LMB Crystallography Course, 2013

Crystals, Symmetry and Space Groups

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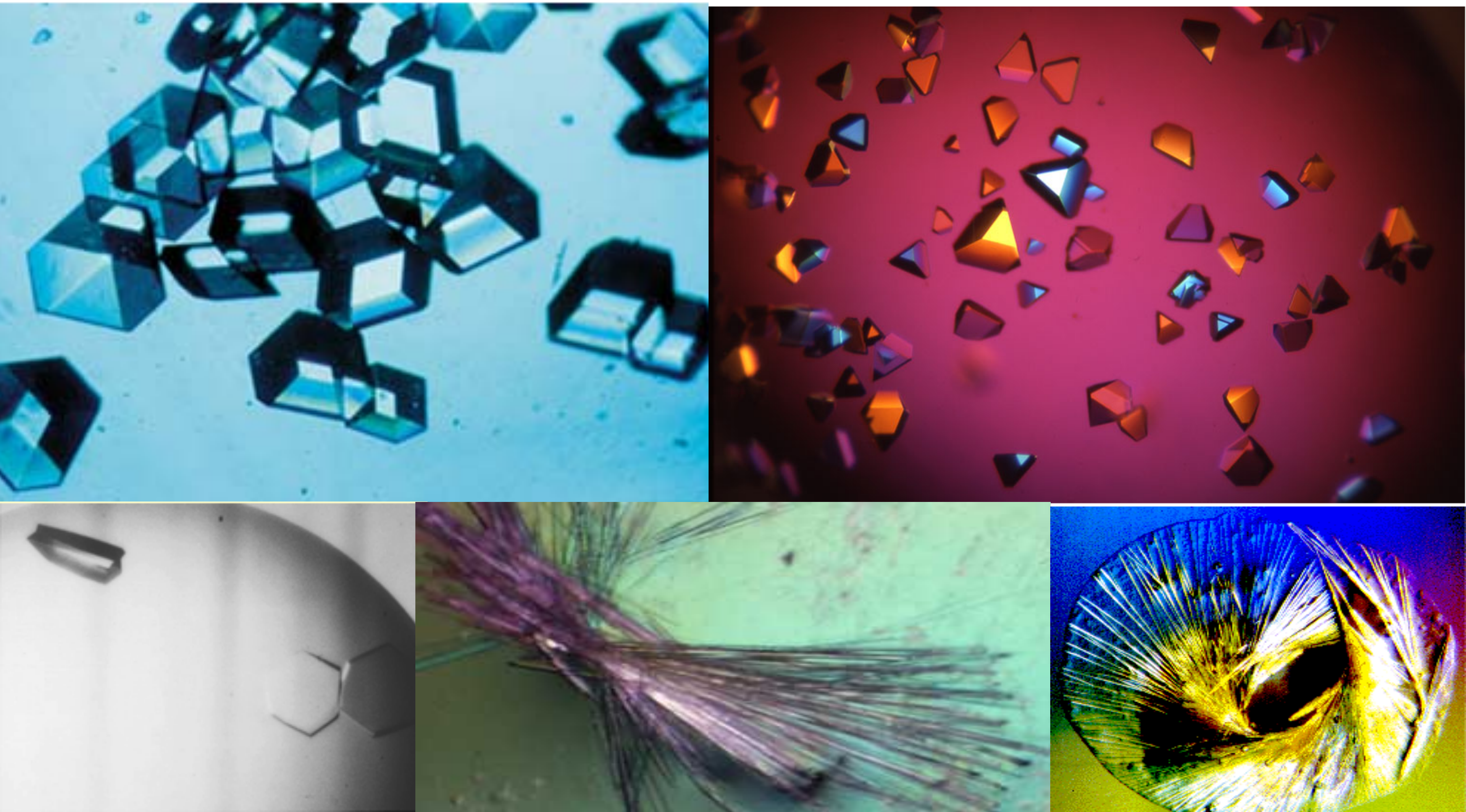
Many of the slides were kindly provided by Erhard Hohenester (Imperial College), several other illustrations are from David Blow's excellent book entitled:

Outline of Crystallography for Biologists (Oxford University Press).

Crystals

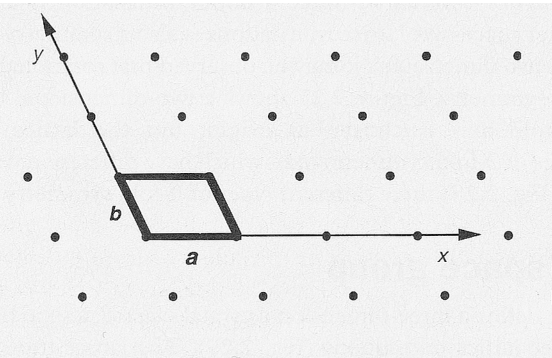
A crystal is a solid in which the constituent atoms, molecules, or ions are packed in a regularly ordered, repeating pattern extending in all three spatial dimensions.

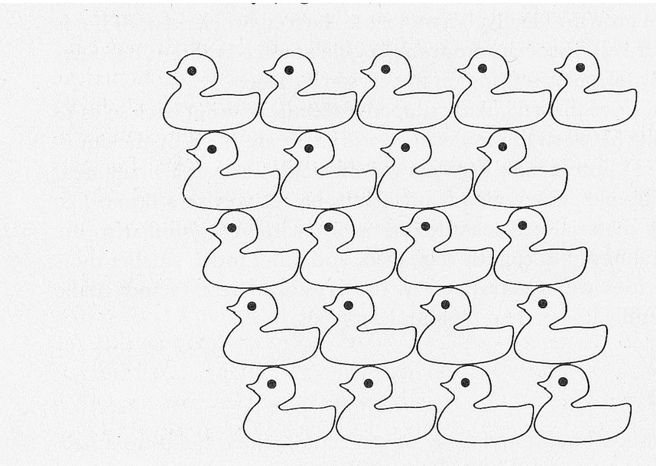
(Wikipedia)



Crystals and Lattices

Lattice: An infinite array of points arranged so that the environment of any point is identical to the environment of any other point.

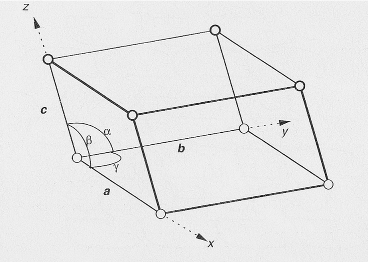




If we take a group of atoms (a molecule) and associate it (in the same way) with every lattice point, this will generate an ideal crystal of those atoms (molecules).

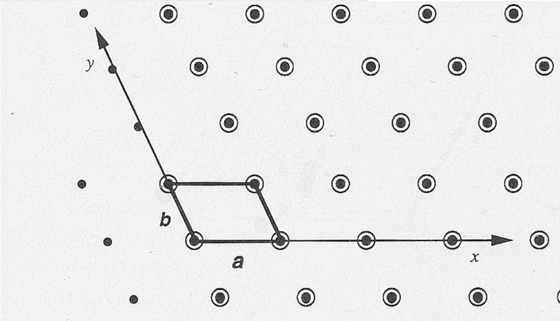
We can define a basic repeat unit of the lattice. In 2D, this is two distances and the angle between them.

In 3D, there are three distances and three inter-axial angles: a, b, c, α, β, γ. These crystal axes define a "unit cell" that forms the basic building block of the crystal.



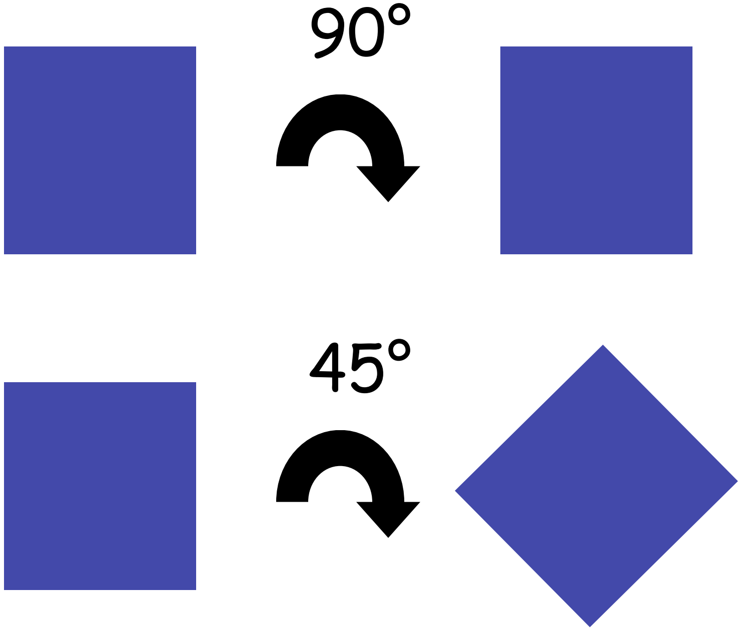
By convention, the unit cell is chosen to have the smallest possible volume, while ensuring that the crystallographic axes show off the lattice symmetry. α, β, γ are chosen to be obtuse, but as close to 90° as possible.

The lattice shows translational symmetry.



Rotational Symmetry

An n-fold rotational symmetry implies that if a rotation of 360/n degrees is applied, the transformed object is identical to the original.

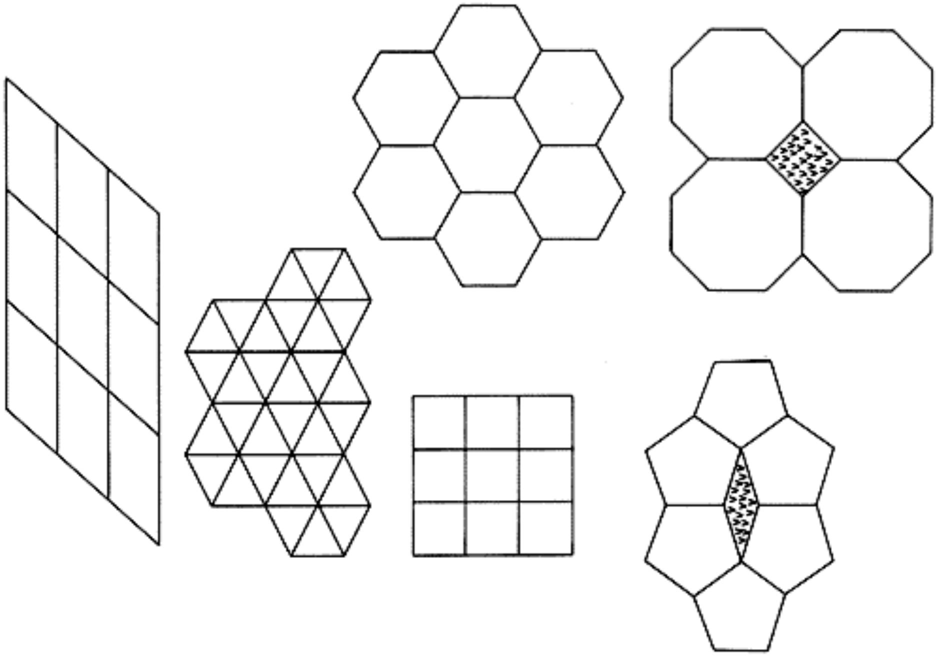


4-fold

Not 8-fold

Not all rotational symmetries are allowed in a crystal

The only rotational symmetries possible in a crystal lattice are 2, 3, 4 and 6, because it is not possible to fill space with other symmetries.

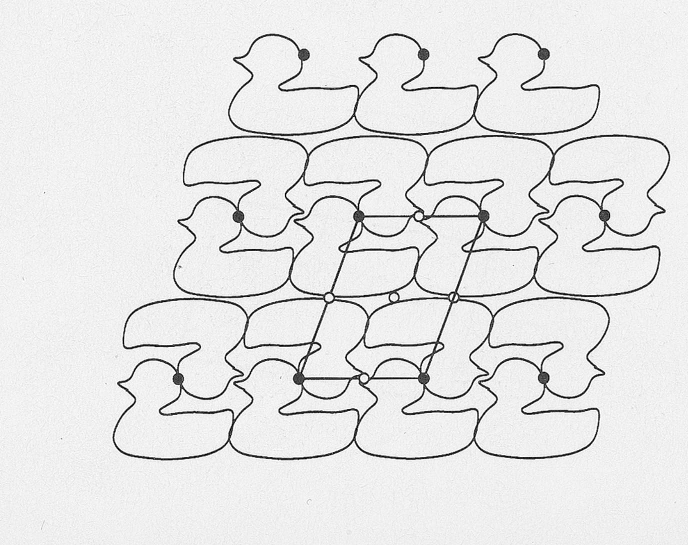


(I am excluding “quasi-crystals” which can show 5-fold symmetry, discovered by Dan Schechtman in 1982, Nobel prize in Chemistry 2011)

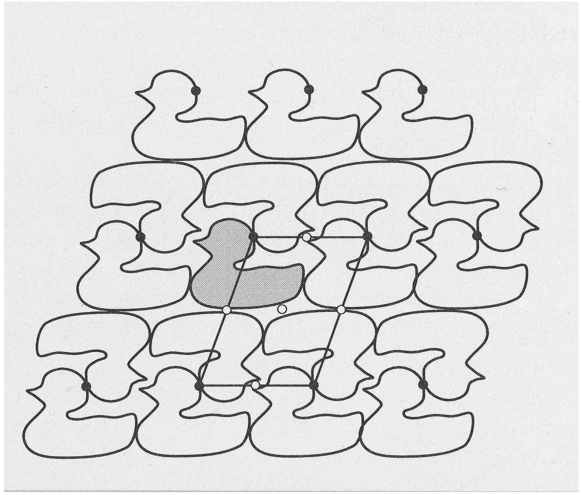
Note this restriction does not apply to molecular symmetry, for example C-reactive protein has 5-fold symmetry, GroEL has 7-fold etc

Combining rotational and lattice symmetries

The translational symmetry of the lattice generates additional rotational symmetry elements.



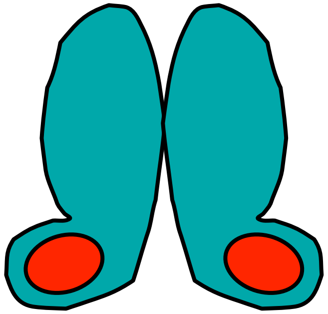
The lattice translation symmetry coupled with one 2-fold symmetry axis (black dots) generates three additional 2-fold axes.



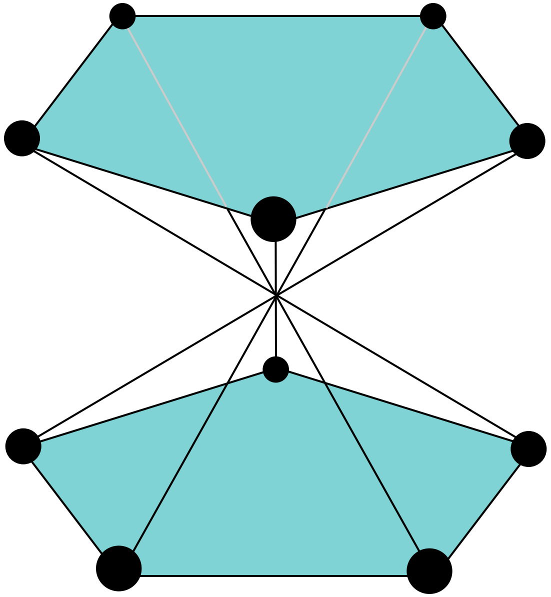
The asymmetric unit (shaded duck) is the smallest unit of structure that can generate the whole crystal after application of the crystal symmetry.

Other crystallographic symmetry elements

Other types of symmetry operation are reflection and inversion.



mirror symmetry



Because macromolecules (protein and nucleic acid) are chiral, macromolecular crystals cannot contain these symmetry elements*.

* Ignoring crystals of racemic mixtures

The seven crystal systems

The seven crystal systems are defined according to the rotational symmetry present, and the rotational symmetry imposes restrictions on the unit cell parameters.

Crystal System	Minimum Symmetry*	Constraints on unit cell
Triclinic	None	None
Monoclinic	One 2-fold (along b)	$\alpha = \gamma = 90$
Orthorhombic	Three 2-folds (along a,b,c)	$\alpha = \beta = \gamma = 90$
Trigonal	3-fold (along c)	$a = b$; $\alpha = \beta = 90$; $\gamma = 120$
Tetragonal	4-fold (along c)	$a = b$; $\alpha = \beta = \gamma = 90$
Hexagonal	6-fold (along c)	$a = b$; $\alpha = \beta = 90$; $\gamma = 120$
Cubic	Four 3-fold axes (along body diagonal)	$a = b = c$; $\alpha = \beta = \gamma = 90$

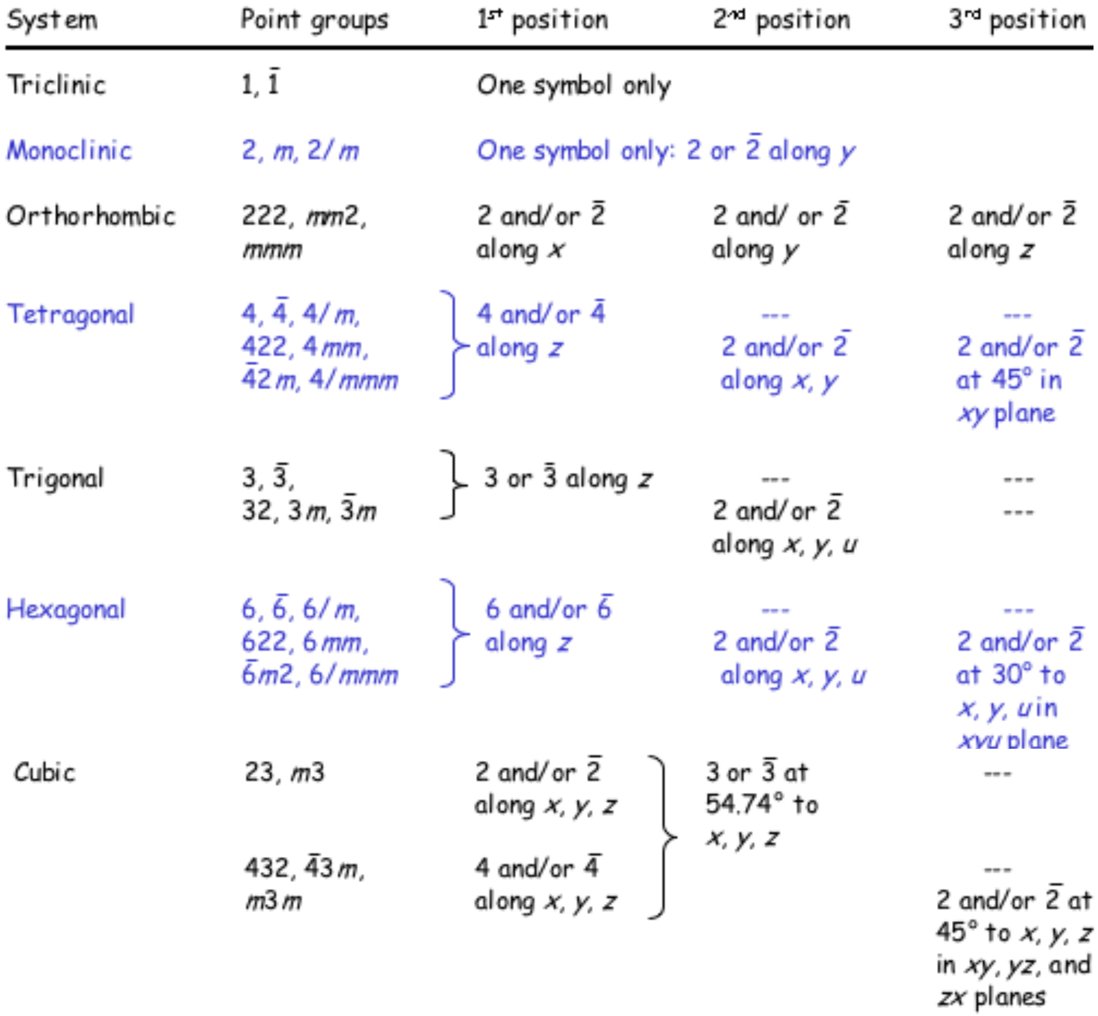
* For chiral molecules. For non-chiral molecules, a mirror plane can replace the 2-fold axis in the monoclinic system or two mirror planes can replace two of the three 2-folds in orthorhombic system.

The axis that is in the direction of the characteristic symmetry axis (if any) is called the unique axis. There are unique axes for monoclinic, trigonal, tetragonal and hexagonal systems.

The 32 crystallographic point groups

Rotations, inversions and reflections (mirror planes) are examples of Point Group symmetry, because they leave the position of one point unchanged (origin, centre of mass).

There are a limited number of ways in which the symmetry operations that are applicable to a lattice can be combined, giving the 32 crystallographic point groups.



System	Point groups	1st position	2nd position	3rd position
Triclinic	$1, \bar{1}$	One symbol only		
Monoclinic	$2, m, 2/m$	One symbol only: 2 or $\bar{2}$ along y		
Orthorhombic	$222, mm2, mmm$	2 and/or $\bar{2}$ along x	2 and/ or $\bar{2}$ along y	2 and/or $\bar{2}$ along z
Tetragonal	$4, \bar{4}, 4/m,$ $422, 4mm,$ $\bar{4}2m, 4/mmm$	4 and/or $\bar{4}$ along z	--- 2 and/or $\bar{2}$ along x, y	--- 2 and/or $\bar{2}$ at 45° in xy plane
Trigonal	$3, \bar{3},$ $32, 3m, \bar{3}m$	3 or $\bar{3}$ along z	--- 2 and/or $\bar{2}$ along x, y, u	--- ---
Hexagonal	$6, \bar{6}, 6/m,$ $622, 6mm,$ $\bar{6}m2, 6/mmm$	6 and/or $\bar{6}$ along z	--- 2 and/or $\bar{2}$ along x, y, u	--- 2 and/or $\bar{2}$ at 30° to x, y, u in xyu plane
Cubic	$23, m3$	2 and/or $\bar{2}$ along x, y, z	3 or $\bar{3}$ at 54.74° to x, y, z	---
	$432, \bar{4}3m,$ $m3m$	4 and/or $\bar{4}$ along x, y, z		--- 2 and/or $\bar{2}$ at 45° to x, y, z in $xy, yz,$ and zx planes

$\bar{2}$ denotes a 2-fold rotation followed by an inversion.

(The u axis bisects the x and y axes)

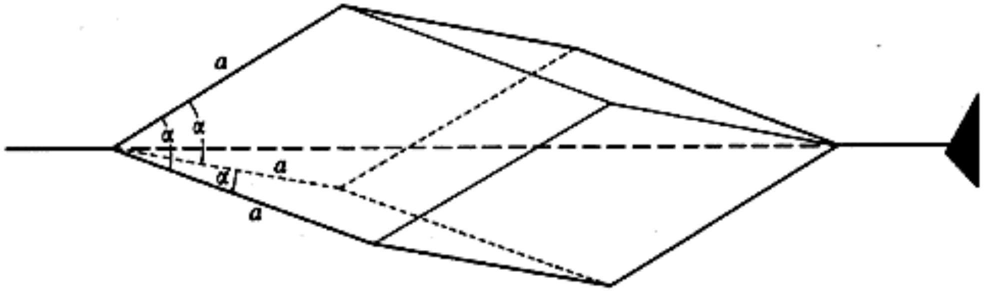
Bravais Lattices

Lattices in which the lattice points lie only at the vertices of the unit cell are Primitive lattices (P).

In some cases, it is conventional to define the unit cell so that there are, in addition, lattice points at the centre of:

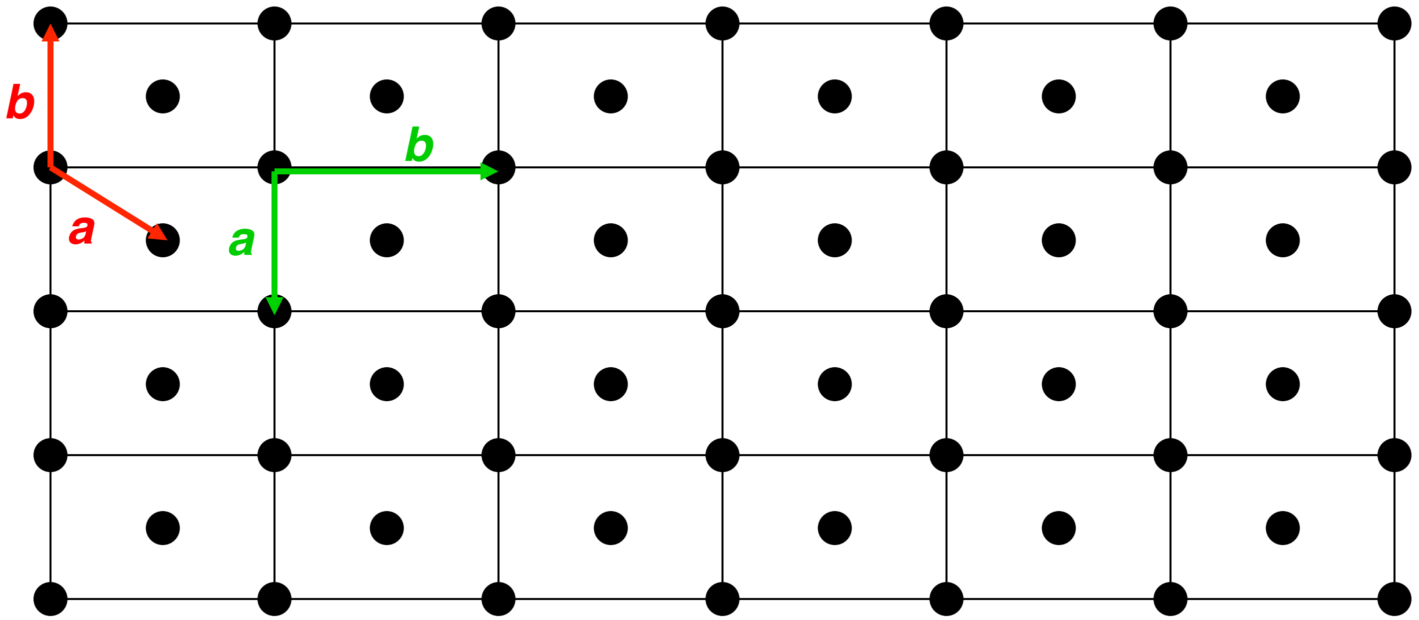
- One face (C) (the face opposite the c axis)
- All faces (F)
- The unit cell (I, body centred)

This is done so that the unit cell axes remain parallel to symmetry axes.



A rhombohedral cell (R) is possible for trigonal crystals. Because it is easier to visualise, such cells are normally treated in an equivalent hexagonal setting (space groups R3 and R32 are handled as H3 and H32).

Choice of unit cell - centered lattices



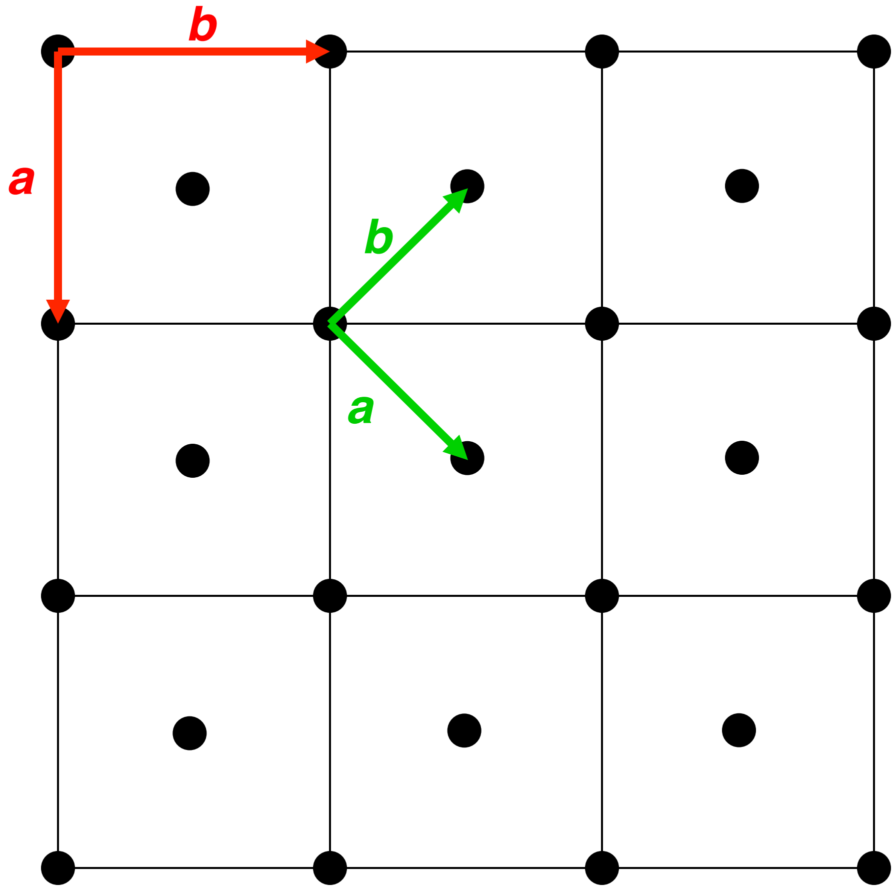
We could choose an oblique set of unit cell vectors...

…but orthogonal vectors better reflect the symmetry.

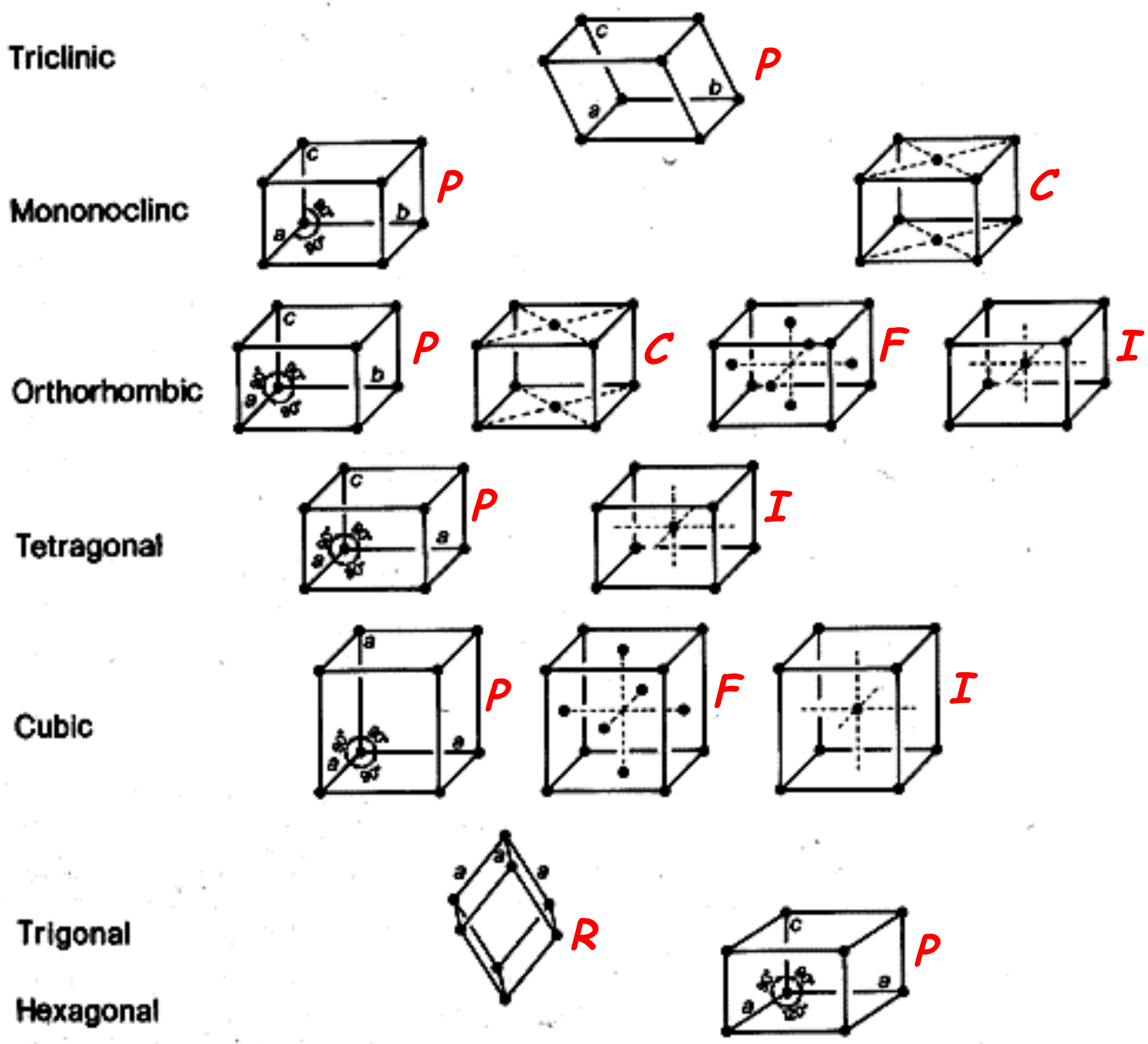
We define a **centered** unit cell, which is orthogonal and has an additional lattice point at 1/2a, 1/2b.

Not all lattices have centred cells

For example, a tetragonal lattice with a C-face centered unit cell can be reduced to primitive unit cell without losing symmetry.



The 14 Bravais lattices



Space Groups

- A point group describes the symmetry of a finite object
- A lattice defines the translational symmetry
- Combining point group and Bravais lattice symmetries generates space group symmetry (but additional symmetry elements involving a translation need to be considered).
- The space group is a complete description of the symmetry of an (ideal) crystal. (Ideal implies infinite !)
- Knowing the space group, and the contents of the asymmetric unit, defines the positions of all atoms in the crystal.
- There are a total of 230 different space groups (first derived in nineteenth century), of which only 65 are possible for chiral molecules.

Symmetry elements involving a translation

When considering an ideal crystal (infinite) we need to consider rotation and reflection operations that include a translation.

Screw axes: involve a rotation and translation

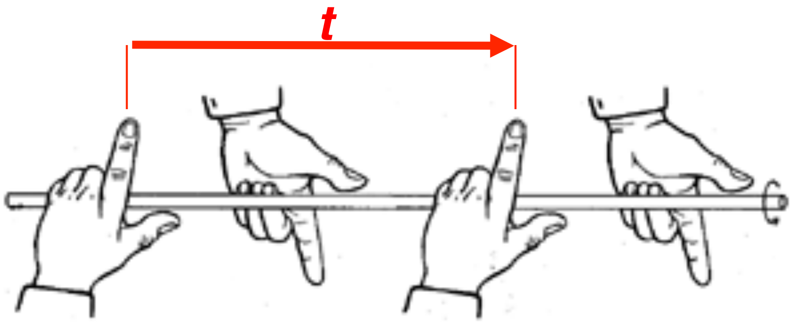
Glide planes: involve reflection and translation … not applicable to chiral molecules.

Screw axes

A screw axis describes the following operation: first, rotate clockwise about an axis, then translate along this axis (think of a spiral staircase).

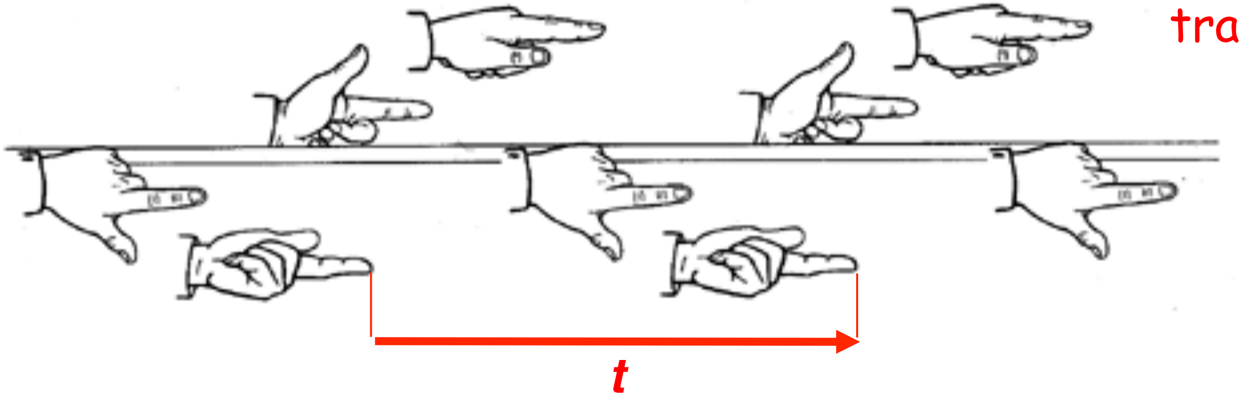
The rotation is expressed as for pure rotation axes, i.e., 1, 2, 3, 4, 6-fold.
The translation is expressed in fractions of the lattice translation parallel to the screw axis (read “2 sub 1”, “4 sub 1” and so on):

2_1



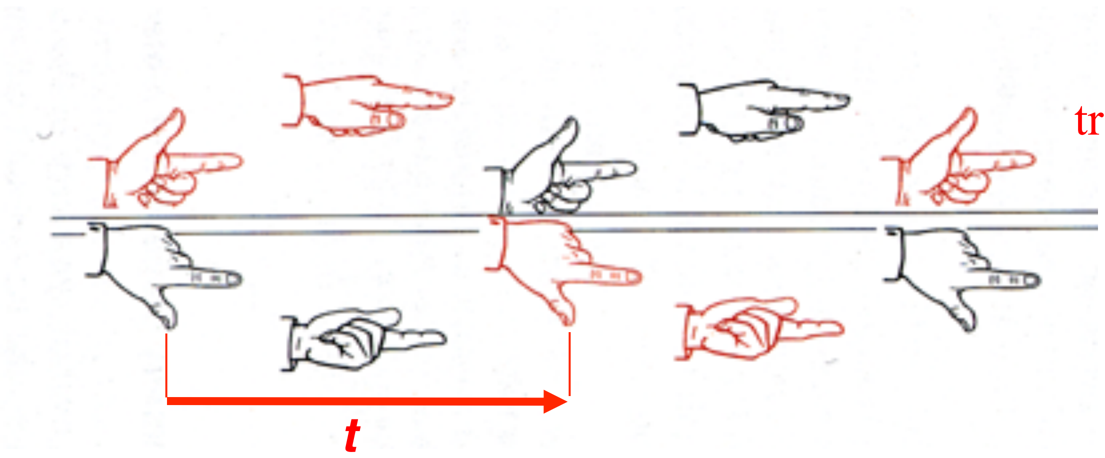
translation of 1/2***t*** per rotation

4_1



translation of 1/4

4_2



translation of 2/4 = 1/2

A 4_2 axis is also a 2 axis.

(6_2 is also 2 and a 3_2 ; 6_4 is also 2 and 3_1 ; 6_3 is also 3 and 2_1).

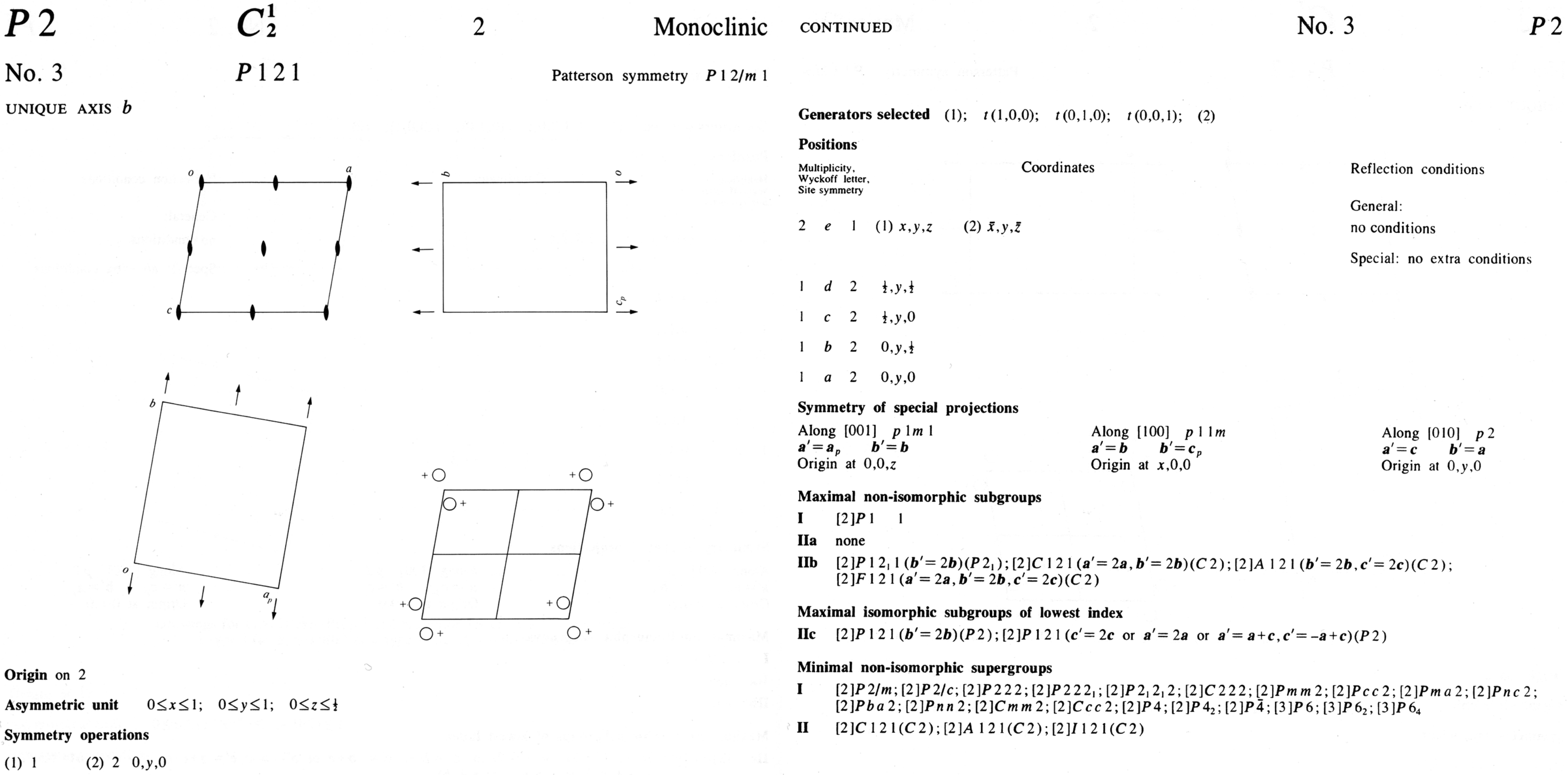
A 3_1 axis corresponds to a right-handed helix, whereas 3_2 corresponds to a left-handed helix (the two helices are *enantiomorphous*).

The same applies to the pairs 4_1 and 4_3, 6_1 and 6_5, and 6_2 and 6_4.

Symbols of Symmetry Axes

Symbol	Symmetry axis	Graphical symbol	Nature of right-handed screw translation along the axis	Symbol	Symmetry axis	Graphical symbol (normal to plane of paper)	Nature of right-handed screw translation along the axis
1	Rotation monad	None	None	4	Rotation tetrad	◆	None
$\bar{1}$	Inversion monad	○	None	4_1	Screw tetrads		$c/4$
				4_2			$2c/4$
2	Rotation diad	⬮ (normal to paper)	None	4_3			$3c/4$
		→ (parallel to paper)		$\bar{4}$	Inversion tetrad		None
2_1	Screw diad	 (normal to paper)	$c/2$	6	Rotation hexad	⬢	None
		⇀ (parallel to paper)	Either $a/2$ or $b/2$	6_1	Screw hexads		$c/6$
		Normal to paper		6_2			$2c/6$
3	Rotation triad	▲	None	6_3			$3c/6$
				6_4			$4c/6$
3_1	Screw triads		$c/3$	6_5			$5c/6$
3_2			$2c/3$				
$\bar{3}$	Inversion triad		None	$\bar{6}$	Inversion hexad		None

This is what a space group entry in the International Tables looks like:



***P* 2** C_2^1 2 Monoclinic

No. 3 *P* 1 2 1 Patterson symmetry *P* 1 2/*m* 1

UNIQUE AXIS *b*

Origin on 2

Asymmetric unit $0 \le x \le 1$; $0 \le y \le 1$; $0 \le z \le \frac{1}{2}$

Symmetry operations

(1) 1 (2) 2 0,*y*,0

CONTINUED No. 3 *P* 2

Generators selected (1); *t*(1,0,0); *t*(0,1,0); *t*(0,0,1); (2)

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates	Reflection conditions
		General:
2 *e* 1	(1) x,y,z (2) $\bar{x},y,\bar{z}$	no conditions
		Special: no extra conditions
1 *d* 2	$\frac{1}{2},y,\frac{1}{2}$	
1 *c* 2	$\frac{1}{2},y,0$	
1 *b* 2	$0,y,\frac{1}{2}$	
1 *a* 2	$0,y,0$	

Symmetry of special projections

Along [001] *p* 1*m* 1	Along [100] *p* 1 1*m*	Along [010] *p* 2
$\mathbf{a}' = \mathbf{a}_p$ $\mathbf{b}' = \mathbf{b}$	$\mathbf{a}' = \mathbf{b}$ $\mathbf{b}' = \mathbf{c}_p$	$\mathbf{a}' = \mathbf{c}$ $\mathbf{b}' = \mathbf{a}$
Origin at 0,0,*z*	Origin at *x*,0,0	Origin at 0,*y*,0

Maximal non-isomorphic subgroups

I [2]*P* 1 1

IIa none

IIb [2]$P12_11$ ($\mathbf{b}' = 2\mathbf{b}$)($P2_1$); [2]$C121$ ($\mathbf{a}' = 2\mathbf{a}$, $\mathbf{b}' = 2\mathbf{b}$)($C2$); [2]$A121$ ($\mathbf{b}' = 2\mathbf{b}$, $\mathbf{c}' = 2\mathbf{c}$)($C2$); [2]$F121$ ($\mathbf{a}' = 2\mathbf{a}$, $\mathbf{b}' = 2\mathbf{b}$, $\mathbf{c}' = 2\mathbf{c}$)($C2$)

Maximal isomorphic subgroups of lowest index

IIc [2]$P121$ ($\mathbf{b}' = 2\mathbf{b}$)($P2$); [2]$P121$ ($\mathbf{c}' = 2\mathbf{c}$ or $\mathbf{a}' = 2\mathbf{a}$ or $\mathbf{a}' = \mathbf{a}+\mathbf{c}$, $\mathbf{c}' = -\mathbf{a}+\mathbf{c}$)($P2$)

Minimal non-isomorphic supergroups

I [2]$P2/m$; [2]$P2/c$; [2]$P222$; [2]$P222_1$; [2]$P2_12_12$; [2]$C222$; [2]$Pmm2$; [2]$Pcc2$; [2]$Pma2$; [2]$Pnc2$; [2]$Pba2$; [2]$Pnn2$; [2]$Cmm2$; [2]$Ccc2$; [2]$P4$; [2]$P4_2$; [2]$P\bar{4}$; [3]$P6$; [3]$P6_2$; [3]$P6_4$

II [2]$C121$($C2$); [2]$A121$($C2$); [2]$I121$($C2$)

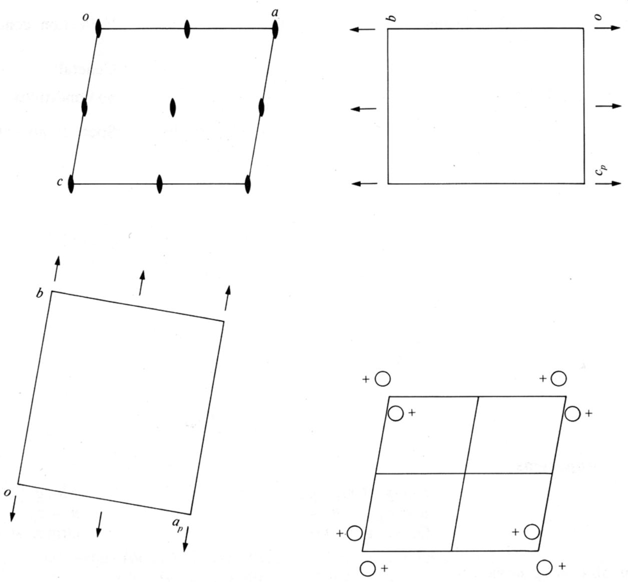
Focus on the most important parts:

Space group name and number

Crystal system

No. 3 $P\,1\,2\,1$ Patterson symmetry $P\,1\,2/m\,1$

UNIQUE AXIS *b*



Origin on 2

Asymmetric unit $0 \le x \le 1$; $0 \le y \le 1$; $0 \le z \le \frac{1}{2}$

Symmetry operations

(1) 1 (2) 2 0,*y*,0

Space group diagram, origin, asymmetric unit

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates
2	*e*	1	(1) x,y,z (2) $\bar{x},y,\bar{z}$
1	*d*	2	$\frac{1}{2},y,$
1	*c*	2	$\frac{1}{2},y,0$
1	*b*	2	$0,y,\frac{1}{2}$
1	*a*	2	$0,y,0$

Equivalent positions

Reflection conditions

General:
no conditions

Special: no extra conditions

Reflection conditions

Symmetry of special projections

Along [001] $p\,1m\,1$
$\mathbf{a}'=\mathbf{a}_p$ $\mathbf{b}'=\mathbf{b}$
Origin at 0,0,*z*

Along [100] $p\,1\,1m$
$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}_p$
Origin at *x*,0,0

Along [010] $p\,2$
$\mathbf{a}'=\mathbf{c}$ $\mathbf{b}'=\mathbf{a}$
Origin at 0,*y*,0

Maximal non-isomorphic subgroups

I [2]$P\,1$ 1

IIa none

IIb [2]$P\,1\,2_1\,1$ ($\mathbf{b}'=2\mathbf{b}$)($P\,2_1$); [2]$C\,1\,2\,1$ ($\mathbf{a}'=2\mathbf{a}, \mathbf{b}'=2\mathbf{b}$)($C\,2$); [2]$A\,1\,2\,1$ ($\mathbf{b}'=2\mathbf{b}, \mathbf{c}'=2\mathbf{c}$)($C\,2$); [2]$F\,1\,2\,1$ ($\mathbf{a}'=2\mathbf{a}, \mathbf{b}'=2\mathbf{b}, \mathbf{c}'=2\mathbf{c}$)($C\,2$)

Maximal isomorphic subgroups of lowest index

IIc [2]$P\,1\,2\,1$ ($\mathbf{b}'=2\mathbf{b}$)($P\,2$); [2]$P\,1\,2\,1$ ($\mathbf{c}'=2\mathbf{c}$ or $\mathbf{a}'=2\mathbf{a}$ or $\mathbf{a}'=\mathbf{a}+\mathbf{c}, \mathbf{c}'=-\mathbf{a}+\mathbf{c}$)($P\,2$)

Minimal non-isomorphic supergroups

I [2]$P\,2/m$; [2]$P\,2/c$; [2]$P\,2\,2\,2$; [2]$P\,2\,2\,2_1$; [2]$P\,2_1\,2_1\,2$; [2]$C\,2\,2\,2$; [2]$P\,m\,m\,2$; [2]$P\,c\,c\,2$; [2]$P\,m\,a\,2$; [2]$P\,n\,c\,2$; [2]$P\,b\,a\,2$; [2]$P\,n\,n\,2$; [2]$C\,m\,m\,2$; [2]$C\,c\,c\,2$; [2]$P\,4$; [2]$P\,4_2$; [2]$P\,\bar{4}$; [3]$P\,6$; [3]$P\,6_2$; [3]$P\,6_4$

II [2]$C\,1\,2\,1$($C\,2$); [2]$A\,1\,2\,1$($C\,2$); [2]$I\,1\,2\,1$($C\,2$)

Let’s look at these items in more detail:

The **crystal system** can be triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, or cubic.

The **space group symbol** consists of a capital letter indicating the unit cell centering (*P*, *C*, *I*, *F* or *R*), followed by the symmetry along one (triclinic and monoclinic) or three directions (all other crystal systems). The definition of these directions in the seven crystal systems is the same as for the crystallographic point groups.

A few examples:

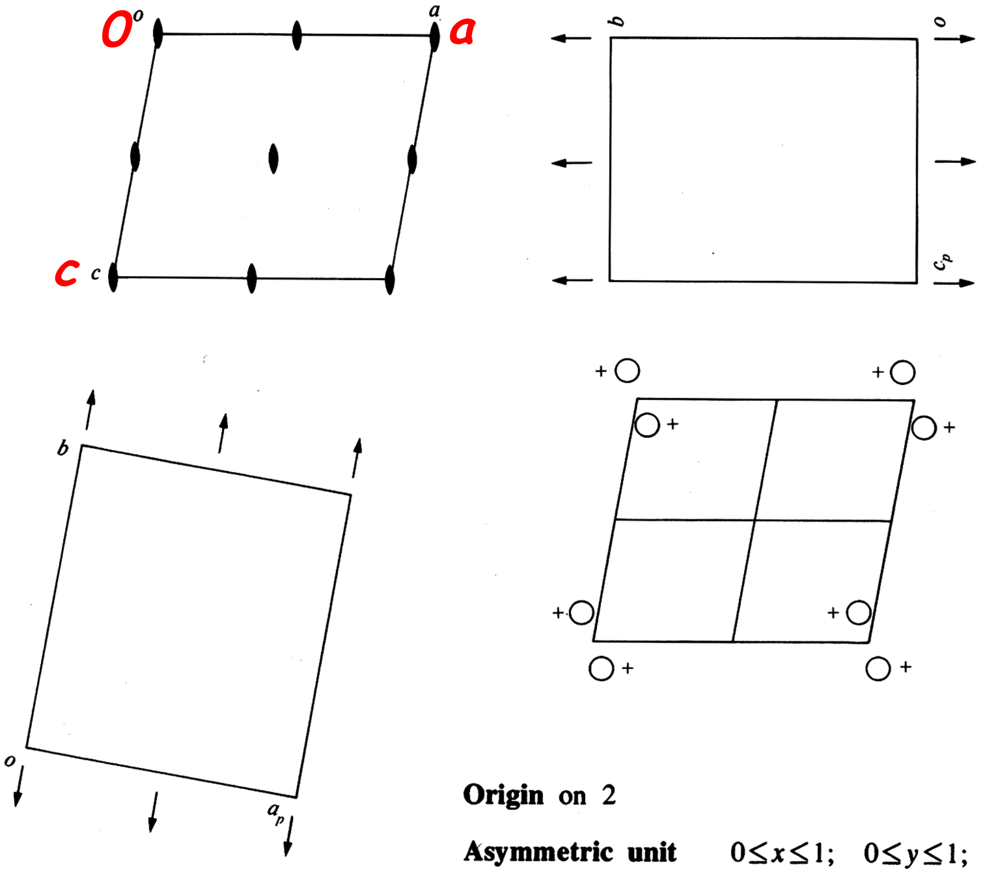
*P*2	monoclinic, primitive, 2-fold axis along ***b***
$C222_1$	orthorhombic, C–centered, 2-fold axes along ***a*** and ***b***, 2_1 along ***c***
$I4_122$	tetragonal, body-centered, 4_1 screw axis along ***c***, 2-fold axis along ***a*** (and ***b***), 2-fold axis along the ***ab*** diagonal
*P*321	trigonal, primitive, 3-fold axis along ***c***, 2-fold axis along ***a*** (and ***b***)

The **space group diagrams** use graphical symbols to indicate symmetry elements. The definition of the **origin** (if constrained by symmetry) is given below the diagram. This is followed by the definition of the **asymmetric unit**.

$P\,2$

No. 3

UNIQUE AXIS b

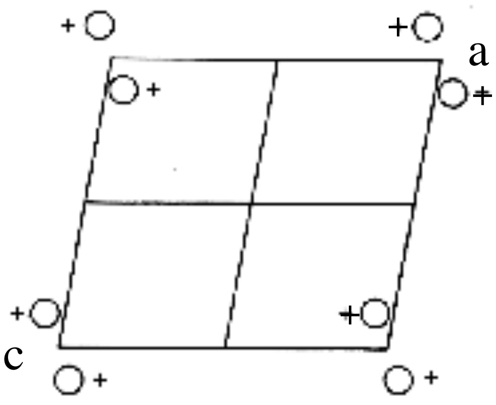


Origin on 2

Asymmetric unit $0 \leq x \leq 1;\quad 0 \leq y \leq 1;\quad 0 \leq z \leq \frac{1}{2}$

The list of **equivalent positions** refers to symmetry-related sites in the unit cell. The maximum number of sites generated by the space group symmetry are called the **general equivalent positions**. Their number is equal to the number of asymmetric units in the unit cell.

In space group *P*2, the entry for the equivalent positions is:



2	e	1	(1) x,y,z	(2) $\bar{x}, y, \bar{z}$
1	d	2	½,y,½	
1	c	2	½,y,0	
1	b	2	0,y,½,	
1	a	2	0,y,0	
---		---	---	---

There are two **general equivalent positions** in the unit cell, which are related by the 2-fold axis along ***b***.

In addition, there are **special positions**, which require an object of symmetry 2 (e.g., a symmetric dimer).

In a space group with a centered unit cell, the equivalent positions generated by the centering operation are given first, followed by those generated by rotation and/or screw axes.

In space group *C*2, for example, the entry for the general equivalent positions is:

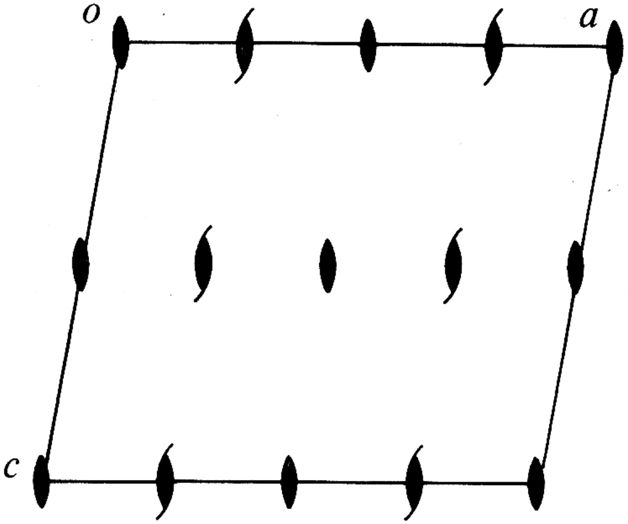
				(0,0,0)+	(1/2,1/2,0)+
4	c	1	(1) x,y,z	(2) $\bar{x}, y, \bar{z}$	

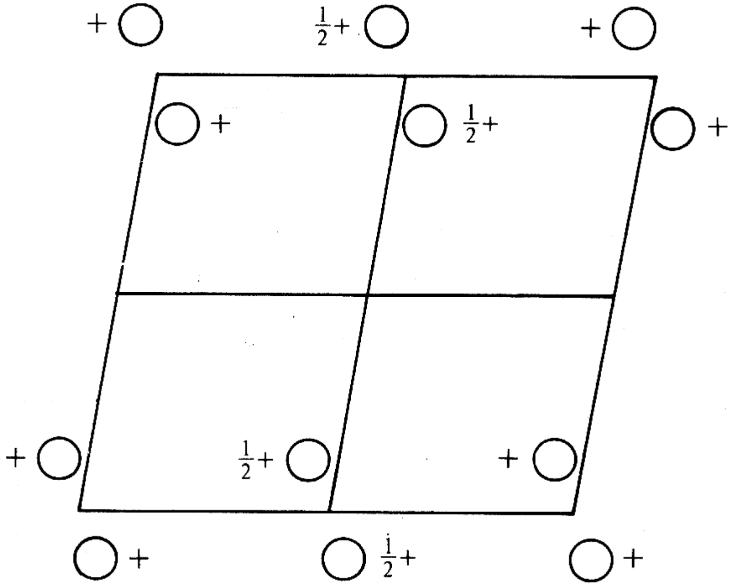
Finally, the **reflection conditions** list classes of reflections that are absent from the diffraction pattern (ie have zero intensity) due to space group symmetry. These are known as systematic absences.

C 2

No. 5

UNIQUE AXIS *b*





Origin on 2

Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{2}$; $0 \le z \le 1$

Symmetry operations

For (0,0,0)+ set

(1) 1 (2) 2 $0,y,0$

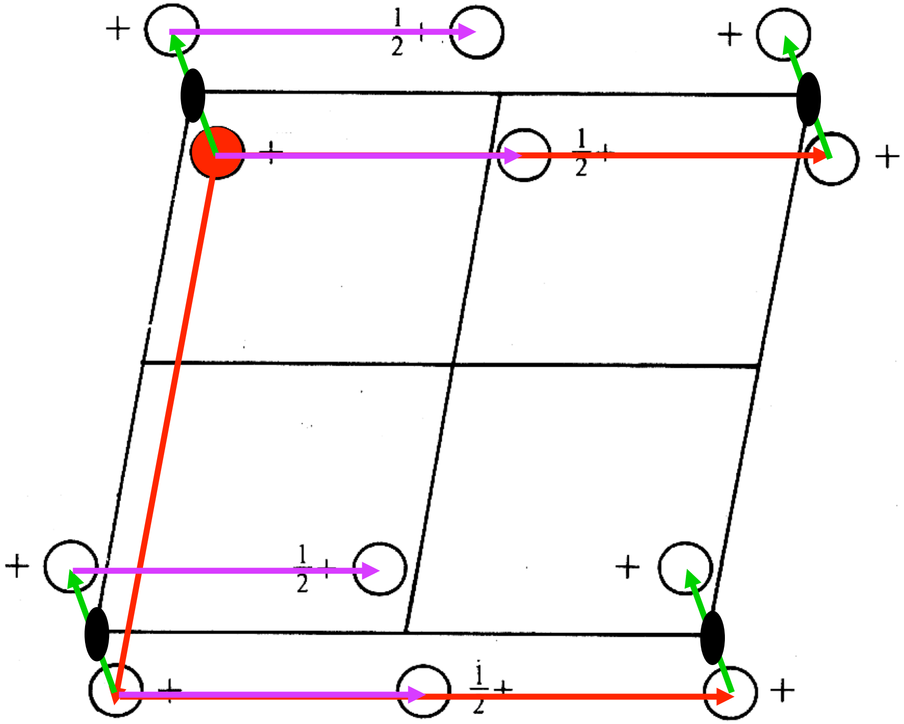
For $(\frac{1}{2},\frac{1}{2},0)$+ set

(1) $t(\frac{1}{2},\frac{1}{2},0)$ (2) $2(0,\frac{1}{2},0)$ $\frac{1}{4},y,0$

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates	
			(0,0,0)+	$(\frac{1}{2},\frac{1}{2},0)$+
4	*c*	1	(1) x,y,z	(2) $\bar{x},y,\bar{z}$

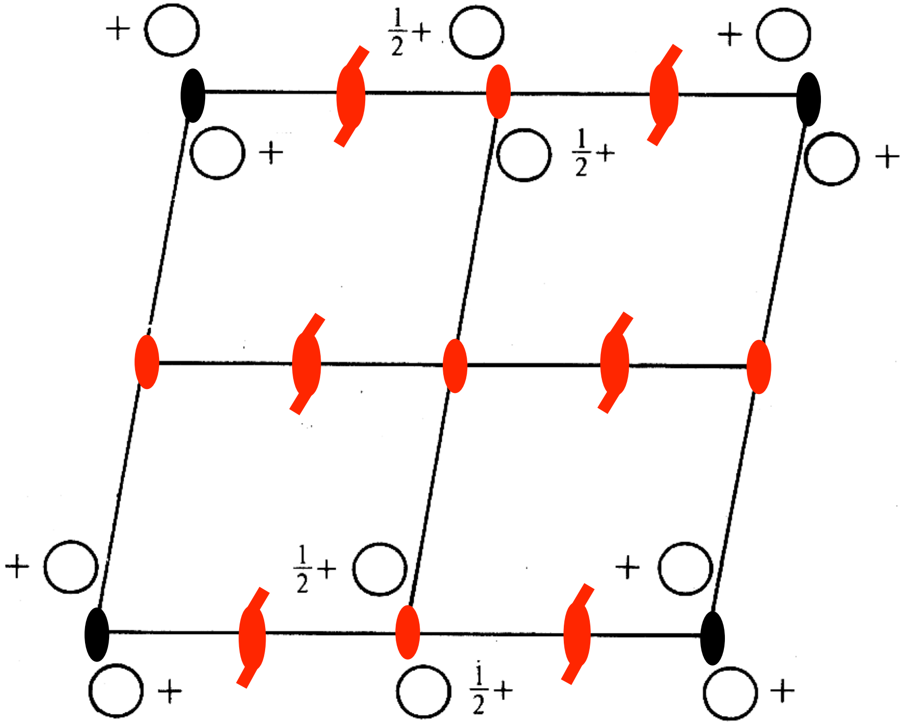
To illustrate the combination of a rotation axis and a centered unit cell, let's build up the equivalent positions from scratch.



1) Apply unit cell translations ***a***, ***c***, and ***a+c***

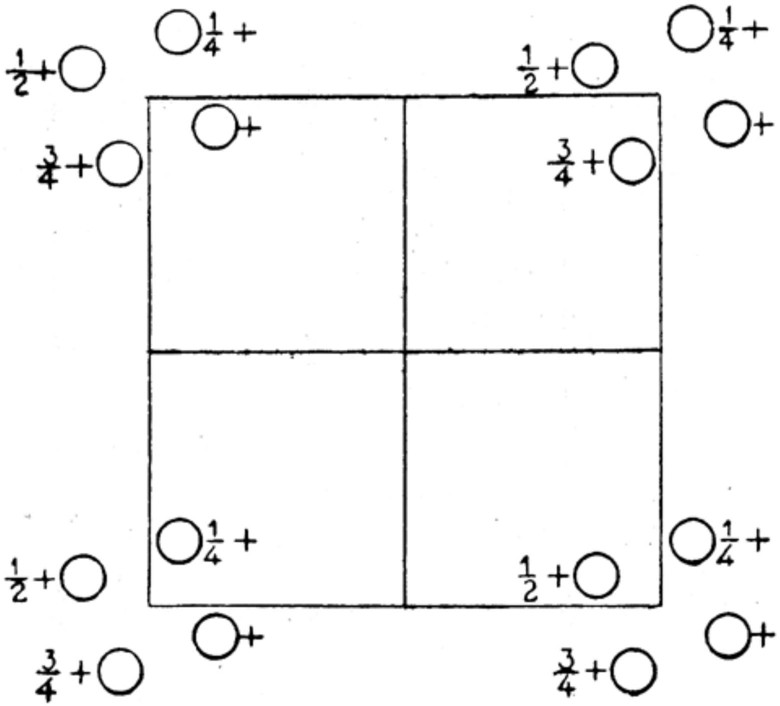
2) Apply 2-fold axis parallel to ***b*** at origin and symmetry-equivalents

3) Apply C-centering (translation by 1/2***a***, 1/2***b***)

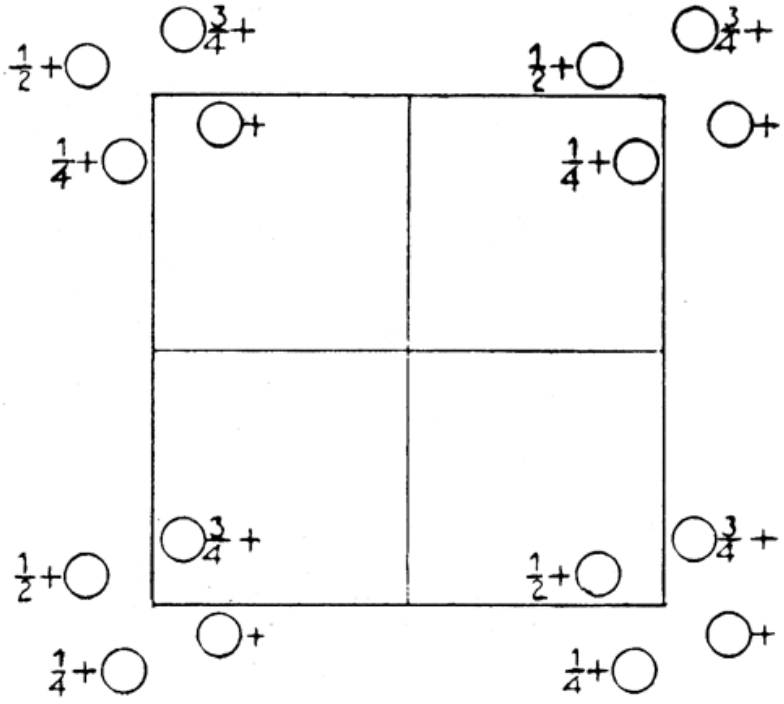


The combination of these symmetry elements generates additional symmetry elements, including 2_1 screw axes.

$P4_1$



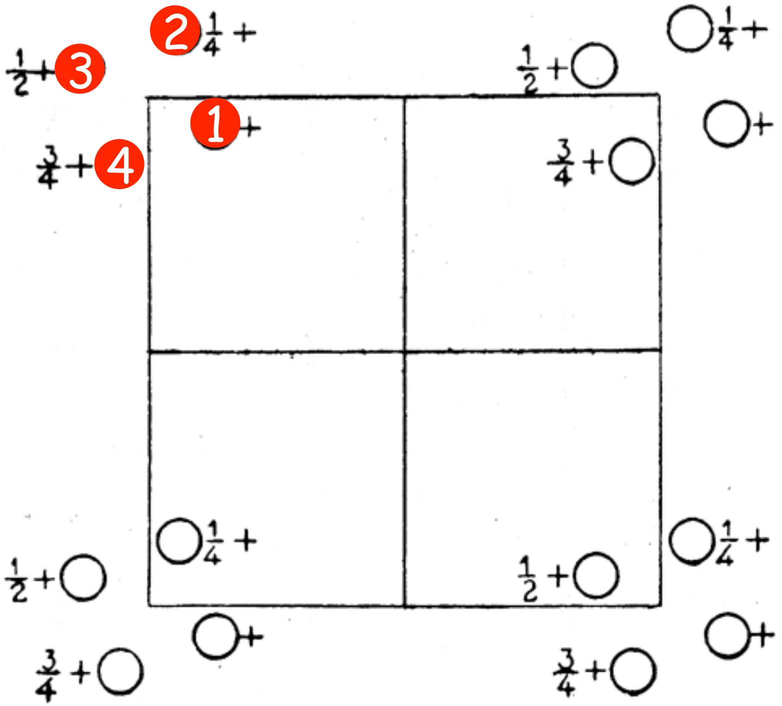
$P4_3$



These two space groups form an enantiomorphous pair, i.e., they are mirror images of each other. Other enantiomorphous pairs are $P3_121$ and $P3_221$, $P6_1$ and $P6_5$, $P6_2$ and $P6_4$, and so on. $P4_2$, $P4_22_12$, $P6_3$ etc. do not have enantiomorphs.

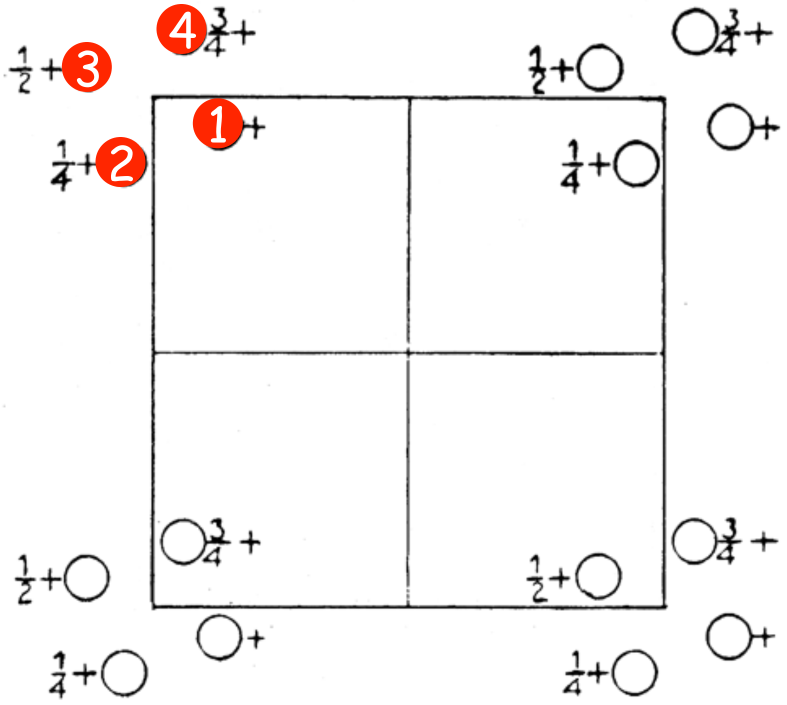
$P\,4_1$

Clockwise (c is up)



$P\,4_3$

Counterclockwise



By looking at the points generated by the 4-fold screw axes, we can see that the two space groups have a different hand.

Content of the asymmetric unit

There can be any number of molecules (N) in the asymmetric unit. If N > 1, there is non-crystallographic symmetry (NCS). NCS elements are not subject to the same restrictions as crystallographic symmetry elements (any rotational symmetry is possible, translations do not have to be fractions of the unit cell).

In the case of oligomeric proteins of identical subunits, the symmetry axes of an oligomer frequently coincide with space group axes, such that only a fraction of the oligomer occupies the asymmetric unit.

Examples: A dimeric protein (symmetry 2) could crystallise in space group *P*2 with only one subunit in the asymmetric unit, or a hexameric protein (symmetry 32) could crystallise in *P*2 with three subunits in the asymmetric unit.

Non-crystallographic symmetry is present in about one third of all protein crystals.

Spacegroup frequencies

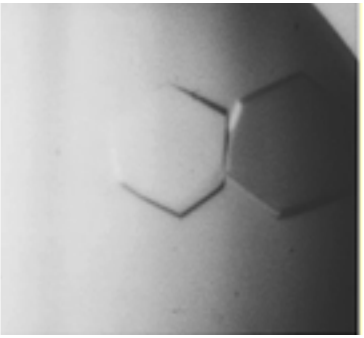
Of the 65 possible chiral space groups some are much more common than others within the Protein Data Bank:

$P2_12_12_1$	24%	$I222$	2.2%
$P2_1$	13%	$P6_122$	2.0%
$C2$	9.0%	$R3$	1.5%
$P3_221$	6.4%	$R32$	1.3%
$P2_12_12$	6.1%	$P6_1$	1.2%
$P4_32_12$	4.9%	$P4_22_12$	1.0%
$C222_1$	4.7%	$P6$	1.0%
$P3_121$	3.9%	$P2_13$	1.0%
$P4_12_12$	2.9%	$P4_1$	0.8%
$P1$	2.6%	$P6_522$	0.8%

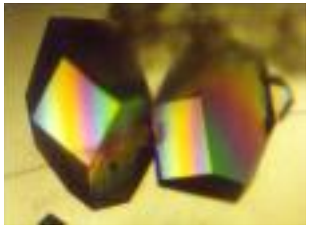
(sample size of 9481 chiral space groups – but many mutants)

How is the symmetry determined ?

- Crystal morphology

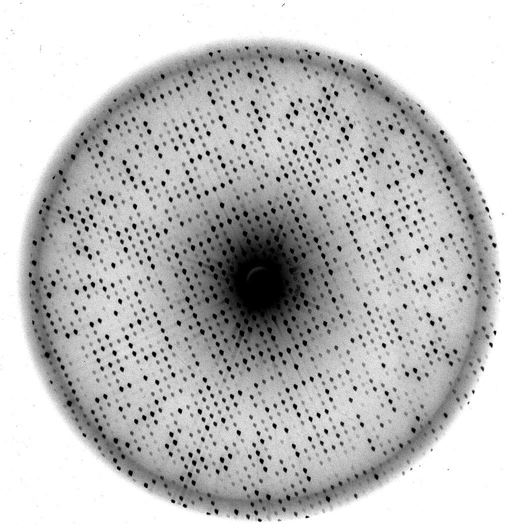


- Physical properties (eg optical properties in polarised light)

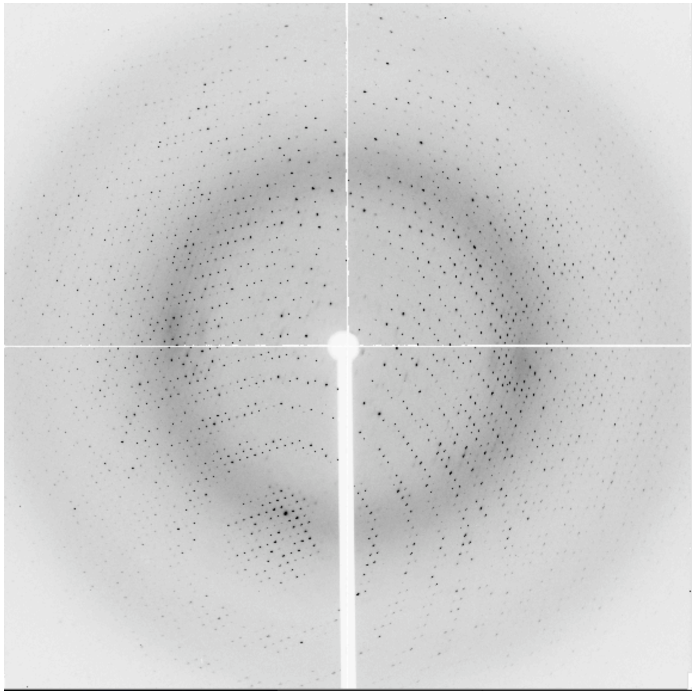


- The diffraction pattern

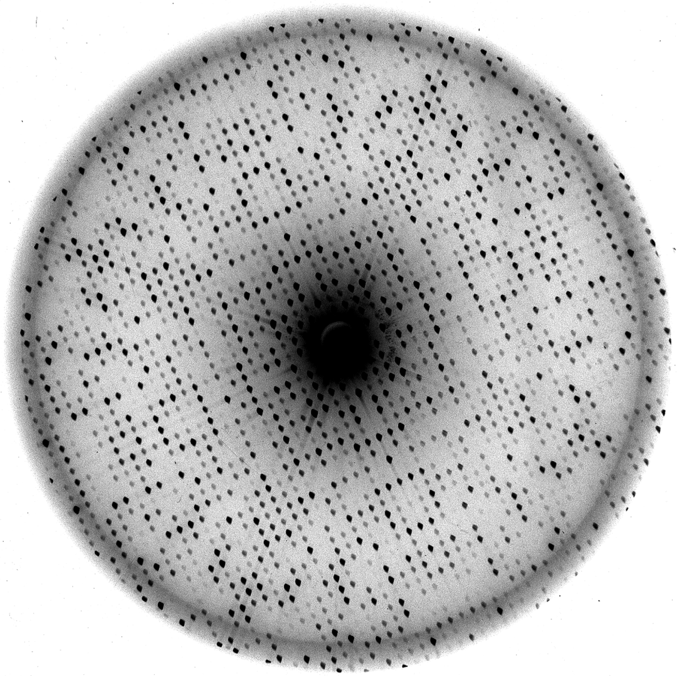
  (POINTLESS)



The spots in a diffraction pattern are arranged on a lattice – the reciprocal lattice.
In the simplest case (all unit cell angles 90°) the reciprocal cell axes, denoted a*, b*, c* are parallel to a, b, c and their lengths are 1/a, 1/b, 1/c.
Each reciprocal lattice point represents a set of (Bragg) planes in the real space lattice, and when the intensity of the scattering is represented in the reciprocal lattice points this gives the **weighted reciprocal lattice**.



An oscillation photograph gives a distorted view of the weighted reciprocal lattice



A precession photograph gives an undistorted view of the weighted reciprocal lattice

Symmetry of the diffraction pattern

The symmetry of the reciprocal lattice is the same as the symmetry of the real space lattice.

Diffraction patterns provide a (distorted) view of the reciprocal lattice, and the positions of spots in the diffraction pattern can be used to work out the dimensions of the reciprocal unit cell (and the real unit cell).

It is important to distinguish between the symmetry of the lattice, which is the symmetry of the reciprocal lattice points, and the symmetry of the diffraction pattern which is both the arrangement of the spots (reciprocal lattice points) and their intensities.

In addition, in the absence of anomalous scattering, Friedel’s law holds:

$$\mathrm{I}(hkl) = \mathrm{I}(\bar{h}\bar{k}\bar{l})$$

Which means that the diffraction pattern has a centre of symmetry (inversion centre).

Laue symmetry

Because of Friedel's Law, the diffraction pattern will have higher symmetry than the crystal. In addition, the diffraction pattern cannot have translational symmetry, because it has a defined origin (the reciprocal lattice point with indices 0,0,0.

To derive the Laue symmetry from the space group symmetry:

- Remove the lattice centring symbol (C, F, I, R)
- Remove the translational symmetry component of screw axes
- Add a centre of symmetry

In this way the 230 space groups are reduced to the 11 Laue groups.

It is the Laue group symmetry that is determined from the symmetry of the diffraction pattern.

The 11 Laue groups

System	Laue group	Examples of space groups
Triclinic	$\bar{1}$	$P1$
Monoclinic	$2/m$	$P2$, $P2_1$, $C2$, $C2_1$
Orthorhombic	mmm	$P2_12_12_1$, $C222_1$, $I222$…
Tetragonal	$4/m$	$P4$, $P4_1$, $P4_2$, $P4_3$, $I4$, $I4_1$
	$4/mmm$	$P42_12$, $P4_322$…
Trigonal	$\bar{3}$	$P3$, $P3_1$, $P3_2$, $R3$
	$\bar{3}/m$	$P321$, $P3_121$, $R32$…
Hexagonal	$6/m$	$P6_1$, $P6_2$, $P6_3$, $P6_4$, $P6_5$
	$6/mmm$	$P622$, $P6_122$…
Cubic	$m3$	$P32$, $I32$..
	$m3m$	$P432$, $P4_132$, $I432$, $F432$...

The symmetry of the diffraction pattern (Laue symmetry) does not uniquely determine the space group of the crystal (unless it is triclinic).

Systematic absences

Systematic absences (extinctions) are classes of reflections (*hkl*) that have zero amplitude. They result from symmetry operations with a translation component. In crystals of chiral compounds (ie macromolecular), these are the unit cell centering operations (C, F, I, R) and screw axes.

Without deriving the structure factor equations (which is the most rigorous way of demonstrating the reason for systematic absences), we can state that systematic absences occur for certain classes of reflections because the contribution of any atom is cancelled out by the contribution of its translated symmetry mate (i.e., $\mathbf{F}_{hkl} = 0$).

Reflection conditions due to centered unit cells

Unit cell type	Limiting condition	
P	None	
C	hkl:	$h + k = 2n$
I	hkl:	$h + k + l = 2n$
F	hkl:	$h + k = 2n$, $h + l = 2n$, $k + l = 2n$
R	hkl:	$-h + k + l = 3n$ (obverse setting)

Reflection conditions due to screw axes (axial reflections)

2_1 along $\boldsymbol{a}$		$h00$:	$h = 2n$
2_1 along $\boldsymbol{b}$		$0k0$:	$k = 2n$
2_1 along $\boldsymbol{c}$	$00l$:	$l = 2n$	
3_1 or 3_2 along $\boldsymbol{c}$		$00l$:	$l = 3n$
4_1 or 4_3 along $\boldsymbol{c}$		$00l$:	$l = 4n$
4_2 along $\boldsymbol{c}$	$00l$:	$l = 2n$	
6_1 or 6_5 along $\boldsymbol{c}$		$00l$:	$l = 6n$
6_2 or 6_4 along $\boldsymbol{c}$		$00l$:	$l = 3n$
6_3 along $\boldsymbol{c}$	$00l$:	$l = 2n$	

Some important points about systematic absences

Systematically absent means that **all** affected reflections must be absent.

For example, a 2_1 screw axis along ***a*** would lead to the absence of all *h*00 with *h* odd. A single weak reflection with *h* odd rules out a screw axis ! (but beware of incompletely resolved reflections if the spots are very close). Note that no constraints apply to *h*00 reflections with *h* even: they can be strong, weak or absent.

Enantiomorphous screw axes produce the same systematic absences. Hence, pairs of enantiomorphous space groups (e.g., $P4_122$ and $P4_322$) cannot be distinguished based on the diffraction pattern alone.

Systematic absences due to unit cell centering may obscure absences due to screw axes. For example, body (I) centering results in the absence of all reflections with $(h + k + l)$ odd, including *h*00 with *h* odd, 0*k*0 with *k* odd, and 00*l* with *l* odd. Hence, it is not possible to distinguish between I222 and $I2_12_12_1$.

The reflection conditions for each space group are given in the International Tables.

Space group determination

This topic will be discussed again in the lecture on Data Processing.

Here, we only note that the process involves, in principle, three steps:

1) Determination of the crystal system, lattice type and probable Laue group based on the geometry (shape) of the unit cell.
2) Determination of the true Laue group based on intensities.
3) Assignment of screw axes based on systematic absences.

If the space group cannot be uniquely determined (enantiomorphous pairs, $I222$ vs. $I2_12_12_1$), do not despair. There are ways of resolving the ambiguity, which will be discussed in future lectures (but typically involve trying all possibilities and seeing which one works !)

Summary

- (Real) Crystals can display only 1, 2, 3, 4 or 6 fold rotation axes.

- Crystals of non-chiral molecules can also contain mirror planes and centres of inversion (excluded for macromolecules)*.

- Crystals belong to one of seven Crystal Systems (determined by the symmetry operators present).

- Combinations of these symmetry operators lead to the 32 Point Groups.

- Lattices can be Primitive, (single) face centred (C) , all face centred (F), body centred (I) or rhombohedral (R). The combination of possible lattices with the seven crystal systems leads to the 14 Bravais Lattices.

- Combining Point Group and Lattice symmetries gives rise to the 230 space groups, of which only 65 are possible for chiral molecules*. Space groups (considering an ideal infinite crystal) may contain symmetry elements (rotation axes, mirror planes) with a translational component (screw axes, glide planes).

- Diffraction patterns do not have translational symmetry but do have a centre of symmetry (Friedel's Law). This reduces the 32 Point Groups to the 11 Laue Groups.

* Except racemic mixtures

Data Processing Practical

This will take place in the Klug seminar room next Tuesday, 30th April, 2-5pm

1. Everyone should have a laptop with version 6.3.0 (or later) of the CCP4 software suite installed.

2. Please bring some of your own data to work with. Test images will be available, but these will take time to install.

3. The exact format will depend on the participants. There can be a “lecturer lead” tutorial if this is thought to be useful, but at some stage students should do their own processing.

4. Any queries, please ask now or contact andrew@mrc-lmb.cam.ac.uk or pre@mrc-lmb.cam.ac.uk