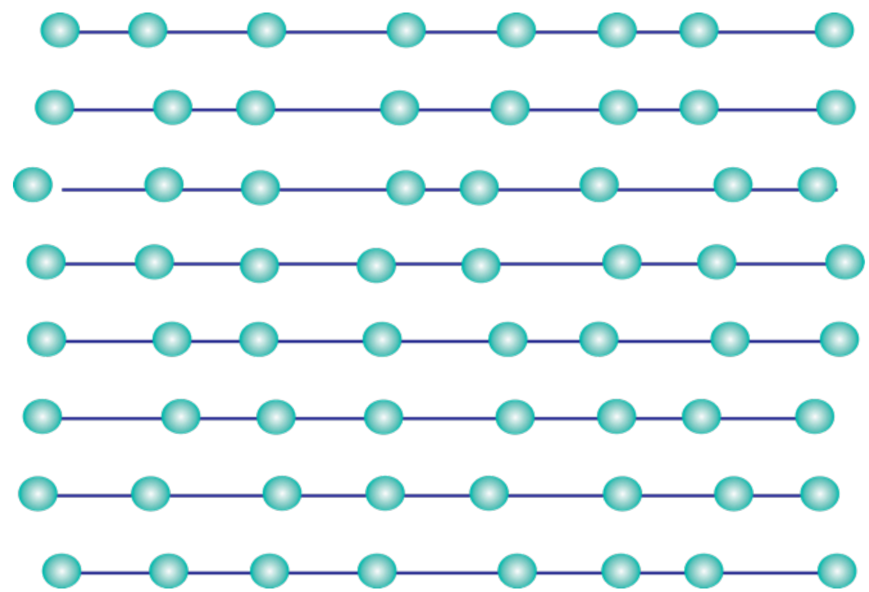


The Spectrum of Crystallinity

- 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

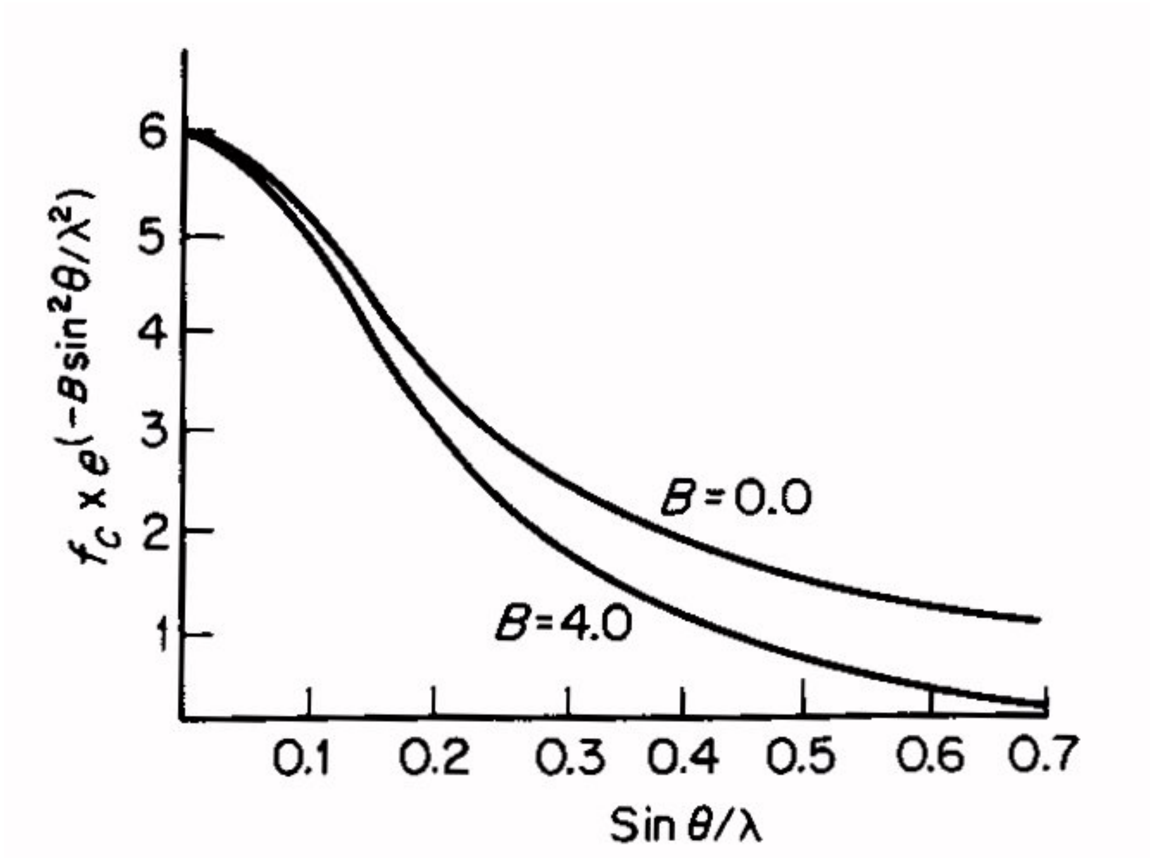
Scattering Efficiency

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

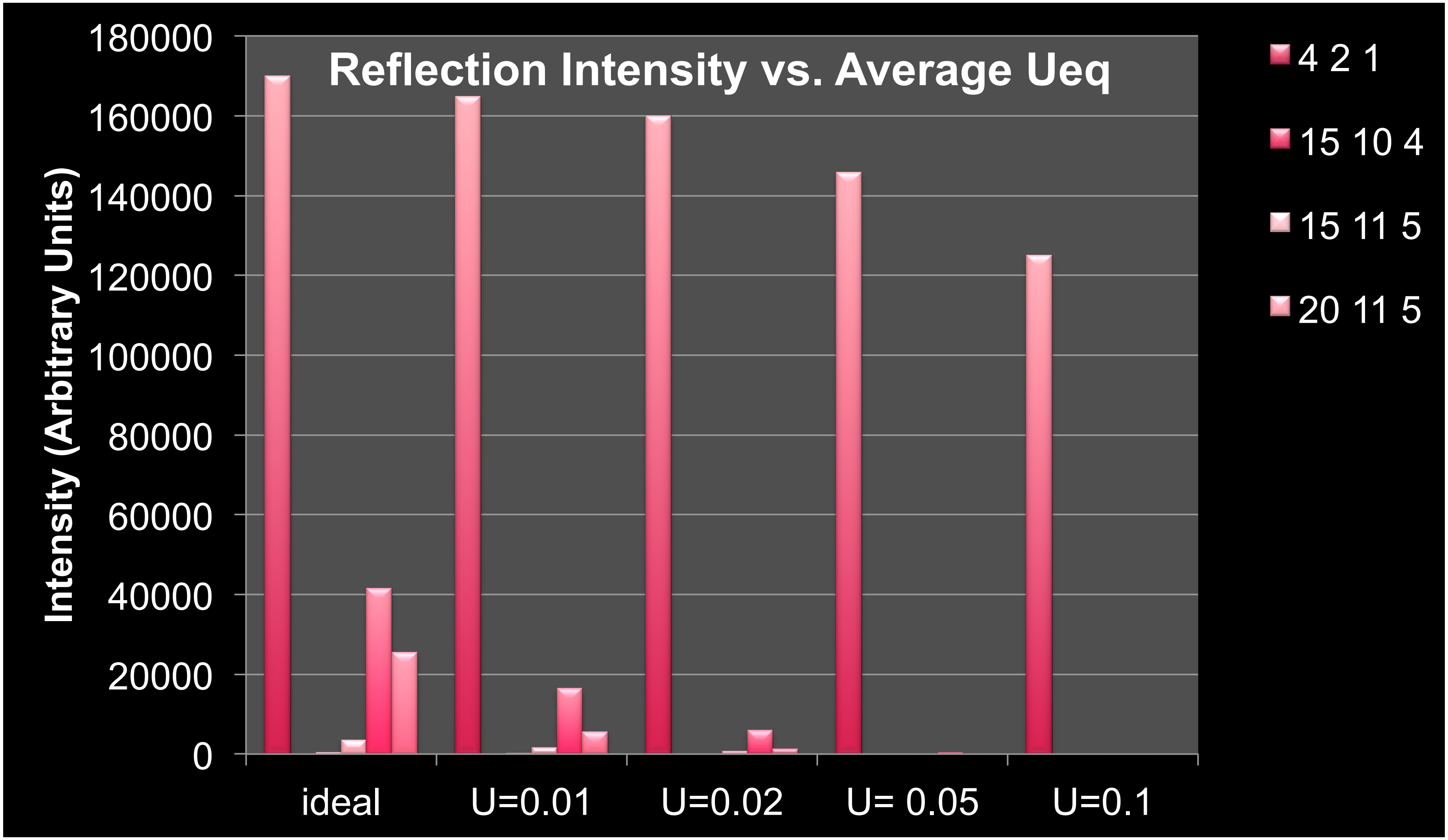
- where:-
- F = number of electrons per atom
- $V_{crystal}$ = volume of the crystal
- V_{cell} = volume of the unit cell

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

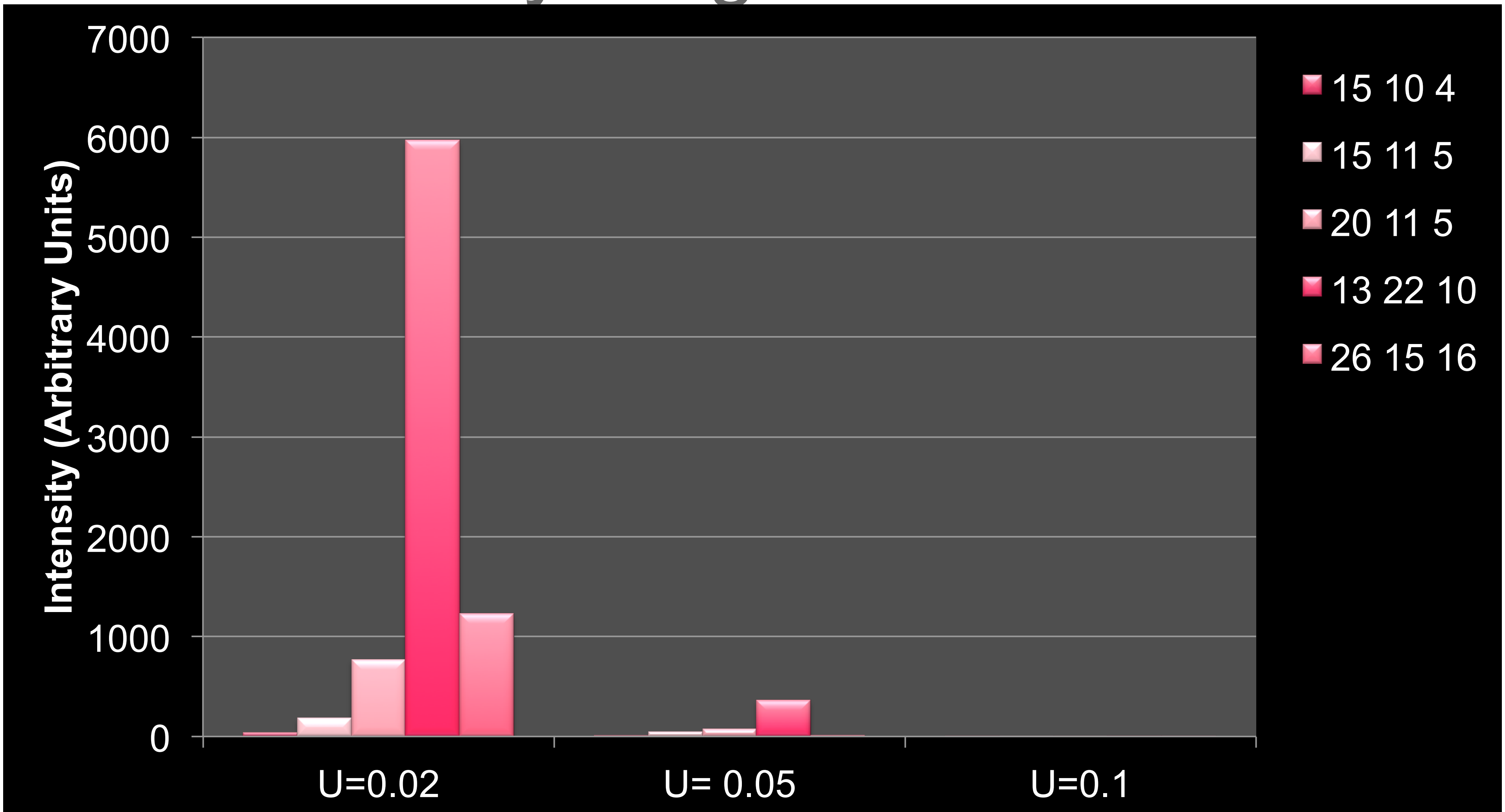
Effect of disorder



Intensity vs. Displacement



Higher Angle Reflections Affected by Larger ADPs



Wavelength

- The material and the wavelength need to be compatible
  - Short wavelengths better for heavy absorbers
  - 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

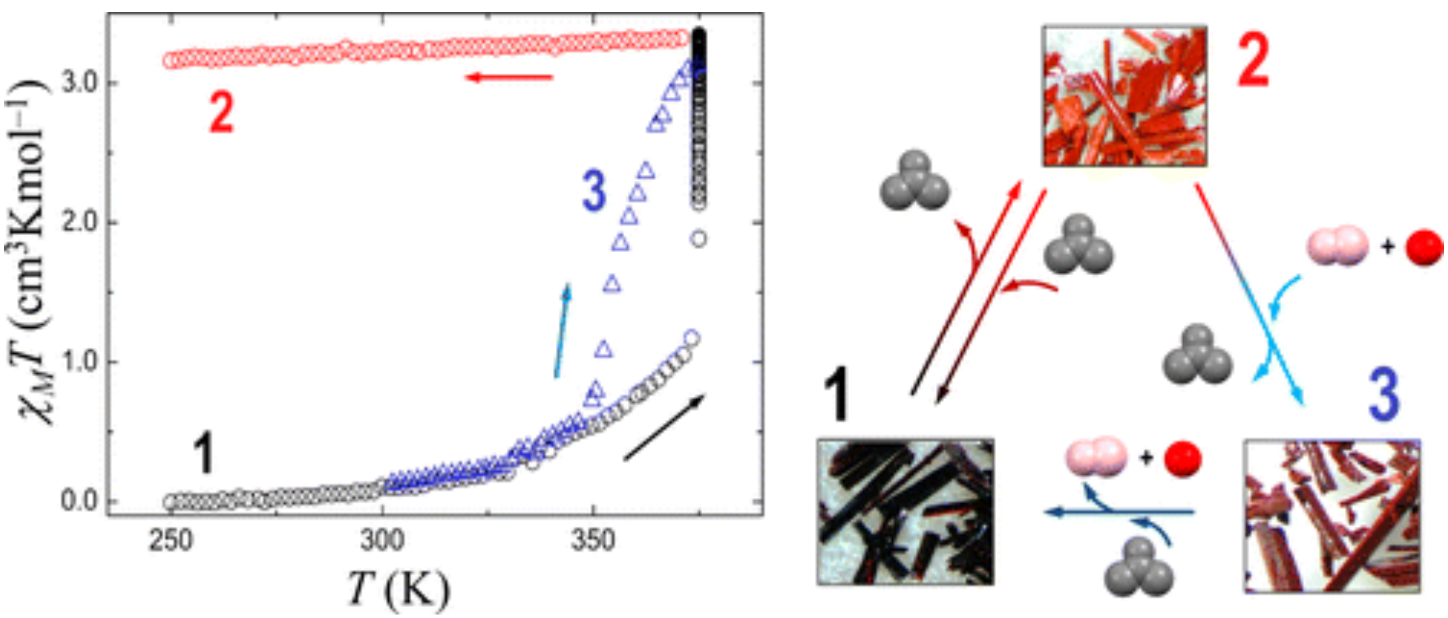
Structures from change:

IN SITU EXPERIMENTS

In-situ Crystallography

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

Desolvation

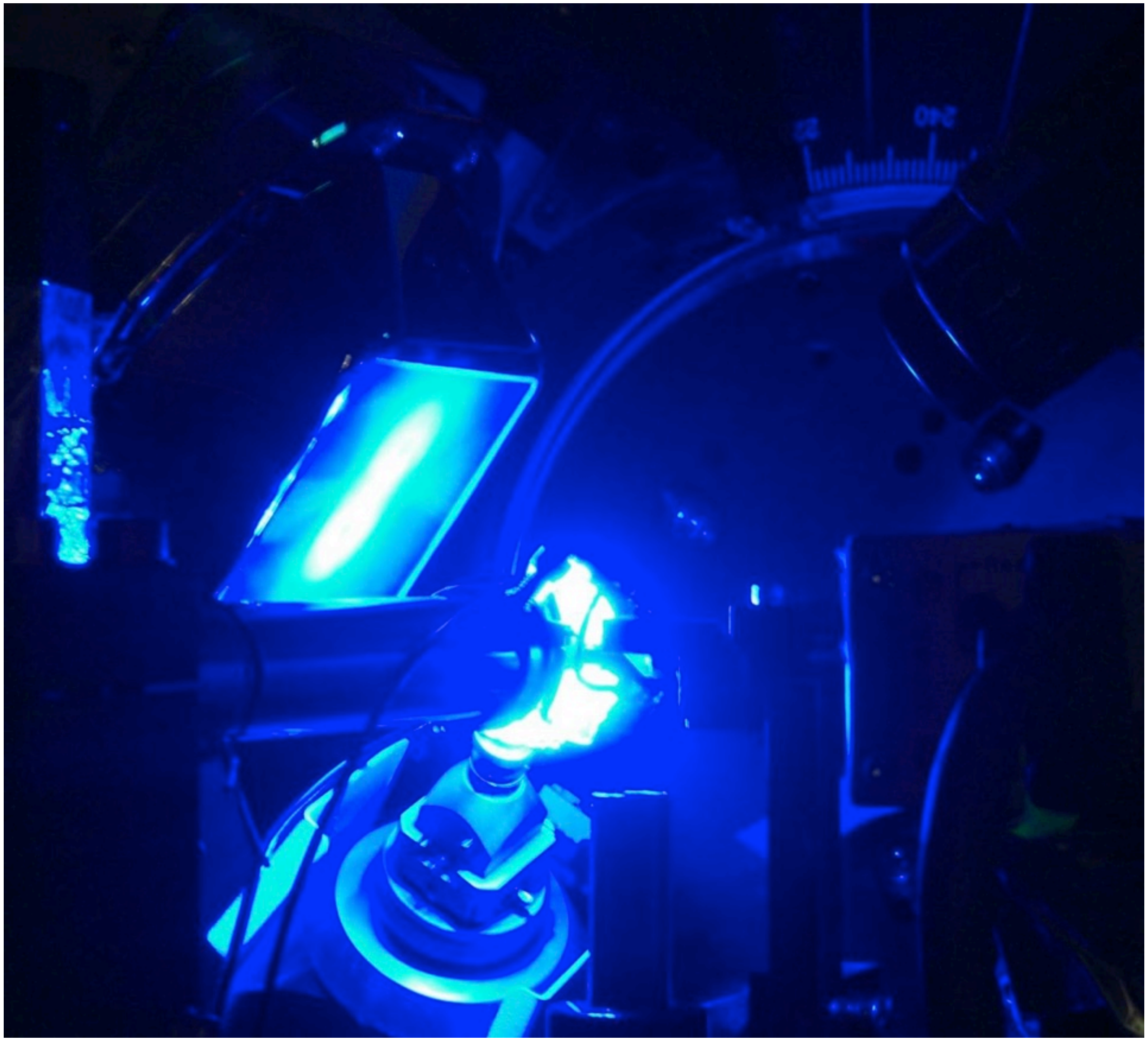


Three-Way Crystal-to-Crystal Reversible Transformation and Controlled Spin Switching by a Nonporous Molecular Material

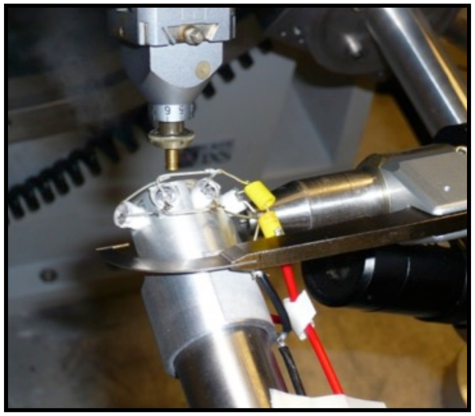
Sanchez Costa et al.,*J. Am. Chem. Soc.*, **2014**, *136* (10), pp 3869–3874

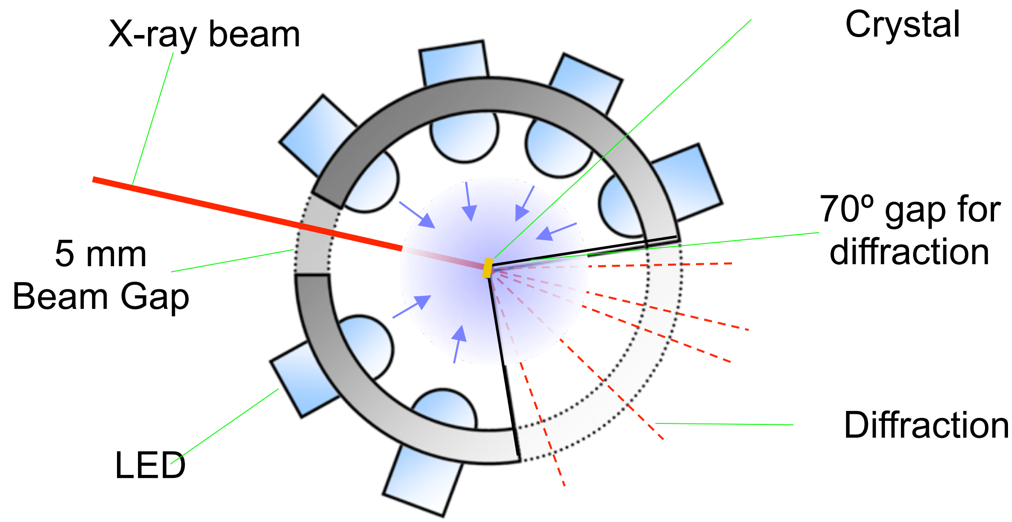
DOI: 10.1021/ja411595y

Photocrystallography



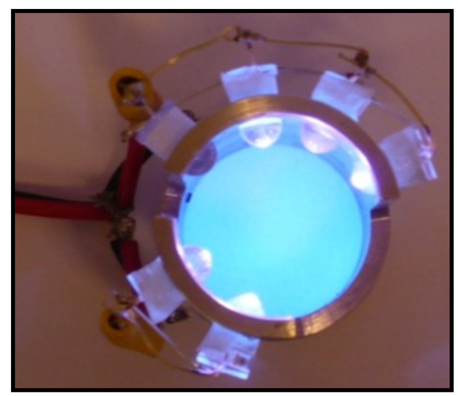
Experimental Procedure





Procedure

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



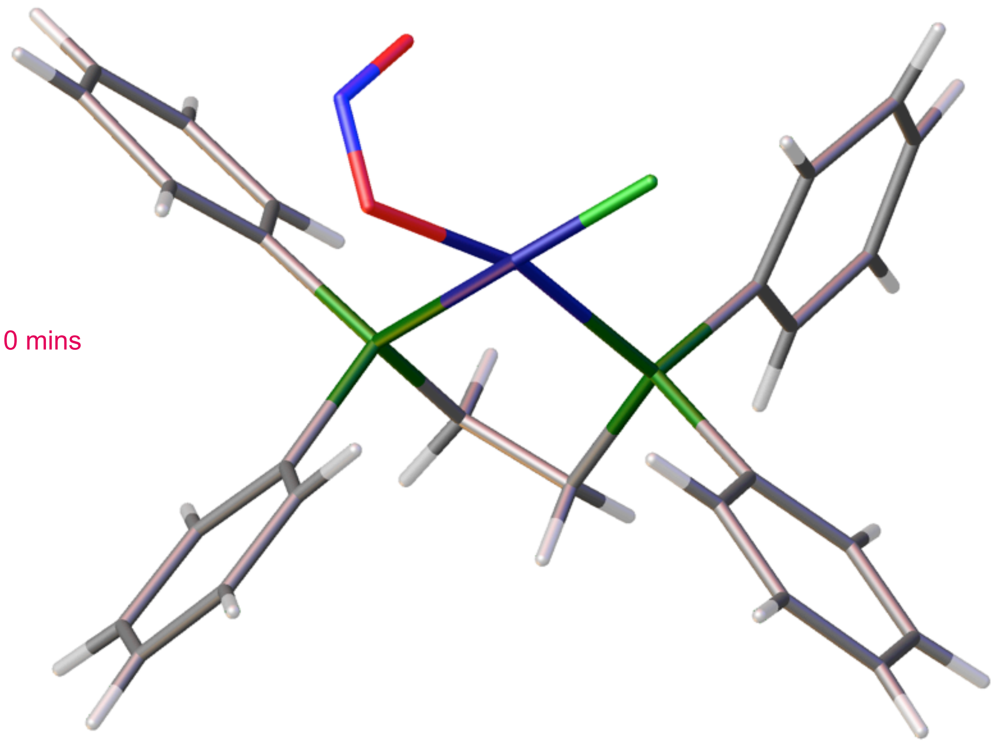
***N*-bound** nitro

***O*-bound** nitrito

0 % **No irradiation**

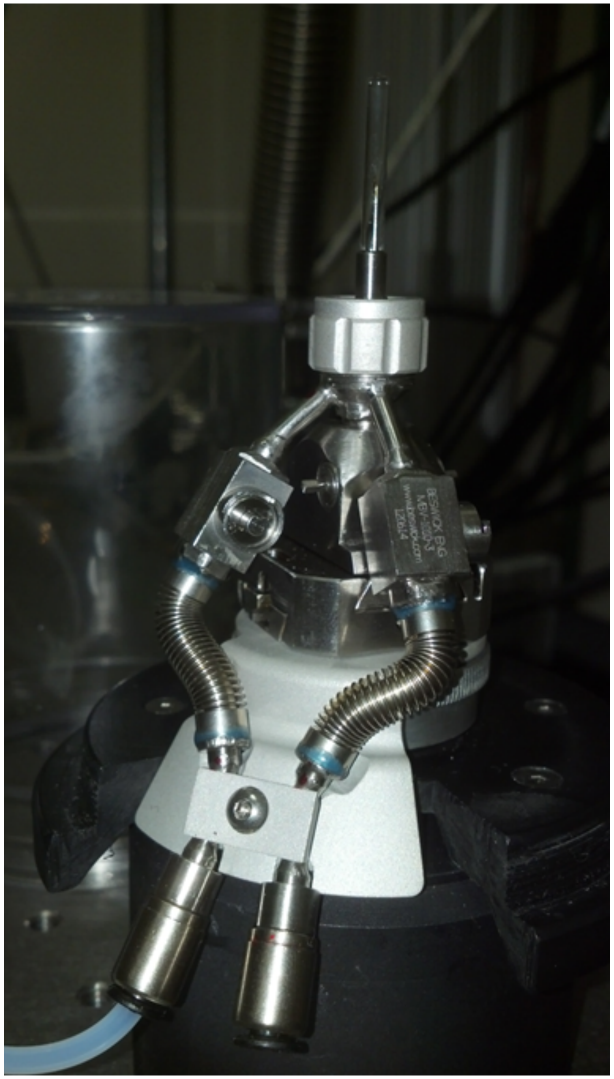
50 % **10 minutes irradiation**

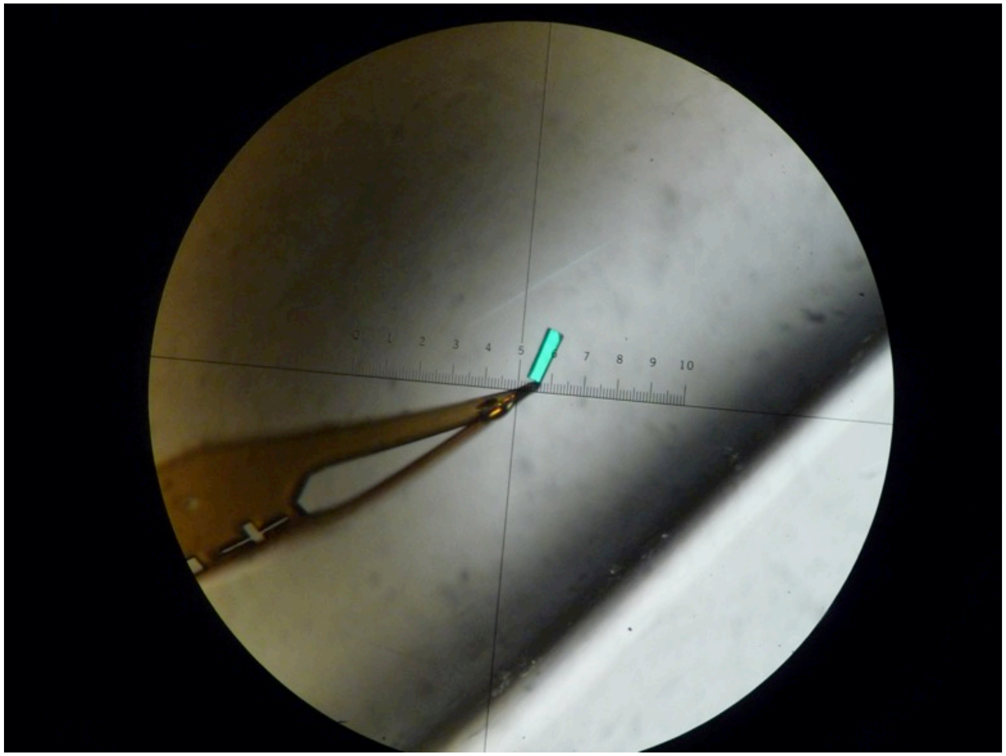
100 % **20 minutes irradiation**



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

Gas Cell





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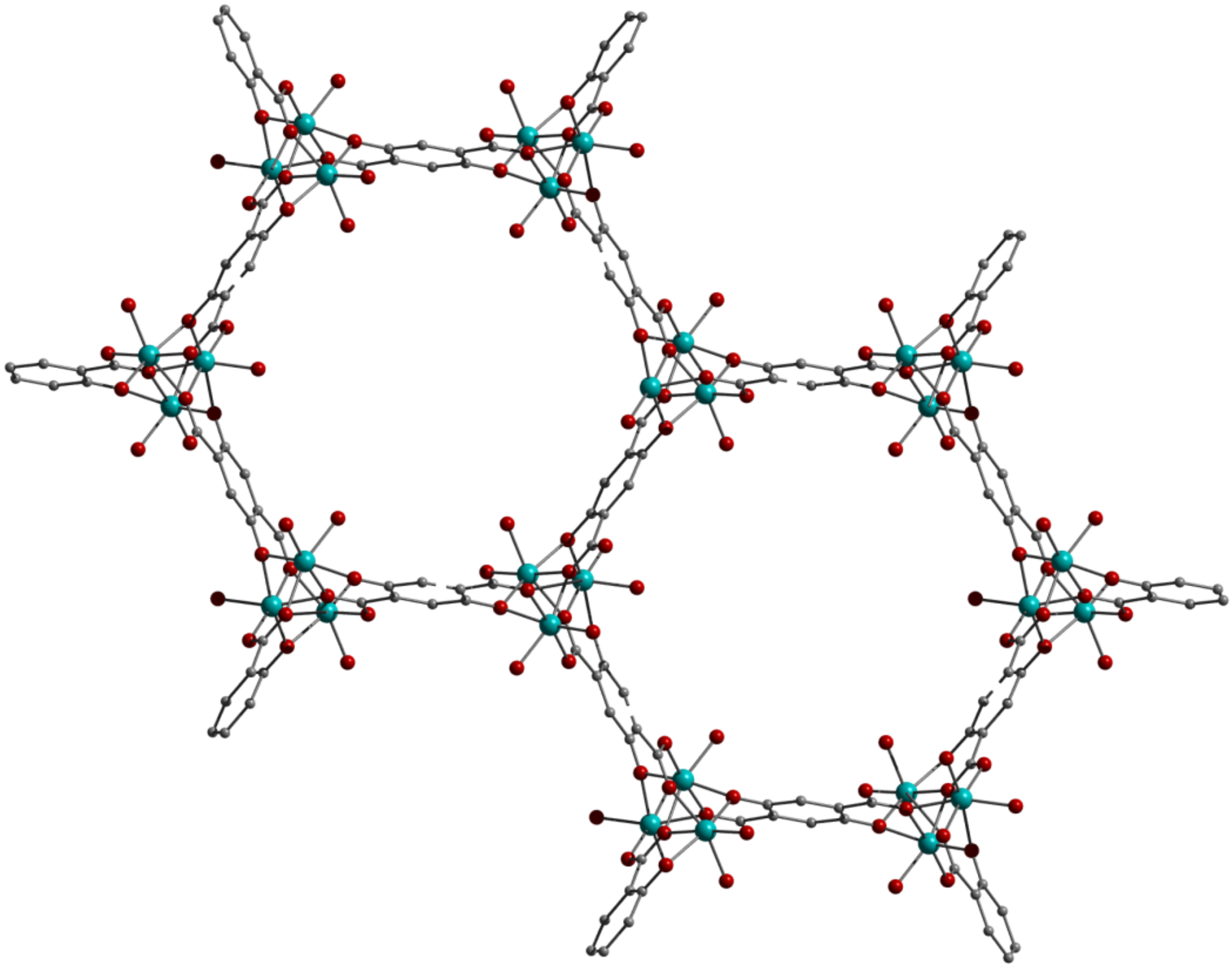
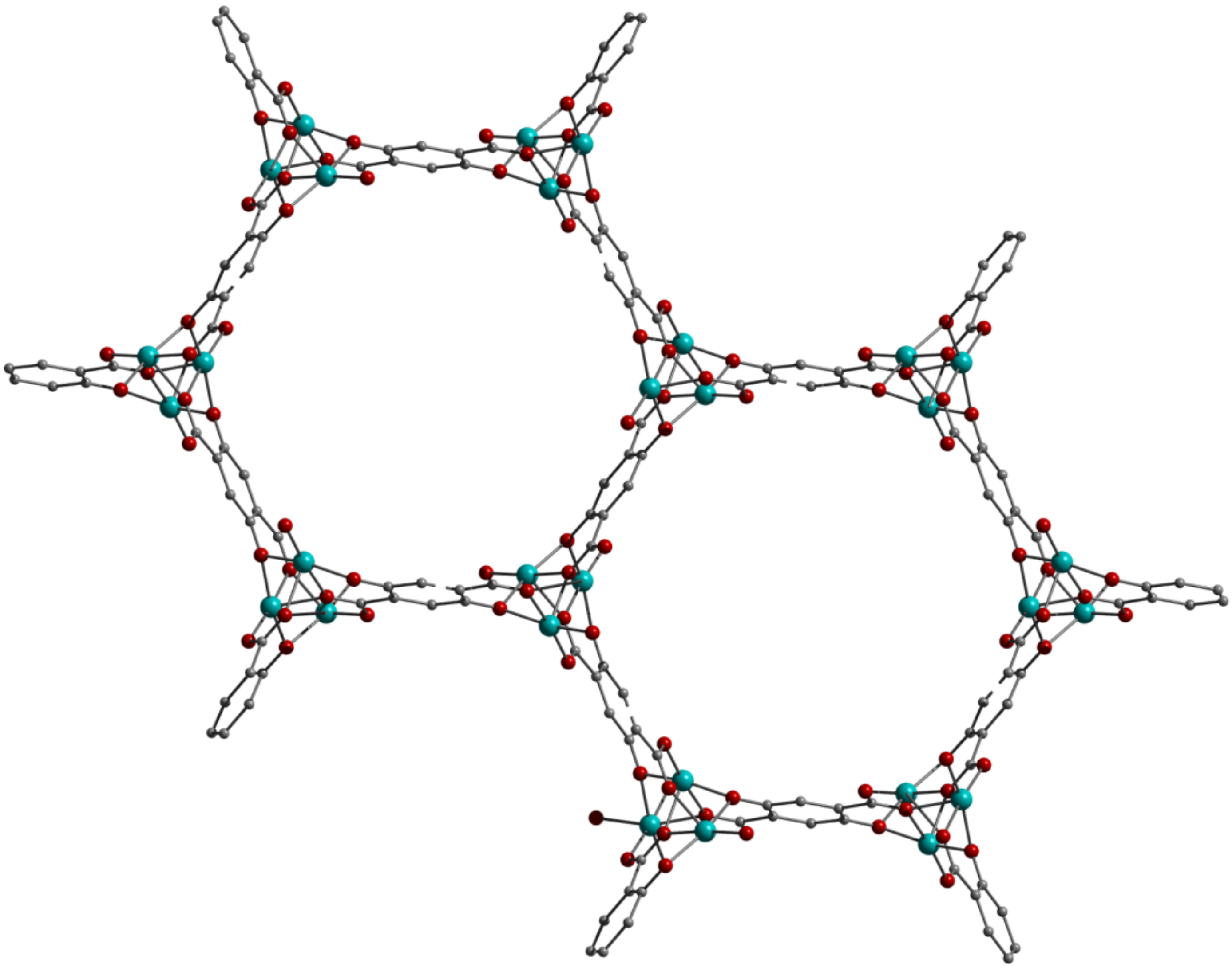
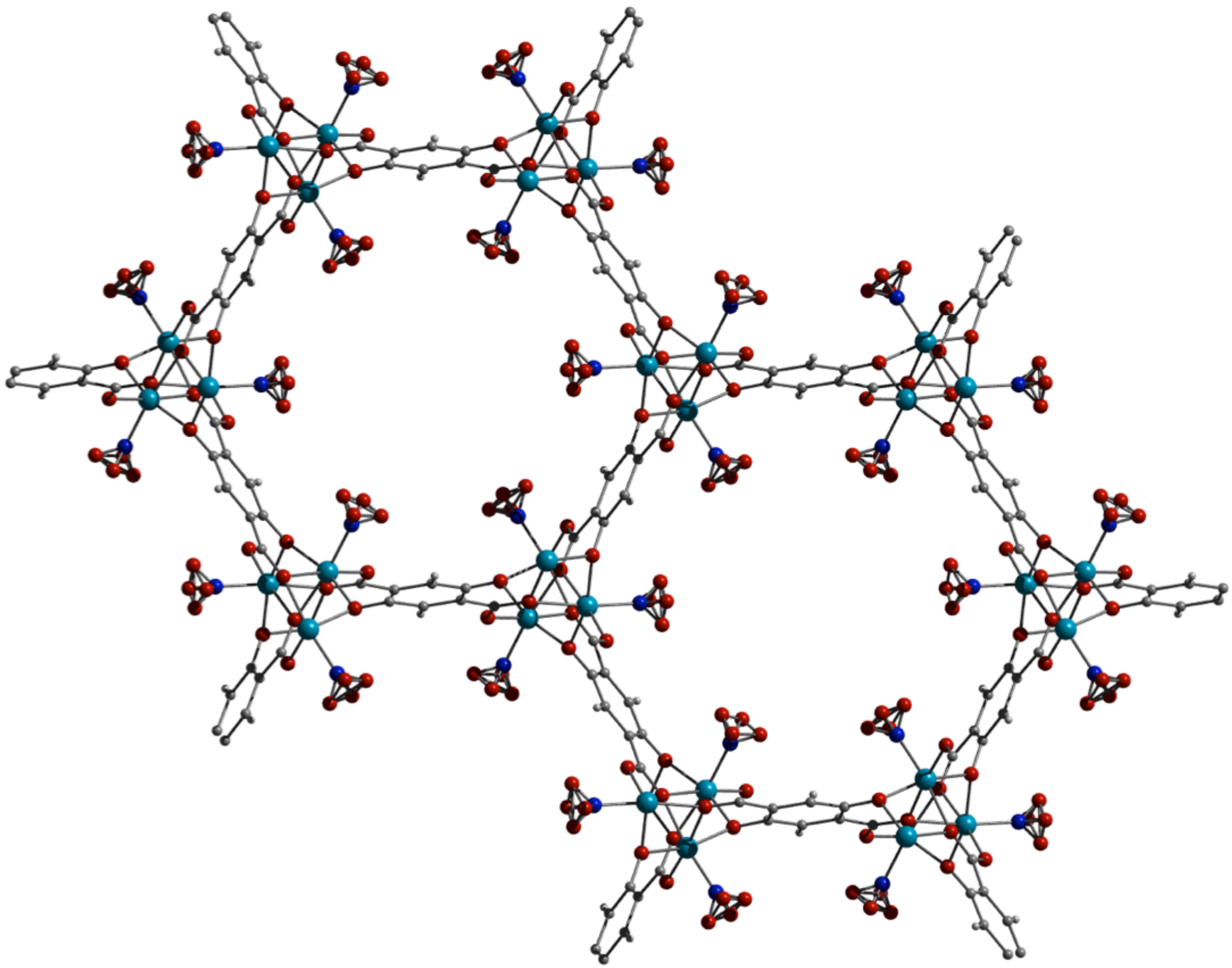
Hydrated MOF



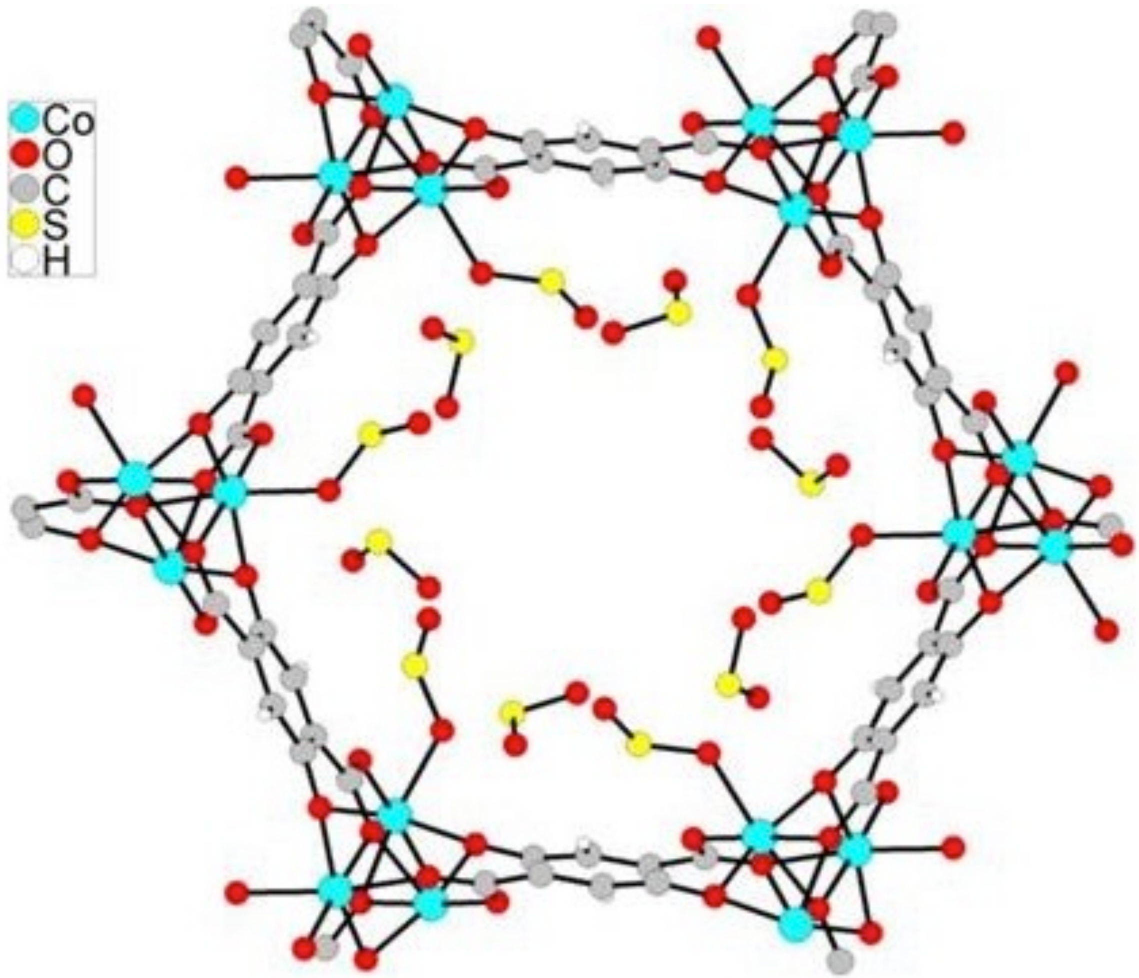
Dehydrated



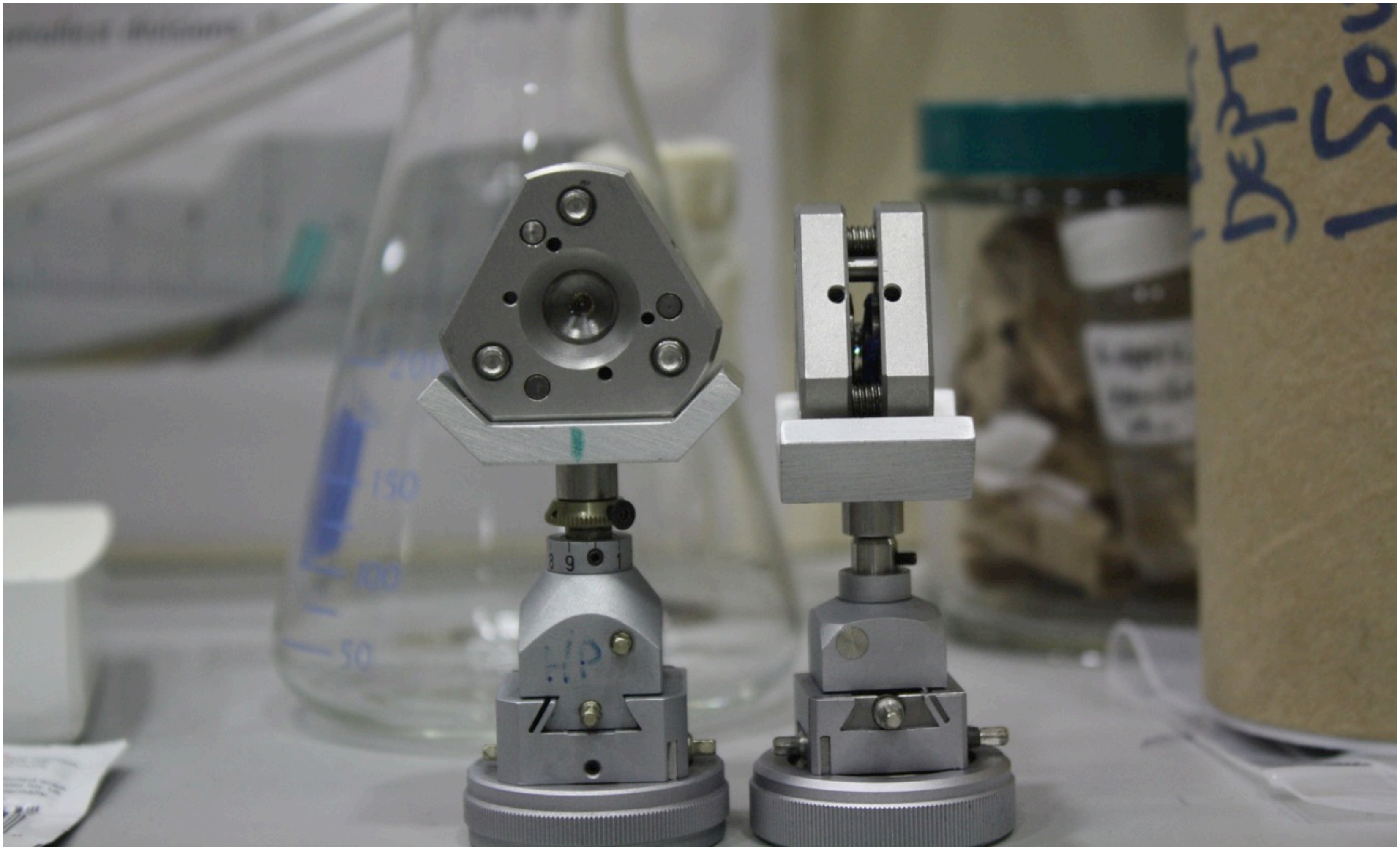
NO absorbed



SO_2 absorbed



High Pressure with Diamond Anvil Cells



Diamond Anvil Cell (DAC)

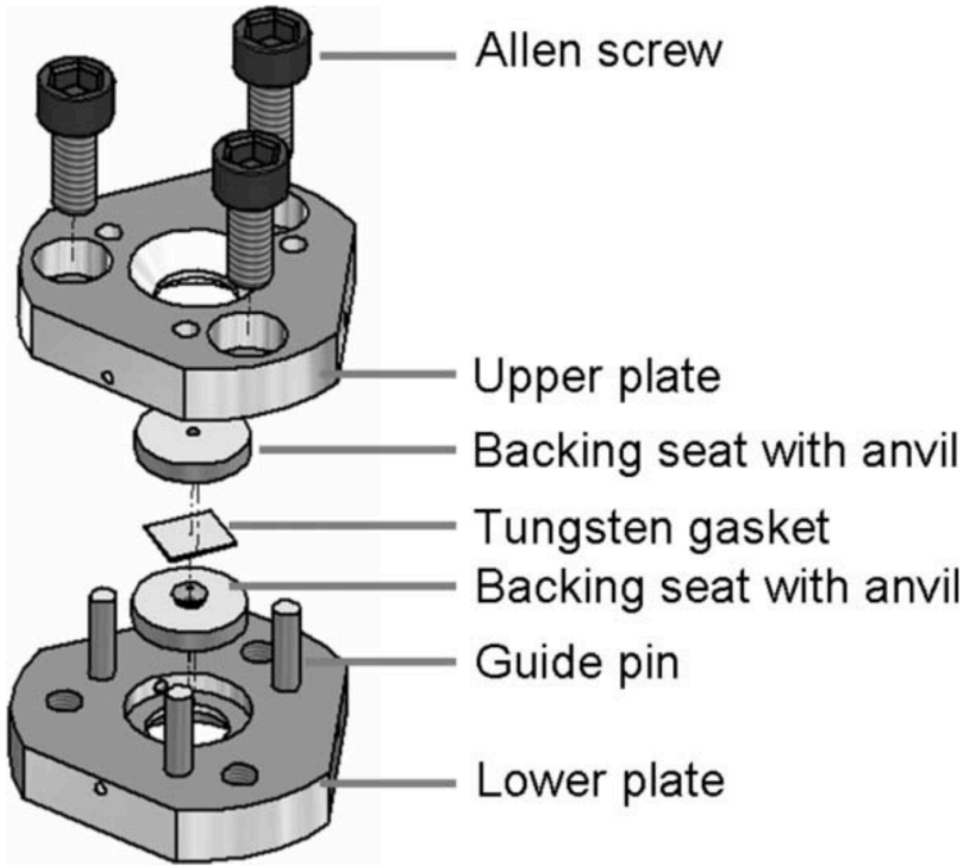
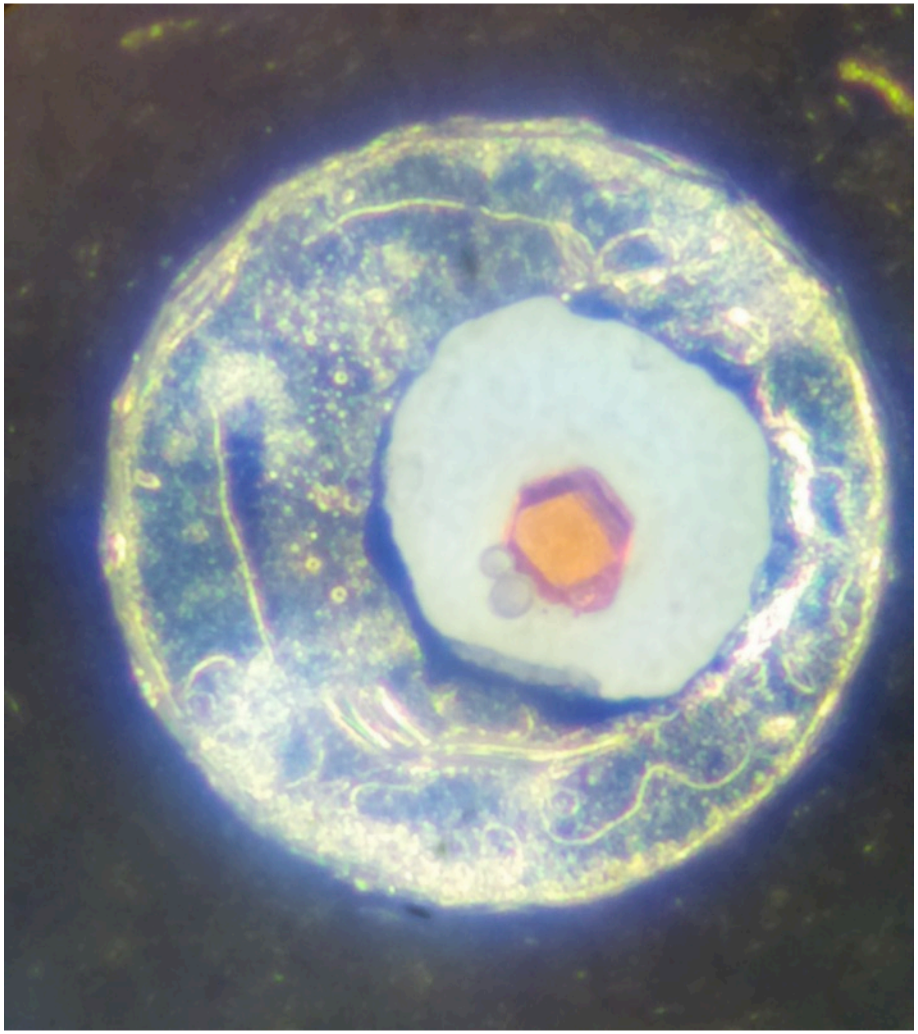


Figure 2
Exploded view of a Merrill–Bassett DAC.

Moggach, S. A. et al. *J. Appl. Crystallogr.* **2008**, *41*, 249-251.

A High Pressure Sample



The Zinc-Alkyl Gate (ZAG) Family

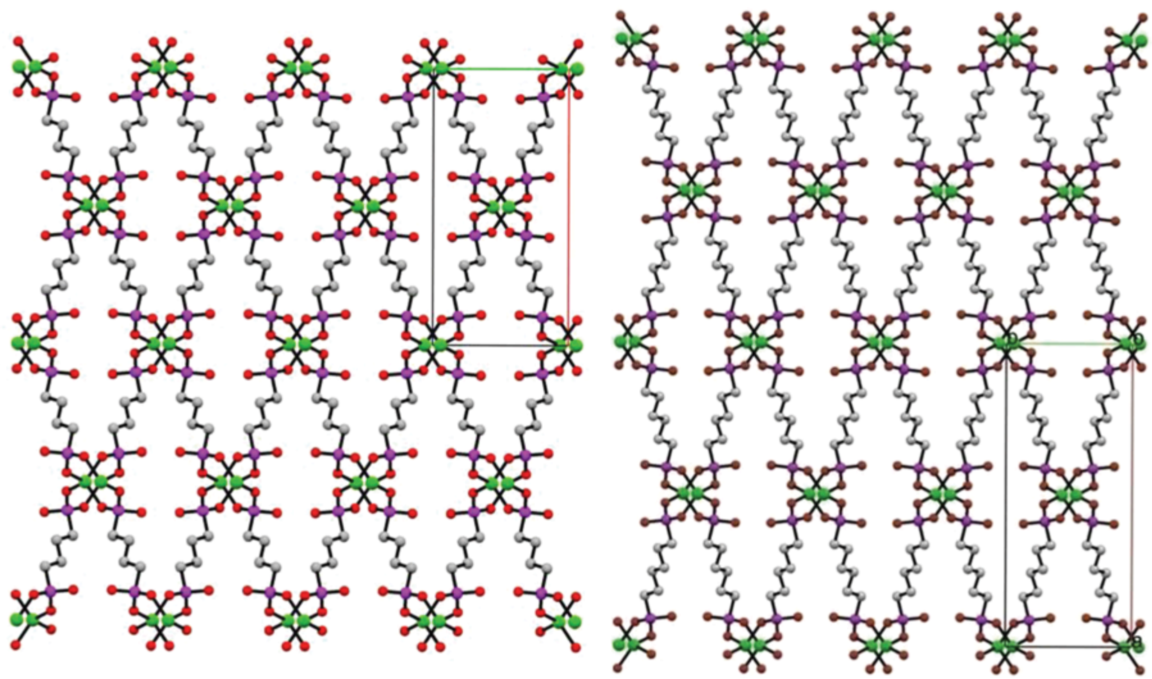
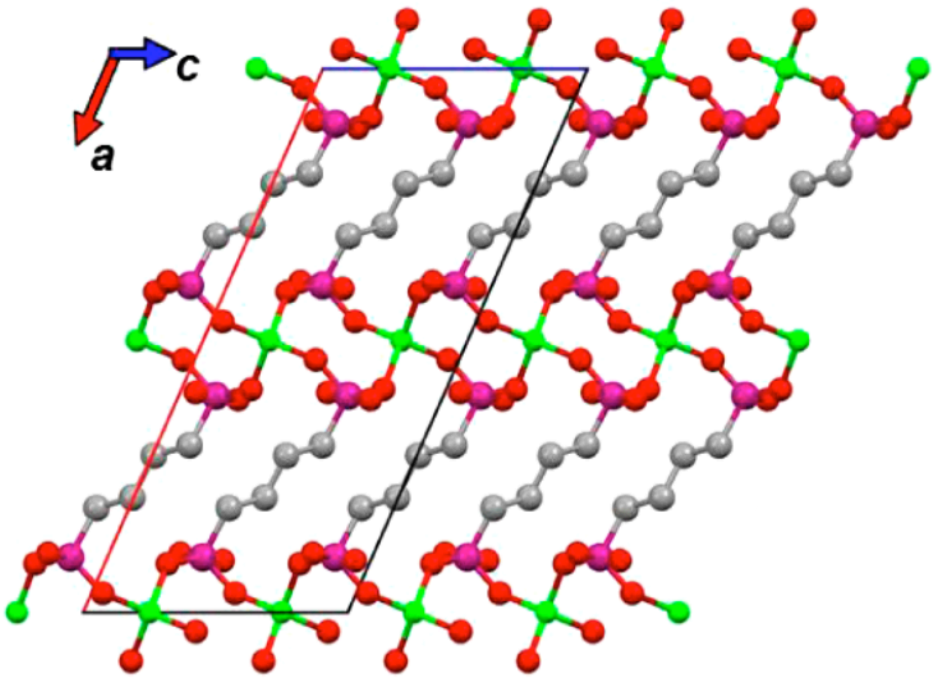


Figure 4. Comparison of ZAG-4 (left) and ZAG-6 (right) as viewed down their *c*-axes.

1037 dx.doi.org/10.1021/cr2002257 | *Chem. Rev.* 2012, 112, 1034–1054

ZAG-4, under pressure



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.

ALS

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Thank You!!