Of Symmetry, Lattices & Space Groups

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What is Symmetry?

- Symmetry is all around us…
  - Just have a look…
- Examples
  - Mirror planes
  - Rotational axes
  - Repetitive motifs, i.e. Lattices
- Outline of Seminar
  - Symmetry Operators
  - Point groups
  - Lattices (2D & 3D)
  - Plane groups (2D)
  - Space groups (3D)
  - Reciprocal Space
  - Space Group Determination

Basic Symmetry Operators

- Rotation axes
- Mirror planes
- Points of inversion
- Screw axes
- Glide planes
- Pseudo-symmetry

Notation

- Schönflies
  - Rotational axes: C_1, C_2, C_3,…
  - Mirror planes: S_1, C_{2v}, C_{3h},…, D_4, D_{4h},…
  - C for cyclic, D for dihedral, S for *spiegel* (mirror)…

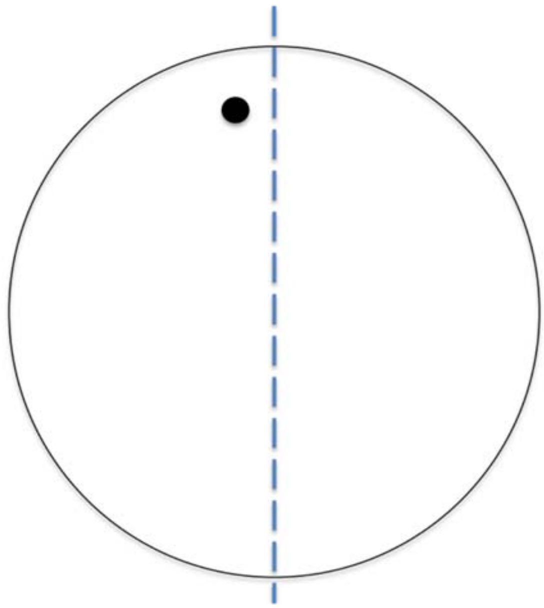
- Hermann-Mauguin
  - Rotational: 1, 2, 3, …
  - Mirror planes: m, 4mmm, 2/m,…
  - IUCr notation

- Others
  - Hall (1981)
    - Explicit
    - e.g. P 2y (= P2 or P 1 2 1 in Hermann-Mauguin)

Asymmetry

Notation: 1 (C_1)

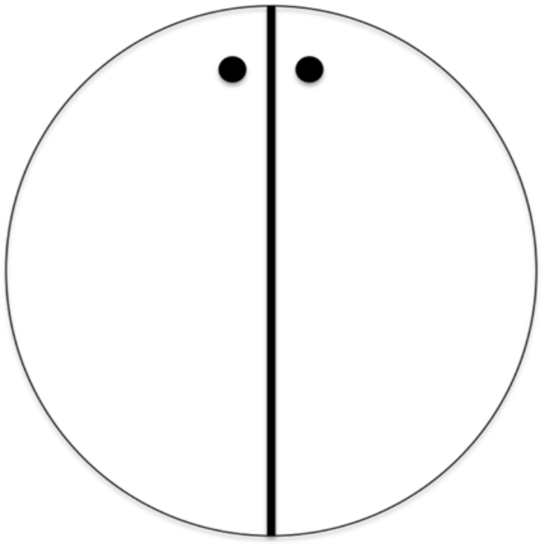
Equivalent positions:
1) x, y, z



Mirror Symmetry

Equivalent positions:

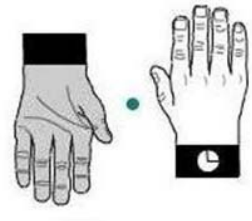
1) x, y, z
2) –x, y, z

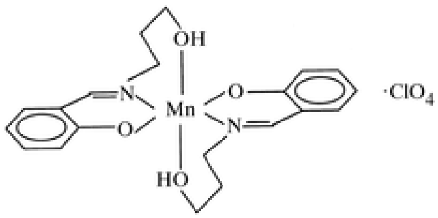


Notation: m

(S_1 or C_s)

Point of Inversion Symmetry



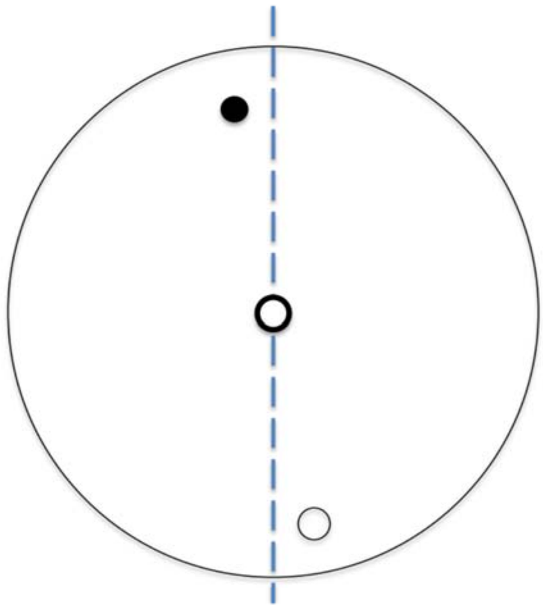


(I)

Equivalent positions:

1) x, y, z

2) -x, -y, -z



Inverted hands catch in rugby

Notation: $\bar{1}$ (C_i)

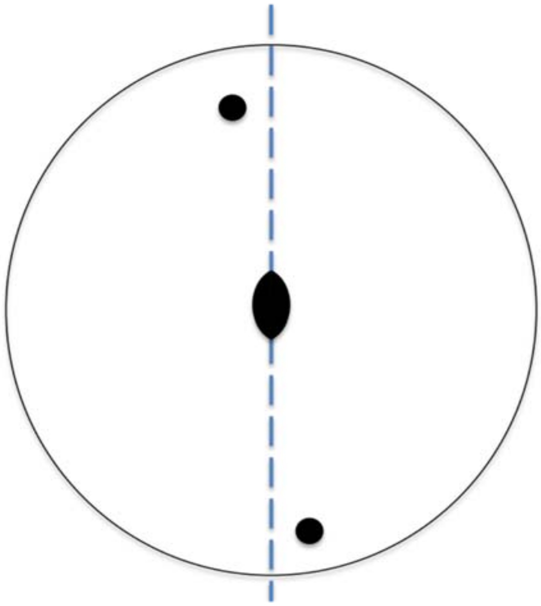
Prononced « one-bar »

2-fold Rotational Symmetry

Notation: 2

Equivalent positions:

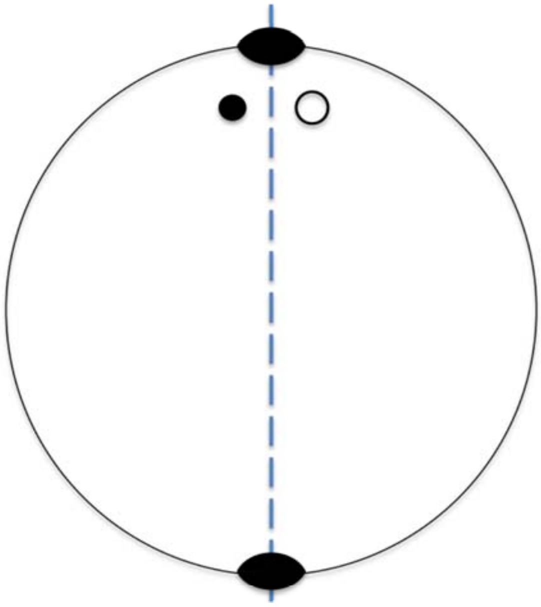
1) x, y, z
2) -x, -y, z



2-fold Rotational Symmetry

Equivalent positions:

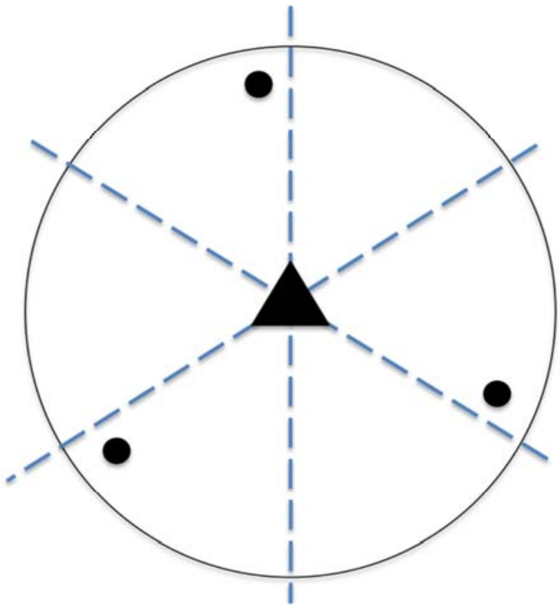
1) x, y, z
2) -x, y, -z



Notation: 2

3-fold Rotational Symmetry

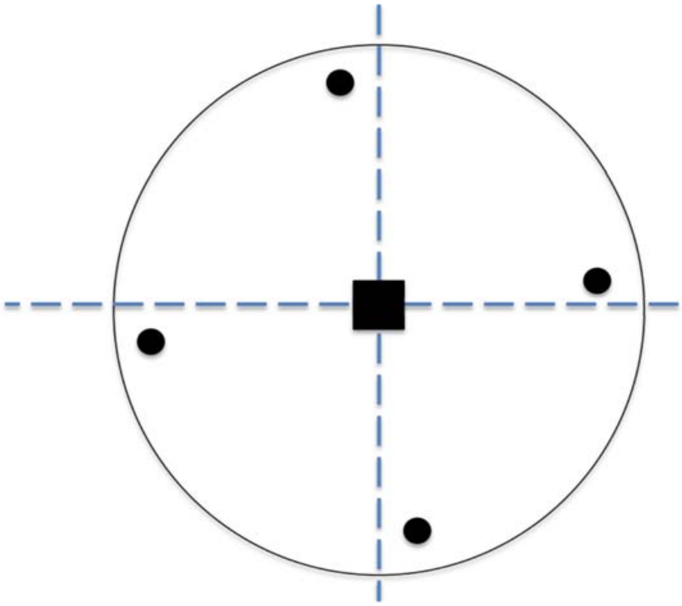
Notation: 3



4-fold Rotational Symmetry

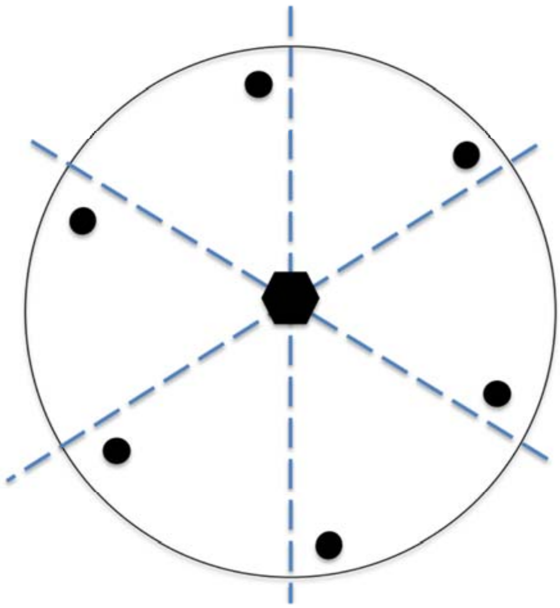
Equivalent positions:

1) x, y, z 3) y, -x, z
2) -x, -y, z 4) -y, x, z



Notation: 4

6-fold Rotational Symmetry



Notation: 6

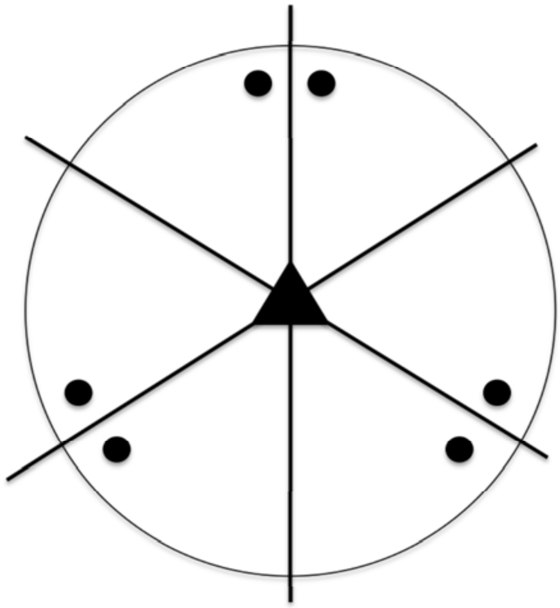
POINT GROUPS (1D)

Point groups

- Definition:
  - Point groups define symmetry about a speficied origin
  - The overall symmetry may combine more than one symmetry element
- Examples
  - 2, 222, 4, 422,…
  - mmm, 3m, 2/m,…

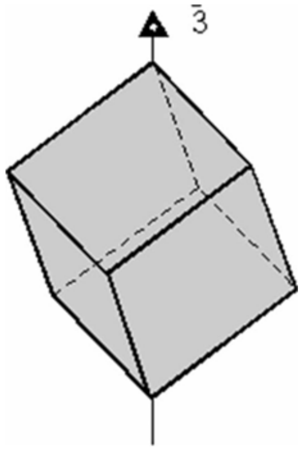
- Reciprocal space has a point group
  - The point group defines equivalent reflections

Point Group 3m

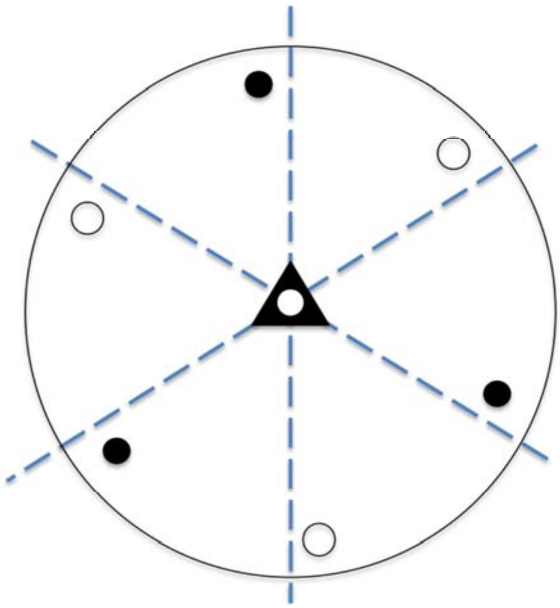


Notation: 3m

3-fold Rotational Symmetry with Inversion

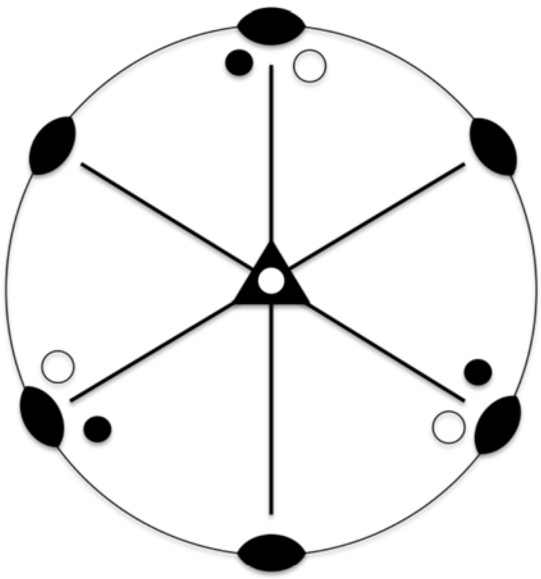


Notation: $\bar{3}$

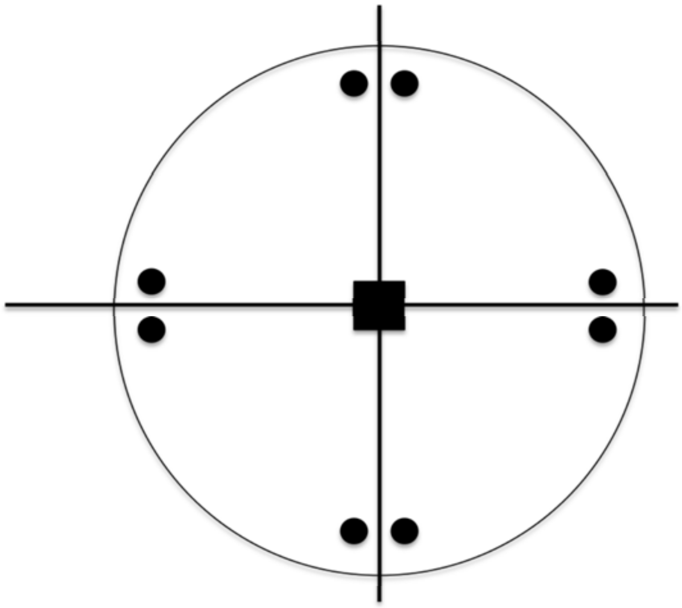


321 Point Group

Notation: 321



4mm point group



Homework

- How many symmetry elements are there in a:
  - Rugby ball?
  - Tennis ball?
  - Football?
  - Shoe box?
  - Cube?

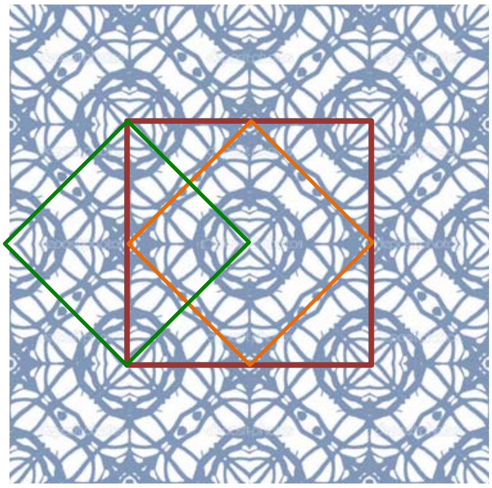


- Which point groups does each belong to?

LATTICES & PLANE GROUPS (2D)

Lattices

- Lattices are objects with a repetitive structure
  - The repetitive *unit*…
    - has a constant size & shape
    - may be formulated several ways
      - definition of the origin
      - centring
    - can reconstruct the entire object
    - may have symmetry elements
      - Rotational, mirror planes,…
      - glide planes & screw axes
- 2-dimensional lattices
  - Wallpaper, tiles & clothing
- 3-dimensional lattices
  - Packing, stacking & crystals

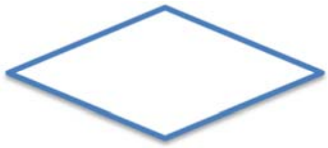


2D Bravais Lattices

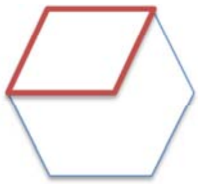
- Oblique (Parallelogram)
  - a ≠ b, $\alpha \neq 90°$

- Rectangular
  - a ≠ b, $\alpha = 90°$

- Rhombic
  - a = b, $\alpha \neq 90°$

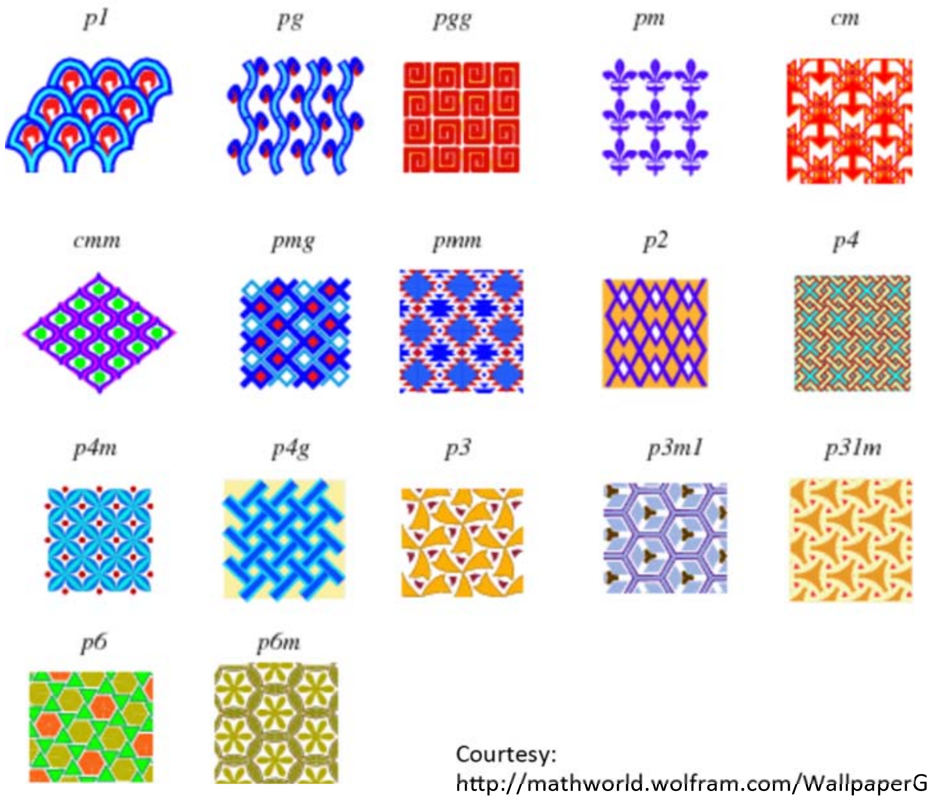


- Hexagonal
  - a = b, $\alpha = 120°$



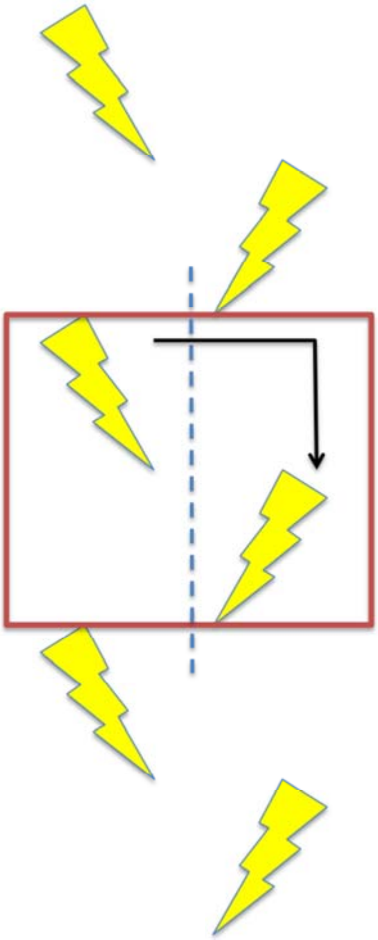
- Square
  - a = b, $\alpha = 90°$

Plane groups (17)



Courtesy:
http://mathworld.wolfram.com/WallpaperGroups.html

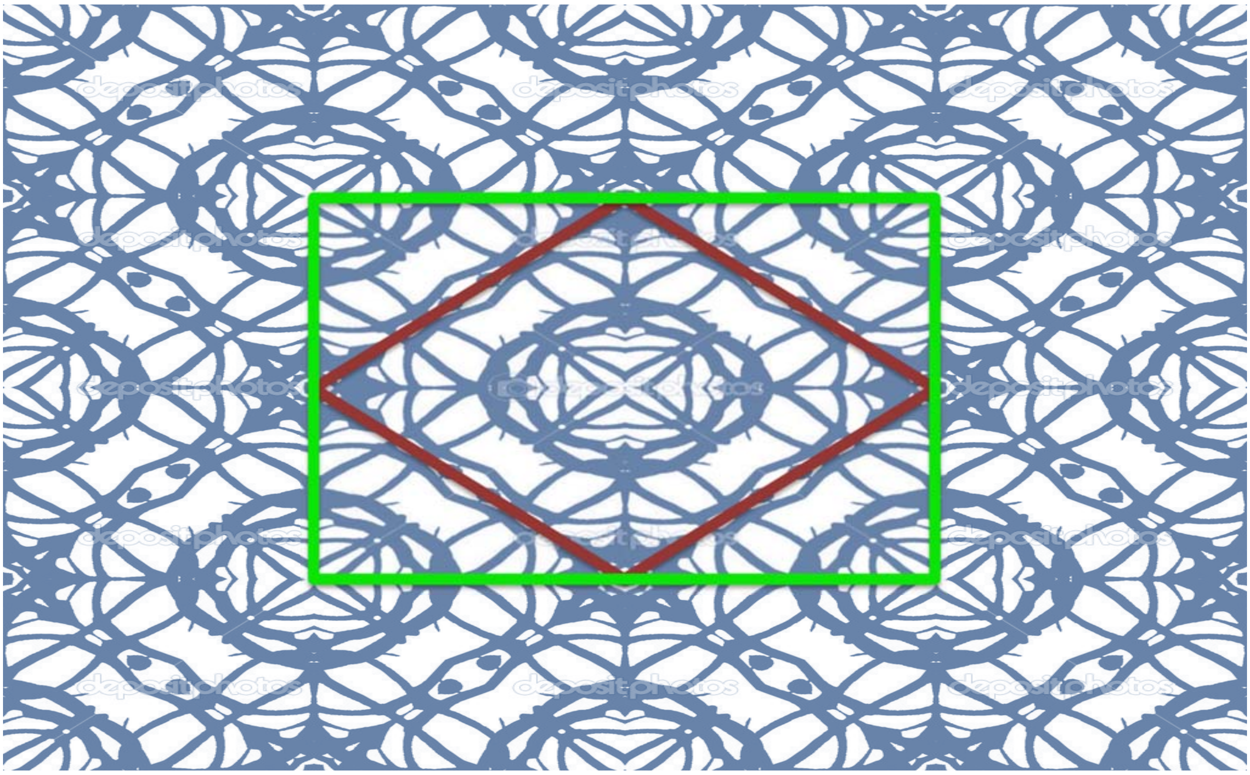
Glide planes



- Mirror plane with translation
  - Translation defined as:
    - along mirror plane
    - ½ unit cell length
- Notation (Herman-Mauguin)
  - 2D: g (glide)
  - 3D: a, b, c, n, e, d
    - a = glide along a-axis of unit cell
- Symbol
  - Right angle arrow
- Common in small molecule crystallography
  - But non-existent for protein/DNA/RNA crystallography…

Centring

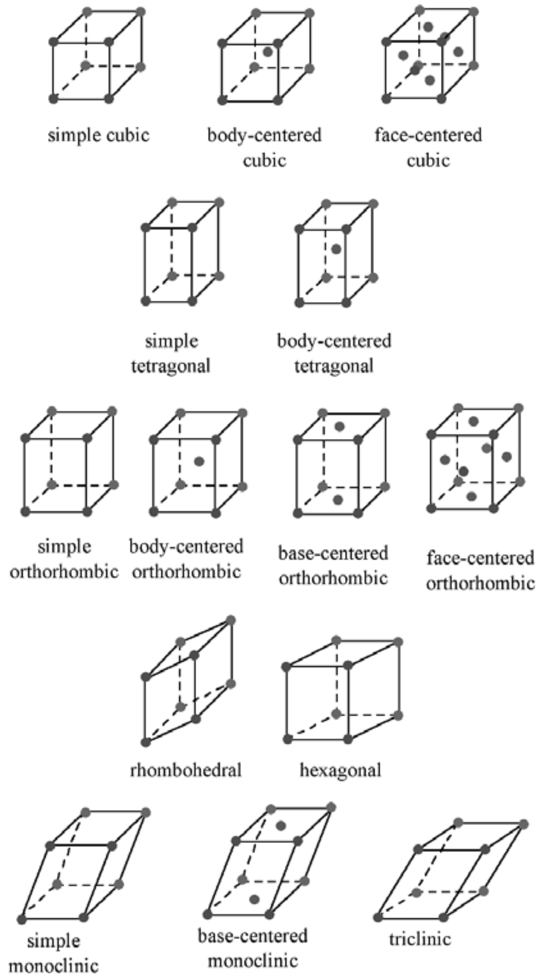
- Which unit cell would you choose? Why?



3D LATTICES & SPACE GROUPS

3D Bravais Lattices

- 14 Bravais Lattices
- 7 Lattice Systems
  - Trinclinic (a ≠ b ≠ c, α ≠ β ≠ γ ≠ 90°)
  - Monoclinic
  - Orthorhombic
  - Tetragonal
  - Rhombohedral/trigonal
  - Hexagonal
  - Cubic
- Centering
  - Primitive (P)
  - Axis centered (A,B,C)
  - Body-centered (I)
    - German *Innenzentriert*
  - Face-centered (F)
  - Rhombohedral (R)



3D Space Groups

- 230 Space groups
  - 65 Sohncke or non-centrosymmetric space groups
    - chiral molecules (i.e. protein, DNA, RNA,…)
- IUCr International Tables Vol. A
  - The « bible » for crystallographers!
  - …which is out of print… but exists in PDF format
- http://img.chem.ucl.ac.uk/sgp/large/sgp.htm
  - Very convenient web site!
  - Jeremy Karl Cockcroft

Space Group Notation

$I4_322$

- Always starts with the type of centering
  - Always a CAPITAL letter for 3D space
  - P, (A, B), C, I, F or R (Hermann Mauguin notation)
- Followed by symmetry elements
  - Rotation/Screw axes
    - 2, 3, 4, 6 or 2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5
  - Mirrors, glide planes & centers of inversion
    - m, a, b, c, n, d, (e) and/or a number with a « bar » over it
    - e.g. $\overline{3}$, pronouced « three-bar »
- Long and short notations
  - $P2_1$ and $P\ 1\ 2_1\ 1$

Space Group Names
(short & long notations)

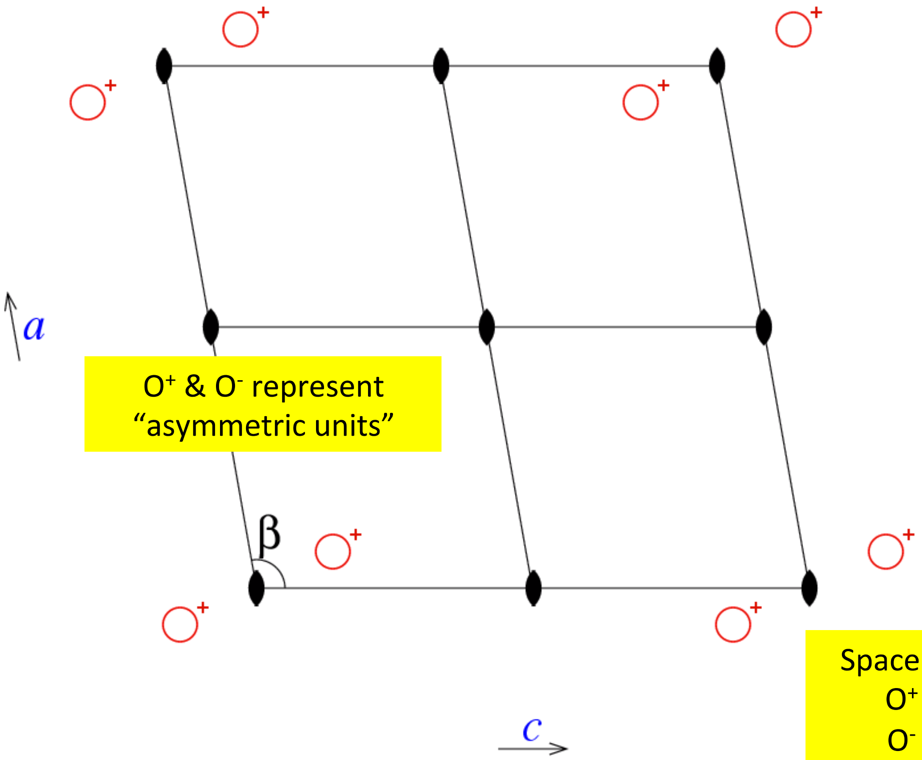
*P*2 *P* 1 2 1

Point Group

2

Space Group
Number

No. 3



O⁺ & O⁻ represent
"asymmetric units"

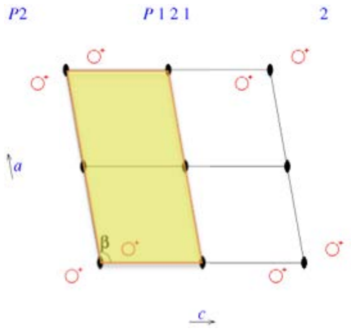
Equivalent
Positions

1 x, y, z

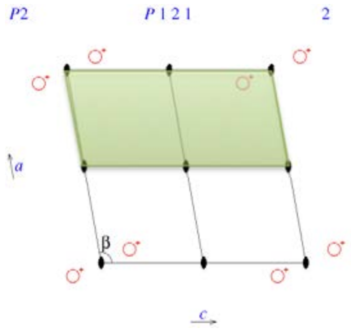
2 $\bar{x}, y, \bar{z}$

Space group diagram
O⁺ above page
O⁻ below page

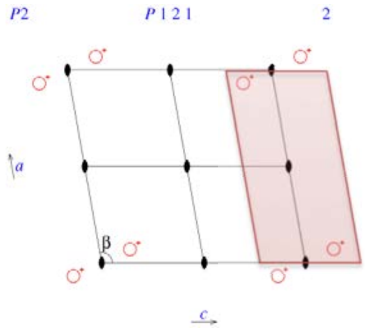
Asymmetric Unit (ASU)



Yes!



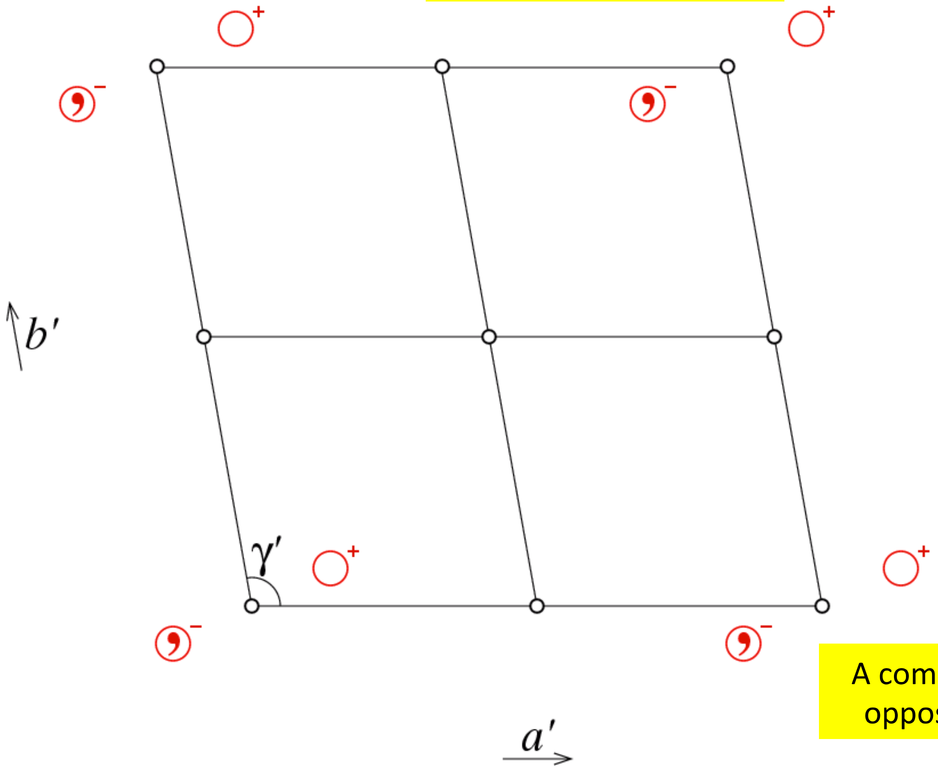
Yes!



No!

- The asymmetric unit (shaded yellow or green) of a space group is the fractional volume that contains <u>no crystallographic symmetry</u>
  - ASU volume = 1/N, where N = number of equivalent positions in the space group
  - The ASU is represented by a single O^+ sign in the space group diagram
- The ASU may contain more than 1 molecule
  - Non-Crystalllographic Symmetry (NCS)
  - Beware: NCS is fairly common in MX!

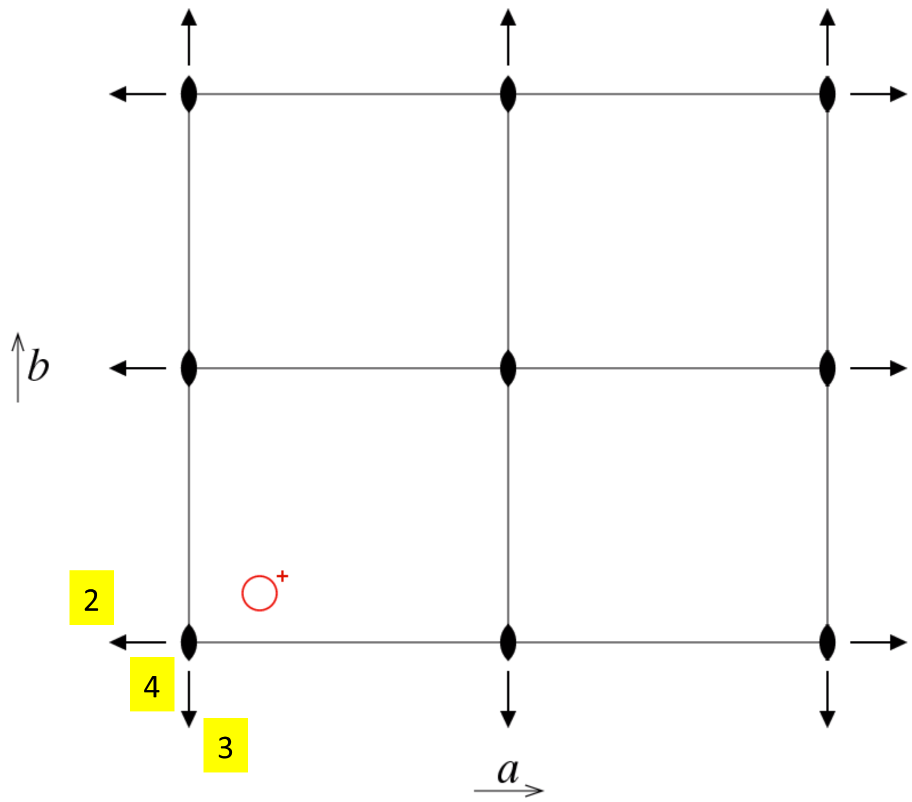
Pronounced “P 1 bar”



1 x, y, z

2 $\bar{x}, \bar{y}, \bar{z}$

A comma indicates the opposite chiral hand

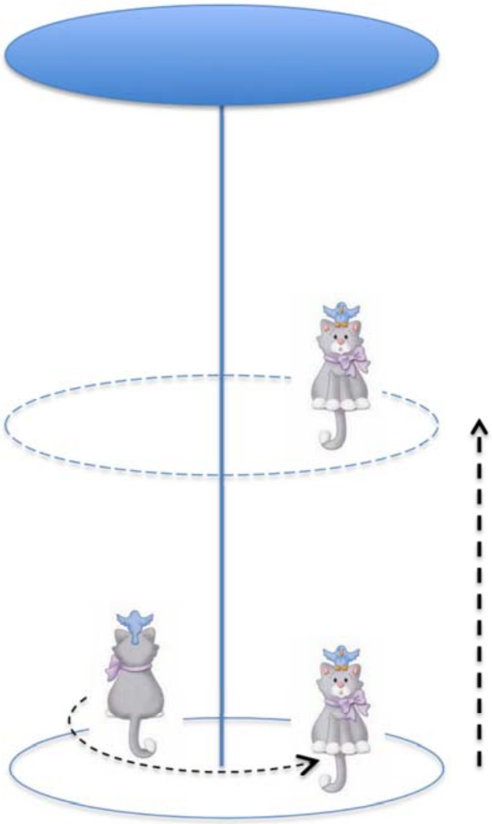


1 x, y, z

2 $x, \bar{y}, \bar{z}$

3 $\bar{x}, y, \bar{z}$

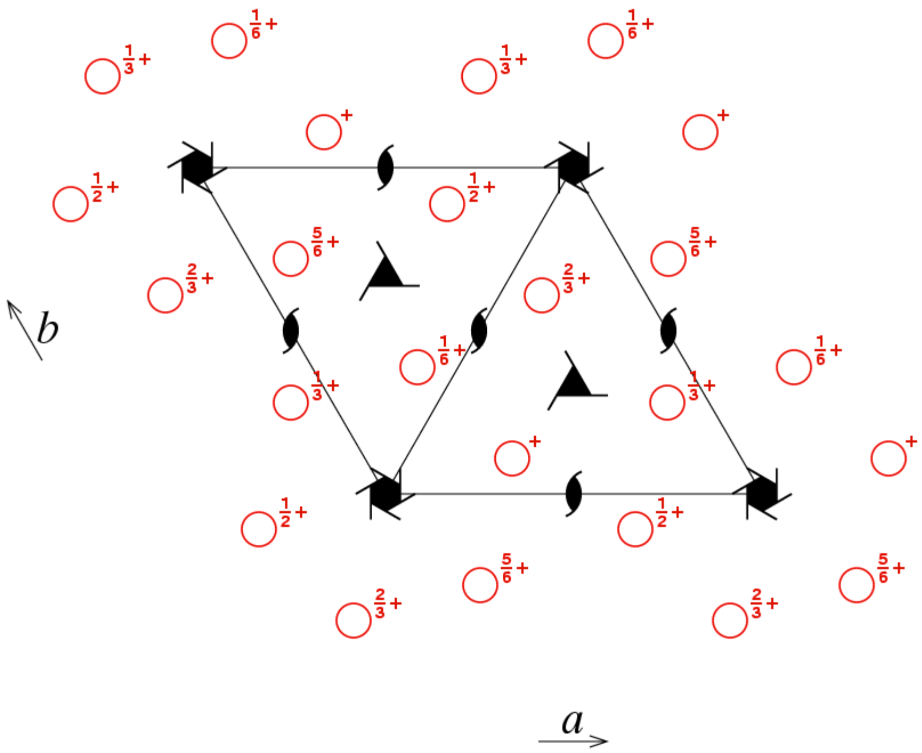
4 $\bar{x}, \bar{y}, z$



Screw axes

- 2-fold screw axis
  - Rotate 180˚
  - Translate ½ unit cell length
  - Notation: 2_1
- 3-fold screw axes
  - Rotate +120˚ or -120˚
  - Translate +⅓ or -⅓ unit cell length
  - Notation: 3_1, 3_2
- 4-fold
  - Rotate ±90˚ or 180˚
  - Translate ±¼, +½ unit cell length
  - Notation: 4_1, 4_2, 4_3
- 6-fold
  - Rotate ±60˚, ±120˚or 180˚
  - Translate ±⅙, ±⅓, +½ unit cell length
  - Notation: 6_1, 6_2, 6_3, 6_4, 6_5
- Enantiomorphic pairs
  - { 3_1|3_2 }, { 4_1|4_3 }, { 6_1|6_5 }, { 6_2| 6_4 }

$P6_1$ $P\,6_1$ 6 No. 169



1 x, y, z

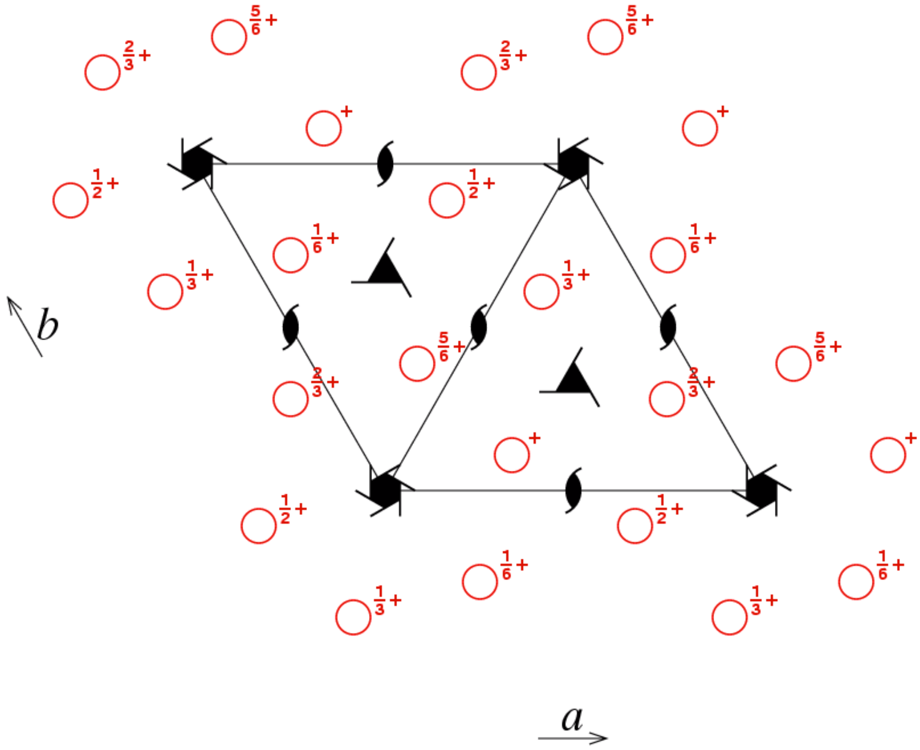
2 $\bar{y}, x-y, \frac{1}{3}+z$

3 $\bar{x}+y, \bar{x}, \frac{2}{3}+z$

4 $\bar{x}, \bar{y}, \frac{1}{2}+z$

5 $x-y, x, \frac{1}{6}+z$

6 $y, \bar{x}+y, \frac{5}{6}+z$



1 x, y, z

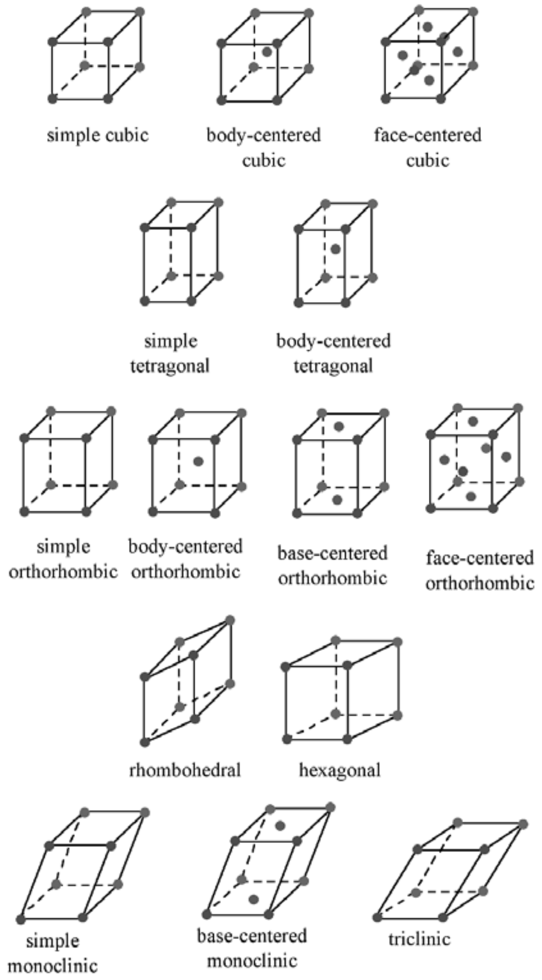
2 $\bar{y}, x-y, \frac{2}{3}+z$

3 $\bar{x}+y, \bar{x}, \frac{1}{3}+z$

4 $\bar{x}, \bar{y}, \frac{1}{2}+z$

5 $x-y, x, \frac{5}{6}+z$

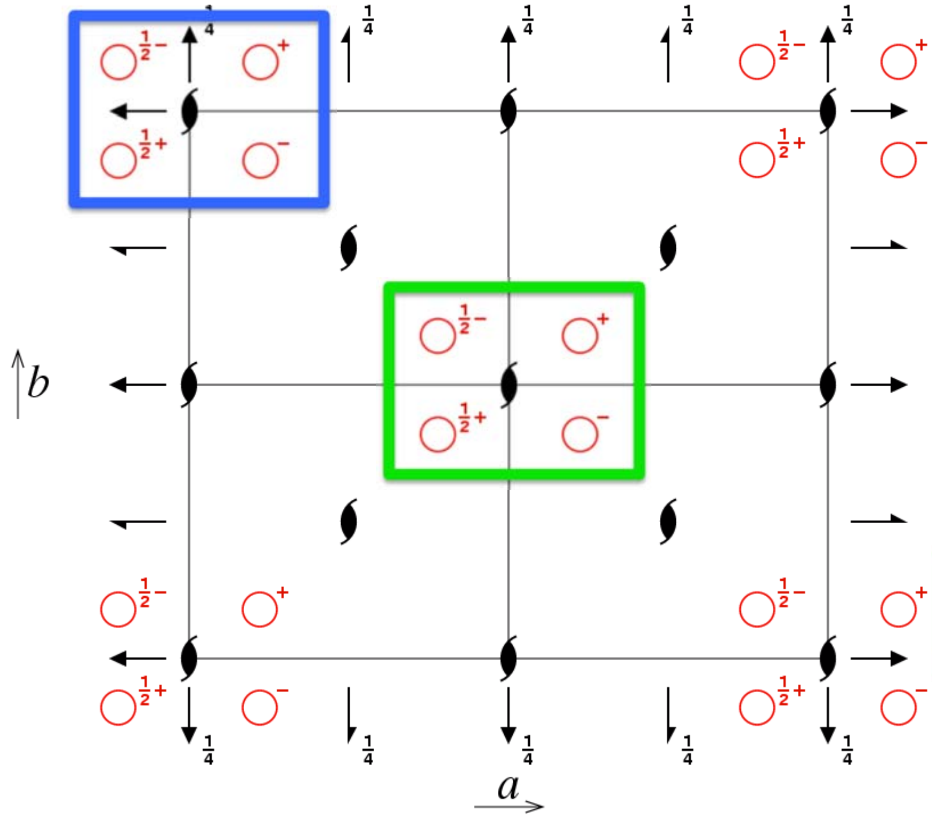
6 $y, \bar{x}+y, \frac{1}{6}+z$



Centering

- Primitive
  - P
- Base centering
  - A, B or C
- Body centering
  - I (*Innenzentriert*)
- Face centering
  - F

$C222_1$ $C\,2\,2\,2_1$ 222 No. 20



1 x, y, z

2 $x, \bar{y}, \bar{z}$

3 $\bar{x}, y, \frac{1}{2} - z$

4 $\bar{x}, \bar{y}, \frac{1}{2} + z$

$+ (\frac{1}{2}, \frac{1}{2}, 0)$

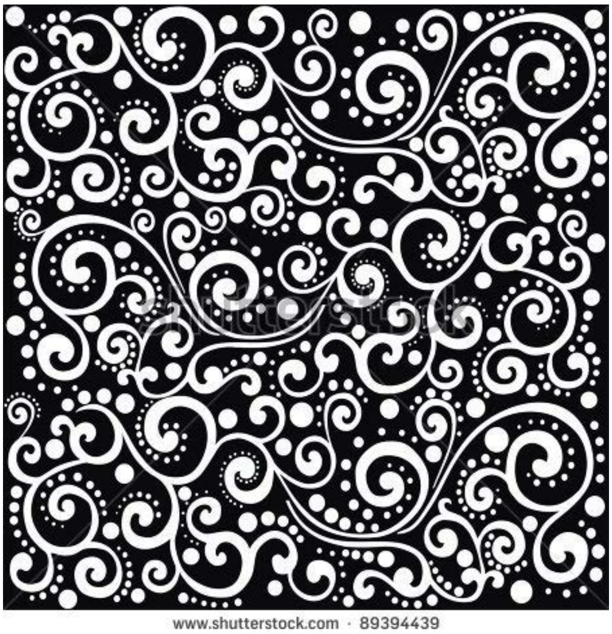
PSEUDO-SYMMETRY

Pseudo-symmetry

- Lots and lots…

- Especially when things don't quite fit right together…
  Like biological macromolecules!
  - e.g. Hemeglobin $\alpha_2\beta_2$
  - Non-Crystallographic Symmetry (NCS) very common
    - More than one molecule in the asymmetric unit

2D Pseudo-symmetry



EXTRA!

Pseudo-Symmetry & Unit Cells

- Some lower symmetry unit cells may look like higher symmetry ones, e.g.
  - Monoclinic unit cells with β ≈ 90° may index as an orthorhombic unit cell
  - An orthorhombic unit cell with a ≈ b may index as a tetragonal unit cell
- Examine the output of the next slide
  - a ≈ b ≈ c
  - In fact the protein displays « polymorphism » and crystallises into more than one crystal form (unit cell)

Indexing & Space Groups

EXTRA!

	LATTICE-CHARACTER	BRAVAIS-LATTICE	QUALITY OF FIT	a	b	c	alpha	beta	gamma
*	44	aP	0.0	98.5	103.5	106.3	90.1	90.0	90.0
*	31	aP	0.0	98.5	103.5	106.3	89.9	90.0	90.0
*	35	mP	0.2	103.5	98.5	106.3	90.0	90.1	90.0
*	34	mP	0.6	98.5	106.3	103.5	90.1	90.0	90.0
*	33	mP	0.7	98.5	103.5	106.3	90.1	90.0	90.0
*	32	oP	0.8	98.5	103.5	106.3	90.1	90.0	90.0
*	25	mC	30.7	148.3	148.4	98.5	90.0	90.0	88.5
*	23	oC	30.8	148.3	148.4	98.5	90.0	90.0	88.5
*	20	mC	30.8	148.4	148.3	98.5	90.0	90.0	91.5
*	21	tP	31.4	103.5	106.3	98.5	90.0	90.0	90.1
*	14	mC	52.1	142.9	142.9	106.3	90.0	90.0	87.2
*	13	oC	52.2	142.9	142.9	106.3	90.0	90.0	87.2
*	10	mC	52.2	142.9	142.9	106.3	90.0	90.0	92.8
*	11	tP	52.3	98.5	103.5	106.3	90.1	90.0	90.0
	4	hR	82.8	142.9	145.0	178.0	93.5	87.8	117.9
	2	hR	83.0	142.9	145.0	178.2	93.6	87.7	118.0
	3	cP	83.4	98.5	103.5	106.3	90.1	90.0	90.0
	5	cI	248.9	144.9	142.9	148.3	59.7	58.3	62.1
	39	mC	249.9	229.2	98.5	106.3	90.0	90.1	64.6
	37	mC	250.1	234.3	98.5	103.5	90.0	90.1	65.1
	38	oC	250.5	98.5	229.2	106.3	89.9	90.0	115.4
	29	mC	250.5	98.5	229.2	106.3	89.9	90.0	64.6
	28	mC	250.6	98.5	234.4	103.5	90.0	90.0	65.1
	36	oC	250.7	98.5	234.3	103.5	89.9	90.0	114.9
	41	mC	275.4	236.4	103.5	98.5	90.0	90.0	64.1
	30	mC	275.4	103.5	236.4	98.5	90.0	90.0	64.1
	40	oC	275.4	103.5	236.4	98.5	90.0	90.0	115.9

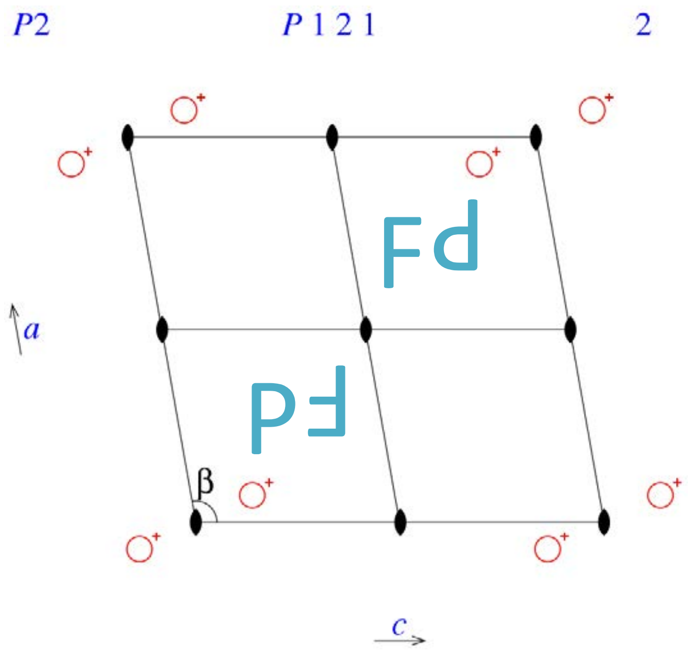
UNIT CELL CONSTANTS (ANGSTROEM & DEGREES)

Possible solutions

Possible polymorphism?
- Proteins may crystallise in more than one lattice and space group

Non-Crystallographic Symmetry (NCS)

EXTRA!



- The above example illustrates NCS
- The P and F resemble each other, and they pack along a pseudo 2-fold axis
- The real space group is P2 with 2 *slightly different* molecules in the ASU

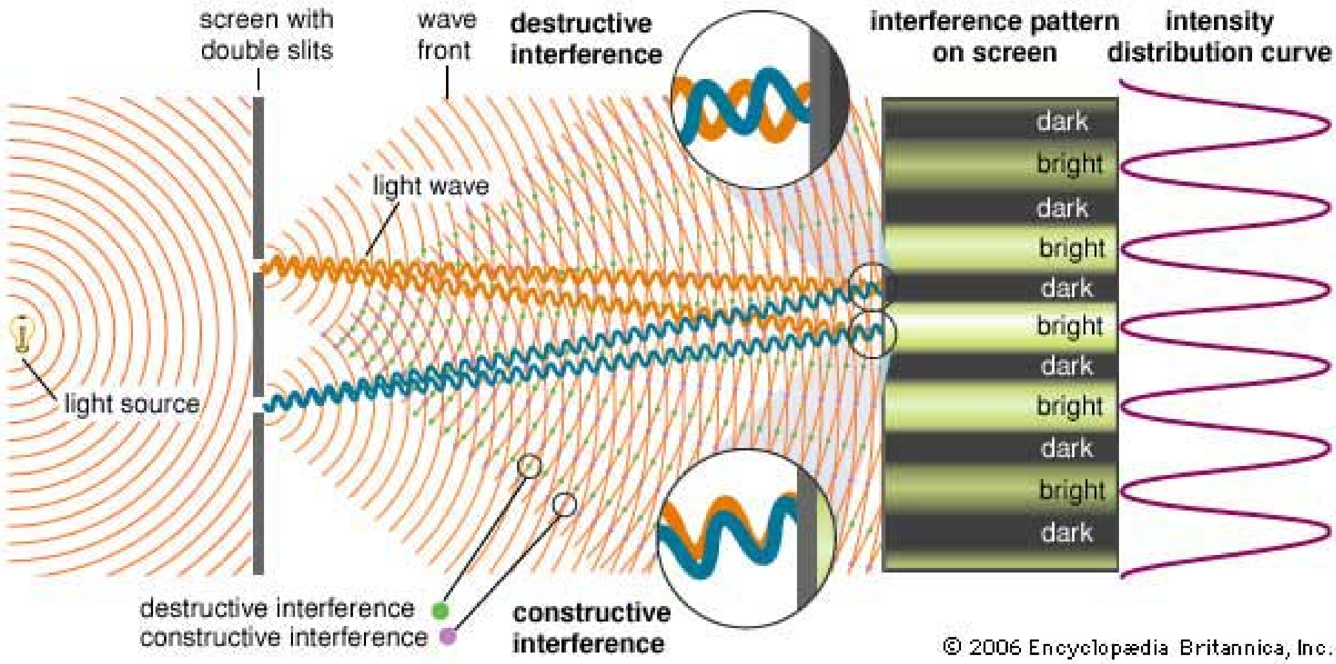
Intermission?

- Next up…
  - Real Space and Reciprocal Space
  - Space Group Determination

Real Space & Reciprocal Space?

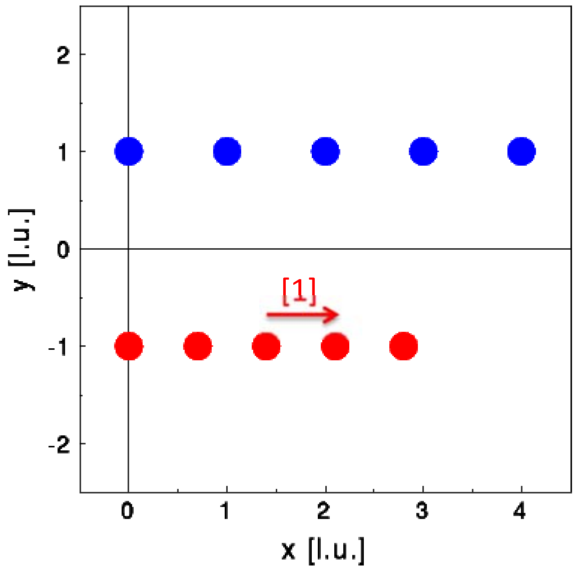
- Reciprocal Space is an abstract concept that explains diffraction…
- It is a relationship between the lattice planes of a crystal in real space, and their corresponding diffraction points generated by Reciprocal Space…
- It also applies to 1D and 2D « crystals »
  - which are easier to visualise and understand…

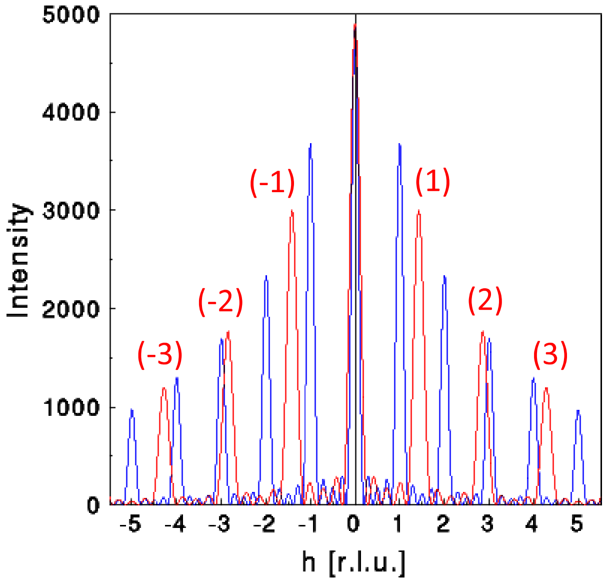
Young's Experiment (1803) Revisited



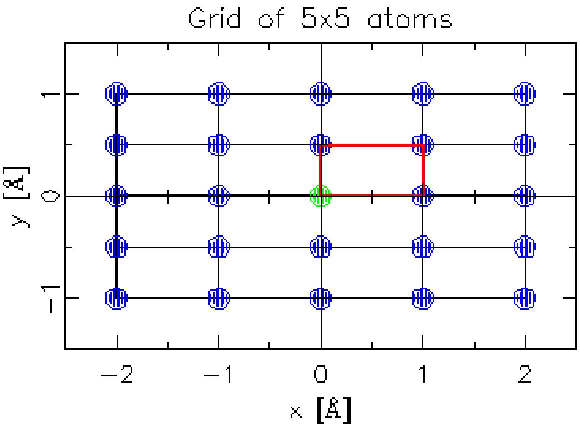
Reciprocity & 1D Reciprocal Space

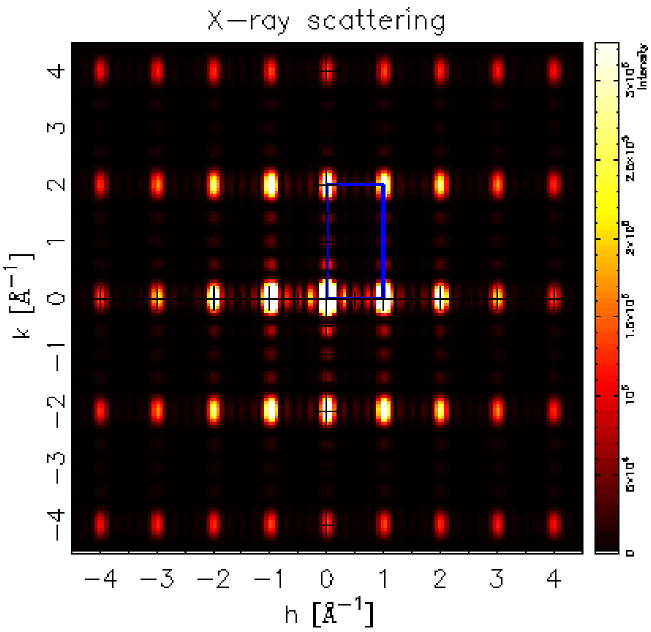
- Consider the multiple atom experiment
- A smaller spacing (x) between slits or atoms in the lattice yields….
  - a larger separation between diffraction spots (1/x)
    - Each diffraction spot has its own Miller index, (h)
    - Each Miller index represents a vector in real space, [h]



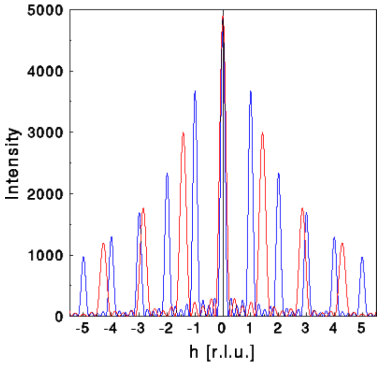


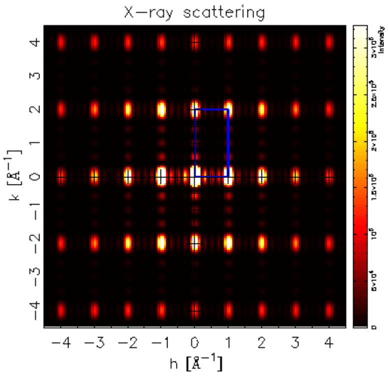
Reciprocal space of a grid

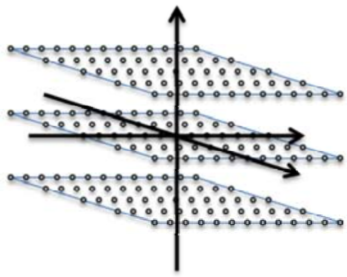




1D, 2D & 3D Reciprocal Space



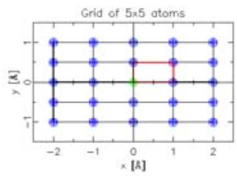


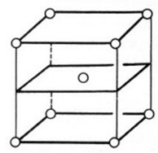


1D
Lattice points
[h]
Unit Spacing = a

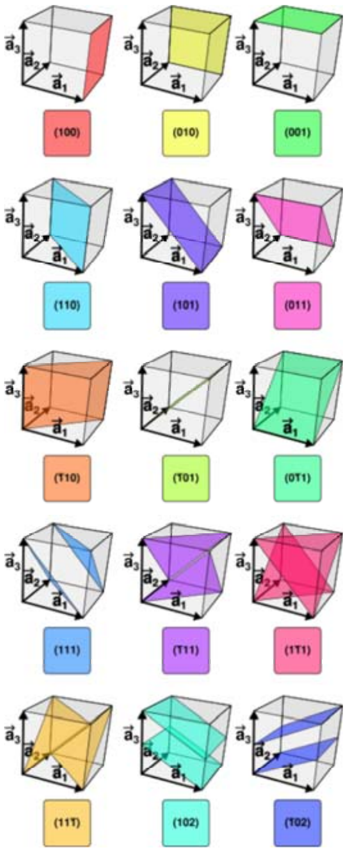
2D
Lattice lines
[hk]
Unit cell constants =
a, b & α

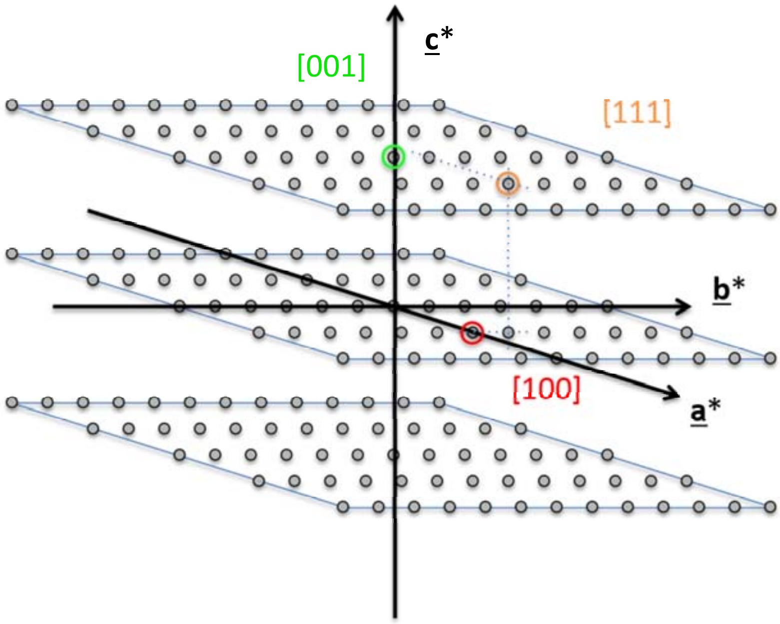
3D
Lattice planes
[hkl]
Unit cell constants =
a, b, c, α, β, γ





3D Reciprocal Space

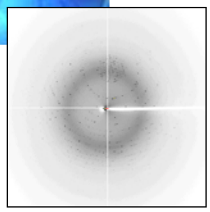




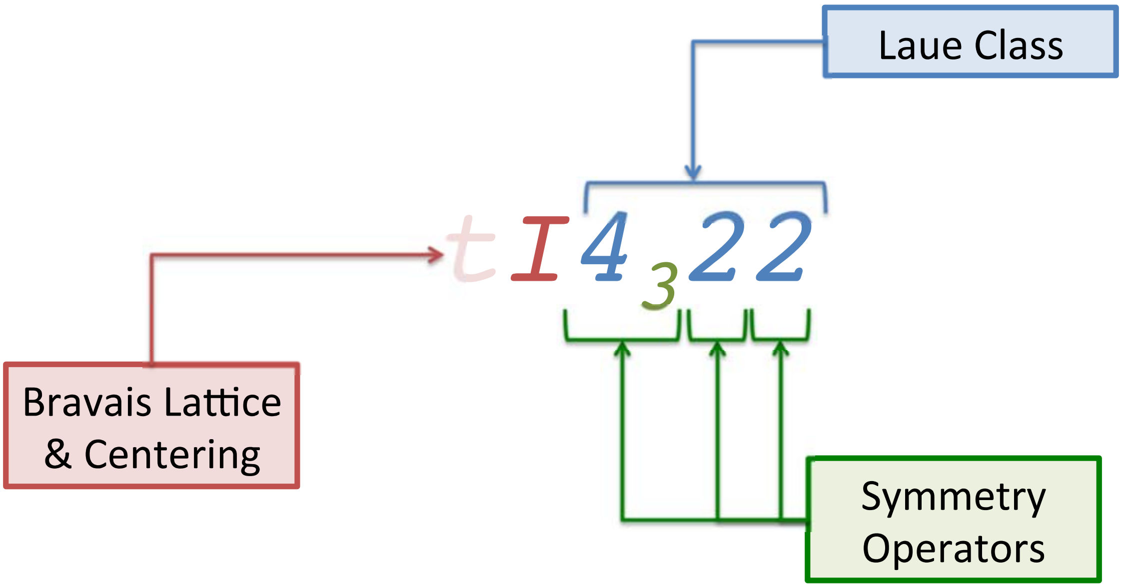
- Lattice planes in Real Space become points in Reciprocal Space

Space Group Determination

- So you have crystals & crystallographic data
  - Congratulations!
  - Now the fun begins…!
- Q: How to determine its space group?
  - 1) Determine the *Bravais Lattice*
  - 2) Determine the *Laue Class*
  - 3) Look for *Systematic Absences*
  - 4) Check for *Enantiomorphic* Space Groups
  - 5) Check *IUCr Conventions*
  - 6) Verify *Equivalent Indexing Solutions*
  - 7) Verify the *Choice of Origin*

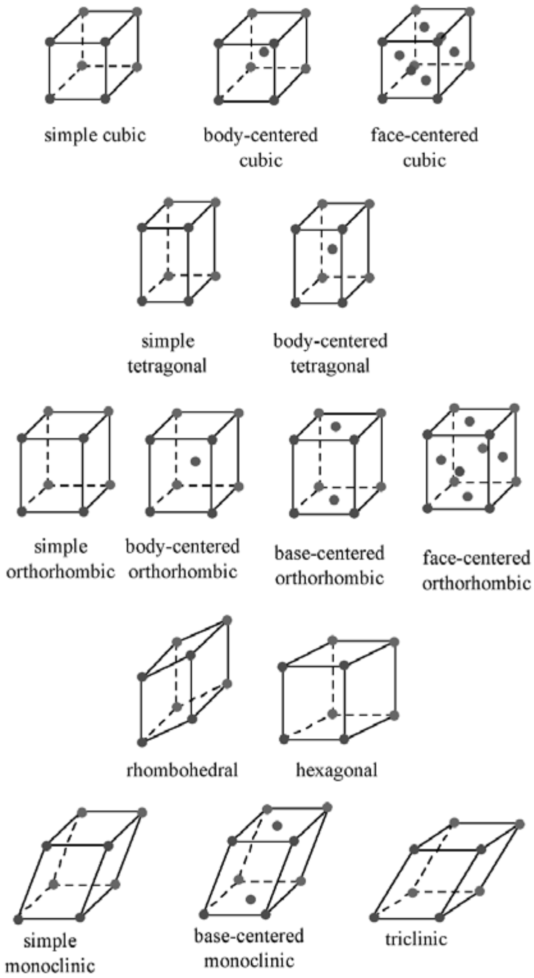
Space Group Notation



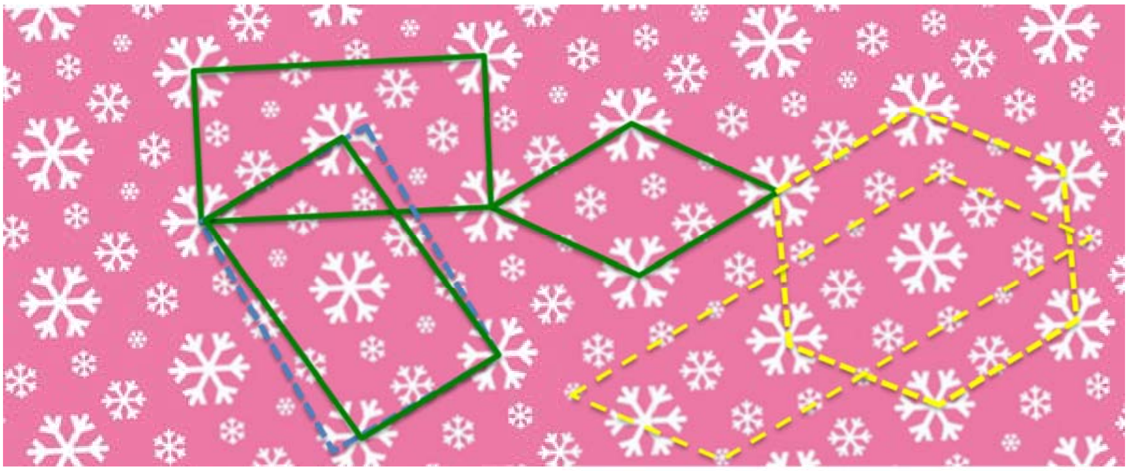
Bravais (3D) Lattices

- 14 Bravais Lattices
- 7 Lattice Systems
  - Triclinic (*a* for anorthic)
    - a ≠ b ≠ c, α ≠ β ≠ γ ≠ 90°
  - Monoclinic (*m*)
    - a ≠ b ≠ c, α = γ = 90° ≠ β
  - Orthorhombic (*o*)
    - a ≠ b ≠ c, α = β = γ = 90°
  - Tetragonal (*t*)
    - a = b ≠ c, α = β = γ = 90°
  - Trigonal / Rhombohedral (*h*)
    - Trigonal a = b ≠ c, α = β = 90°, γ = 120°
    - Rhombahedral a = b = c, α = β = γ ≠ 90°
  - Hexagonal (*h*)
    - a = b ≠ c, α = β = 90°, γ = 120°
  - Cubic (*c*)
    - a = b = c, α = β = γ = 90°
- Centering
  - Primitive (P)
  - Axis centered (A,B,C)
  - Body-centered (I)
    - German *Innenzentriert*
  - Face-centered (F)
  - Rhombohedral (R)

Where « ≠ » means not necessarily equal to



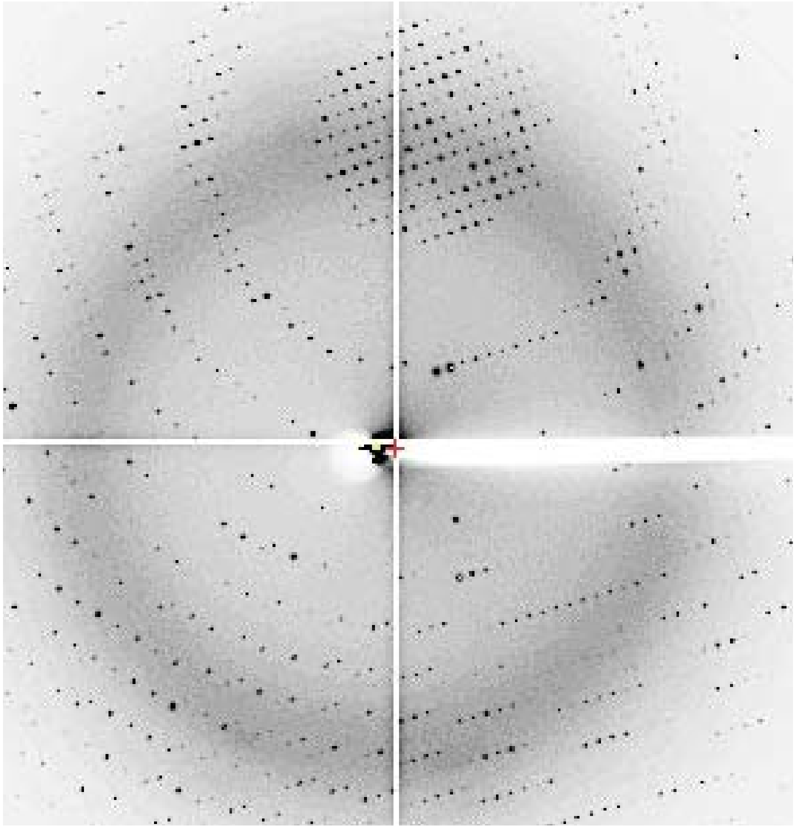
Which Bravais Lattice in Real Space?



- What is a Unit Cell?
  - Smallest *unique repeating unit* of a crystal
  - Many possibilities… but only one ***reduced cell***… which ***transforms*** to other cells
  - The final choice should obey IUCr conventions (i.e. rules)
    - → cube-like unit cell
    - Preference for α, β, γ = 90°
      - α, β, γ > 90°
    - a < b < c, except for unique symmetry axes

Find Spots & Index

- Find strong spots
  - X_{det}, Y_{det}, ω (angle)
- Convert spot positions to reciprocal space
- Calculate a ***reduced*** unit cell and its transformations:
  - a, b, c, α, β, γ
- Assign a Miller indice (h,k,l) to each spot

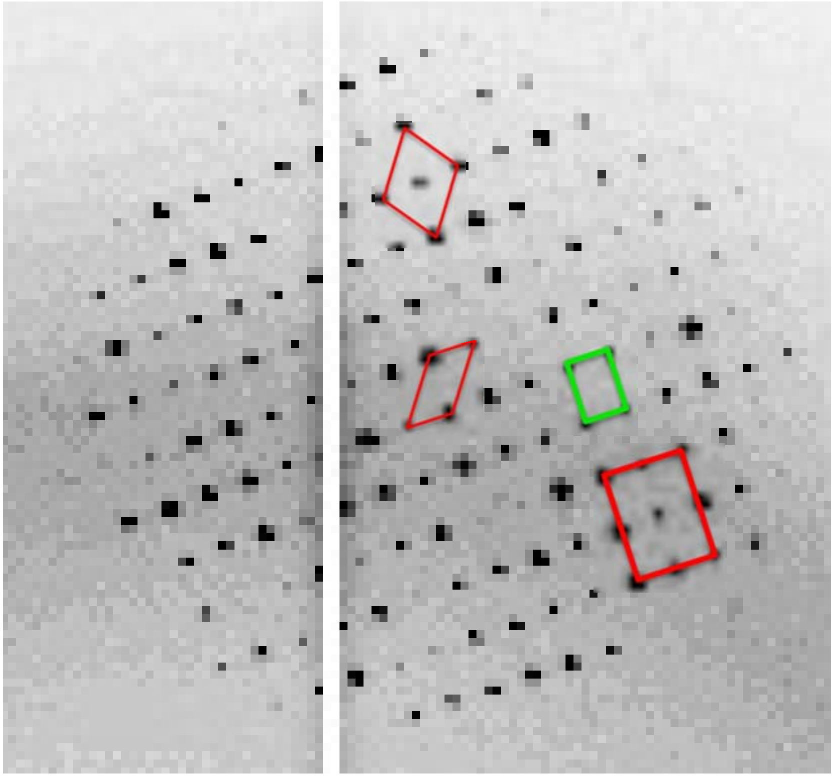


Which Bravais Lattice in Reciprocal Space?

- Look at this diffraction pattern
  - obviously we prefer: α, β, γ = 90°

- NOTE: Miller Indices (h,k,l) must be integers!

- Note: Centered Lattices will have *systematic absences*
  - C-centered: h+k = 2n
  - I-centered: h+k+l = 2n



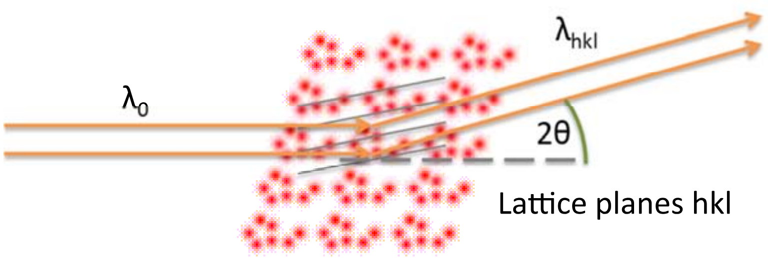
Example: Indexing & Space Groups

LATTICE-CHARACTER	BRAVAIS-LATTICE	QUALITY OF FIT	a	b	c	alpha	beta	gamma
* 44	aP	0.0	98.5	103.5	106.3	90.1	90.0	90.0
* 31	aP	0.0	98.5	103.5	106.3	89.9	90.0	90.0
* 35	mP	0.2	103.5	98.5	106.3	90.0	90.1	90.0
* 34	mP	0.6	98.5	106.3	103.5	90.1	90.0	90.0
* 33	mP	0.7	98.5	103.5	106.3	90.1	90.0	90.0
* 32	oP	0.8	98.5	103.5	106.3	90.1	90.0	90.0
* 25	mC	30.7	148.3	148.4	98.5	90.0	90.0	88.5
* 23	oC	30.8	148.3	148.4	98.5	90.0	90.0	88.5
* 20	mC	30.8	148.4	148.3	98.5	90.0	90.0	91.5
* 21	tP	31.4	103.5	106.3	98.5	90.0	90.0	90.1
* 14	mC	52.1	142.9	142.9	106.3	90.0	90.0	87.2
* 13	oC	52.2	142.9	142.9	106.3	90.0	90.0	87.2
* 10	mC	52.2	142.9	142.9	106.3	90.0	90.0	92.8
* 11	tP	52.3	98.5	103.5	106.3	90.1	90.0	90.0
4	hR	82.8	142.9	145.0	178.0	93.5	87.8	117.9
2	hR	83.0	142.9	145				
3	cP	83.4	98.5	103				
5	cI	248.9	144.9	142				
39	mC	249.9	229.2	98				
37	mC	250.1	234.3	98				
38	oC	250.5	98.5	229				
29	mC	250.5	98.5	229				
28	mC	250.6	98.5	234				
36	oC	250.7	98.5	234				
41	mC	275.4	236.4	103				
30	mC	275.4	103.5	236				
40	oC	275.4	103.5	236				

UNIT CELL CONSTANTS (ANGSTROEM & DEGREES)

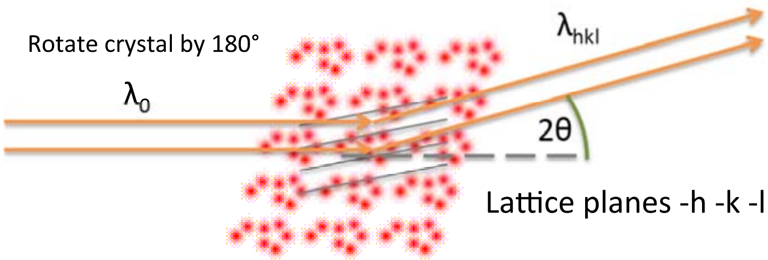
Possible solutions:
- All likely, because β = 90° for monoclinic unit cell (for example)
- Usually we select the solution with the highest symmetry, but BEWARE the correct unit cell could have lower symmetry
- CAUTION: The quality of fit depends strongly on correct experimental parameters:
    - Distance
    - X-ray wavelength
    - Beam center
    - tilt & twist of detector

Friedel's Law (1913)



$\underline{F}(hkl) = \underline{f}_1 + \underline{f}_2 + \underline{f}_3 + \underline{f}_4 + \underline{f}_5 + \underline{f}_6 + \underline{f}_7$

Front to back direction



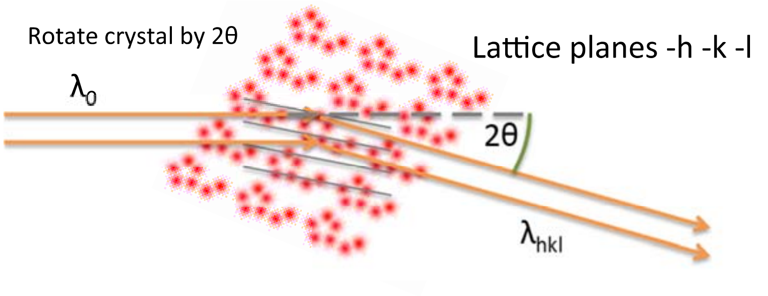
$\underline{F}(-h\ -k\ -l) = -\underline{f}_7 - \underline{f}_6 - \underline{f}_5 - \underline{f}_4 - \underline{f}_3 - \underline{f}_2 - \underline{f}_1$

Back to front direction

$|F(h,k,l)|^2 = I(h,k,l)$

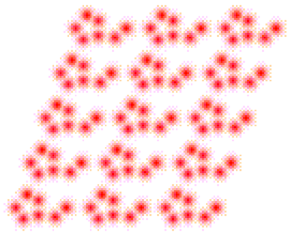
$|F(h,k,l)| = |F(-h,-k,-l)|$

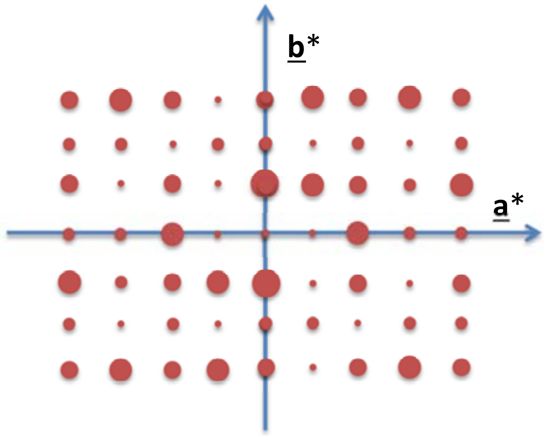
$I(h,k,l) = I(-h,-k,-l)$



Diffraction adds a symmetry of inversion!

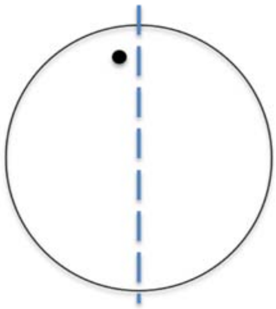
Point Group & Laue Class





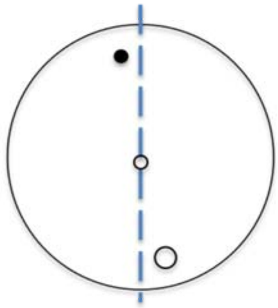
Point Group 1

[x, y, z]



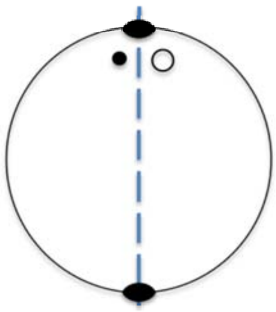
Laue Class $\bar{1}$

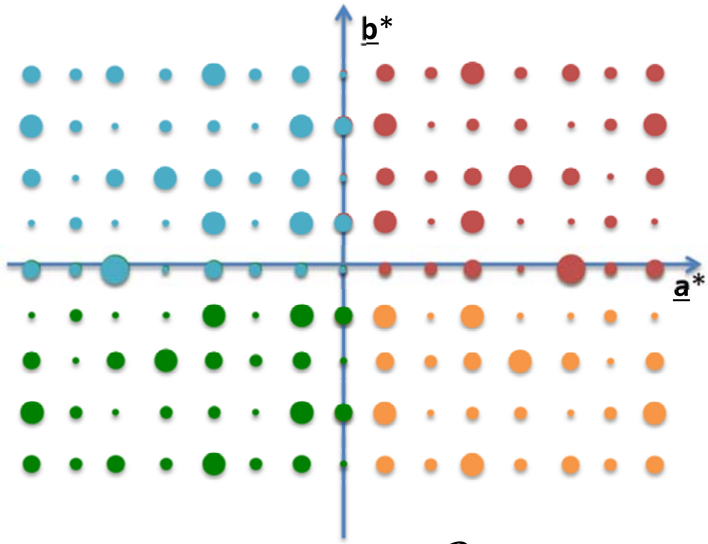
$hkl = \overline{hkl}$



Point Group 2

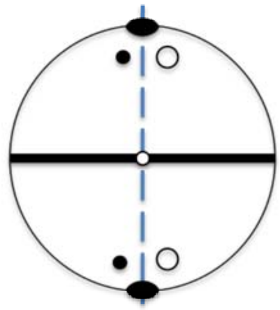
[x, y, z], [-x, y, -z]





Laue Class $^{2}/_{m}$

$$hkl = \overline{hkl} = h\bar{k}l = \bar{h}k\bar{l}$$



Point Group & Laue Class

Table 3.1.2.1. *Laue classes and crystal systems*

Laue class	Crystal system	Conditions imposed on cell geometry
$\bar{1}$	Triclinic	None
$2/m$	Monoclinic	$\alpha = \gamma = 90°$ (b unique) $\alpha = \beta = 90°$ (c unique)
mmm	Orthorhombic	$\alpha = \beta = \gamma = 90°$
$4/m$ $4/mmm$	Tetragonal	$a = b; \alpha = \beta = \gamma = 90°$
$\bar{3}$ $\bar{3}m$	Trigonal	$a = b; \alpha = \beta = 90°; \gamma = 120°$ (hexagonal axes) $a = b = c; \alpha = \beta = \gamma$ (rhombohedral axes)
$6/m$ $6/mmm$	Hexagonal	$a = b; \alpha = \beta = 90°; \gamma = 120°$
$m\bar{3}$ $m\bar{3}m$	Cubic	$a = b = c; \alpha = \beta = \gamma = 90°$

Table 2.1.2.1. *Crystal families, crystal systems, conventional coordinate systems and Bravais lattices in one, two and three dimensions*

Laue Classes

Crystal family	Symbol*	Crystal system	Crystallographic point groups†	No. of space groups	Conventional coordinate system		Bravais lattices*
					Restrictions on cell parameters	Parameters to be determined	
Three dimensions							
Triclinic (anorthic)	a	Triclinic	$1, \bar{1}$	2	None	$a, b, c, \alpha, \beta, \gamma$	aP
Monoclinic	m	Monoclinic	$2, m, 2/m$	13	b-unique setting $\alpha = \gamma = 90°$	a, b, c β‡	mP mS (mC, mA, mI)
					c-unique setting $\alpha = \beta = 90°$	$a, b, c,$ γ‡	mP mS (mA, mB, mI)
Orthorhombic	o	Orthorhombic	$222, mm2, mmm$	59	$\alpha = \beta = \gamma = 90°$	a, b, c	oP oS (oC, oA, oB) oI oF
Tetragonal	t	Tetragonal	$4, \bar{4}, 4/m$ $422, 4mm, \bar{4}2m,$ $4/mmm$	68	$a = b$ $\alpha = \beta = \gamma = 90°$	a, c	tP tI
Hexagonal	h	Trigonal	$3, \bar{3}$ $32, 3m, \bar{3}m$	18	$a = b$ $\alpha = \beta = 90°, \gamma = 120°$	a, c	hP
				7	$a = b = c$ $\alpha = \beta = \gamma$ (rhombohedral axes, primitive cell) $a = b$ $\alpha = \beta = 90°, \gamma = 120°$ (hexagonal axes, triple obverse cell)	a, α	hR
		Hexagonal	$6, \bar{6}, 6/m$ $622, 6mm, \bar{6}2m,$ $6/mmm$	27	$a = b$ $\alpha = \beta = 90°, \gamma = 120°$	a, c	hP
Cubic	c	Cubic	$23, m\bar{3}$ $432, \bar{4}3m, m\bar{3}m$	36	$a = b = c$ $\alpha = \beta = \gamma = 90°$	a	cP cI cF

Laue Class & Equivalent Reflections

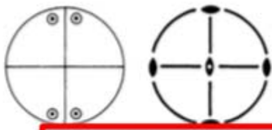
10. POINT GROUPS AND CRYSTAL CLASSES

Table 10.1.2.2. *The 32 three-dimensional crystallographic point groups*

General, special and limiting face forms and *point forms* (italics), oriented face and site symmetries, and Miller indices (*hkl*) of equivalent faces [for trigonal and hexagonal groups Bravais–Miller indices (*hkil*) are used if referred to hexagonal axes]; for point coordinates see text.

mmm D_{2h}

$\frac{2}{m}\frac{2}{m}\frac{2}{m}$



8	*g*	1	Rhombic dipyramid *Quad* (α)	(hkl) $(\bar{h}\bar{k}l)$ $(\bar{h}k\bar{l})$ $(h\bar{k}\bar{l})$ $(\bar{h}\bar{k}\bar{l})$ $(hk\bar{l})$ $(h\bar{k}l)$ $(\bar{h}kl)$
4	*f*	*..m*	Rhombic prism *Rectangle through origin* (*y*)	$(hk0)$ $(\bar{h}\bar{k}0)$ $(\bar{h}k0)$ $(h\bar{k}0)$
4	*e*	*.m.*	Rhombic prism *Rectangle through origin* (*w*)	$(h0l)$ $(\bar{h}0l)$ $(\bar{h}0\bar{l})$ $(h0\bar{l})$
4	*d*	*m..*	Rhombic prism *Rectangle through origin* (*u*)	$(0kl)$ $(0\bar{k}l)$ $(0k\bar{l})$ $(0\bar{k}\bar{l})$
2	*c*	*mm*2	Pinacoid or parallelohedron *Line segment through origin* (*q*)	(001) $(00\bar{1})$
2	*b*	*m*2*m*	Pinacoid or parallelohedron *Line segment through origin* (*m*)	(010) $(0\bar{1}0)$
2	*a*	2*mm*	Pinacoid or parallelohedron *Line segment through origin* (*i*)	(100) $(\bar{1}00)$

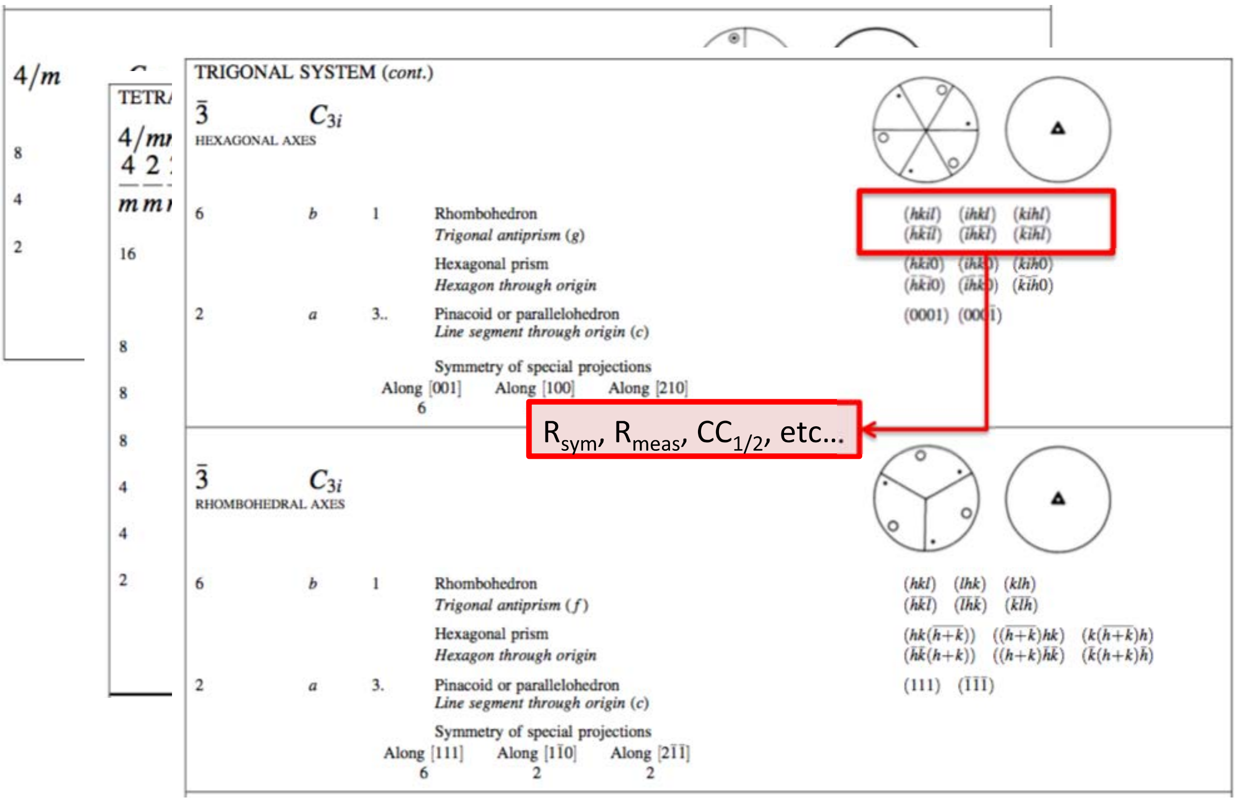
Symmetry of special projections

Along [100]	Along [010]	Along [001]
2*mm*	2*mm*	2*mm*

10. POINT GROUPS AND CRYSTAL CLASSES

Table 10.1.2.2. *The 32 three-dimensional crystallographic point groups*

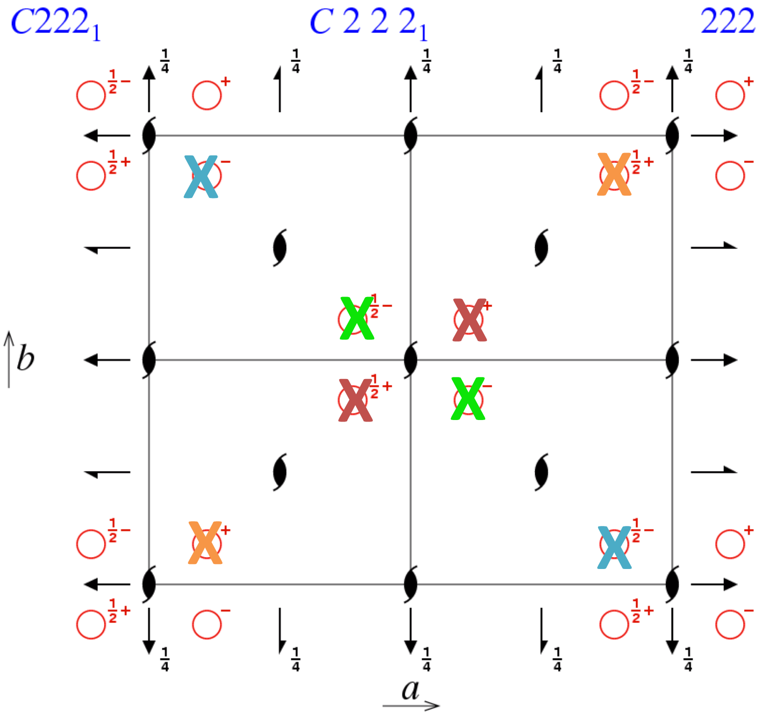
General, special and limiting face forms and *point forms* (italics), oriented face and site symmetries, and Miller indices (*hkl*) of equivalent faces [for trigonal and hexagonal groups Bravais–Miller indices (*hkil*) are used if referred to hexagonal axes]; for point coordinates see text.



Reflection Conditions & Systematic Absences

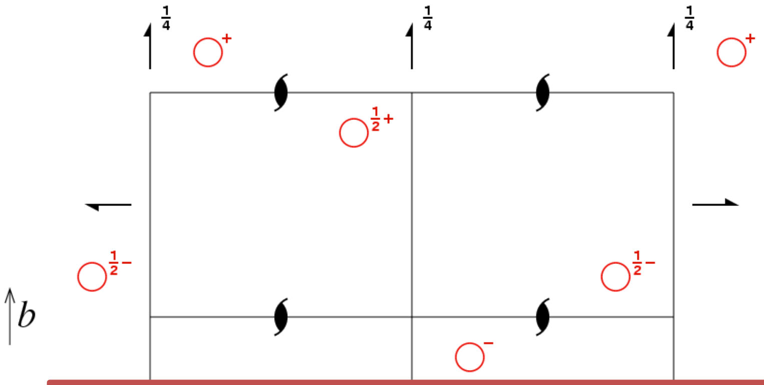
- Certain symmetry operators generate ***reflection conditions,*** also known as ***systematic absences***
- The structure factors (intensities) of the atomic positons generated by these symmetry operators ***cancel out*** for certain ***families of reflections*** (e.g. 00l)
  - Example $C222_1$
    - Reflection conditions
    - hkl : h+k = 2n
    - 00l: k = 2n

F(0k0) = 0 for k = 2n+1, and is ***systematically absent for k = odd numbers***



Equivalent Positions & Systematic Absences

$P2_12_12_1$ $\quad P\,2_1\,2_1\,2_1$ $\quad 222$ $\quad$ No. 19



1 x, y, z

2 $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$

3 $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$

$P2_12_12_1$ No. 19

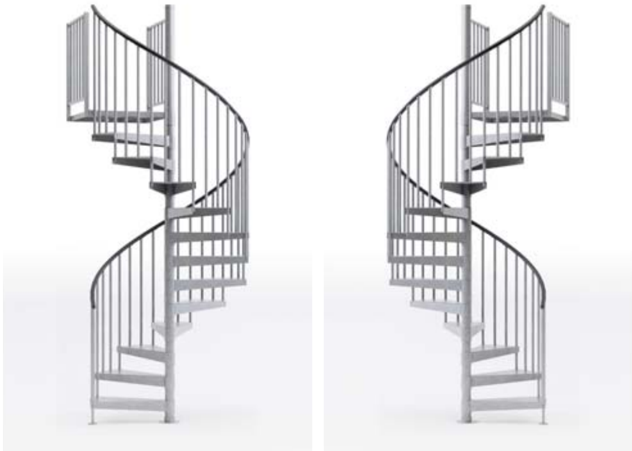
Symmetry Operators		Reflection Conditions (general)
1 x, y, z	1	$h00: h = 2n$
2 $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$	2_1 $(x, \frac{1}{4}, 0)$ $[\frac{1}{2}, 0, 0]$	$0k0: k = 2n$
3 $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$	2_1 $(0, y, \frac{1}{4})$ $[0, \frac{1}{2}, 0]$	$00l: l = 2n$
4 $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	2_1 $(\frac{1}{4}, 0, z)$ $[0, 0, \frac{1}{2}]$	

Systematic Absences

- Centering
  - C-centering, hkl: h+k = 2n
  - I-centering, hkl: h+k+l = 2n
  - F-centering, hkl: h+k, h+l, k+l = 2n
- Screw Axes
  - 2_1 or 4_2 or 6_3 along a-axis
    - h00: h =2n
  - 3_1 or 3_2 or 6_2 or 6_4 along a-axis
    - h00: h =3n
  - 4_1 or 4_3 along a-axis
    - h00: h =4n
  - 6_1 or 6_5 along a-axis
    - h00: h =6n
- Rhombohedral lattices
  - For example R3
    - hkil: -h+k+l = 3n (hexagonal axes) or
    - hkl: none (rhombohedral axes)
- Glide planes (centrosymmetric space groups)
  - c-glide for space group Pc (monoclinic No.7)
    - h0l: l = 2n
  - etc…

Enantiomorphic Space Groups

- Certian space groups are enantiomorphs and are *indistinguishable*, because the diffraction experiment adds a symmetry of inversion
  - $P3_1$ and $P3_2$
  - $P4_1$ and $P4_3$
  - $P6_1$ and $P6_5$
  - $P6_2$ and $P6_4$
  - $P6_1$ and $P6_5$
  - $P4_122$ and $P4_322$
  - $P4_12_12$ and $P4_32_12$
  - $P3_112$ and $P3_212$
  - $P3_121$ and $P3_221$
  - $P6_122$ and $P6_522$
  - etc…



- The only way to distinguish them is to solve the structure!

Some IUCr Conventions

- Axes form right-handed system
- Prefer C-centering rather than A- or B-centering
- Unique angles should be close to 90° and obtuse
  - For monoclinic $\beta > 90°$
- Axial lengths in increasing order
  - $a < b < c$
- Placement of unique symmetry operator?
  - $P2_12_12$ or $P22_12_1$ or $P2_122_1$?
  - $P2_122$ or $P222_1$?
  - Human Transthyretin
    - $P2_12_12$, a = 43.21Å b = 85.99Å c = 63.82Å

Indexing & Equivalent Solutions

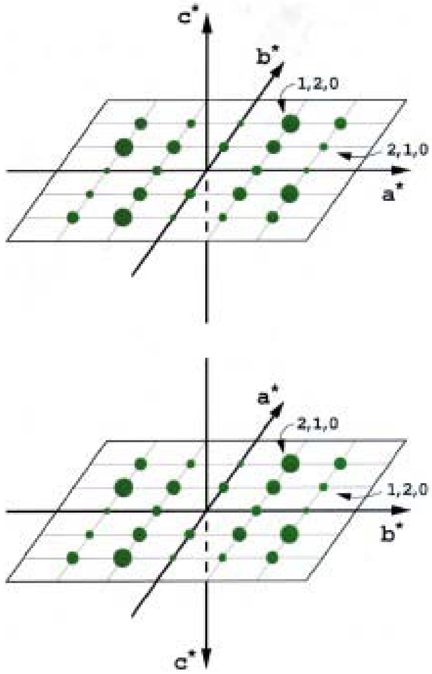
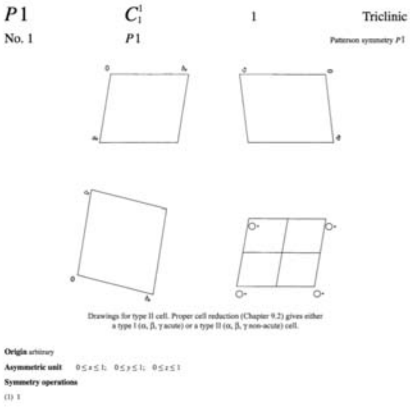


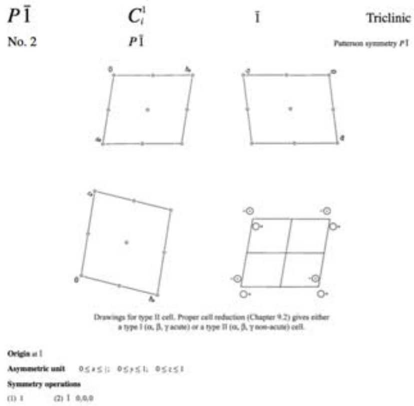
Figure 23
Two ways of indexing the tetragonal lattice in point group 4, with the fourfold axis directed 'up' or 'down'. These two ways are not equivalent, since reflections with the same indices will have different intensities. In this case the symmetry of reflection positions (lattice) is higher than the symmetry of their intensities.

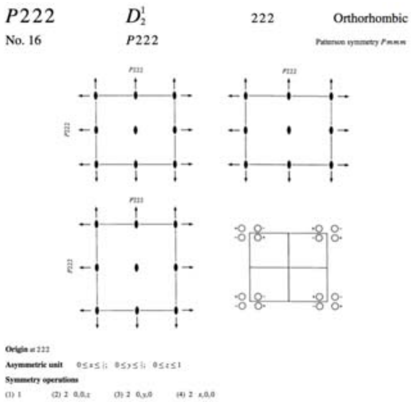
- Caution!
  - Certain space groups have equivalent indexing solutions
  - Where axes can be swapped
    - Tetragonal
    - Trigonal
    - Hexagonal
    - Cubic
  - Experiments that merge data sets together need to verify the indexing solutions for each data set
    - S-SAD, MAD, Serial MX,…

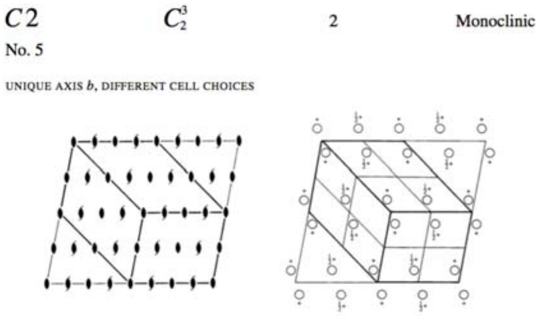
Dauter (1999)

Choice of Origin







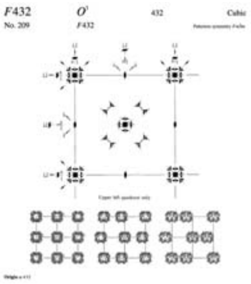


Conclusions

Look for symmetry…

…it is everywhere!

Symmetry is tricky….



…but fun!

Resources

- http://en.wikipedia.org/wiki/Hermann%E2%80%93Mauguin_notation
- http://newton.ex.ac.uk/research/qsystems/people/goss/symmetry/Solids.html
- http://img.chem.ucl.ac.uk/sgp/large/sgp.htm
- http://en.wikipedia.org/wiki/Wallpaper_group#Group_pg
- More…