From X-rays to Point Groups, one step at a time

CCCW25

June 20, 2025

Andreas Decken (via Brian Patrick via Kate Markzenko via Mike Katz)

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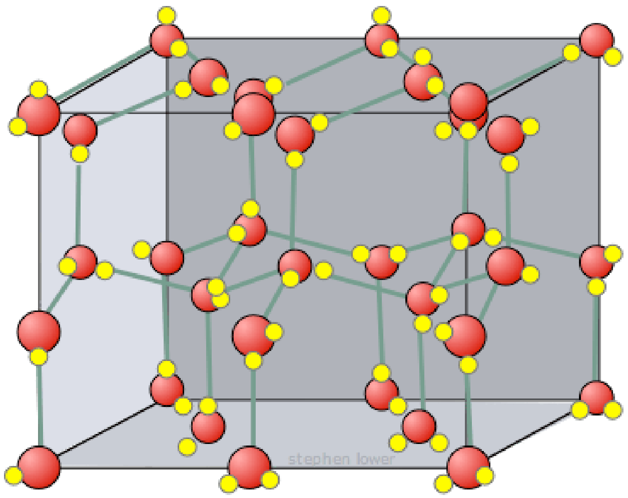
Introduction

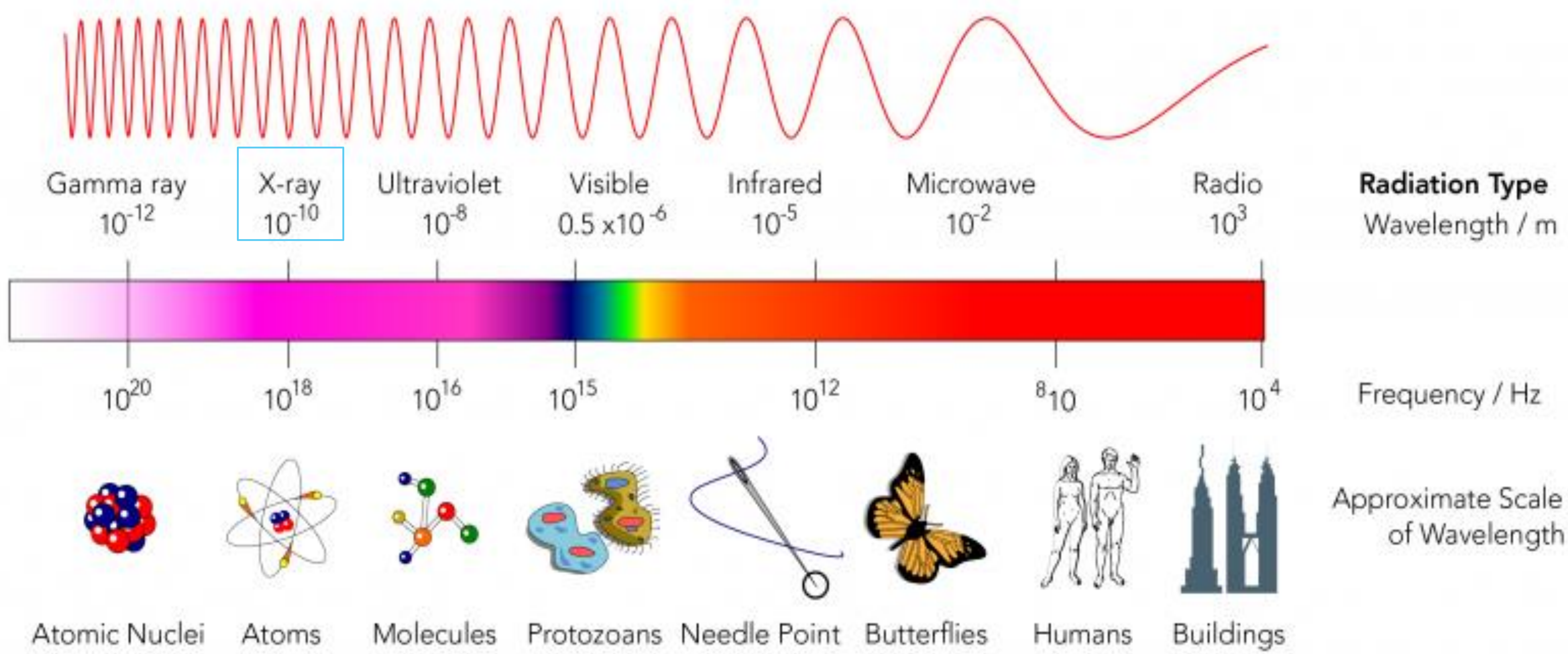
Understanding the Structure of Materials

- We use **crystallography** to understand the structure of **crystalline** solids.
  - Crystallography: The study of *crystal structures*.
  - Crystal structure: A description of the ordered arrangement of atoms, ions, or molecules in a crystalline solid.
  - Crystalline solid: A material whose constituents are arranged in a high order, forming a crystal lattice
  - Crystal lattice: 3D arrangements of atoms in a crystal
  - Crystal: or crystalline solid…
  - Why do you care about the structure of your crystalline solids?



Hexagonal Ice, I_h

Electromagnetic Radiation



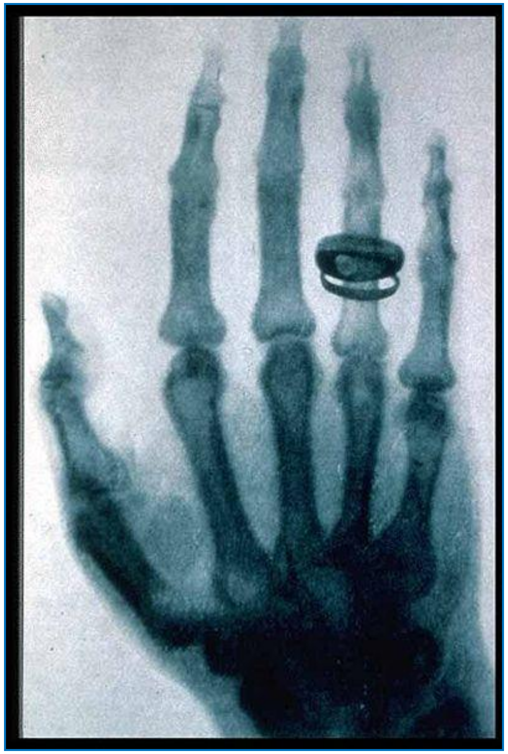
- Observing small objects requires short wavelength
- X-rays can penetrate matter more easily than visible light.

A New Kind of Rays

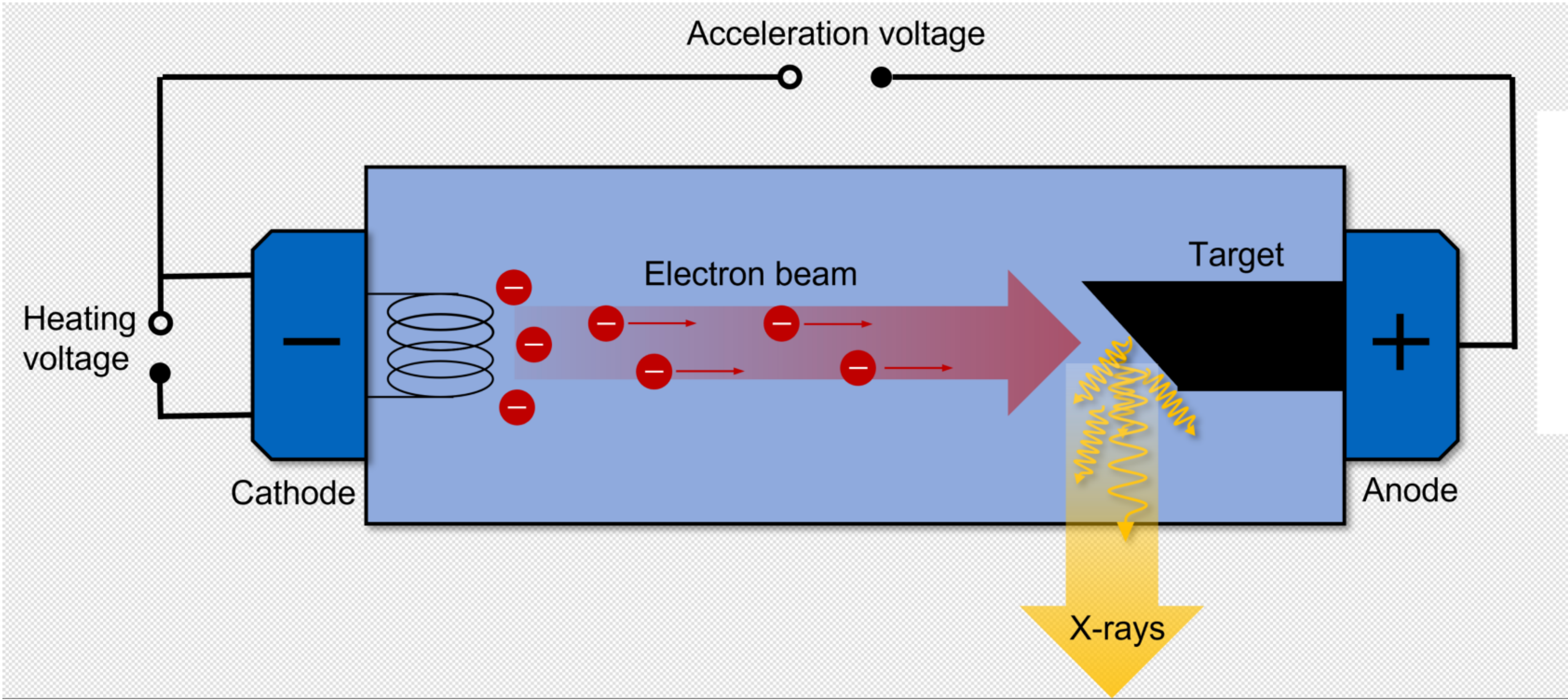
- Wilhelm Conrad Röntgen

He gave his first public lecture on X-rays in January 1896 and showed the rays' ability to photograph the bones within living flesh. A few weeks later in Canada, an X-ray was used to find a bullet in a patient's leg.

Röntgen deliberately didn't patent his discovery, feeling that scientific advances belonged to the world and should not be for profit.



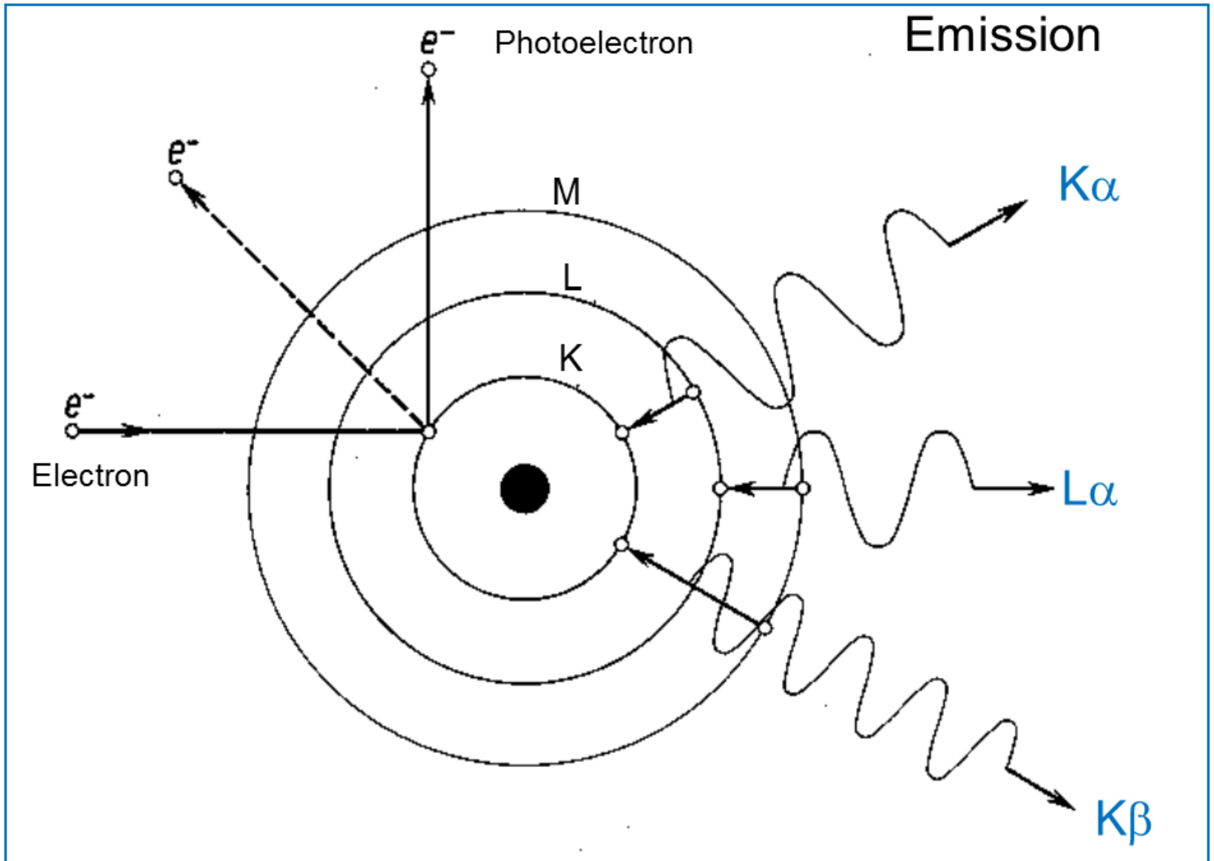
X-Ray Tube



Source: Andreas Eckmüller

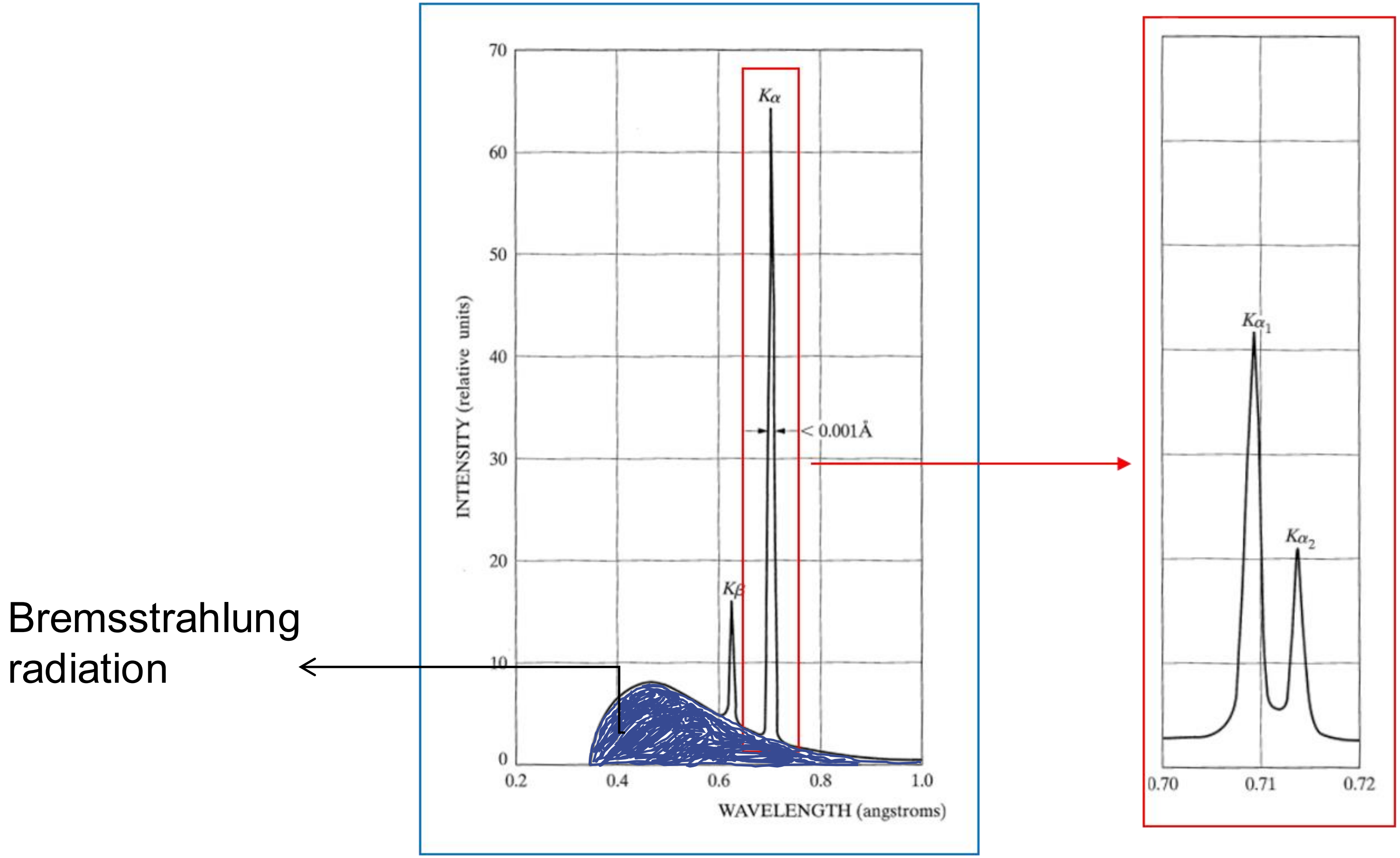
- Generation of lots of heat
- More powerful variants are Rotating X-ray sources
- Liquid Metal Stream
- Microfocus Tubes

Generation of Characteristic Radiation



- Incoming electron knocks out an electron from the inner shell of an atom.
- Designation K,L,M correspond to shells with a different principal quantum number.

Emission Spectrum of an X-Ray Tube: Close-up of Kα



Cullity, B.D. and Stock, S.R., 2001, Elements of X-Ray Diffraction, 3rd Ed., Addison-Wesley

Characteristic Wavelength

The X-rays we use for diffraction have a wavelength of 0.7-1.5 Å.

- Cu radiation (1.54 Å)
  - Great for organic compounds and chiral molecules.
  - Diffracted spots are more widely spread; great for large unit cells.

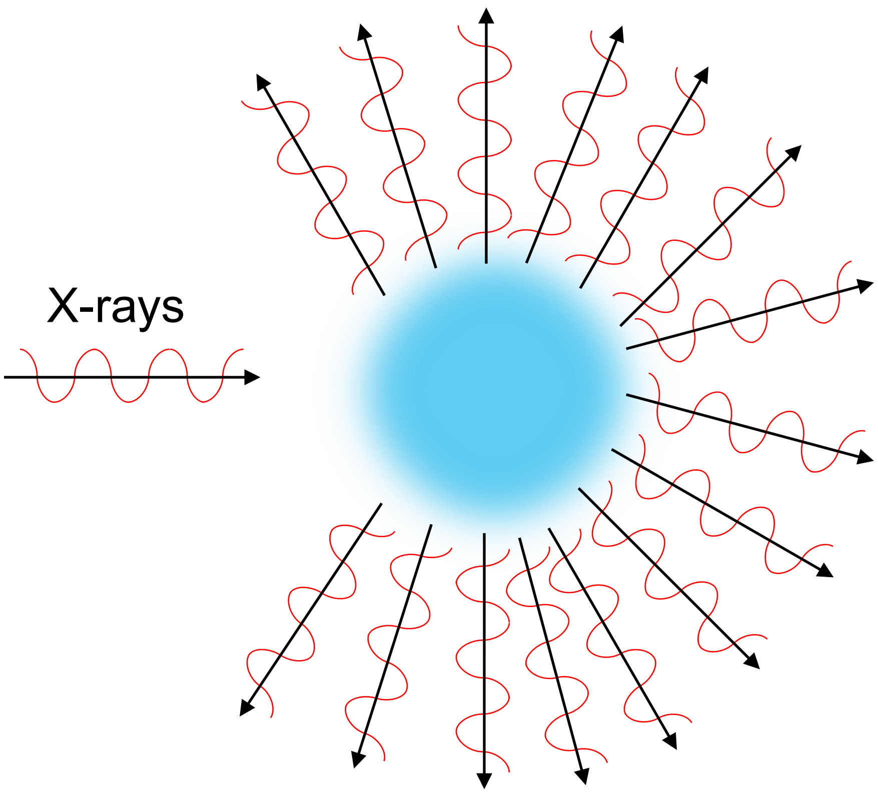
- Mo radiation (0.71 Å)
  - Great for inorganic compounds.
  - Fast data collection.

Element	Wavelength (λ) Å ($K\alpha_1$)
Ag	**0.5594**
Mo	**0.7097**
Cu	**1.5405**
Co	1.7889
Fe	1.9360
Cr	2.2896

PXRD Analysis

X-Ray Scattering

How does electromagnetic radiation interaction with matter?

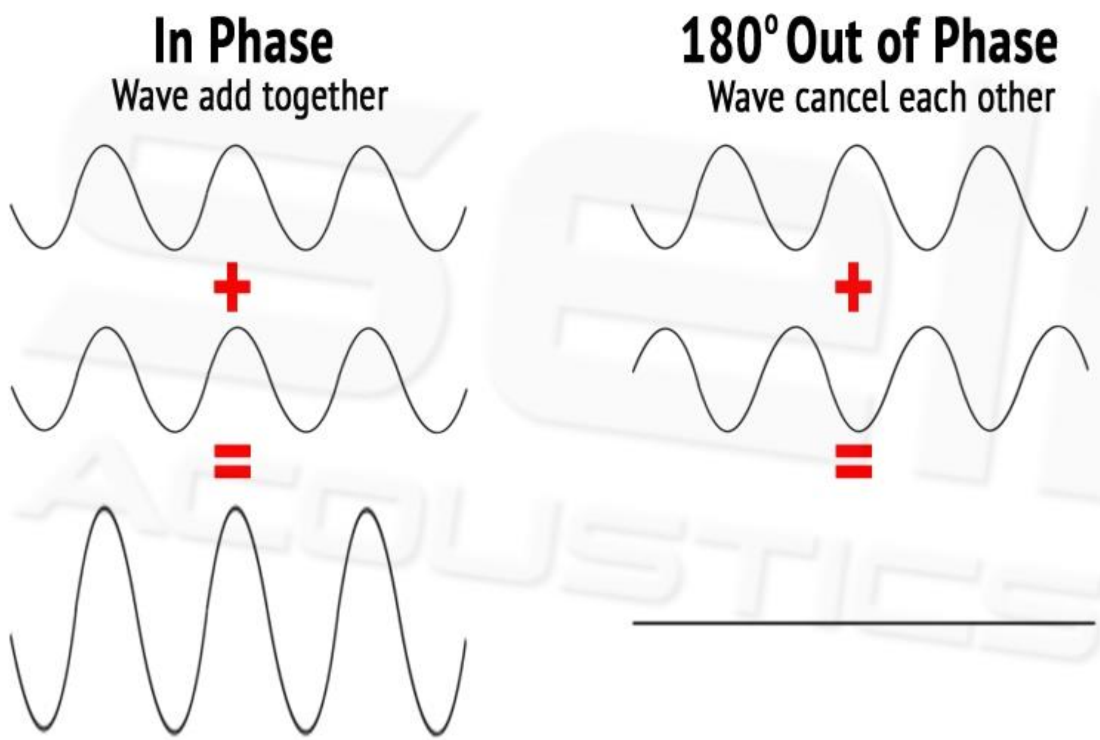


- X-rays interact with the electrons in an atom, causing them to change directions and scatter.
  - **Elastic**: Same wavelength and energy.
  - Inelastic: Different wavelength and energy.
- With multielectron atoms, the whole electron cloud oscillates.

X-Ray Scattering

What happens when we have more than one atom?

The scattered waves from each atom can **interfere** with each other.



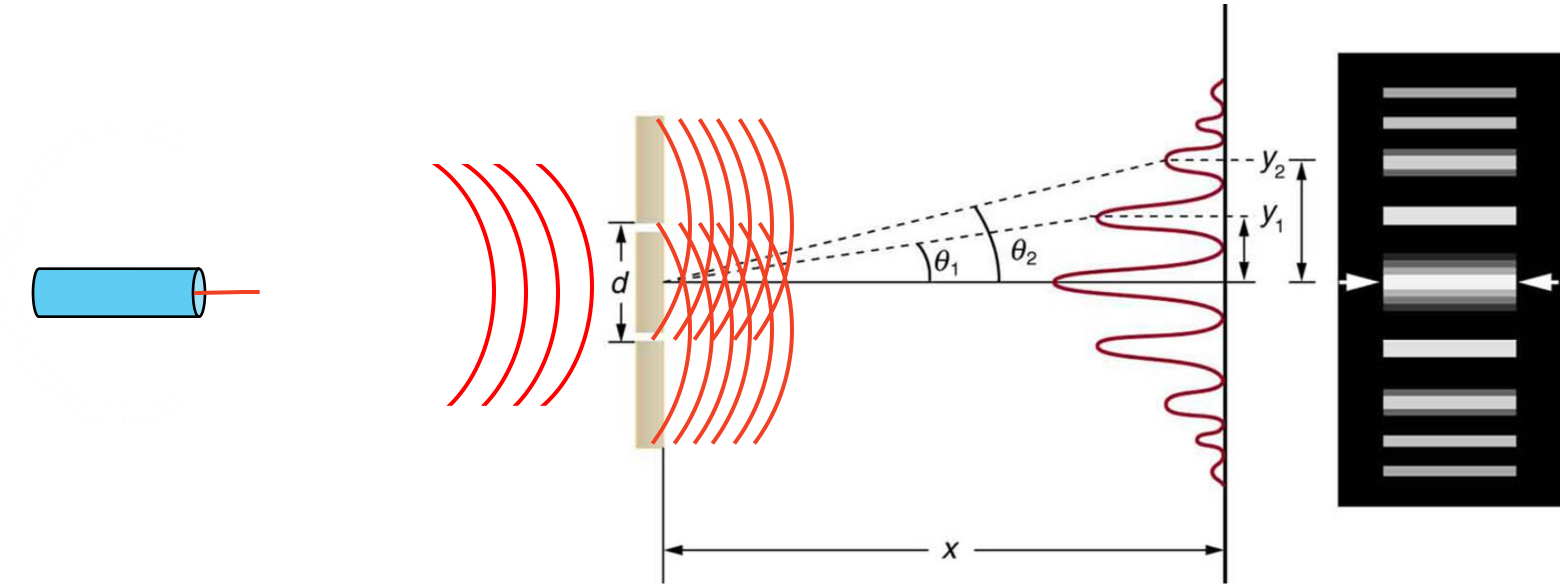
Constructive Interference

Destructive Interference

Source:

X-Ray Scattering

Young's Double Slit Experiment

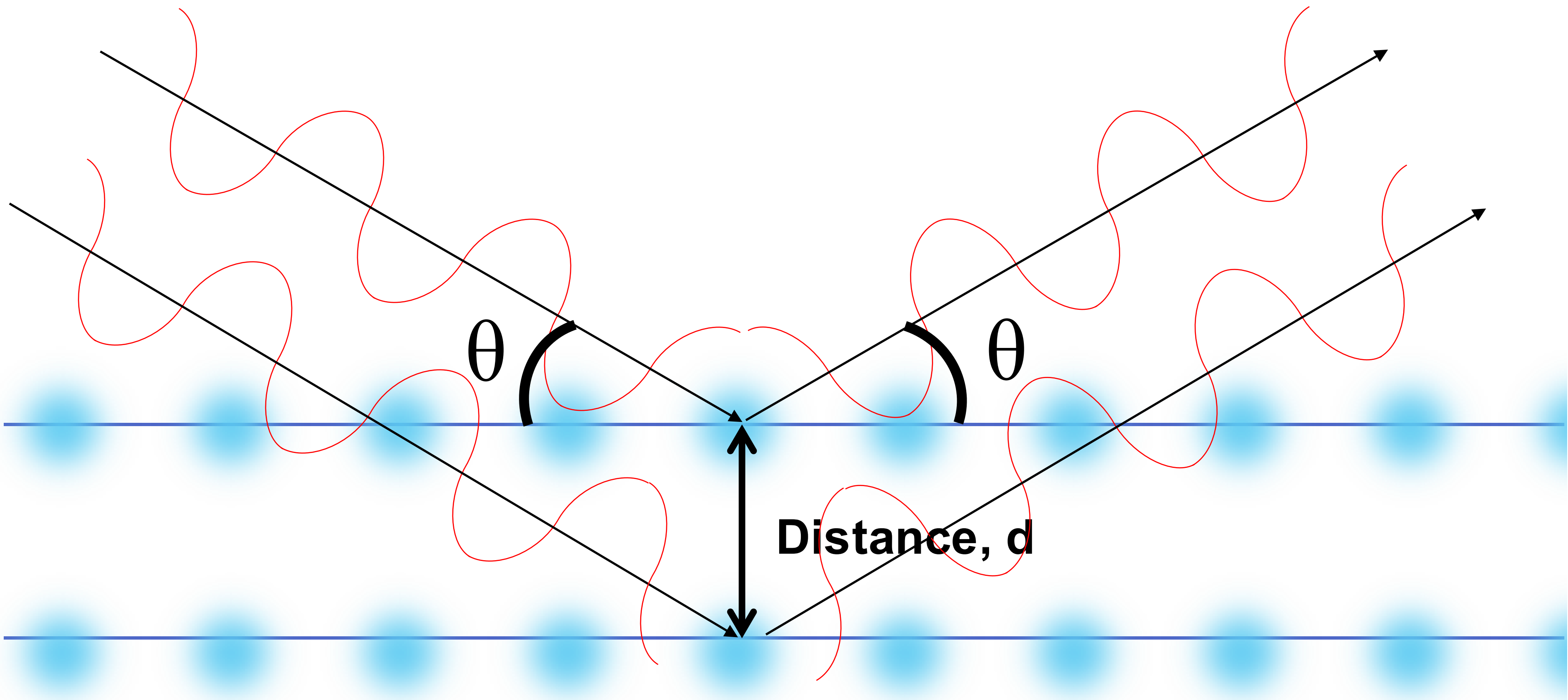


- Light passing through the slits creates two separate wavefronts that can interfere either:
    - Constructively (amplitudes of waves add).
    - Destructively (amplitudes of waves cancel).

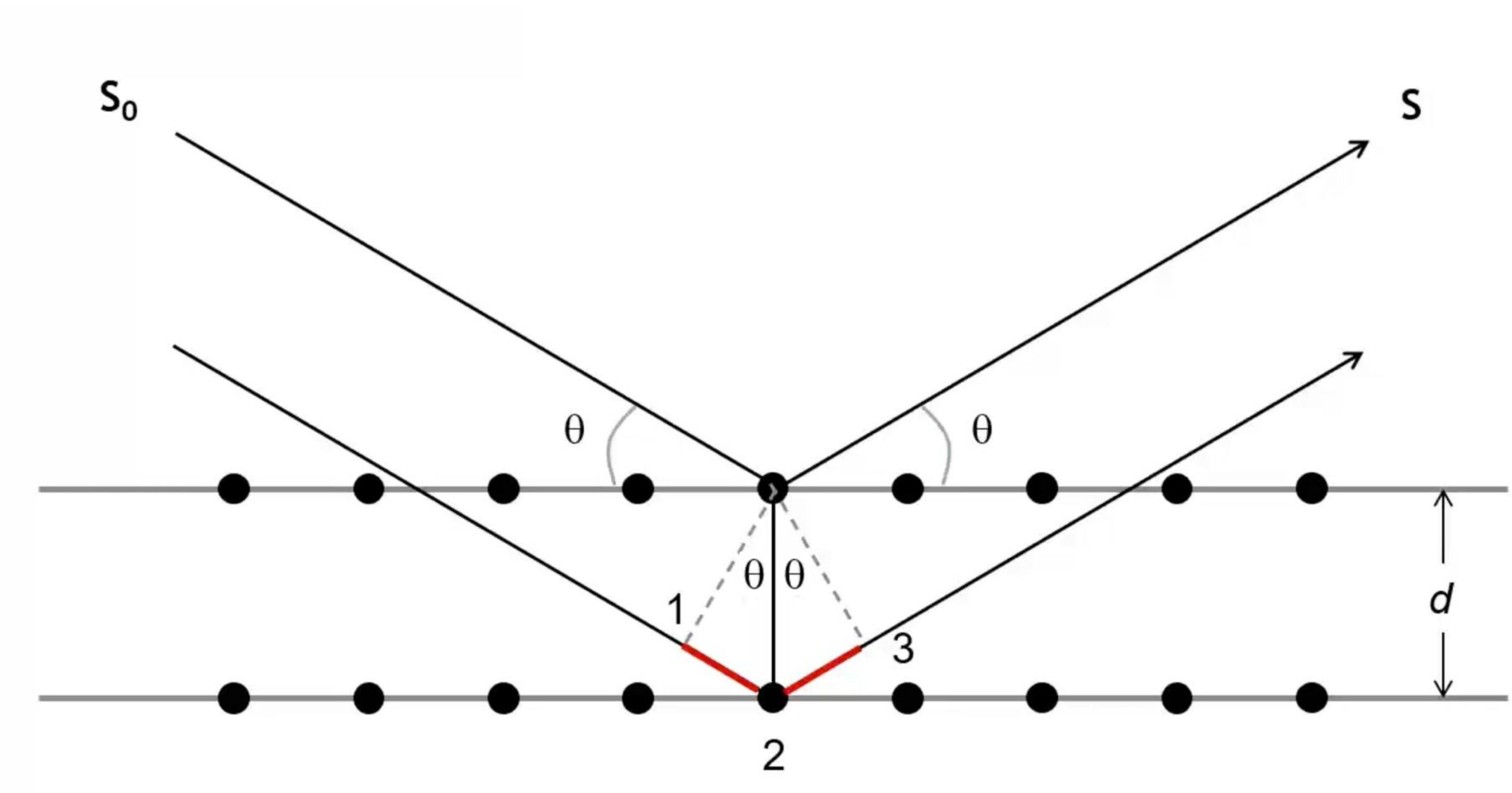
Bragg's Law

Model

- Crystal is a set of discrete parallel planes.



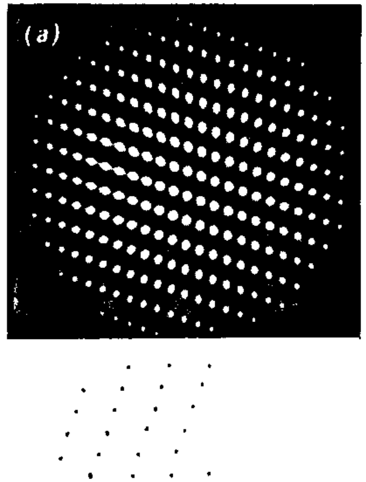
Derivation of Bragg's Law



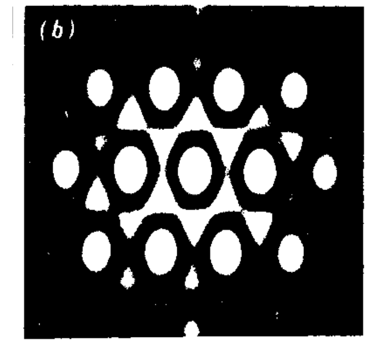
$\sin \Theta = n\,\lambda / 2\,d$

$n\,\lambda = 2d \sin \Theta$

Source: Patrick Woodward



Source: Taylor & Lipson, Optical Transforms



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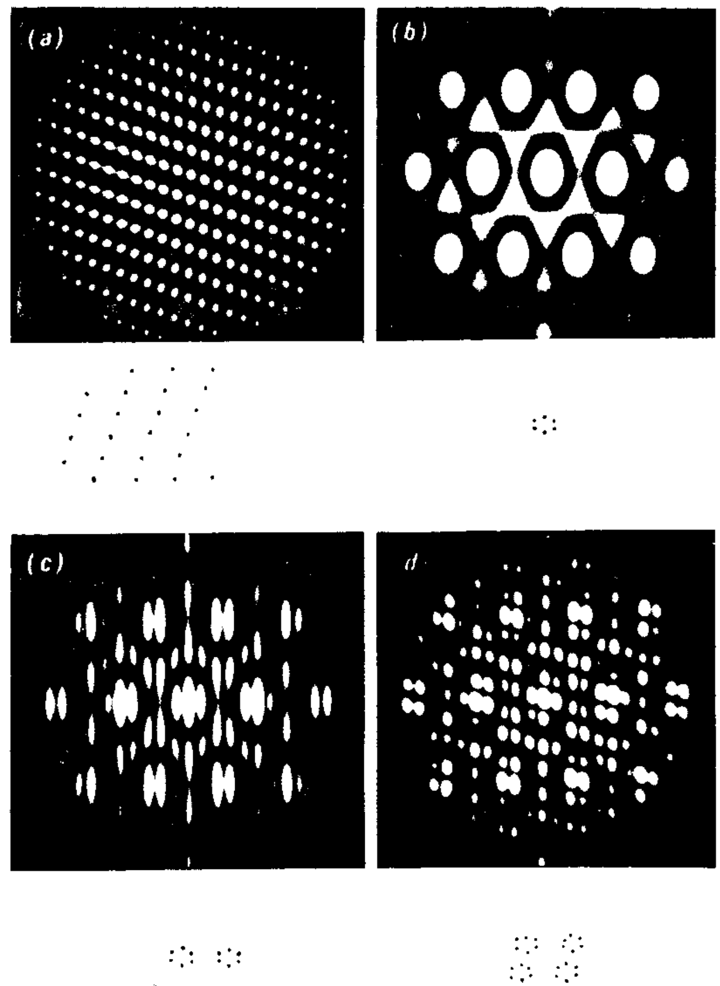

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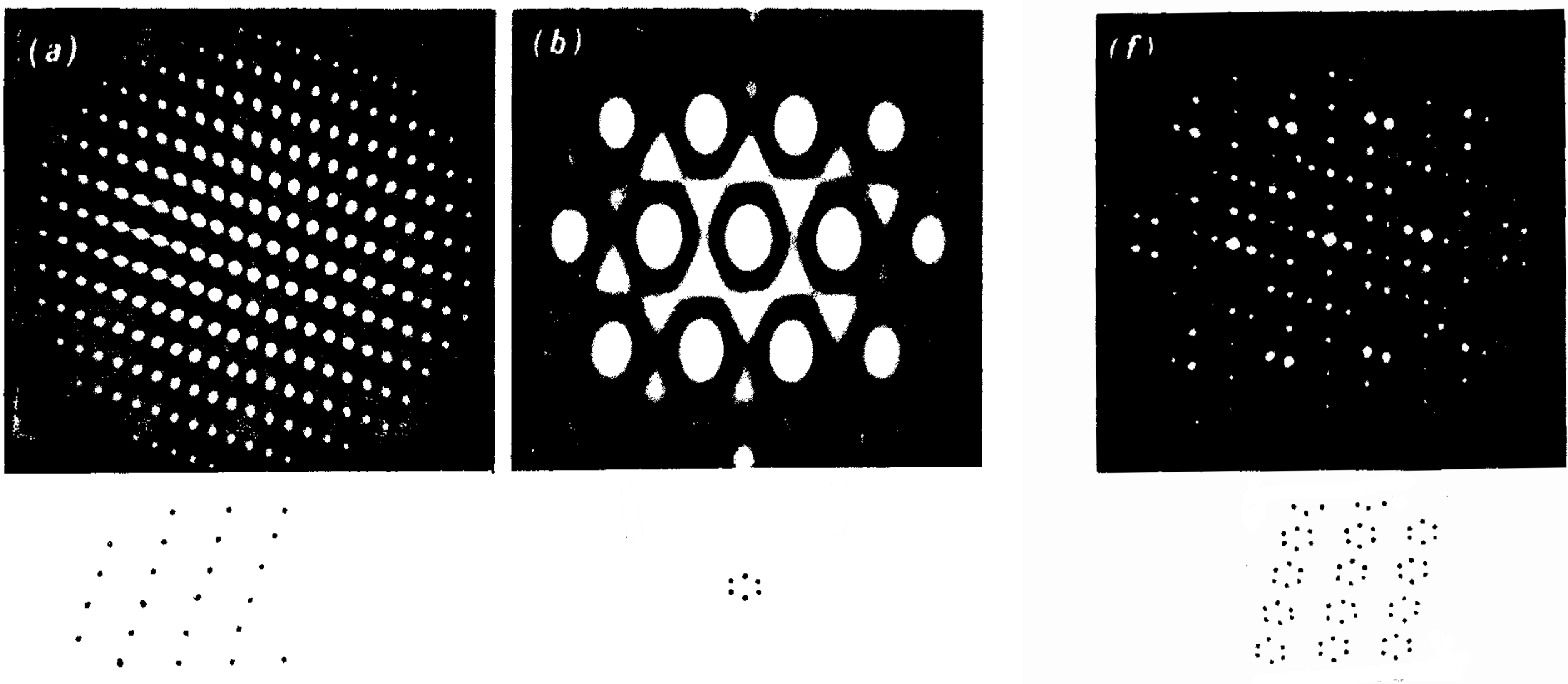

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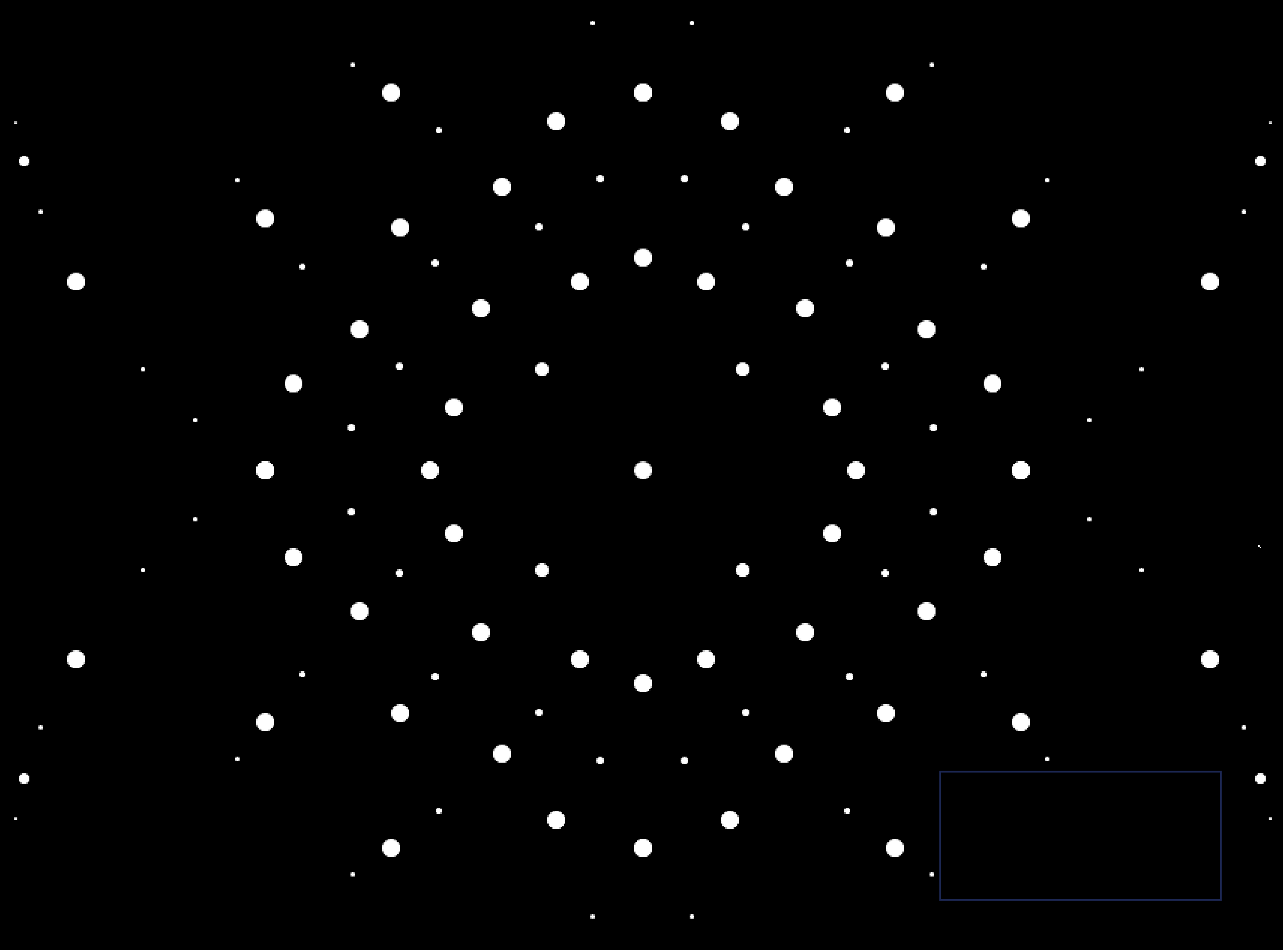
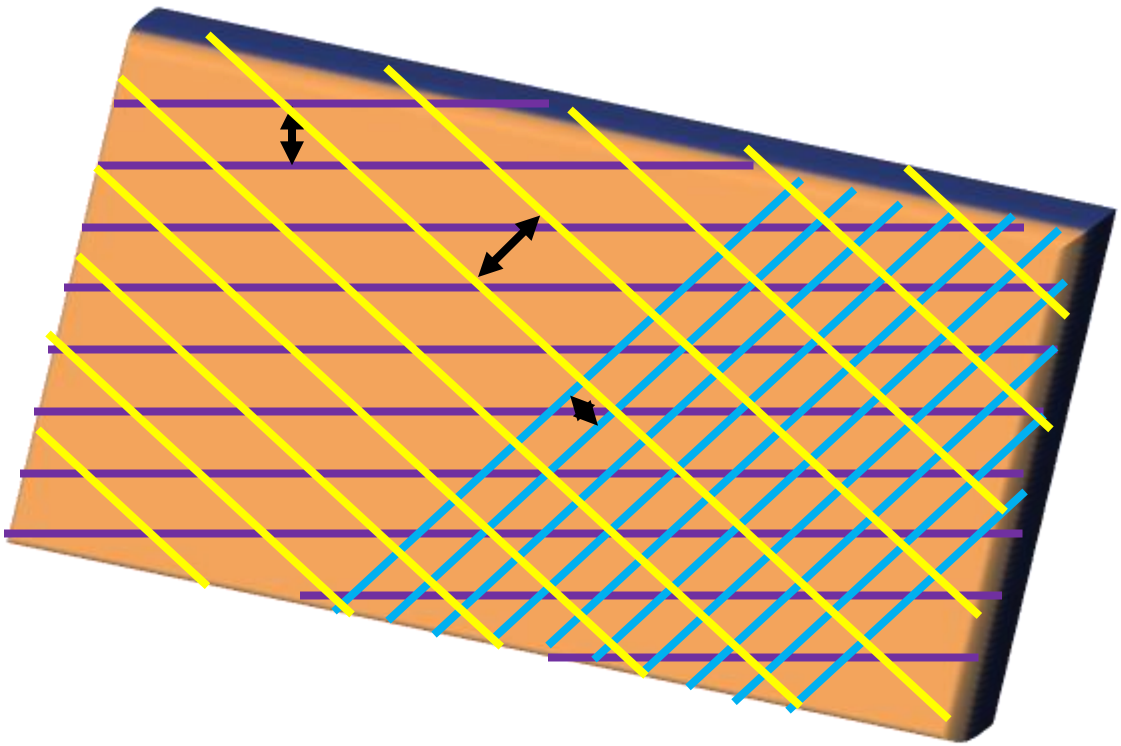


Planes and Distances



- We can draw an infinite number of parallel planes through a crystal.
- The family of planes are a distance d apart from each other.
- Only when we satisfy Bragg's Law, do we see "diffraction" from the planes.

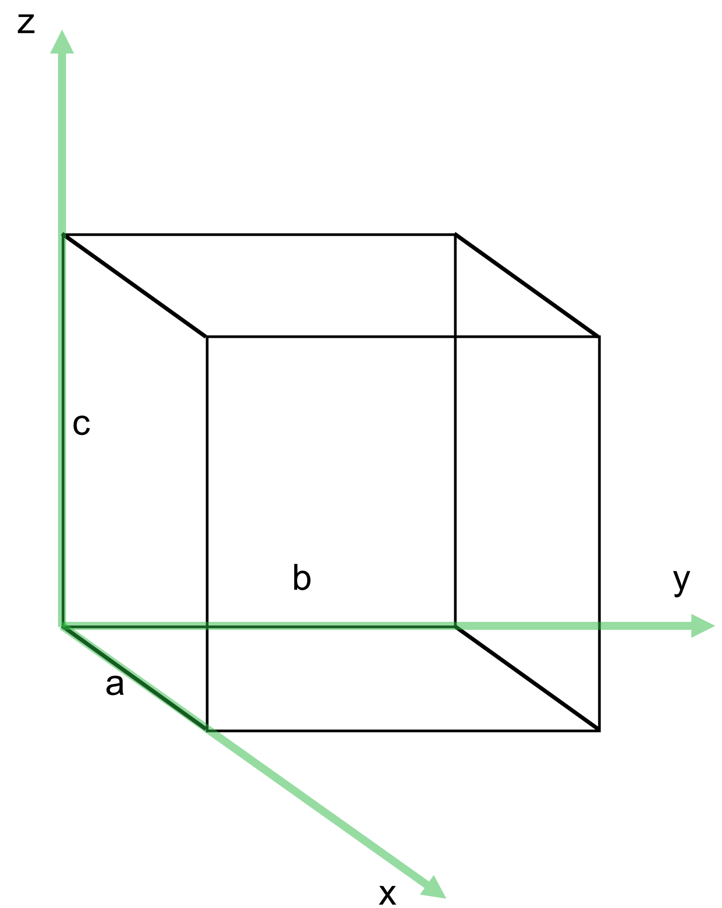
$$2d*\sin(\theta) = n*\lambda$$

Planes and Distances

Miller Planes

- In 1839, William Hallowes Miller came up with a notation for these planes.

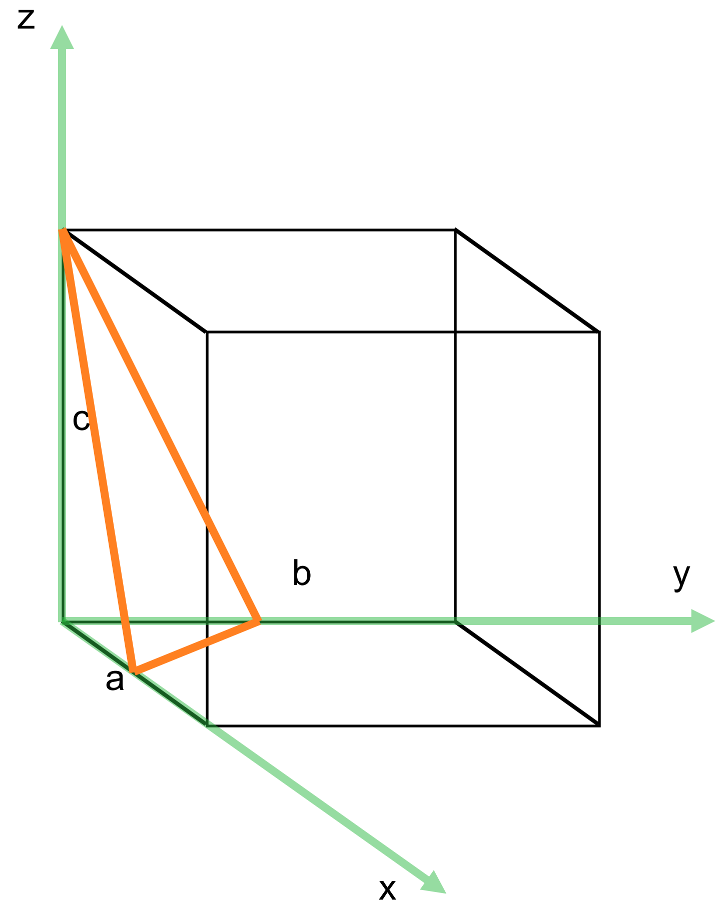
- We don't need to consider the whole crystal. We just need to look at the unit cell.



Planes and Distances

Miller Planes

- Every plane that we can draw in the unit cell, intersects at some fraction of the way along the unit cell axis (a, b, c).



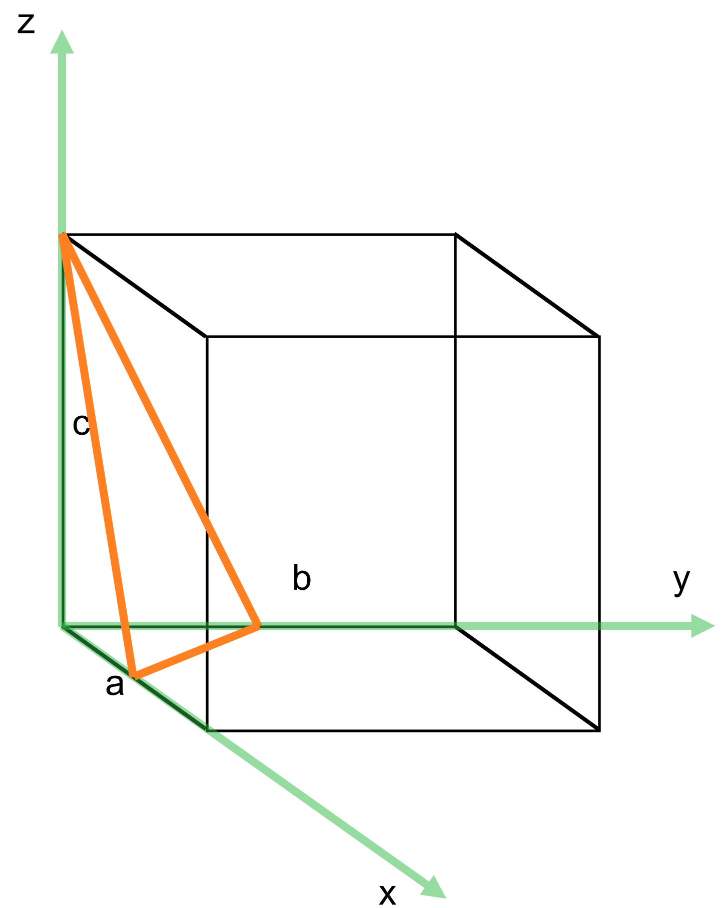
Planes and Distances

Miller Planes

- Every plane that we can draw in the unit cell, intersects at some fraction of the way along the unit cell axis (a, b, c).

The orange plane:

- Intersects **a** at 0.5
- Intersects **b** at 0.5
- Intersects **c** at 1



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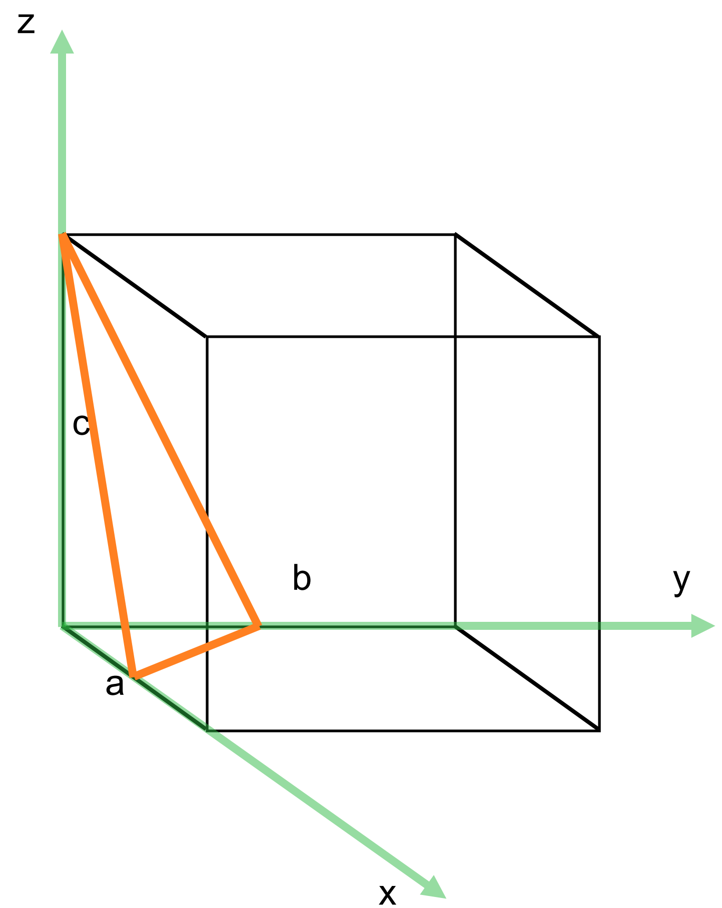

We refer to these planes as (h k l).

- h is the inverse of the fractional coordinate along **a**.
- k is the inverse of the fractional coordinate along **b**.
- l is the inverse of the fractional coordinate along **c**.

Planes and Distances

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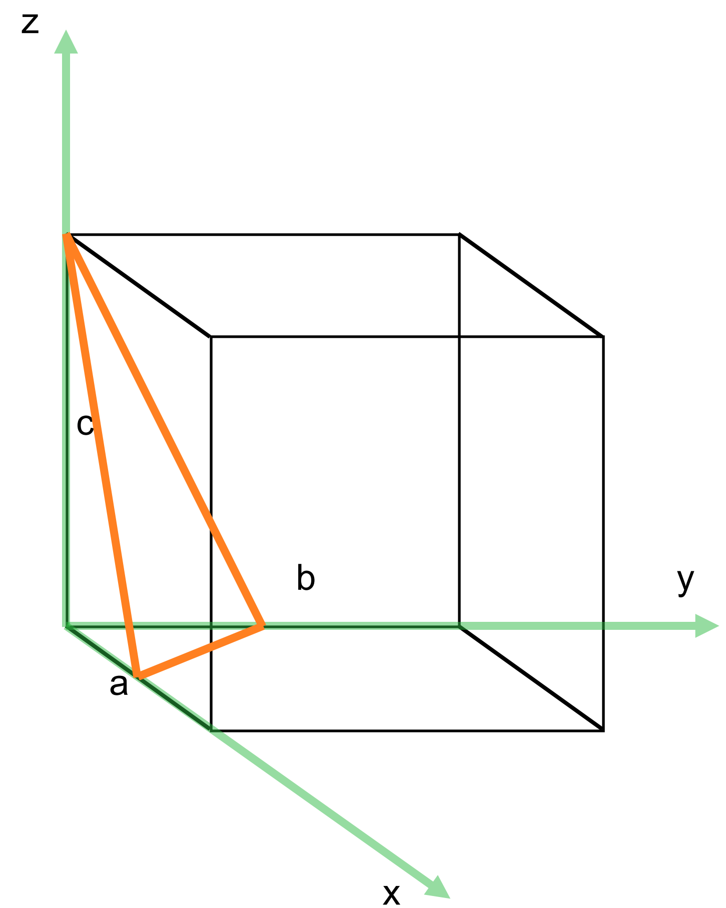
- Intersects **c** at 1

- h is the inverse of the fractional coordinate along **a**.
- h = 1/0.5 = 2
- k is the inverse of the fractional coordinate along **b**.
- k = 1/0.5 = 2
- l is the inverse of the fractional coordinate along **c**.
- l = 1/1 = 1



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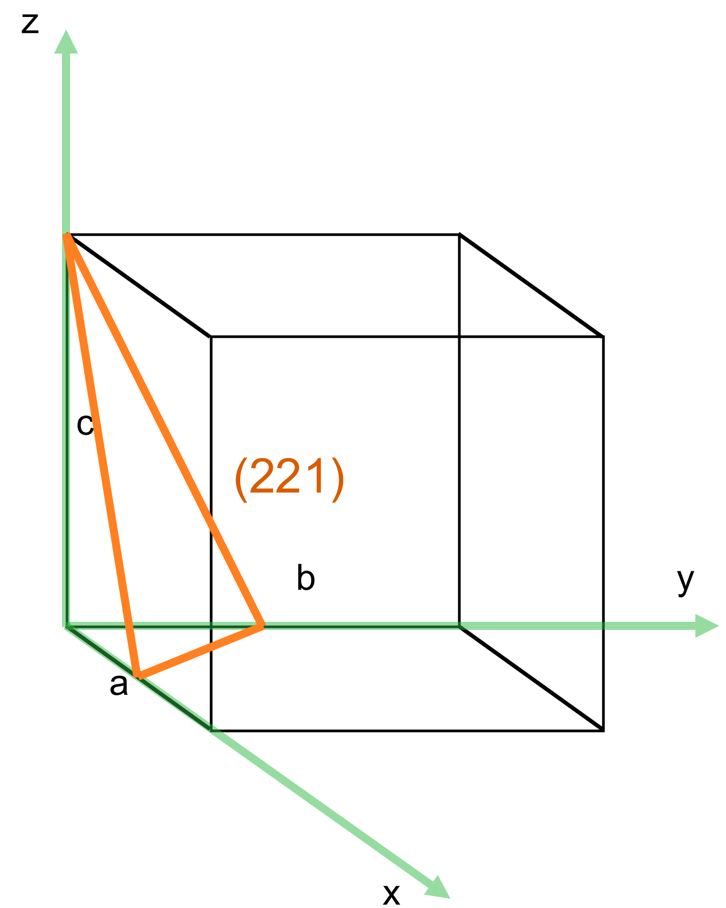

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- l = 1/1 = 1

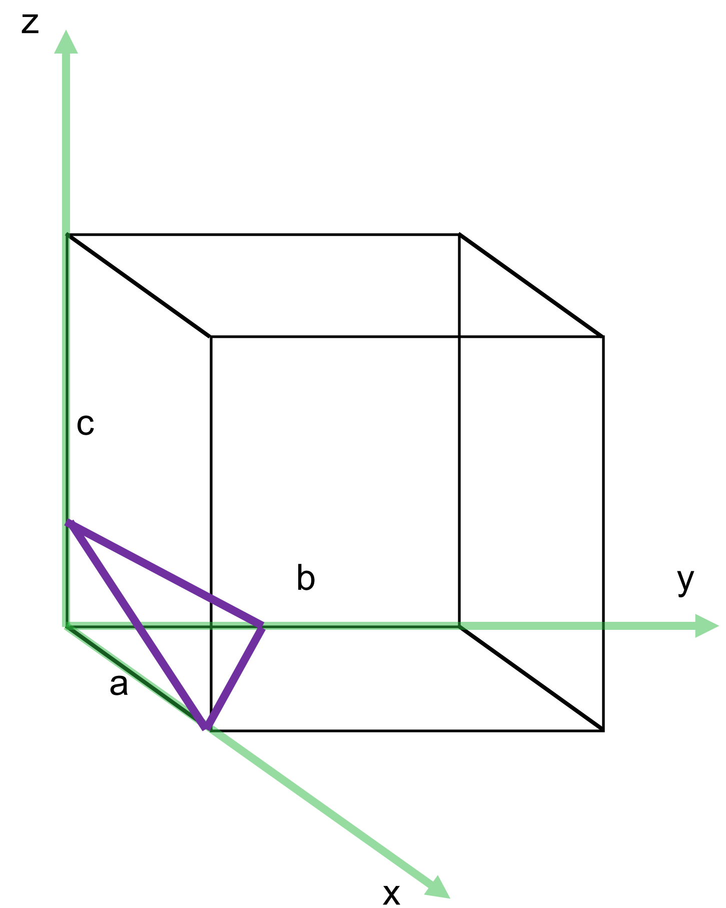
Planes and Distances

Miller Planes

- Every plane that we can draw in the unit cell, intersects at some fraction of the way along the unit cell axis (a, b, c).

The purple plane:

- Intersects a at 1
- Intersects b at 0.5
- Intersects c at 0.33



Planes and Distances

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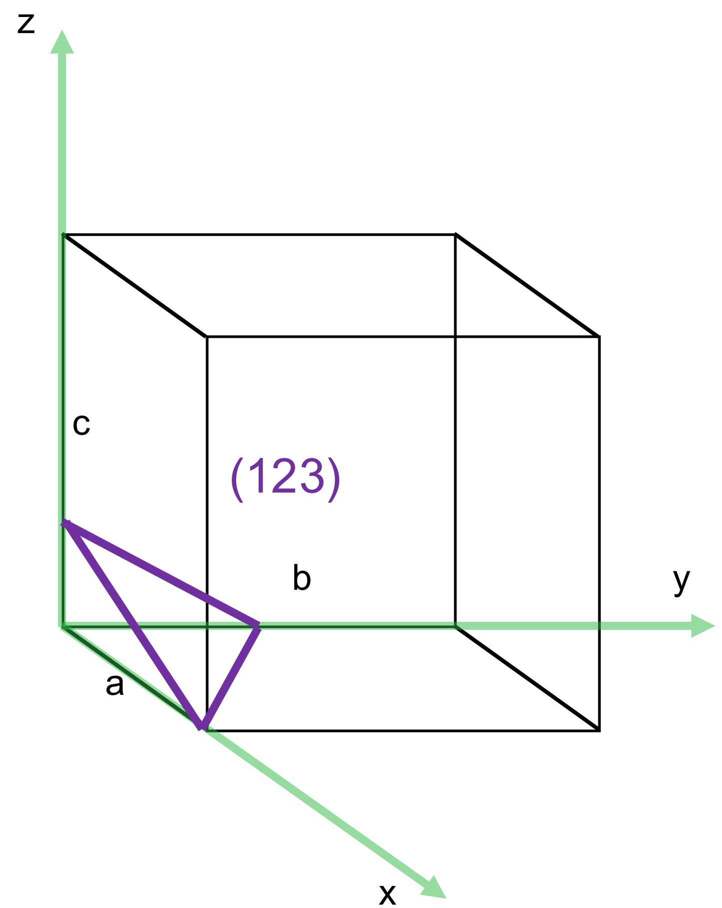

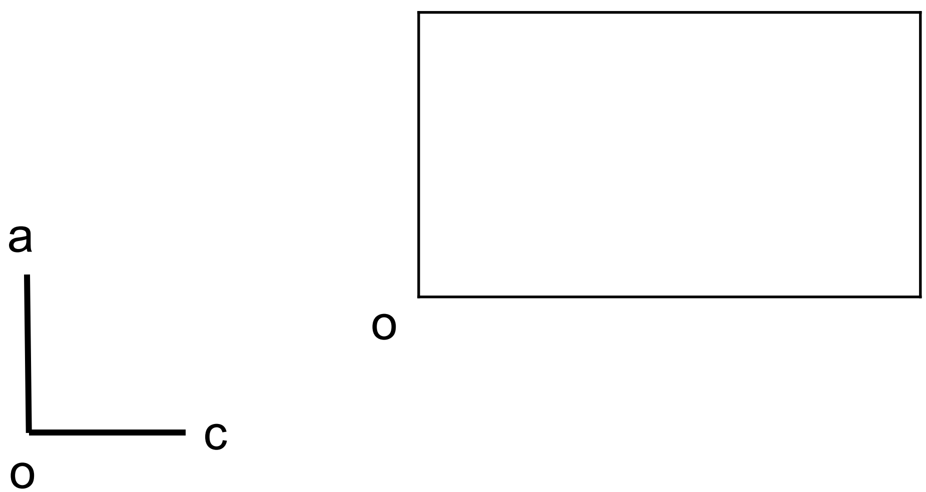
a
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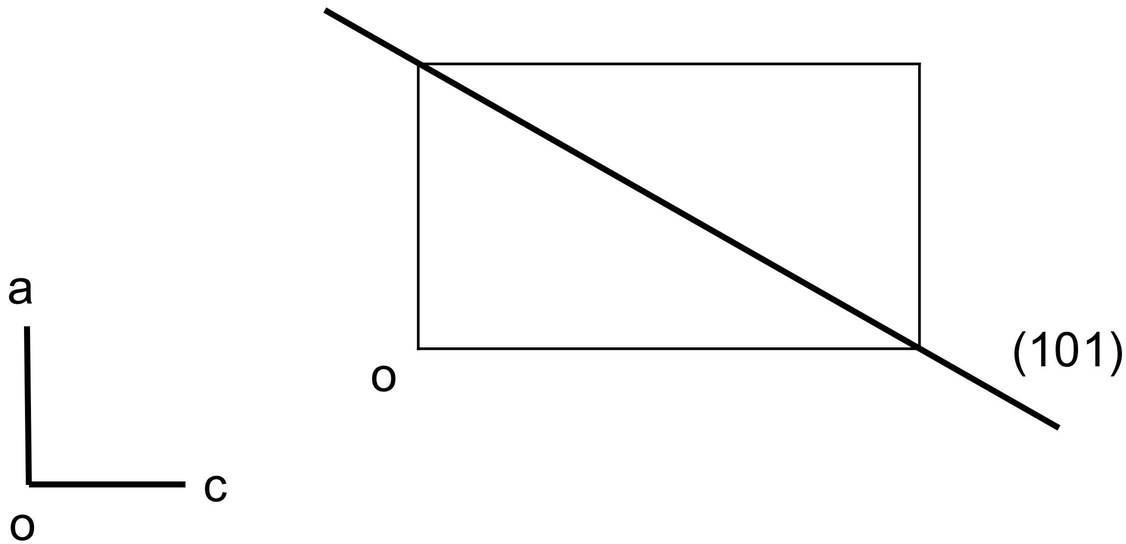
a
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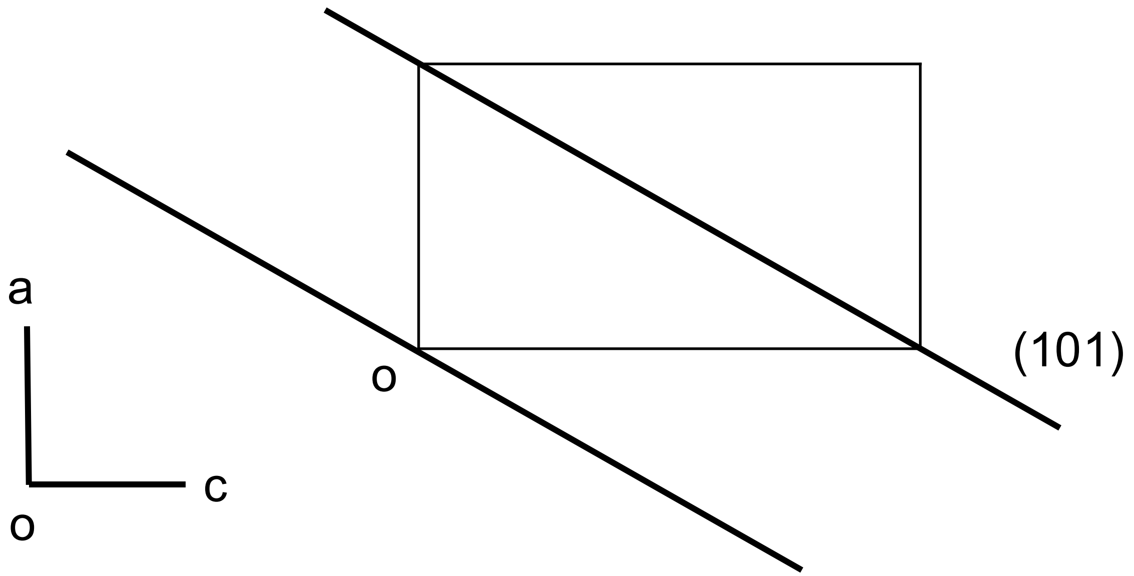
(101)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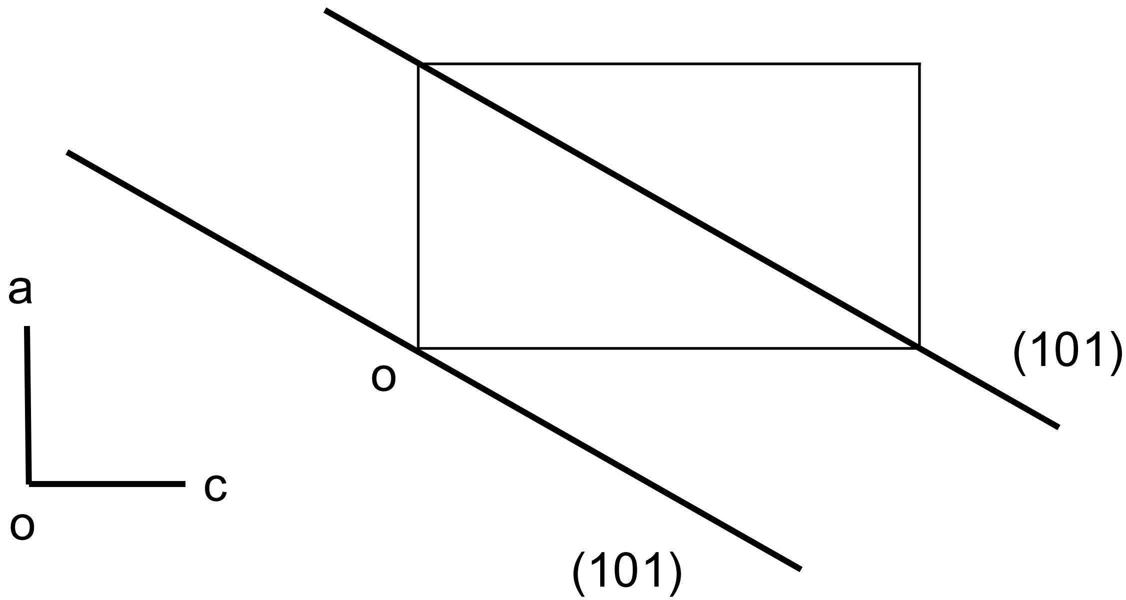

a
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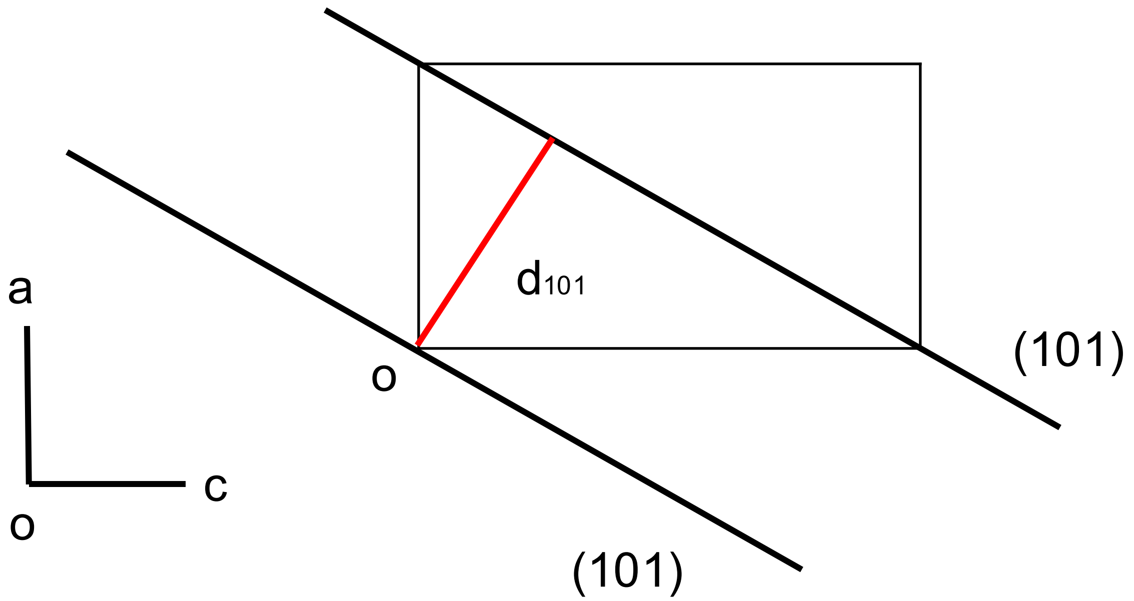
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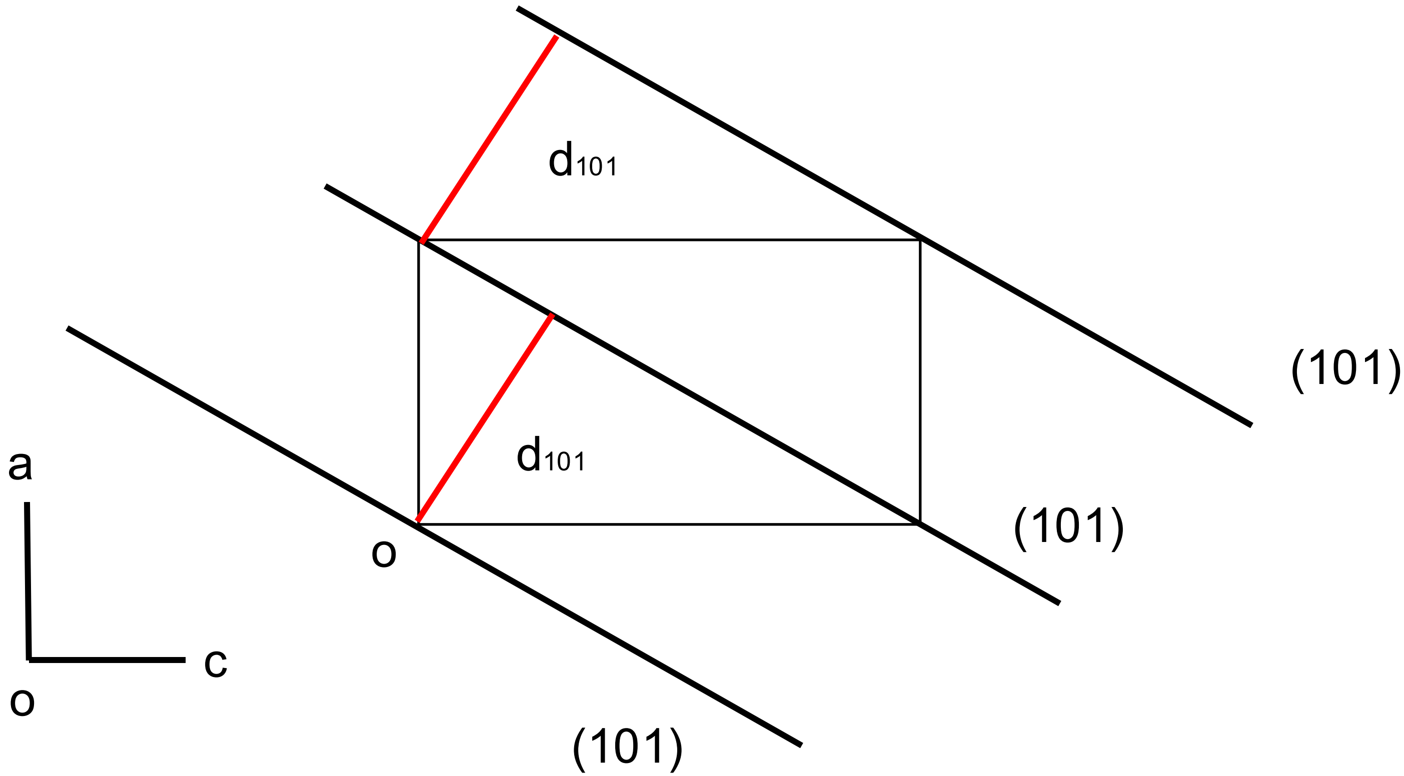

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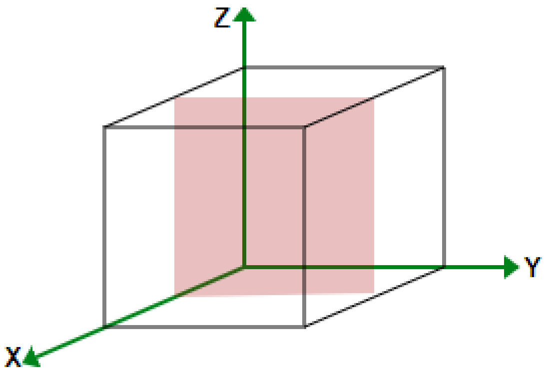
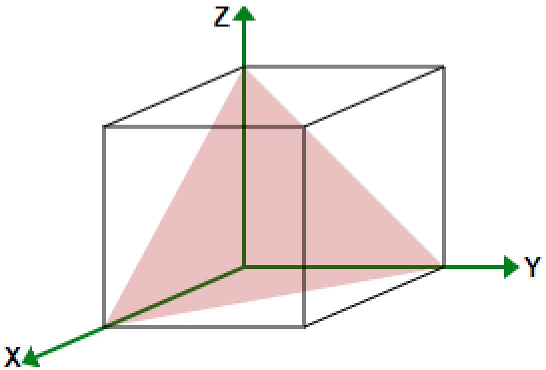
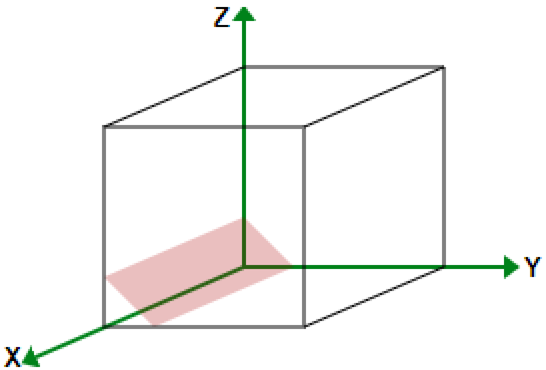
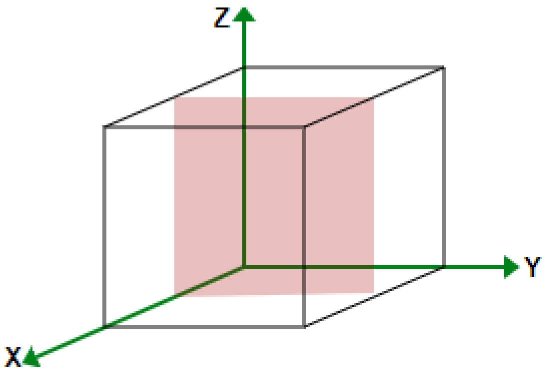
Practice







Practice



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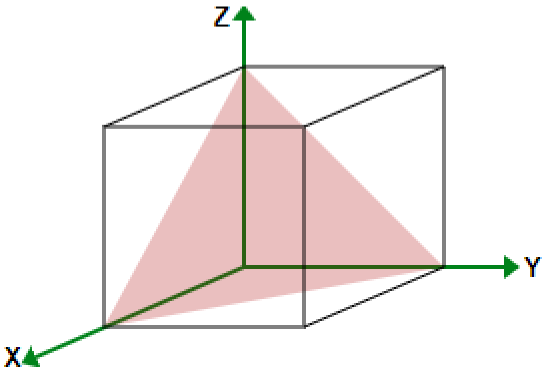
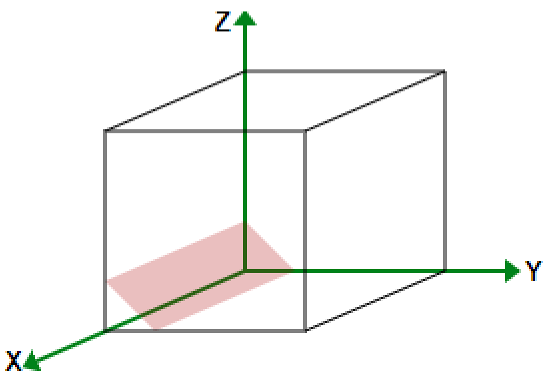
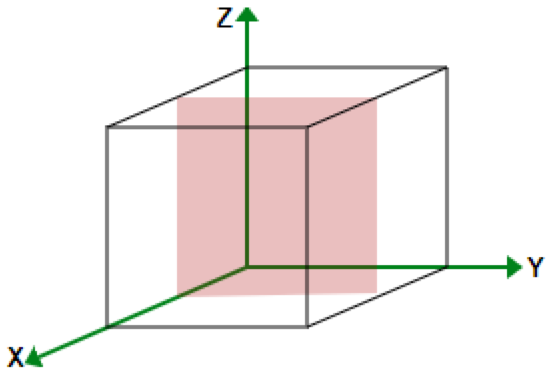




Practice



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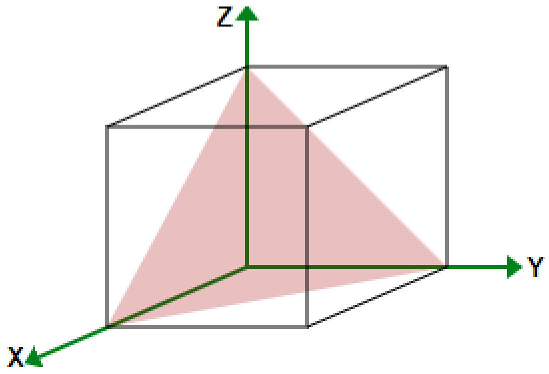

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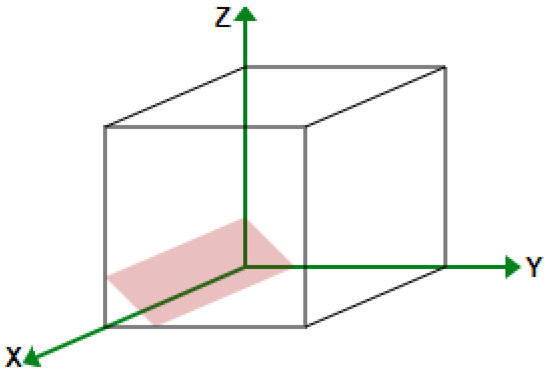
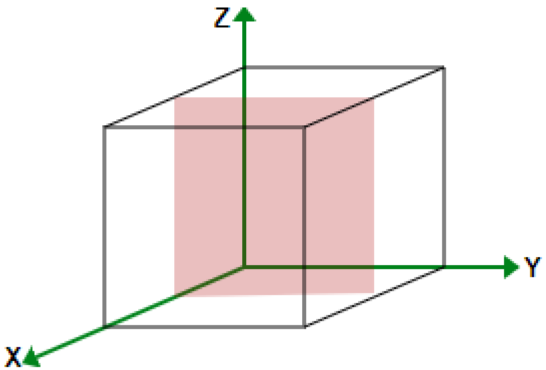


Practice



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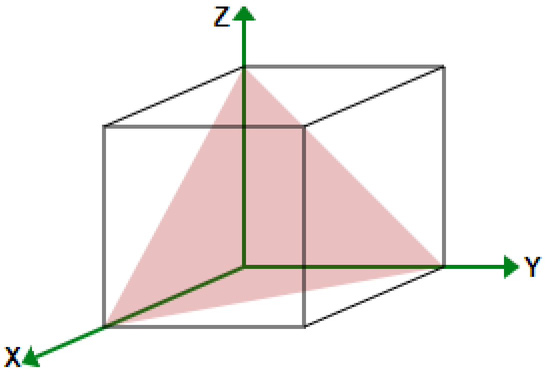

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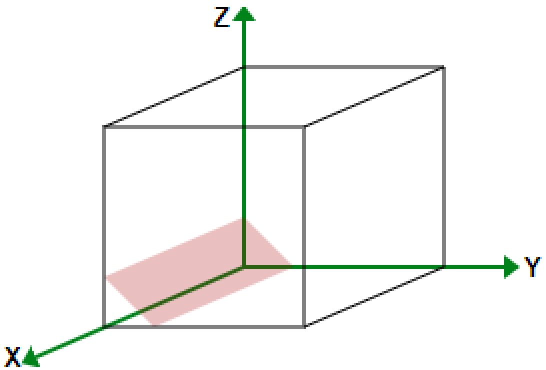

(044)

Miller Plane Calculator, Michael Katz

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MEMORIAL UNIVERSITY

Dr. Michael Katz - Porous Materials

Miller Planes

Below you will find a Miller plane viewer. Miller planes can be viewed as planes that slice through a unit cell. It can be used to visualize crystal growth directions. It can also be used to consider how X-ray "diffraction" (actually scattering) occurs off of a plane. We define each plane using a set of indices, *h*, *k*, and *l*. Each index represents the inverse of how far along a unit cell the plane passes through along *x*, *y*, and *z* respectively. For example, if *h* = 1, then the plane intersects the *x*-axis at *a*. Furthermore, if *h* = 2, then the plane intersects the *x*-axis at half of *a* (*1/h = 1/2*). We label planes as "(*h k l*)". So the plane (*1 1 0*) intesects the *x*-axis at *a*, the *y*-axis at *b*, and it runs parallel to the *z*-axis *1/l = 1/0 = ∞*).

Use the viewer below to explore the viewer. Be careful with negative values of *h*, *k*, and *l*.

Miller Plane 1 (green):

h:

k:

l:

Miller Plane 2 (purple):

☐ Enable

h:

k:

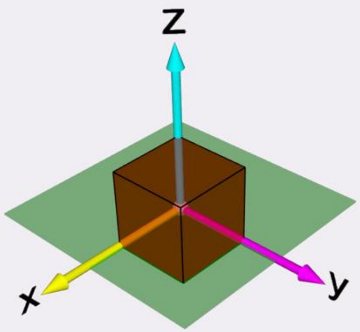
l:

a length: 1

b length: 1

c length: 1

Apply Changes



Contact Details

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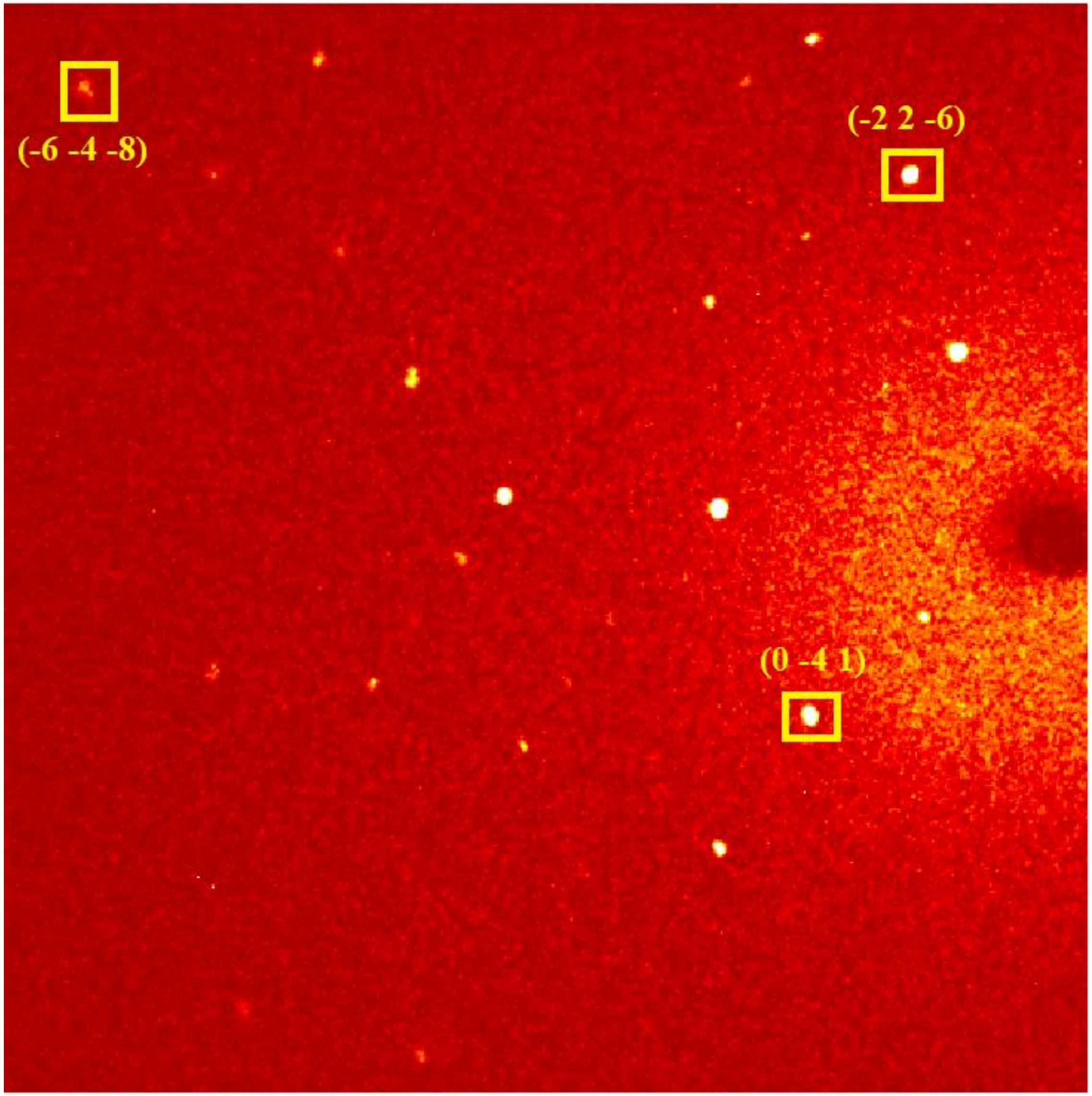

If we know the unit cell, and how it is oriented on the instrument, we can calculate exactly where a reflection should strike the detector!

Crystal Systems and Crystallographic Point Groups

Andreas Decken via Paul D. Boyle

Crystal Systems and Crystallographic Point Groups

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Crystal Systems and Crystallographic Point Groups

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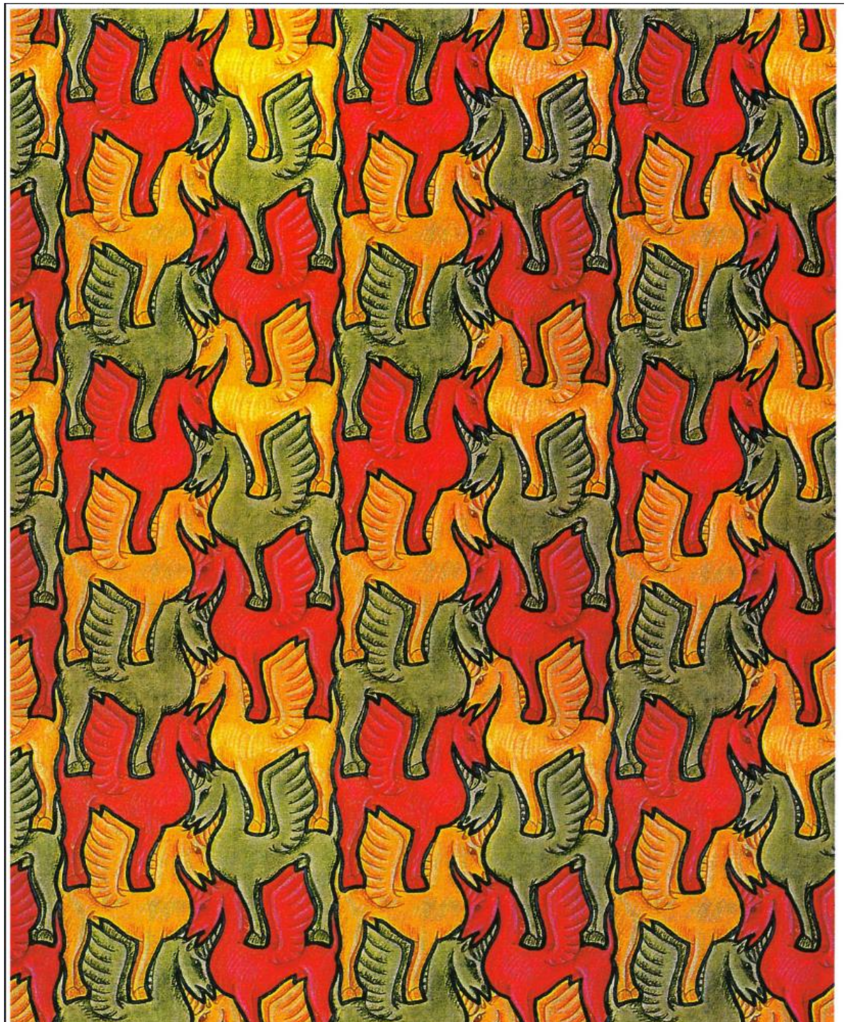


Your Data is Precious

How many data points do we need to solve the following equation?

$y = ax + b$

$y = ax^2 + bx +c$

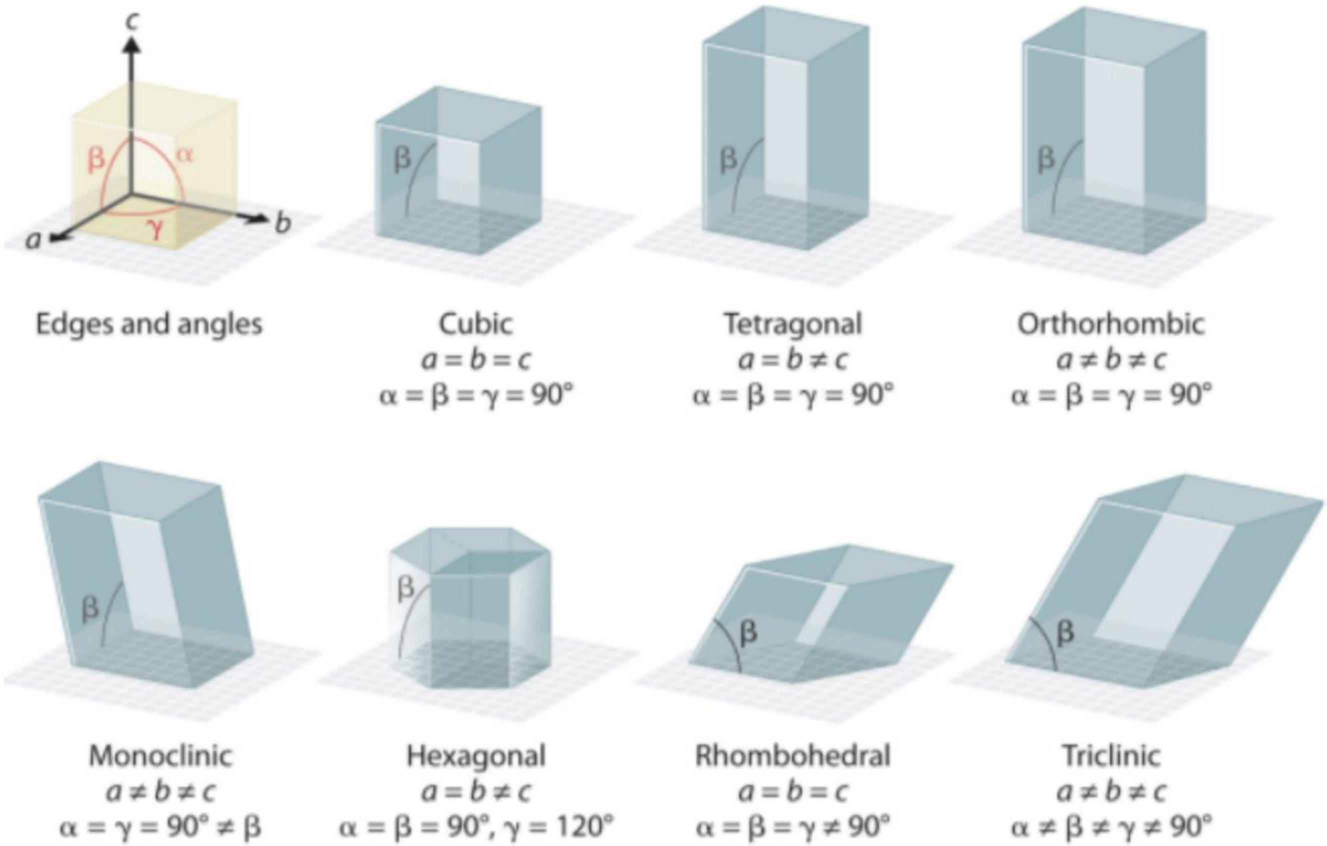
In an X-ray diffraction experiment we obtain a limited amount of data

If we want precise bond length/angles we want to optimize
how we use our data

Source:

NDK Synth. Quartz

Crystal Systems



Crystal Systems

Crystal System	Metric Constraints
Triclinic	$a \neq b \neq c;\ \alpha \neq \beta \neq \gamma$
Monoclinic	$a \neq b \neq c;\ \alpha = \gamma = 90^o,\ \beta \neq 90^o$
Orthorhombic	$a \neq b \neq c;\ \alpha = \beta = \gamma = 90^o$
Tetragonal	$a = b \neq c;\ \alpha = \beta = \gamma = 90^o$
Trigonal	
rhombohedral setting	$a = b = c;\ \alpha = \beta = \gamma \neq 90^o$
hexagonal setting	$a = b \neq c;\ \alpha = \beta = 90^o, \gamma = 120^o$
	$a = b \neq c;\ \alpha = \beta = 90^o, \gamma = 120^o$
Hexagonal	$a = b \neq c;\ \alpha = \beta = 90^o, \gamma = 120^o$
Cubic	$a = b = c;\ \alpha = \beta = \gamma = 90^o$

Metric Constraints

NOTE: ”=“ means “**constrained to be equal**”
“≠” means “**not constrained to be equal to**”
it does not mean “not equal to”

Systems – Point Groups – Space Groups

System
Triclinic
Monoclinic
Orthorhombic
Tetragonal

Trigonal/rhombohedral

Hexagonal

Cubic

Crystallographic Point Groups

A group of symmetry operations all for which leave at least one point unmoved. It maps a point lattice onto itself.

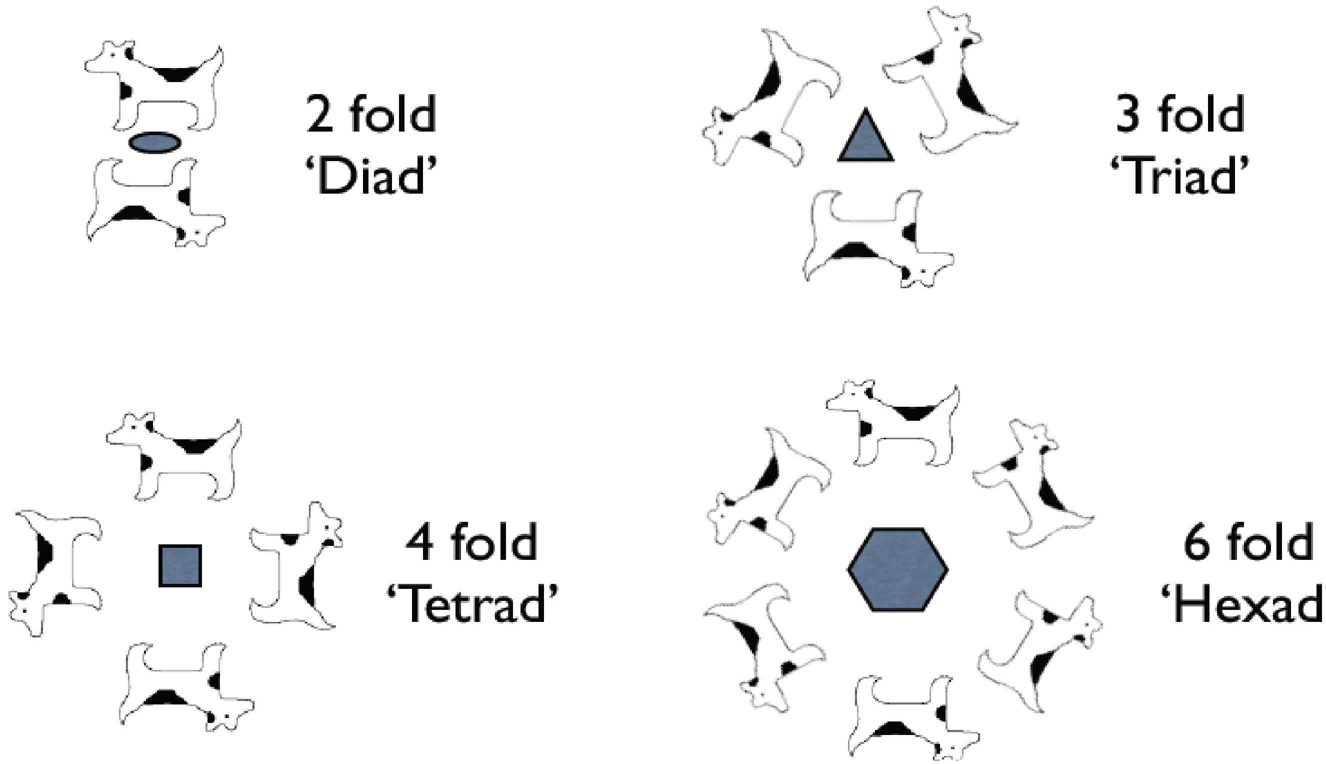
In 3D, the symmetry elements are restricted to:

- Proper rotation axes (n)
- Mirror planes (m)
- Inversion centre ($\bar{1}$, or no explicit symbol)
- Rotary inversion axes ($\bar{n}$)

Source: International Union of Crystallography (IUCr)

Proper Rotation Axes

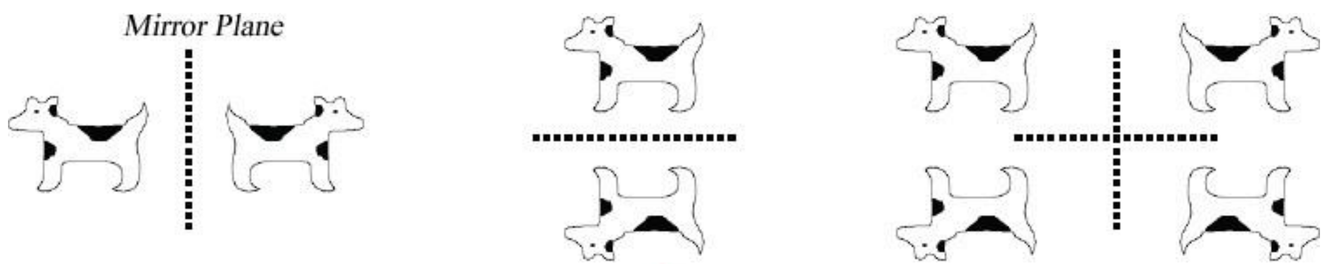
- Rotation about an axis by 360º/n
- Doesn't change handedness of object

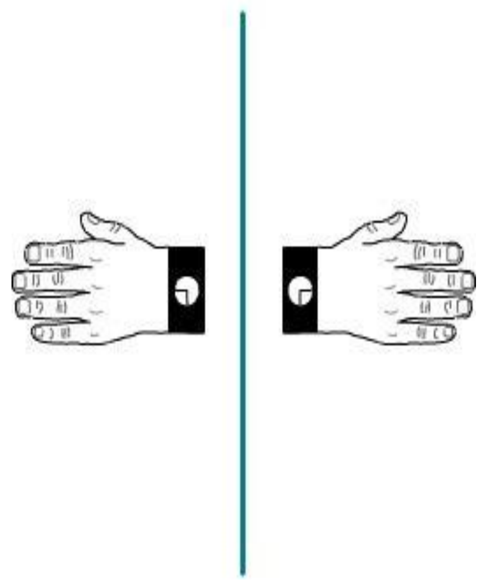


- Only n-fold axes where n = 1, 2, 3, 4, 6 are allowed for space filling 3 dimensional objects

Mirror plane

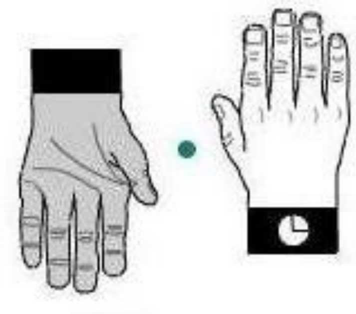
- Creates a reflected object
- Changes handedness of object





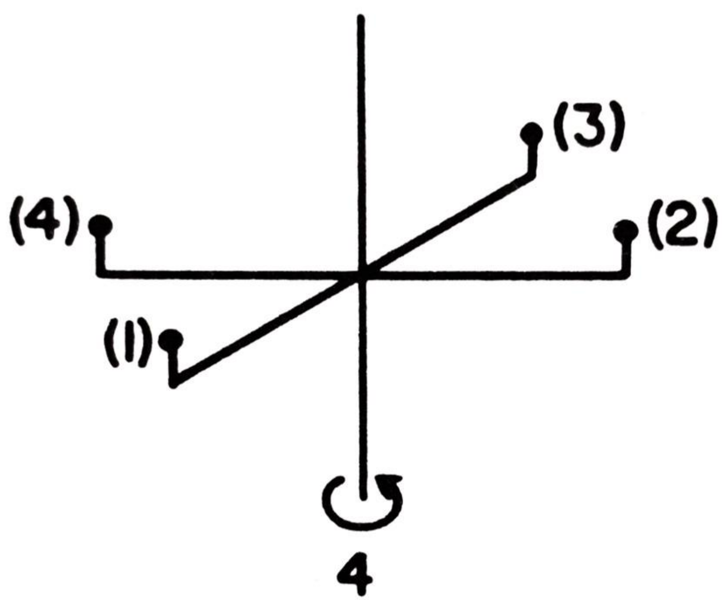
Inversion Centre

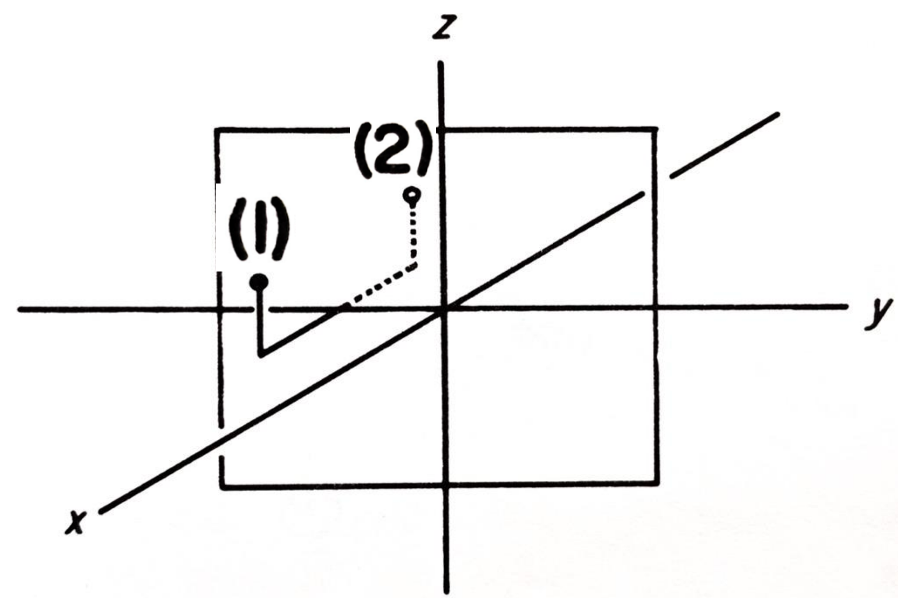
- Transforms x, y, z into $\bar{x}$, $\bar{y}$, $\bar{z}$
- Changes handedness of object



No cows, no hands

Proper Rotation   Mirror

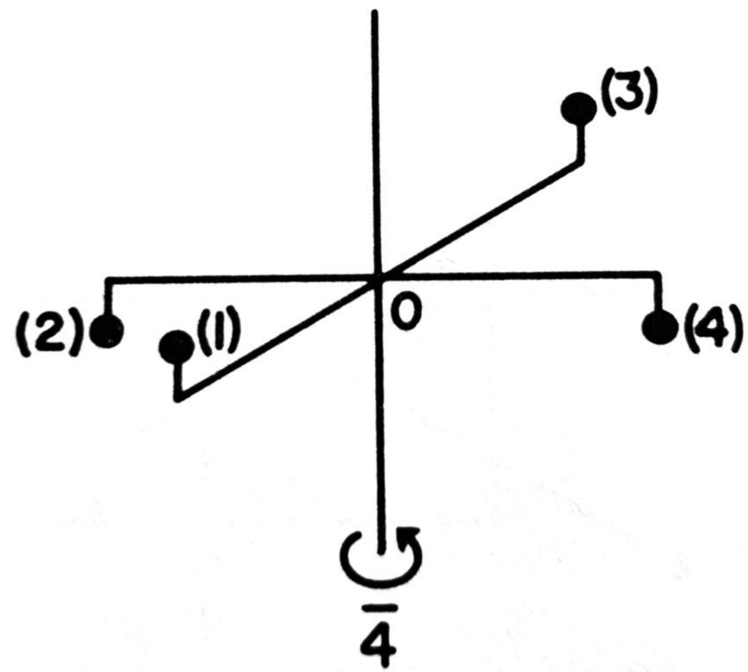




Source: Stout & Jensen

Rotary Inversion Axes

- Rotation of 360º/n followed by inversion
- Changes handedness of object
- $\overline{1}$ is equivalent to an inversion centre
- $\overline{2}$ is equivalent to a mirror plane



Source: Stout & Jensen

Crystallographic Point Groups

- 32 unique crystallographic point groups are obtained from combining the various allowed rotation axes, mirror planes, and inversions

- 11 of the 32 crystallographic point groups are ***centrosymmetric*** *and are the* ***Laue Groups***

- Laue Groups describe the symmetry of the diffraction pattern as determined from the observed intensities

- Determining the Laue Group is an important step when solving a crystal structure

Systems – Point Groups – Space Groups

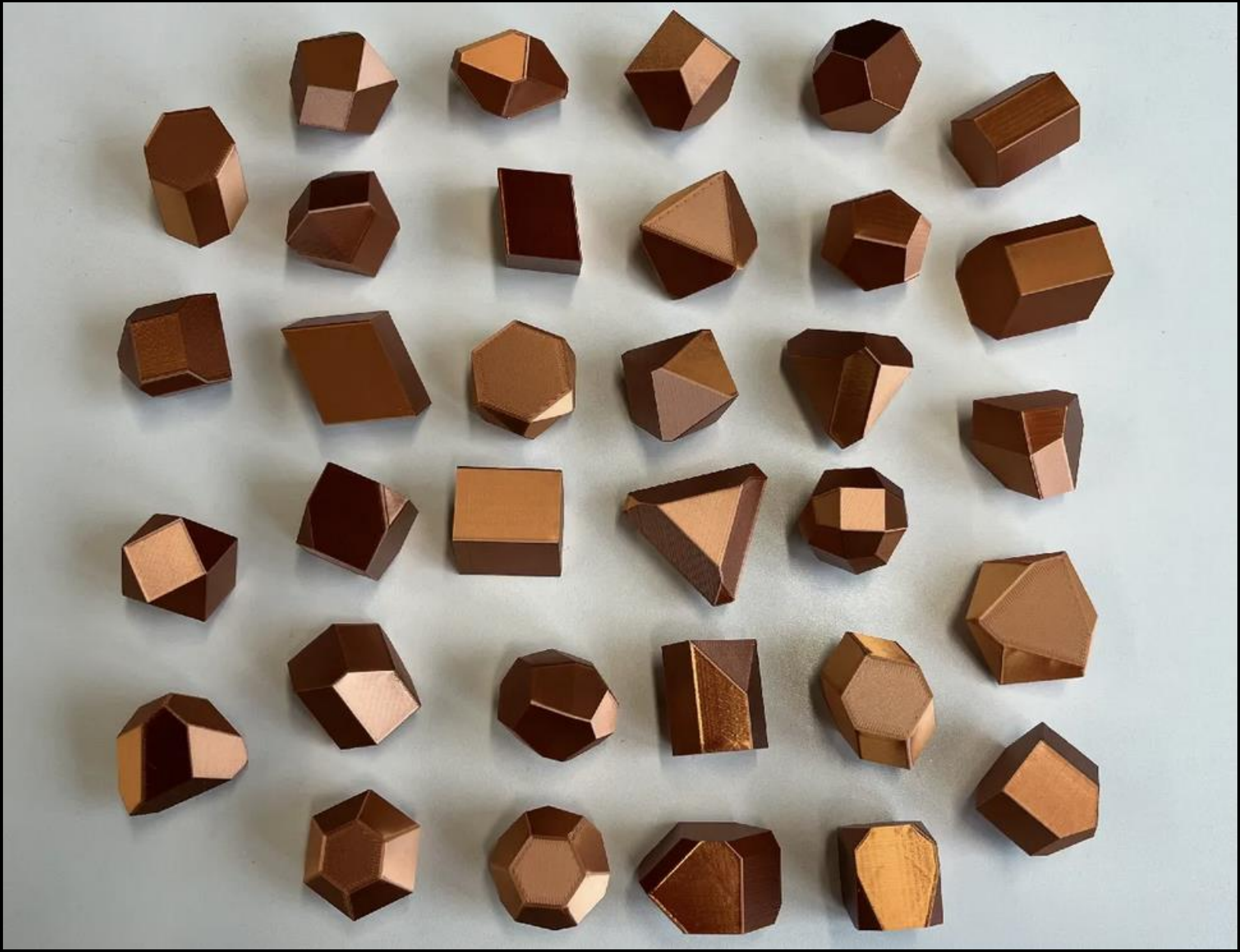
System	Point Group
Triclinic	1 $\bar{1}$
Monoclinic	2 m $2/m$
Orthorhombic	222 $mm2$ mmm
Tetragonal	4 $\bar{4}$ $4/m$
	422 $4mm$ $\bar{4}2m$

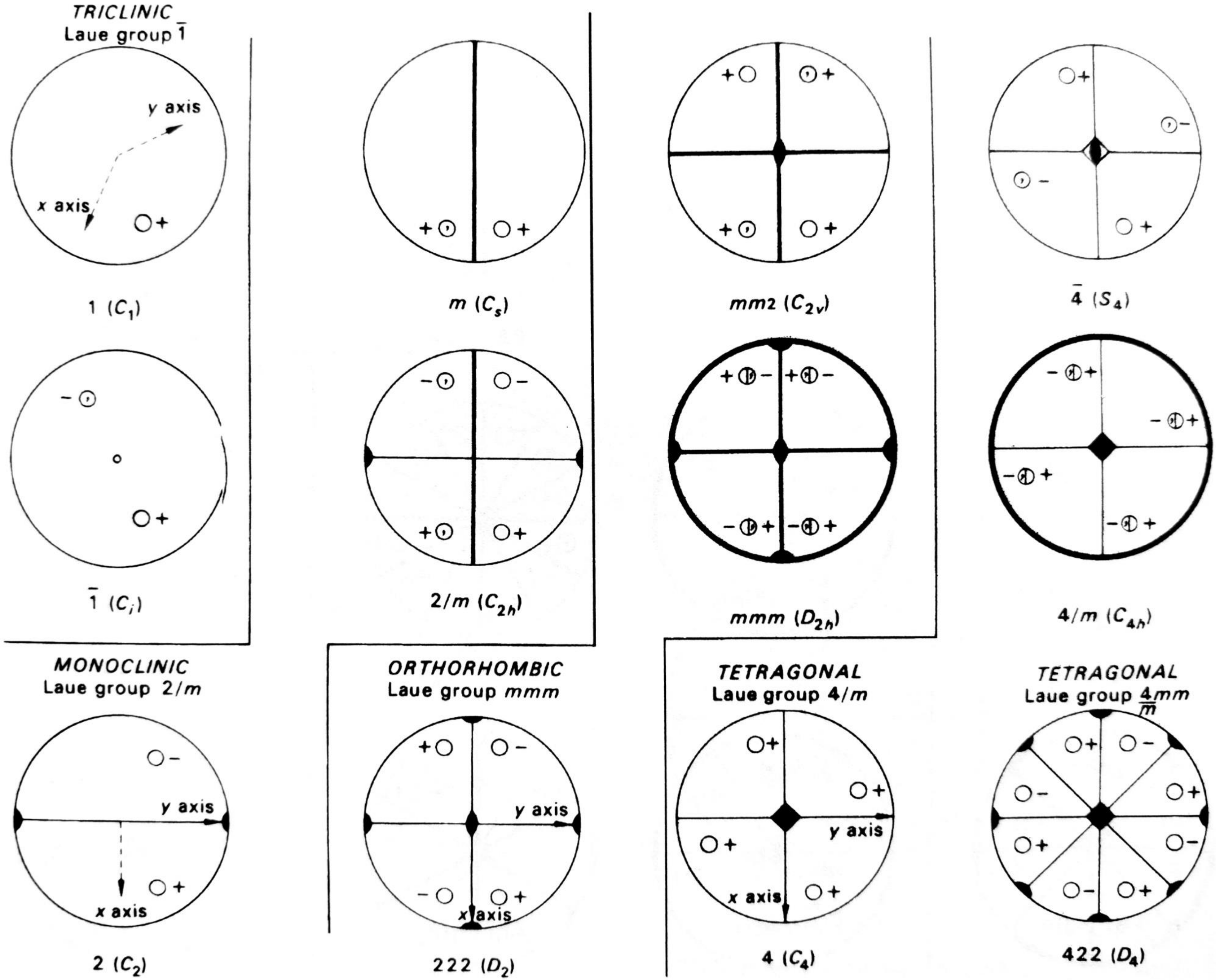
	$4/mmm$
Trigonal/rhombohedral	3
	$\bar{3}$
	32
	$3m$
	$\bar{3}m$
Hexagonal	6
	$\bar{6}$
	$6/m$
	622
	$6mm$
	$\bar{6}m\bar{2}$
	$6/mmm$
Cubic	23
	$m3$
	432
	$\bar{4}3m$
	$m3m$

Hermann-Mauguin Symmetry Notation

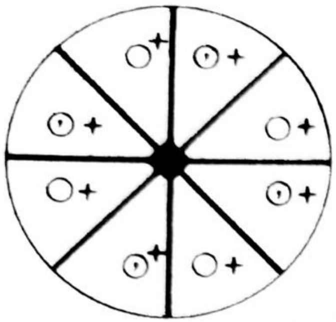
- Spectroscopists use Schoenflies notation to describe symmetry (*e.g.* C_{2v}, D_{4h})
- Crystallographers use Hermann-Mauguin notation (International notation)
- Was introduced by Carl Hermann in 1928
- Modified by Charles-Victor Mauguin in 1931
- Adopted for the 1935 edition of the *International Tables for Crystallography*
- Hermann-Mauguin notation is preferred for crystallography
    - Easier to add translational symmetry elements
    - Directions of symmetry axes are specified

Crystal family	Crystal system	Hermann-Mauguin		Shubnikov[2]	Schoenflies	Orbifold	Coxeter	Order
		(full)	(short)					
Triclinic		1	1	1	C_1	11	$[\ ]^+$	1
		$\bar{1}$	$\bar{1}$	$\tilde{2}$	$C_i = S_2$	×	$[2^+,2^+]$	2
Monoclinic		2	2	2	C_2	22	$[2]^+$	2
		m	m	m	$C_s = C_{1h}$	*	[ ]	2
		$\frac{2}{m}$	2/m	$2 : m$	C_{2h}	2*	$[2,2^+]$	4
Orthorhombic		222	222	$2 : 2$	$D_2 = V$	222	$[2,2]^+$	4
		mm2	mm2	$2 \cdot m$	C_{2v}	*22	[2]	4
		$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	mmm	$m \cdot 2 : m$	$D_{2h} = V_h$	*222	[2,2]	8
Tetragonal		4	4	4	C_4	44	$[4]^+$	4
		$\bar{4}$	$\bar{4}$	$\tilde{4}$	S_4	2×	$[2^+,4^+]$	4
		$\frac{4}{m}$	4/m	$4 : m$	C_{4h}	4*	$[2,4^+]$	8
		422	422	$4 : 2$	D_4	422	$[4,2]^+$	8
		4mm	4mm	$4 \cdot m$	C_{4v}	*44	[4]	8
		$\bar{4}$2m	$\bar{4}$2m	$\tilde{4} \cdot m$	$D_{2d} = V_d$	2*2	$[2^+,4]$	8
		$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	4/mmm	$m \cdot 4 : m$	D_{4h}	*422	[4,2]	16
Hexagonal	Trigonal	3	3	3	C_3	33	$[3]^+$	3
		$\bar{3}$	$\bar{3}$	$\tilde{6}$	$C_{3i} = S_6$	3×	$[2^+,6^+]$	6
		32	32	$3 : 2$	D_3	322	$[3,2]^+$	6
		3m	3m	$3 \cdot m$	C_{3v}	*33	[3]	6
		$\bar{3}\frac{2}{m}$	$\bar{3}$m	$\tilde{6} \cdot m$	D_{3d}	2*3	$[2^+,6]$	12
	Hexagonal	6	6	6	C_6	66	$[6]^+$	6
		$\bar{6}$	$\bar{6}$	$3 : m$	C_{3h}	3*	$[2,3^+]$	6
		$\frac{6}{m}$	6/m	$6 : m$	C_{6h}	6*	$[2,6^+]$	12
		622	622	$6 : 2$	D_6	622	$[6,2]^+$	12
		6mm	6mm	$6 \cdot m$	C_{6v}	*66	[6]	12
		$\bar{6}$m2	$\bar{6}$m2	$m \cdot 3 : m$	D_{3h}	*322	[3,2]	12
		$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	6/mmm	$m \cdot 6 : m$	D_{6h}	*622	[6,2]	24
Cubic		23	23	$3/2$	T	332	$[3,3]^+$	12
		$\frac{2}{m}\bar{3}$	m$\bar{3}$	$\tilde{6}/2$	T_h	3*2	$[3^+,4]$	24
		432	432	$3/4$	O	432	$[4,3]^+$	24
		$\bar{4}$3m	$\bar{4}$3m	$3/\tilde{4}$	T_d	*332	[3,3]	24
		$\frac{4}{m}\bar{3}\frac{2}{m}$	m$\bar{3}$m	$\tilde{6}/4$	O_h	*432	[4,3]	48

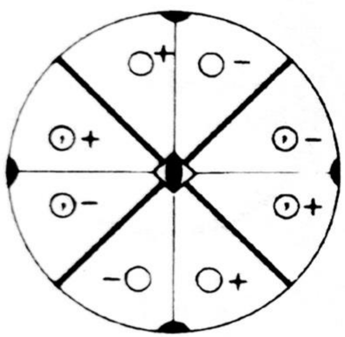




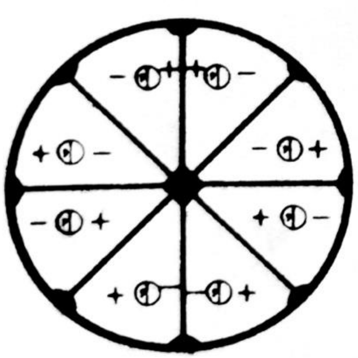
TRICLINIC
Laue group $\bar{1}$
y axis
x axis
1 (C_1)
$\bar{1}$ (C_i)
m (C_s)
2/m (C_{2h})
mm2 (C_{2v})
mmm (D_{2h})
$\bar{4}$ (S_4)
4/m (C_{4h})
MONOCLINIC
Laue group 2/m
y axis
x axis
2 (C_2)
ORTHORHOMBIC
Laue group mmm
y axis
x axis
222 (D_2)
TETRAGONAL
Laue group 4/m
y axis
x axis
4 (C_4)
TETRAGONAL
Laue group $\frac{4}{m}mm$
422 (D_4)



$4mm$ (C_{4v})



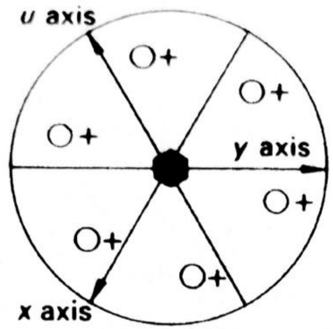
$\bar{4}2m$ (D_{2d})



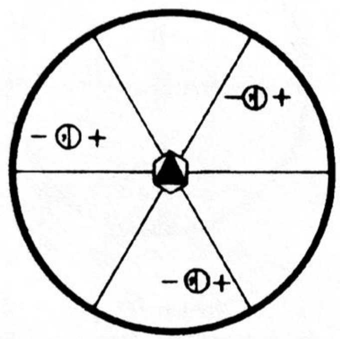
$\frac{4}{m}mm$ (D_{4h})

HEXAGONAL

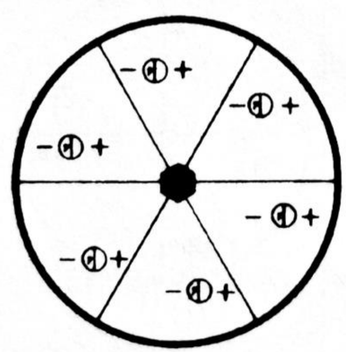
Laue group $6/m$



6 (C_6)

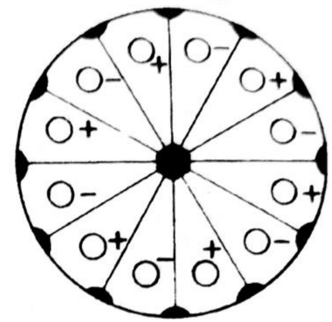


$\bar{6}$ (C_{3h})

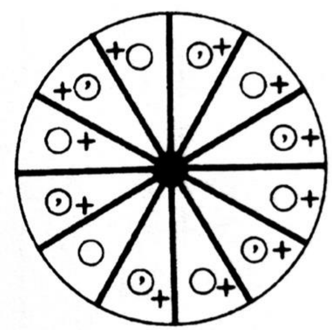


$6/m$ (C_{6h})

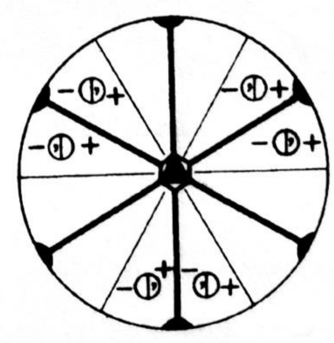
Laue group $\frac{6}{m}mm$



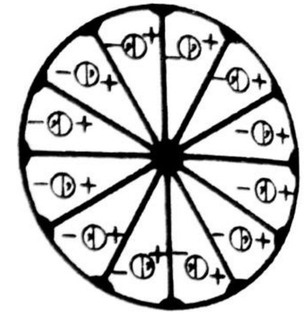
622 (D_6)



$6mm$ (C_{6v})

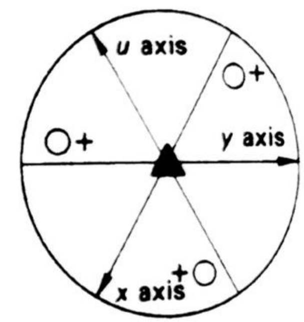


$\bar{6}m2$ (D_{3h})

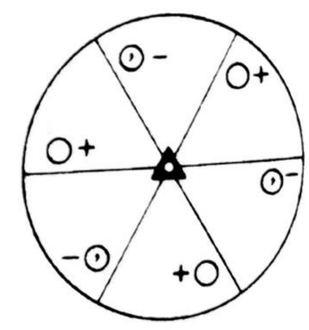


$\frac{6}{m}mm$ (D_{6h})

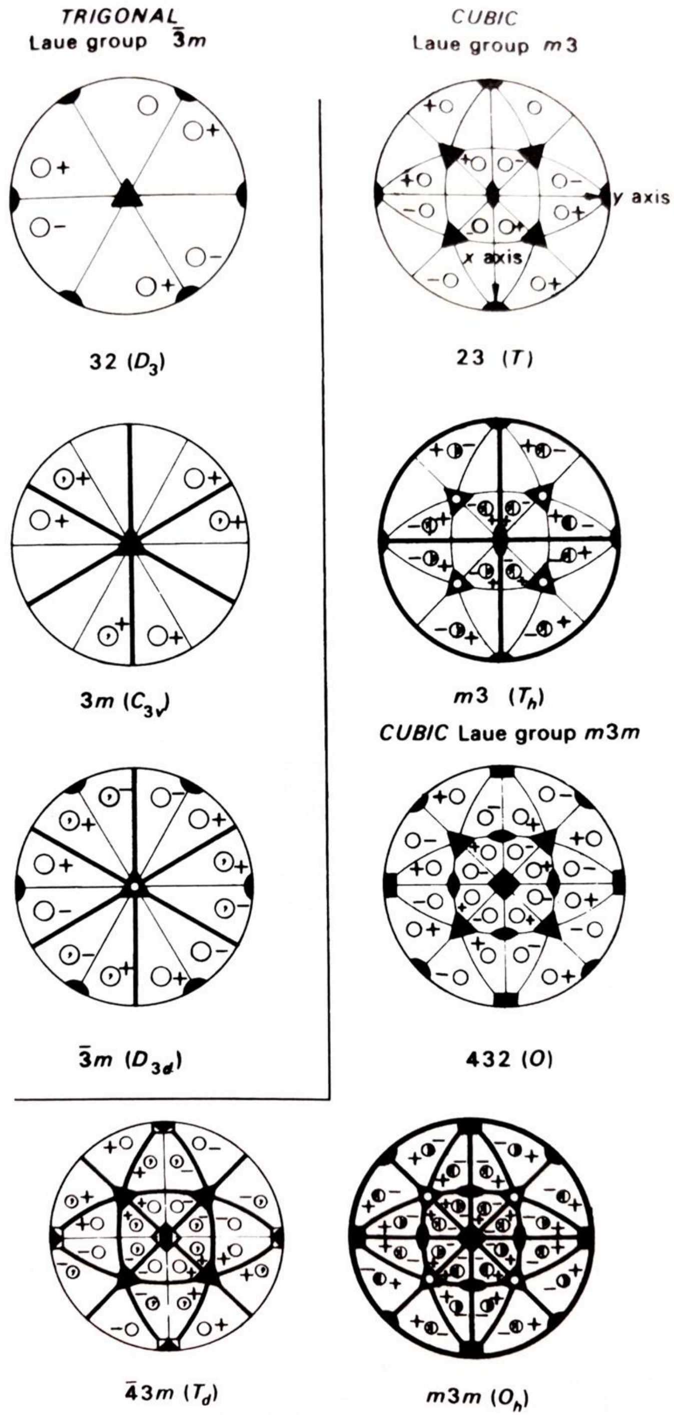
TRIGONAL Laue group $\bar{3}$



3 (C_3)



$\bar{3}$ (S_6)



Source: Ladd & Palmer

Choosing the Correct Crystal System

- Do not assume the metric relations indicate the correct point group and crystal system!!!
- Correctly identify the Laue group symmetry of the diffraction pattern (equivalent intensities, R_{sym})
- The Laue symmetry indicates the crystal system of your sample
- Correct Laue group assignment narrows space group choices

Space Groups

- Space groups vs Point groups
  - Point groups describe symmetry of isolated objects
  - Space groups describe symmetry of infinitely repeating space filling objects
- Space groups include point symmetry elements

Space Groups

- Space groups vs Point groups
  - Point groups describe symmetry of isolated objects
  - Space groups describe symmetry of infinitely repeating space filling objects
- Space groups include point symmetry elements
- After the break - yeah