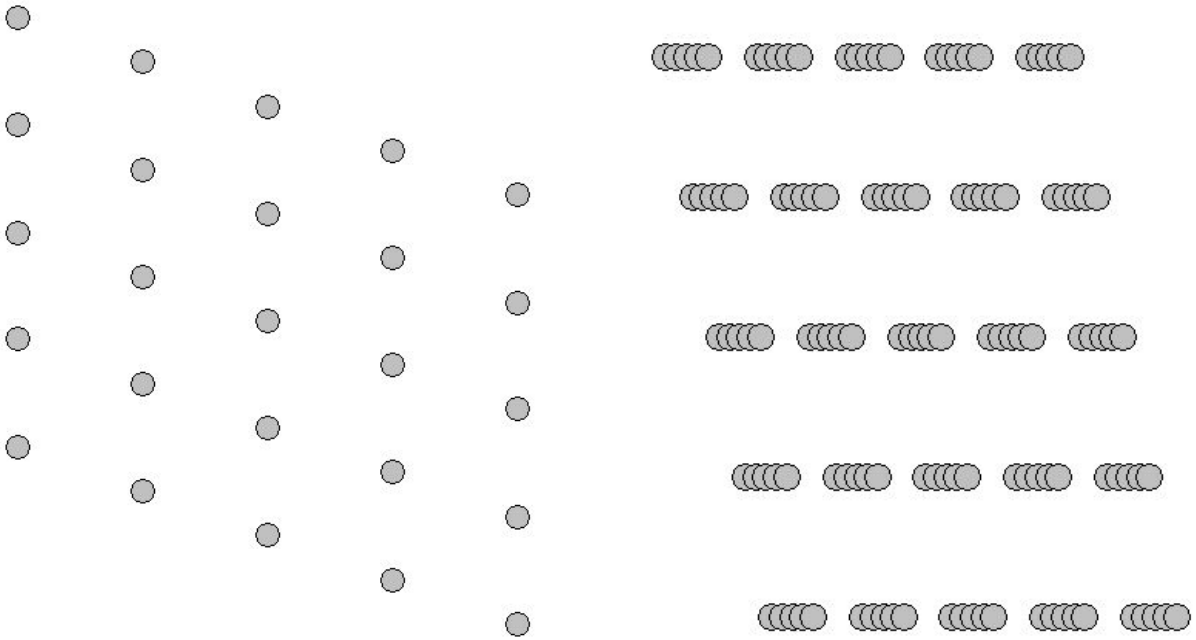
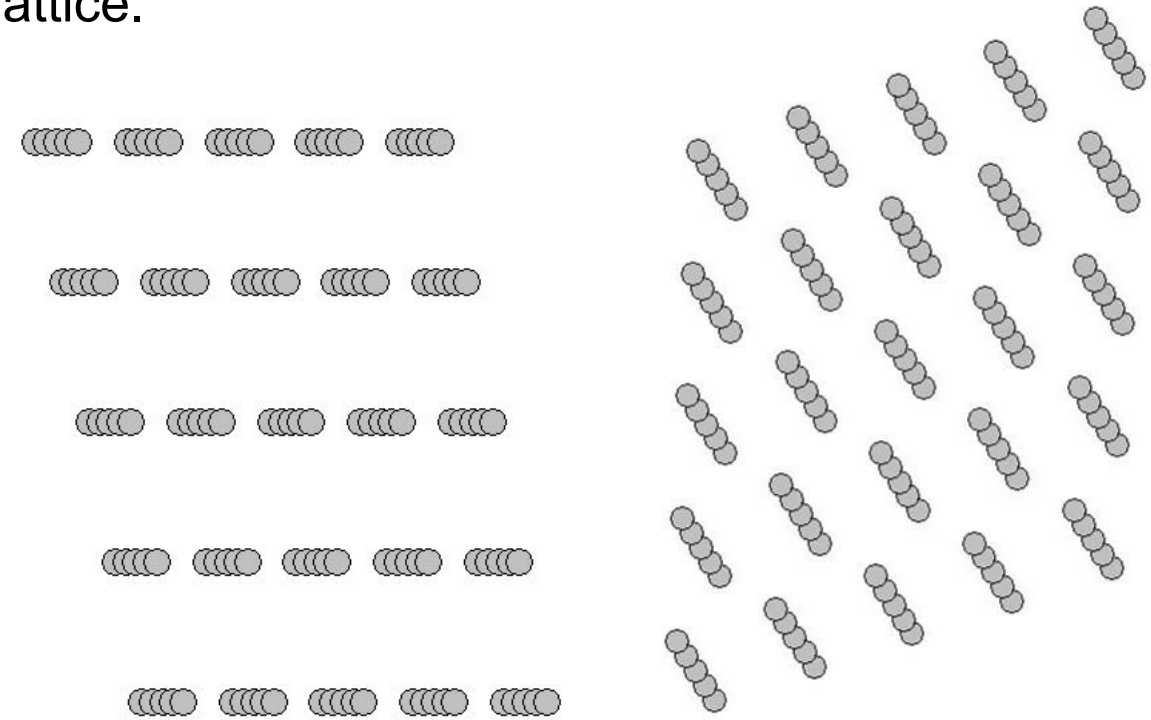
Lattices

By definition, crystals are periodic in three dimensions and the X-ray diffraction experiment must be understood in the context of the crystal lattice and the space group. A lattice is a regular infinite arrangement of points in which every point has the same environment as any other point. A lattice in 2 dimensions is called a *net* and a regular stacking of nets gives us a 3-dimensional lattice.



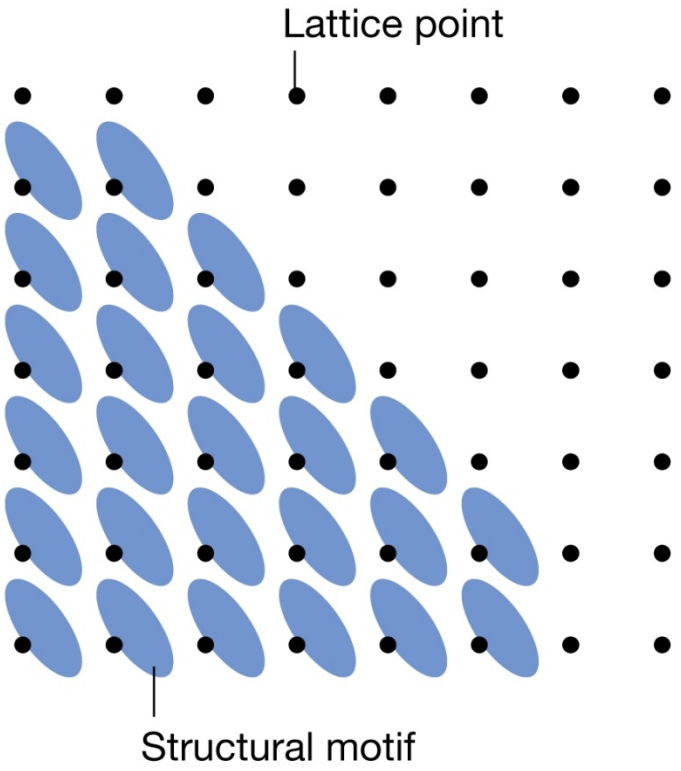
2-D net

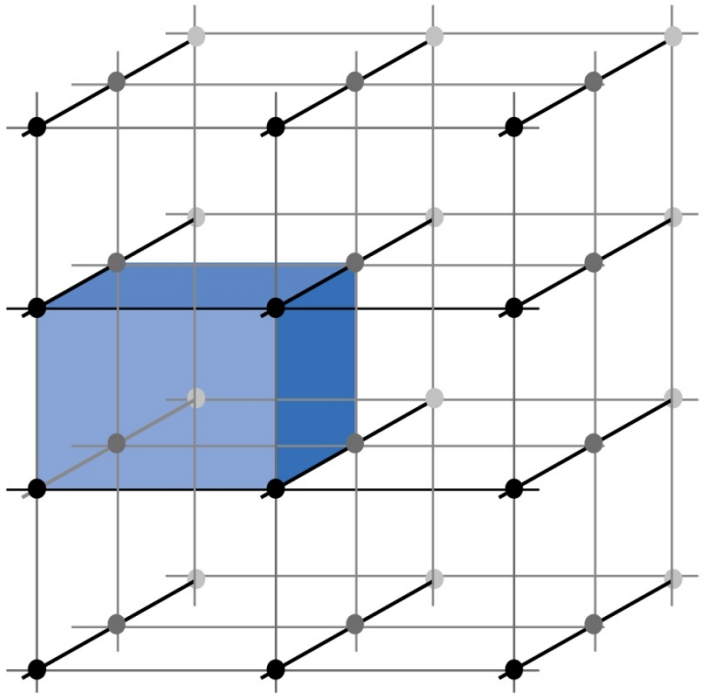


Stacks of 2-D nets produce 3-D lattices.

Lattices

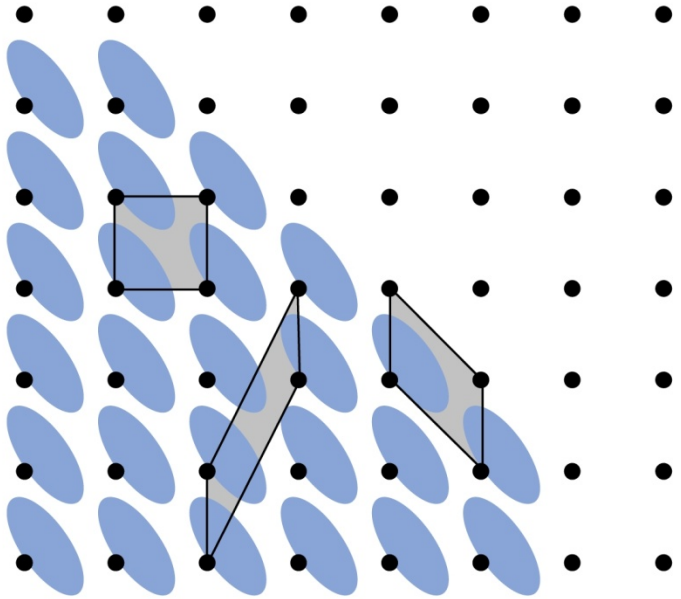
The lattice can be considered as a kind of scaffold upon which the structure of the crystal is built. For a crystal, the lattice is a 3-dimensional array and the structural motif will be located in a hypothetical box called the unit cell.

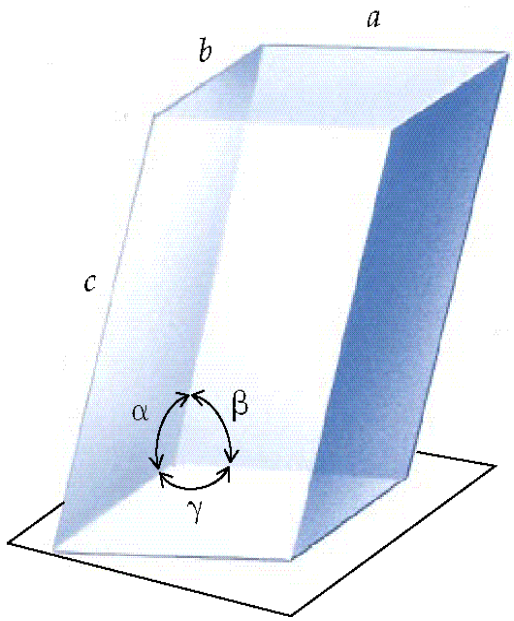




Lattices

Since lattices consist of infinitely repeating patterns, one needs only to look at a the smallest repeat unit to describe the lattice. The smallest repeat unit that will generate the entire lattice (by translation) is called the *Unit Cell*. It is defined by three repeat distances (*a*, *b*, and *c*) and three angles (α, β, γ), where α is the angle between *b* and *c*, β is the angle between *a* and *c*, and γ is the angle between *a* and *b*.

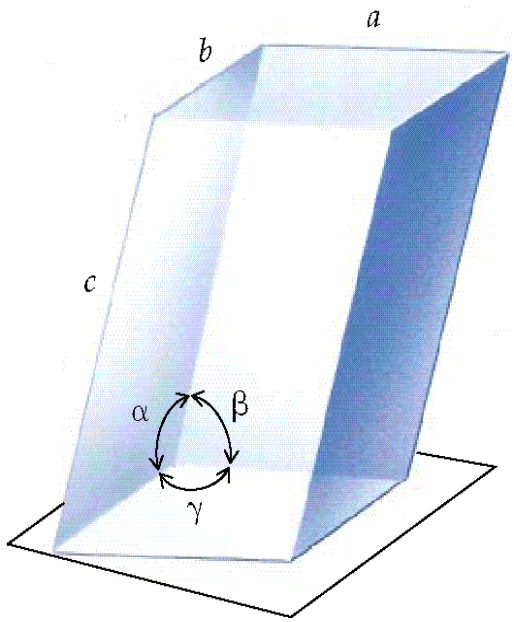




Unit cell parameters (*a*, *b*, *c*, α, β, γ) are chosen to best represent the highest-possible symmetry of the crystal and are given right-handed axes (*a* is along x, *b* is along y and *c* is along z) with angles that are either all ≥ 90º or all ≤ 90º.

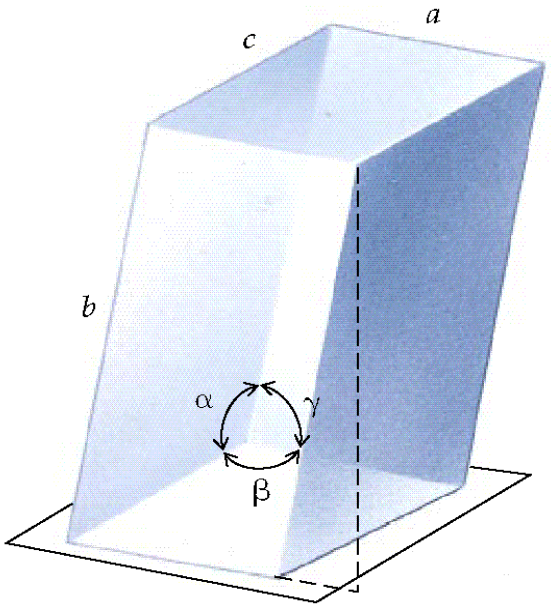
Unit Cells and Crystal Systems

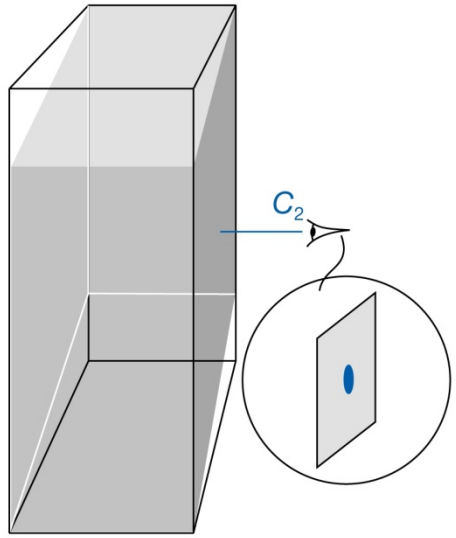
There are seven different classes of unit cells that, each defined by different limiting conditions on the unit cell parameters (*a*, *b*, *c*, α, β, γ). The most general system is called "Triclinic" in which none of the distances and angles are restricted to have any particular value. Please note that the symbol "≠" means "is not necessarily equal to" i.e. they might have the same value but it is not a requirement of the crystal system.



Triclinic

$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$





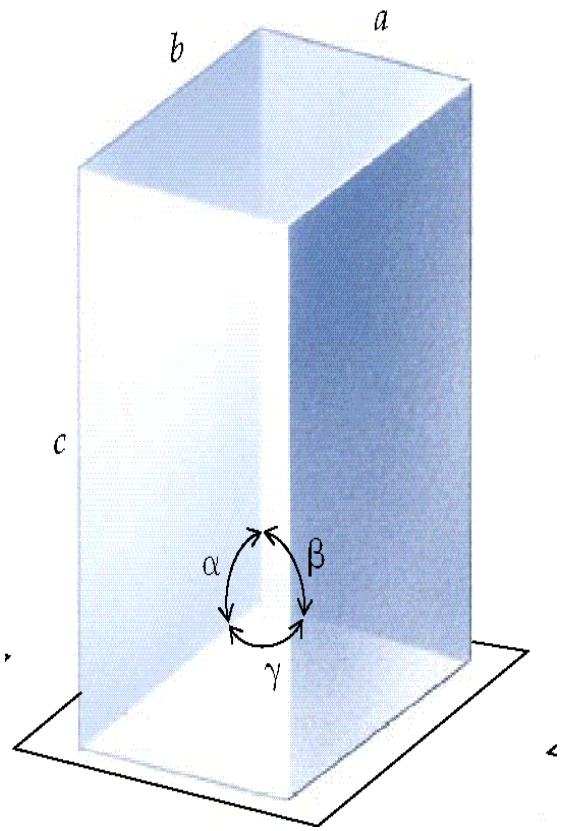
Monoclinic

$a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$

(by convention *b* is the unique axis)

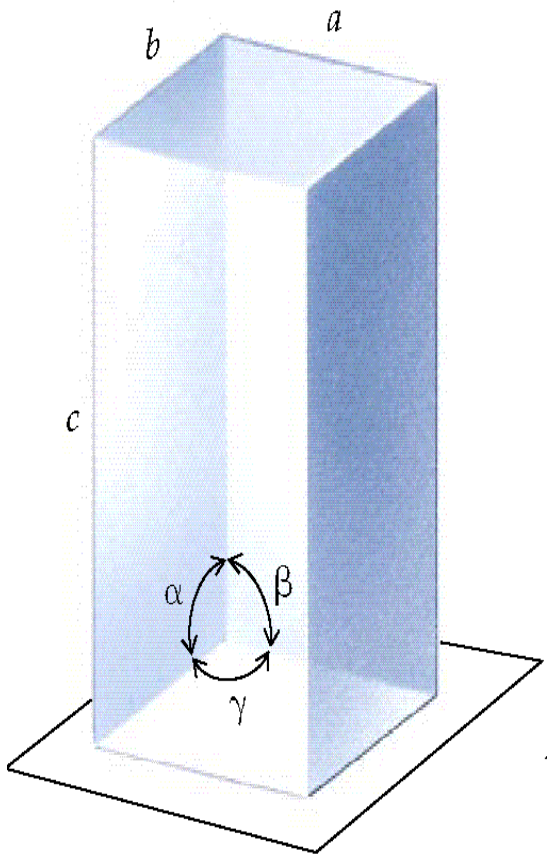
Unit Cells and Crystal Systems

As more of the angles and distances are restricted, the box becomes more symmetric.



Orthorhombic

$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$



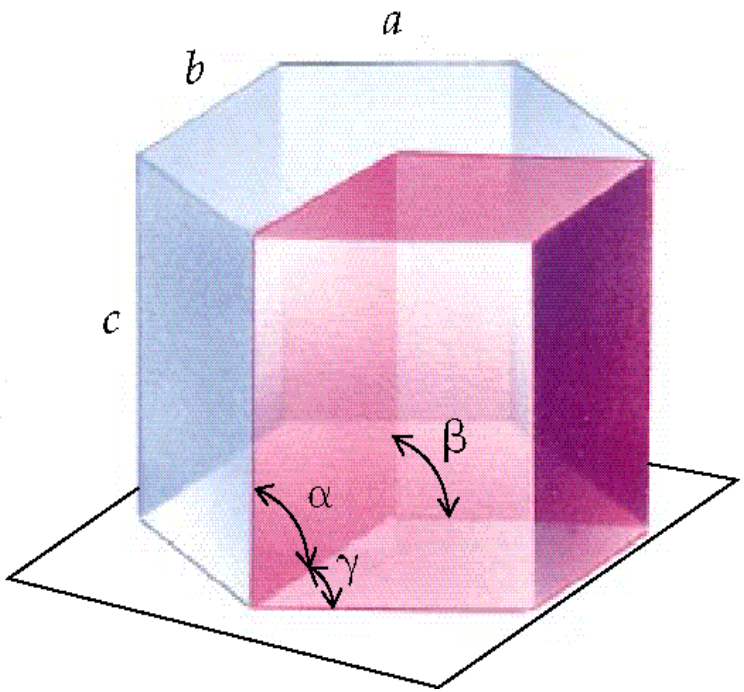
Tetragonal

$a = b \neq c$, $\alpha = \beta = \gamma = 90°$

(by definition c is the unique axis)

Unit Cells and Crystal Systems

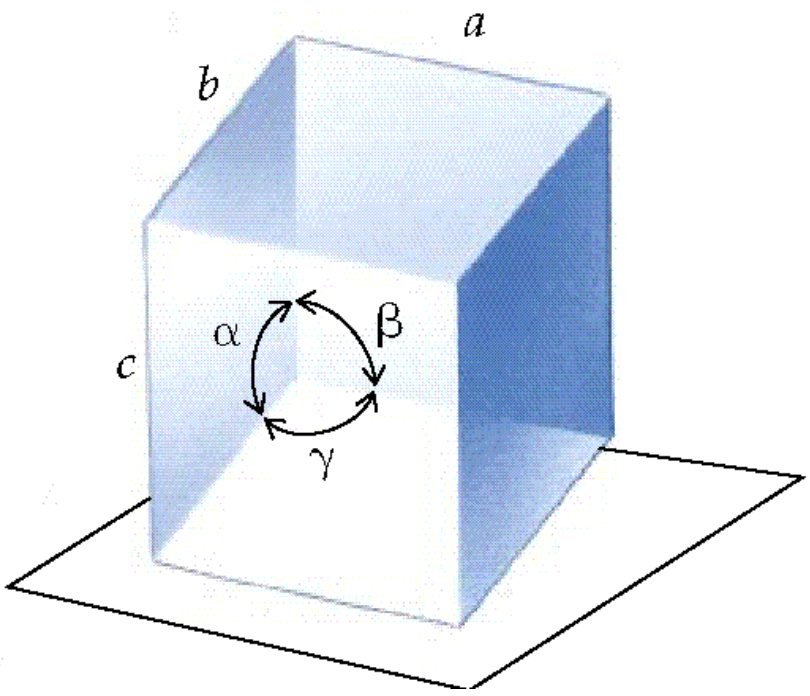
Note that for the hexagonal or trigonal systems, three unit cells are necessary to see the symmetry of the system. The choice of trigonal or hexagonal is dependent on the contents of the cell (more on this later).



Hexagonal or Trigonal

$a = b \neq c$, $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$

(by definition c is the unique axis)

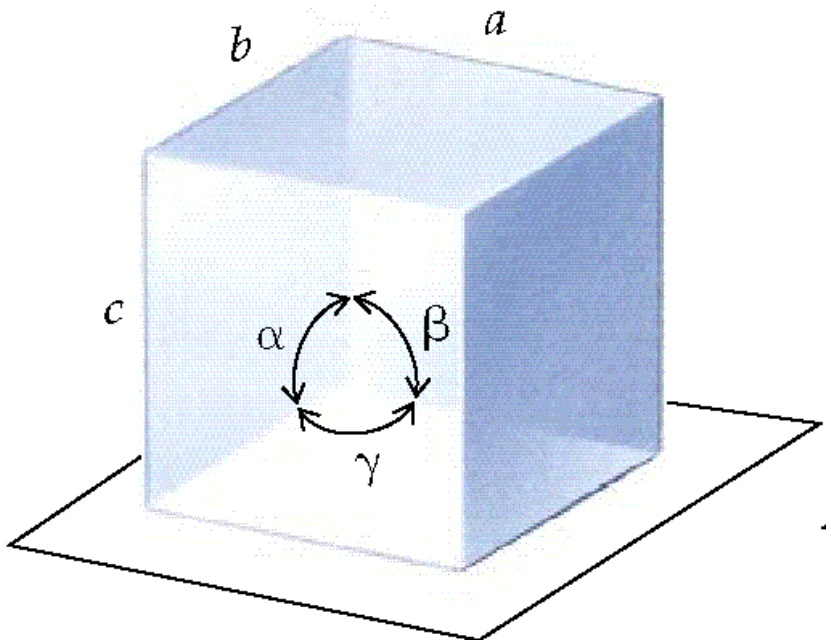


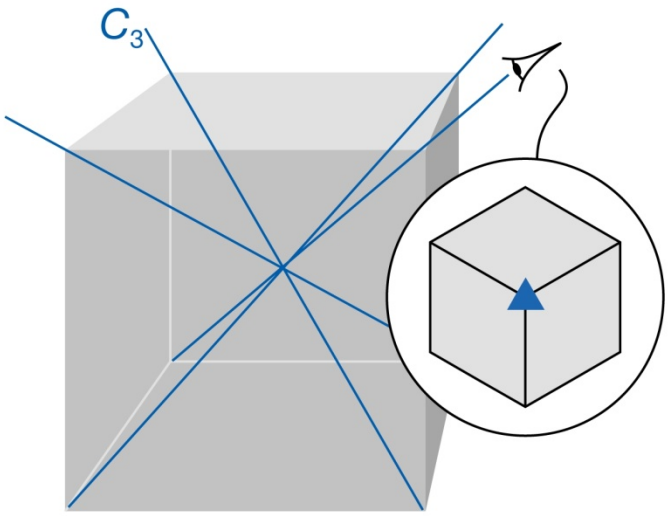
Rhombohedral

$a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$

Unit Cells and Crystal Systems

The most symmetric boxes are cubic and have only one variable parameter.





Cubic

$a = b = c$, $\alpha = \beta = \gamma = 90^{o}$

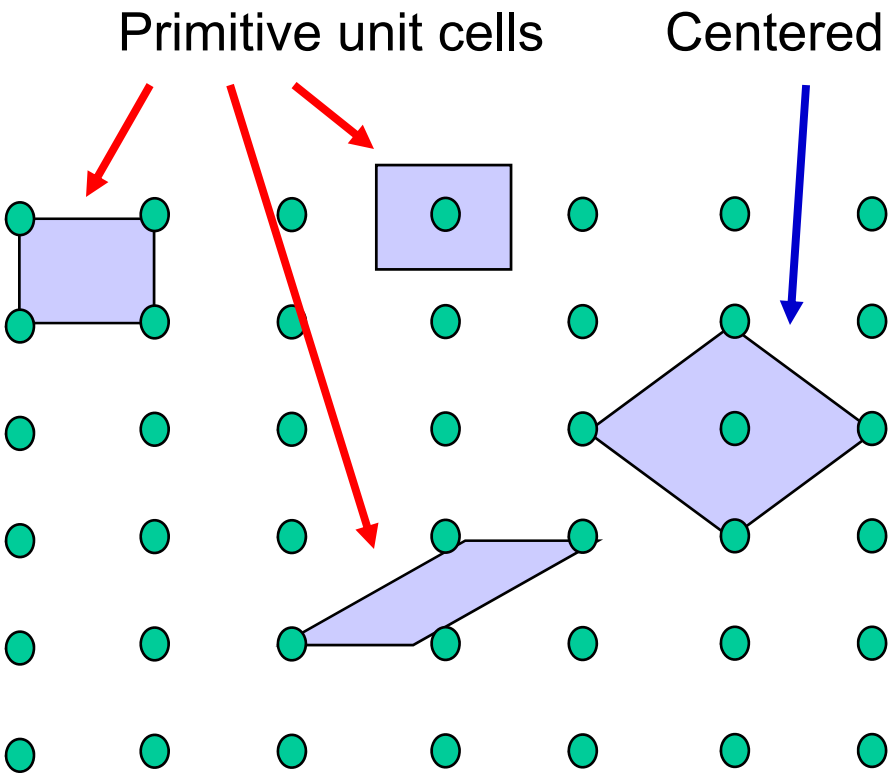
Unit Cells and Crystal Systems

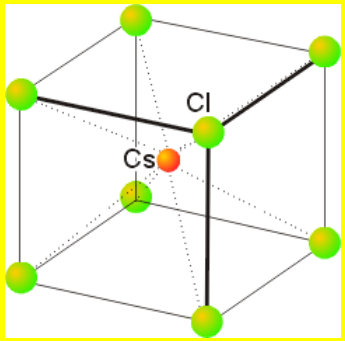
A summary of the different crystal systems shows how the number of variables in the unit cell parameters decreases with increasing lattice symmetry.

Crystal System	**#**	**Parameters***
Triclinic	6	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$
Monoclinic	4	$a \neq b \neq c$; $\alpha = \gamma = 90°$ $\beta \geq 90°$
Orthorhombic	3	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$
Tetragonal	2	$a = b \neq c$; $\alpha = \beta = \gamma = 90°$
Trigonal		
hexagonal	2	$a = b \neq c$; $\alpha = \beta = 90°$ $\gamma = 120°$
rhombohedral	2	$a = b = c$; $\alpha = \beta = \gamma \neq 90°$
Hexagonal	2	$a = b \neq c$; $\alpha = \beta = 90°$ $\gamma = 120°$
Cubic	1	$a = b = c$; $\alpha = \beta = \gamma = 90°$

Centering in Unit Cells

Note that to best indicate the symmetry of the crystal lattice, it is sometimes necessary to choose a unit cell that contains more than one lattice point. Unit cells that contain only one lattice point are called “Primitive” and are indicated with a “*P*”. There are only a limited number of unique ways to choose centered cells and the number and composition of possible centered cells depend on the crystal system.

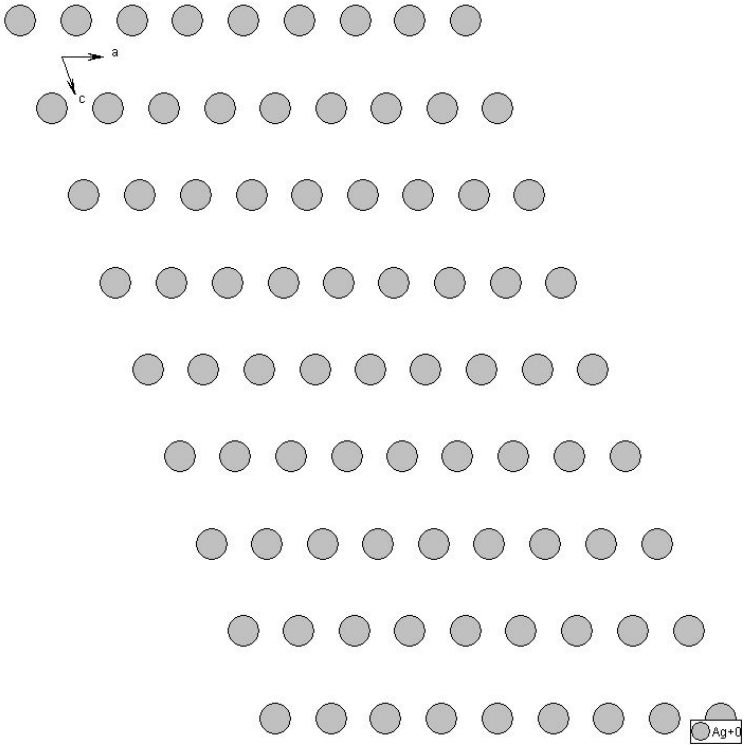




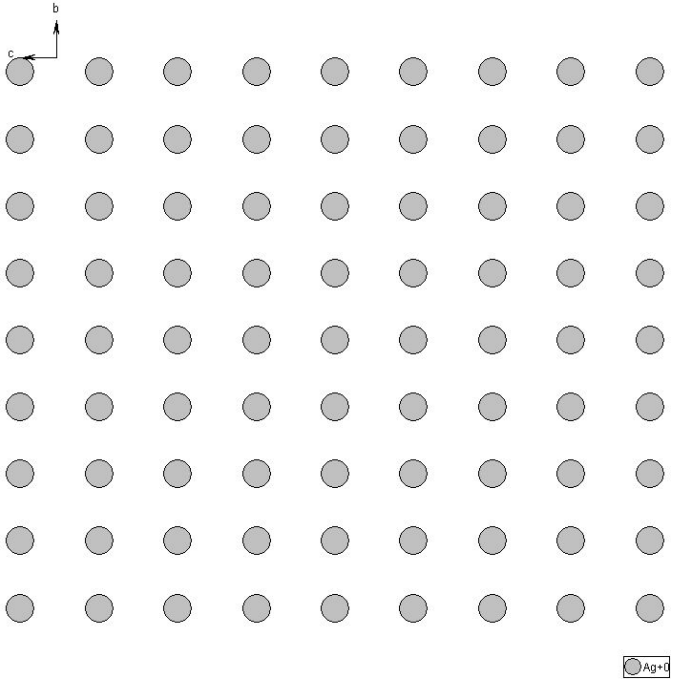
Remember that only 1/8th of an atom at the corner of the cell is actually in that cell. This CsCl lattice is primitive.

Centering in Unit Cells

An example of useful cell centering is shown below for a monoclinic system. When we look down the unique *b* axis, a primitive cell would conform to the monoclinic system. Similarly, when we look down the *a* axis, we can see that the preferred 90º angle for α is apparent.



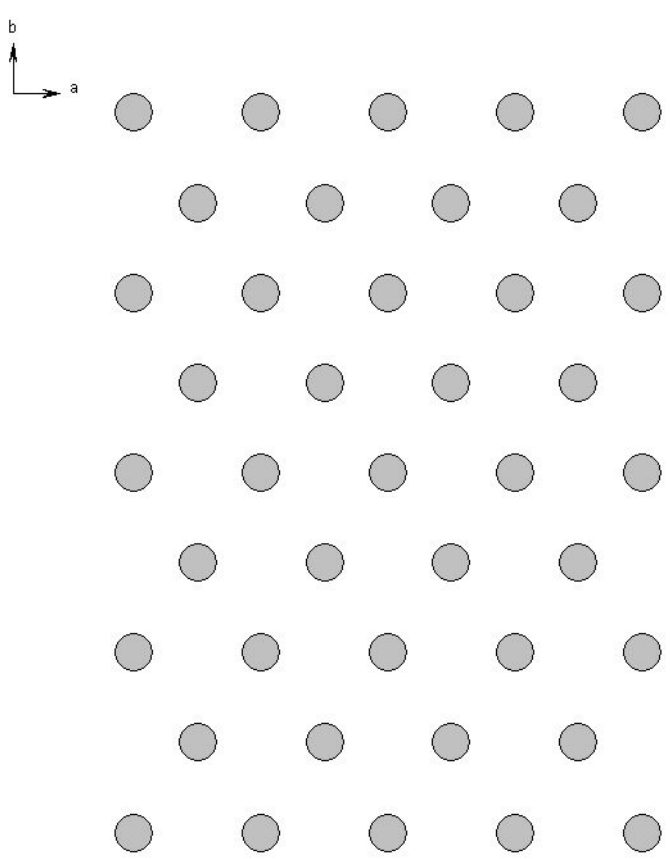
View down *b*



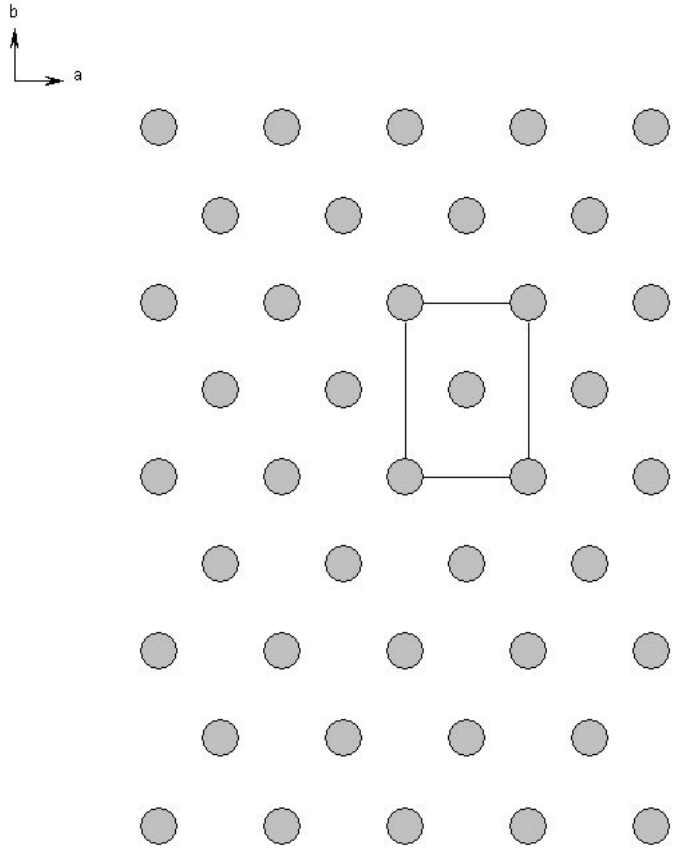
View down *a*

Centering in Unit Cells

However, when we look down the *c* axis, the necessary 90º angle for γ is not observed for a primitive cell, however a face centered unit cell does provide the 90º angle for γ and better indicates the symmetry of the lattice.



View down *c*

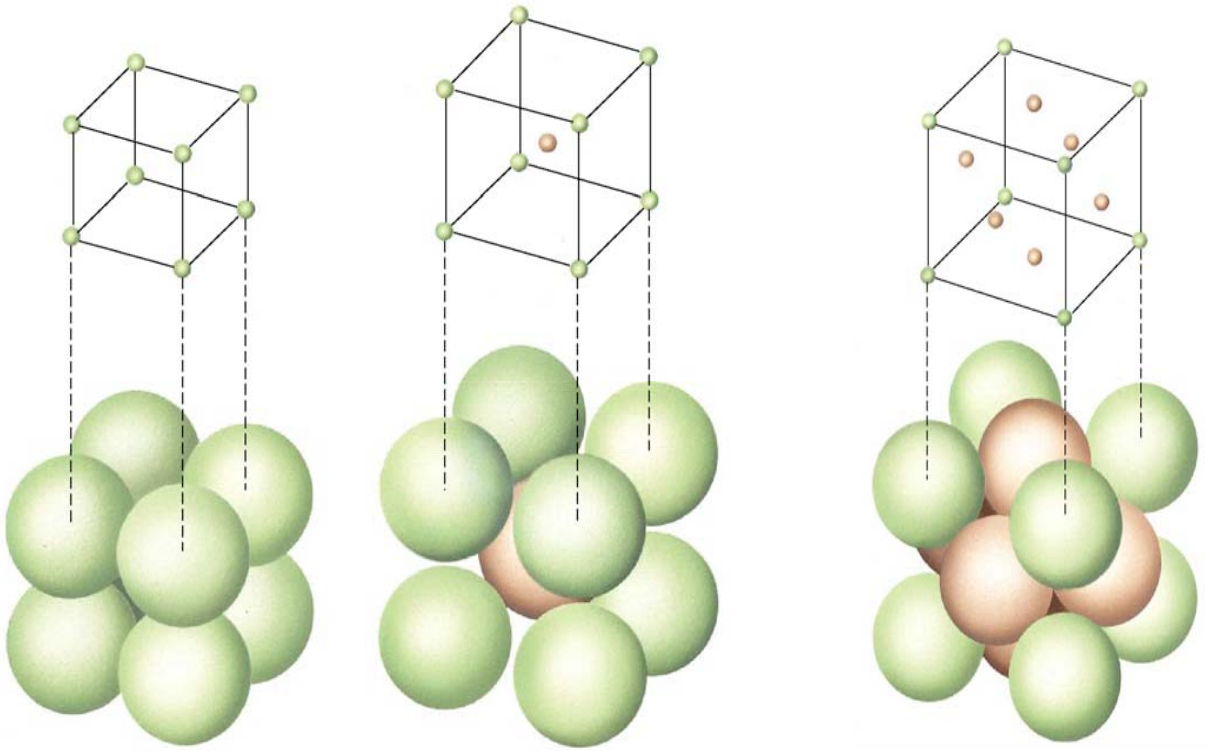


This is an example of a "face centered" cell because the additional lattice point lies in the center of one side of the cell.

Because the face that is centered is looking down the c axis, the lattice is designated with a "*C*" instead of a "*P*".

Centering in Unit Cells

For monoclinic cells, no other form of centering provides a different solution, however for other crystal systems different types of centering are possible. These include centering of specific faces (“A”, “B” or “C”), centering of all faces “F” or body centering “I”, in which there is a lattice point at the geometric center of the unit cell.



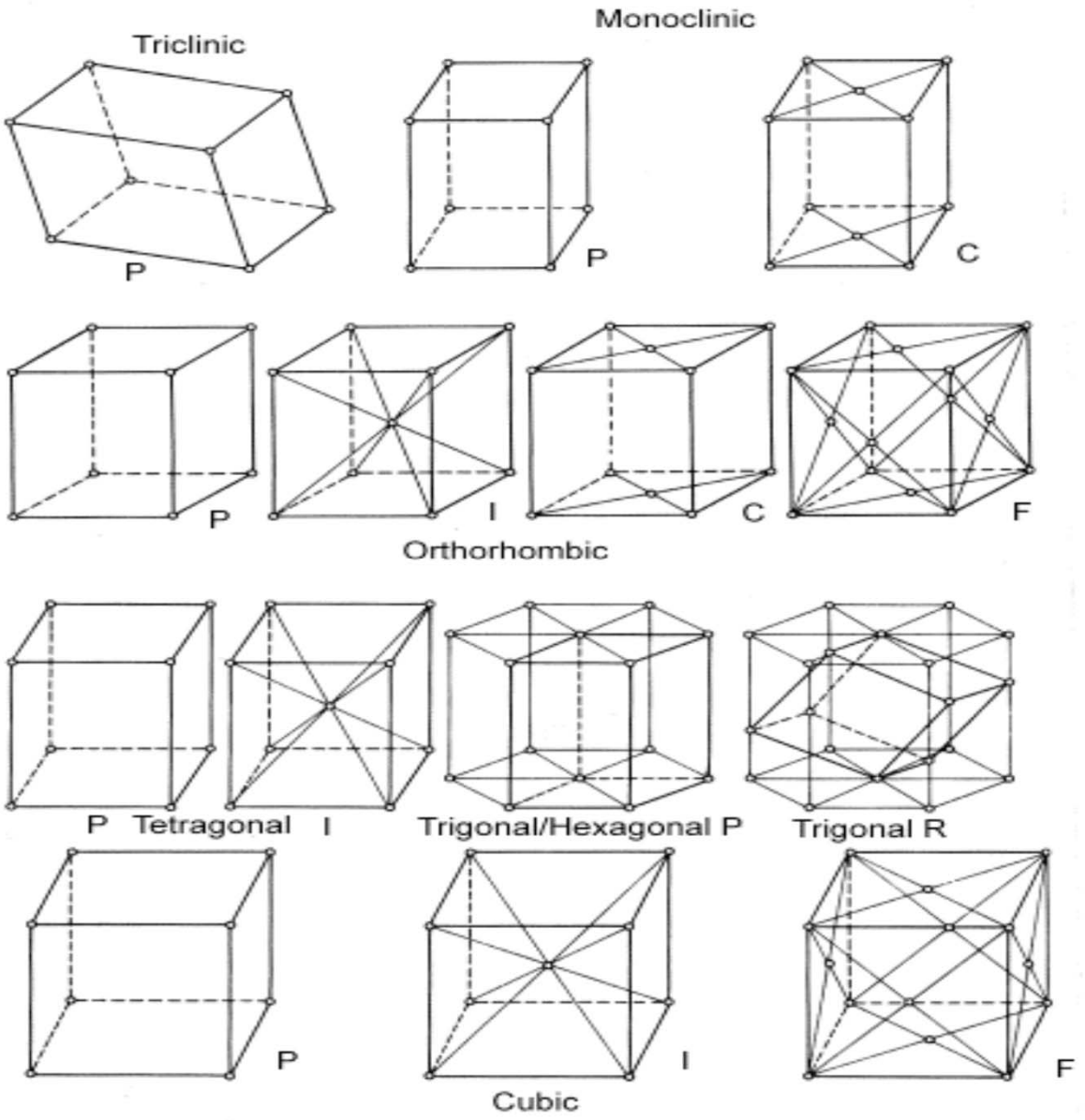
Primitive, *P* Body-centered, *I* Face-centered, *F*

All of the different possible lattices, including unique centering schemes were determined by A. Bravais and thus the 14 unique lattices are called “Bravais Lattices”

Bravais Lattices

These 14 lattices are the unique scaffolds in which atoms or molecules may be arranged to form crystalline materials.

However there is a further aspect of symmetry in crystals which must be considered to describe the actual arrangement of atoms in a crystal. These are the various crystallogaphic *Point Groups*.



Point Groups

Point groups have symmetry about a single point at the center of mass of the system.

Symmetry elements are geometric entities about which a *symmetry operation* can be performed. In a point group, all symmetry elements must pass through the center of mass (the point). A symmetry operation is the action that produces an object identical to the initial object.

The symmetry elements and related operations that we find in discrete objects (such as molecules) are:

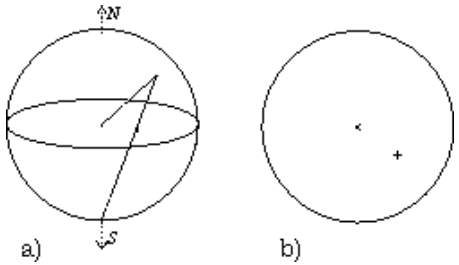
Element	Schoenflies	Hermann-Mauguin	Operation
Rotation axis	C_n	n	n-fold rotation (360º/n)
Identity	E	1	nothing
Plane of symmetry	σ	m	Reflection
Center of symmetry	i	-1 or $\bar{1}$	Inversion
Improper rotation axis	S_n	-	n-fold rotation + reflection
Rotary Inversion axis	-	-n or “n bar”	n-fold rotation + inversion

Point Groups

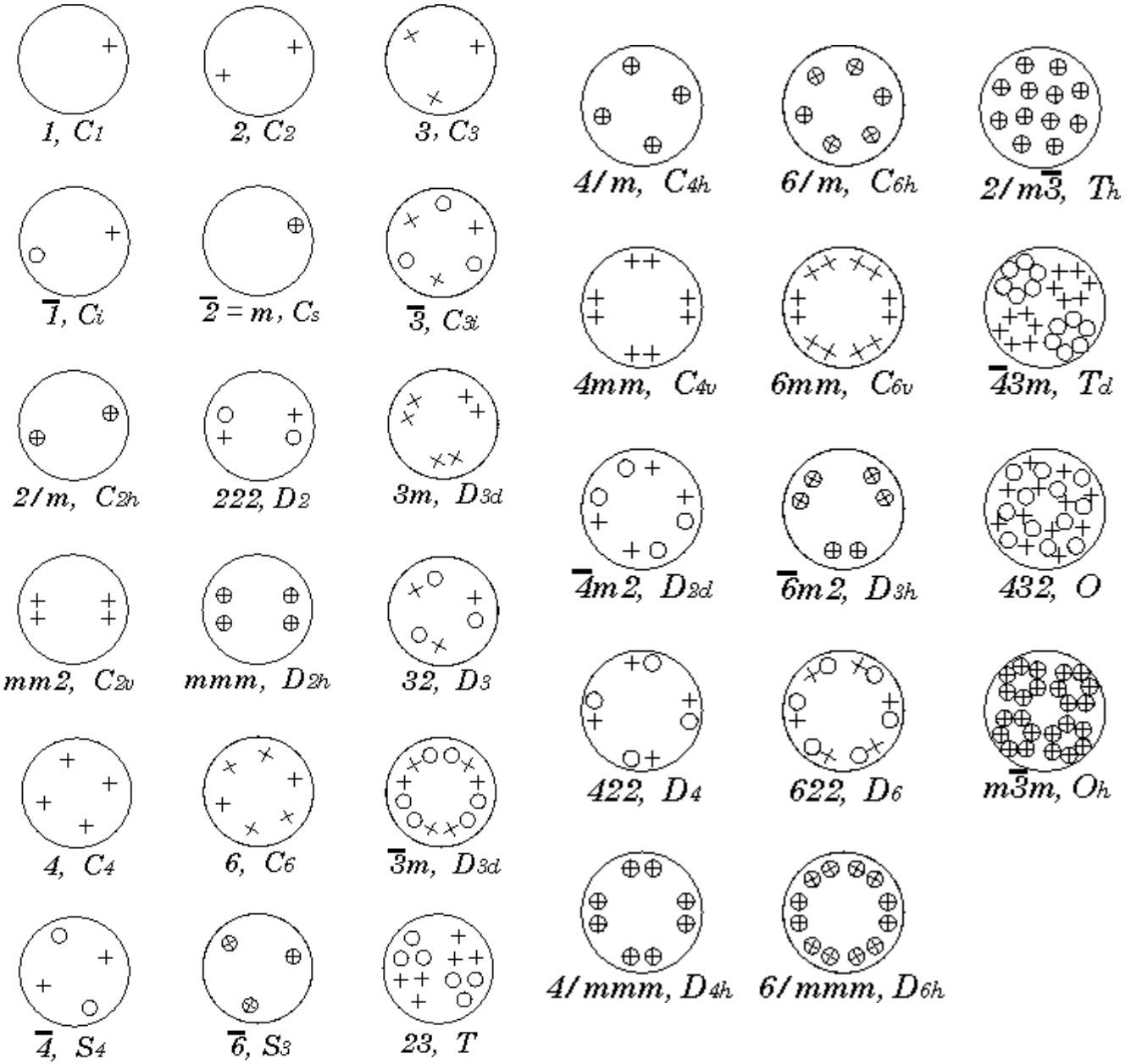
Whereas there is an infinite number of point groups available for discrete molecules and objects, the only point groups that can combine with lattices are those that conform to the periodicity of the lattice. This means that the result of a rotation of a lattice point must coincide with another lattice point. The only such rotations are 1, 2, 3, 4, and 6. There are a total of 32 point groups that conform to this rule (the "crystallographic point groups") and the combination of crystallographically acceptable point groups with the 14 Bravais lattices gives rise to *space groups*.

Crystal System	Point groups	Laue Class	Patterson Symmetry
Triclinc	1, -1	-1	P-1
Monoclinic	2, m, 2/m	2/m	P2/m, C2/m
Orthorhombic	222, mm2 , mmm	mmm	Pmmm, Cmmm, Fmmm, Immm
Tetragonal	4, -4, 4/m, 422, 4mm, -42m, 4/mmm	4/m, 4/mmm	P4/m, I4/m, P4/mmm, I4/mmm
Trigonal	3, -3, 32, 3m, -3 m	-3, -3m	P-3, R-3, P-3m1, P-31m, R-3m
Hexagonal	6, -6, 6/m, 622, 6mm, -62m, 6/mmm	6/m, 6/mmm	P6/m, P6/mmm
Cubic	23, m-3, 432, -43m, m3m	m3, m3m	Pm-3, Im-3, F-3m, Pm-3m, Fm-3m, Im-3m

Crystallographic Point Groups



Stereographic projections of point group symmetry ("+" is in the northern hemisphere and "o" is in the southern hemisphere)

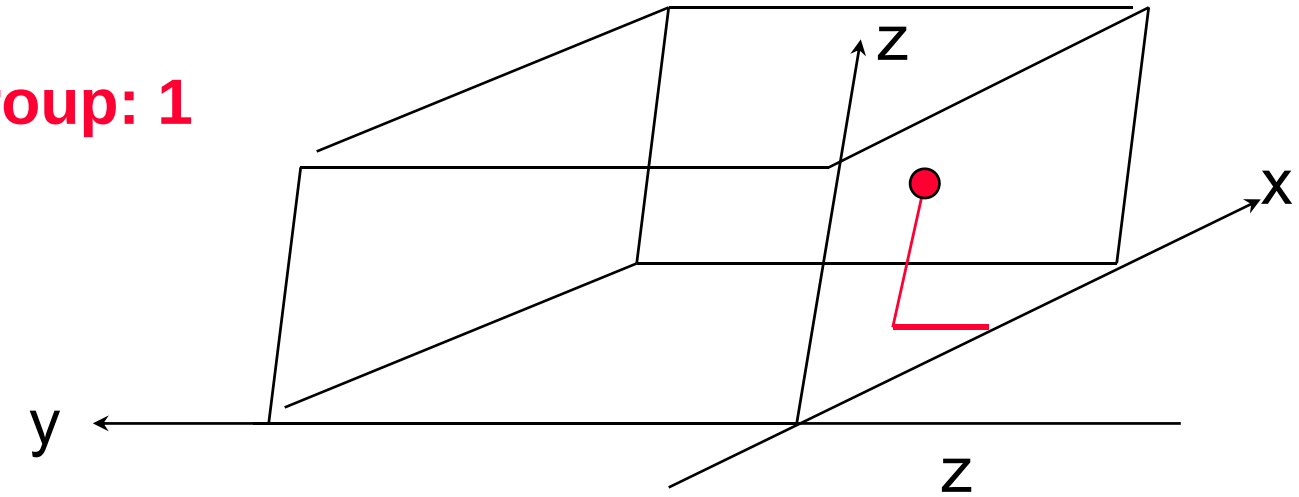


Triclinic Systems

xyz is a *general position* in *fractional coordinates*. This means that x is a number between 0 and 1 that describes the distance in the *a* direction. Similarly, y is the fraction of the *b* distance and z is a fraction of the *c* distance. Because of the periodicity of the lattice, an object found at x = 1.3 means that there must be an identical object in the origin unit cell at x = 0.3. This is the most convenient way to represent coordinates in a lattice. Note: to determine the actual distance in a given direction, all one must do is multiply the fractional coordinate by the corresponding cell parameter (x*a* = distance in the *a* direction from the bc plane using the unit cell axes, but remember that these are not Cartesian axes.)

Point group: 1

xyz

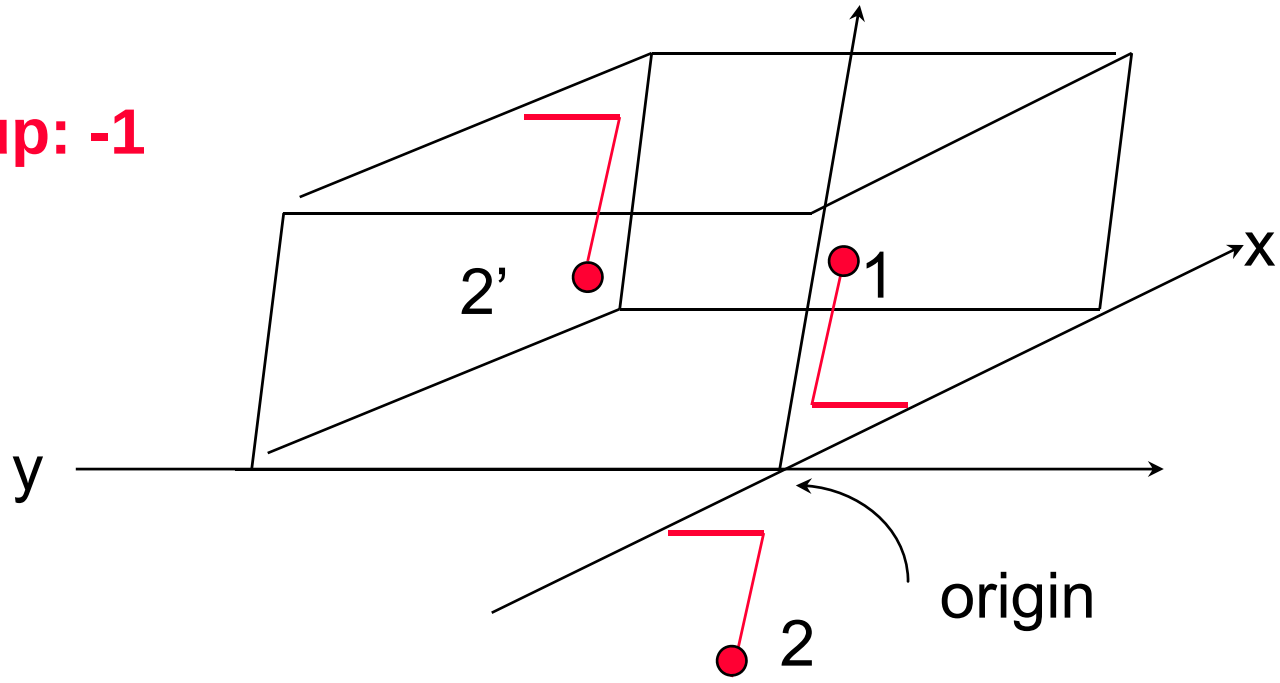


Triclinic Systems

xyz is a *general position* in *fractional coordinates*, the addition of point group symmetry creates *equivalent positions* that **must** also be found in the unit cell.

Point group: -1

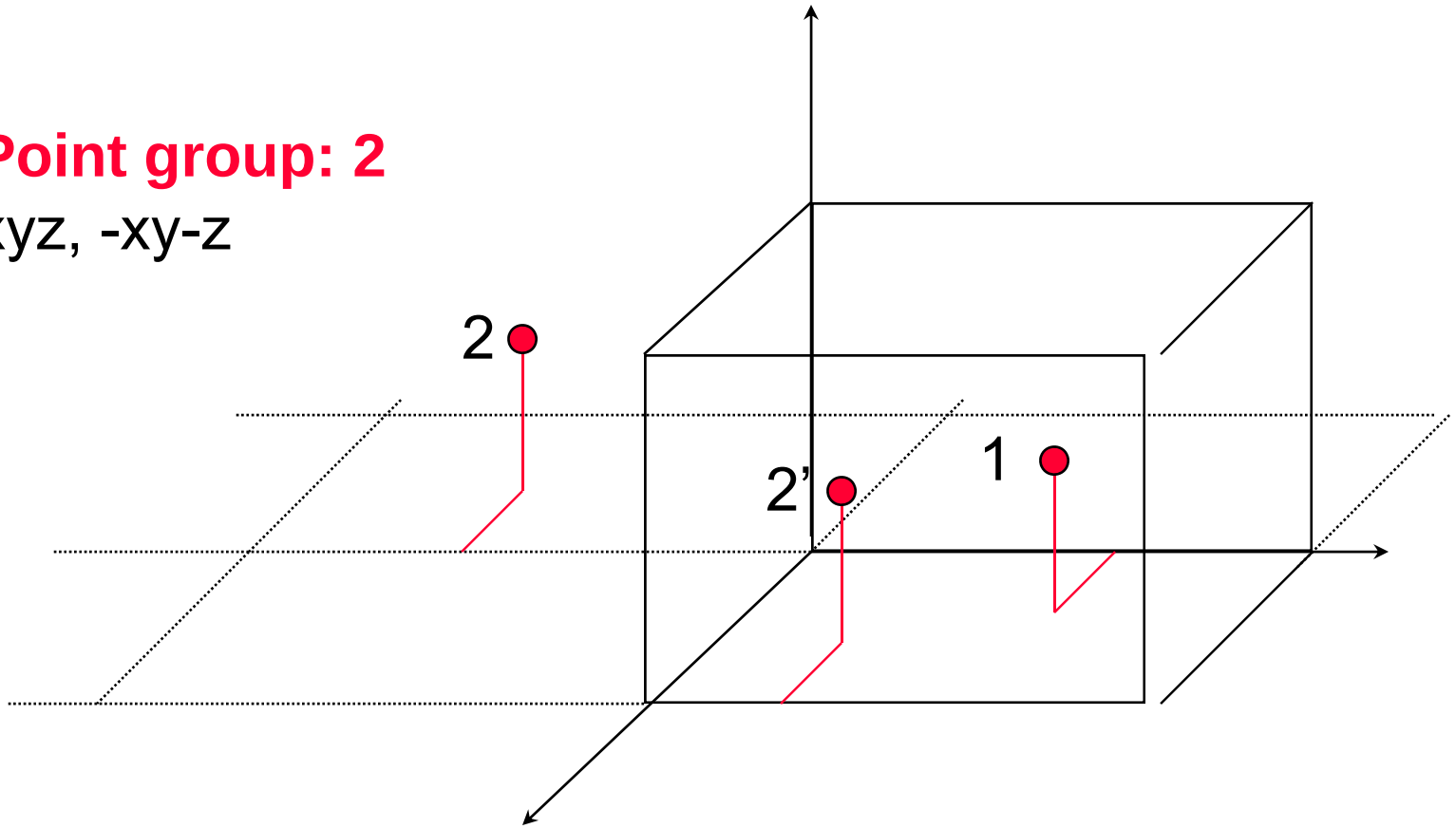
xyz, -x-y-z



Monoclinic Systems

Point group: 2

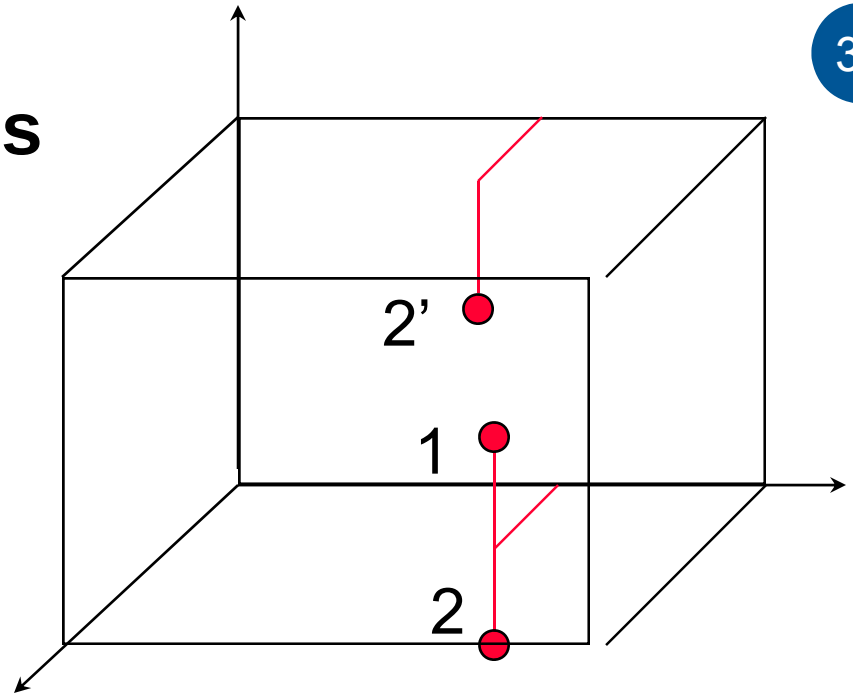
xyz, -xy-z



Monoclinic Systems

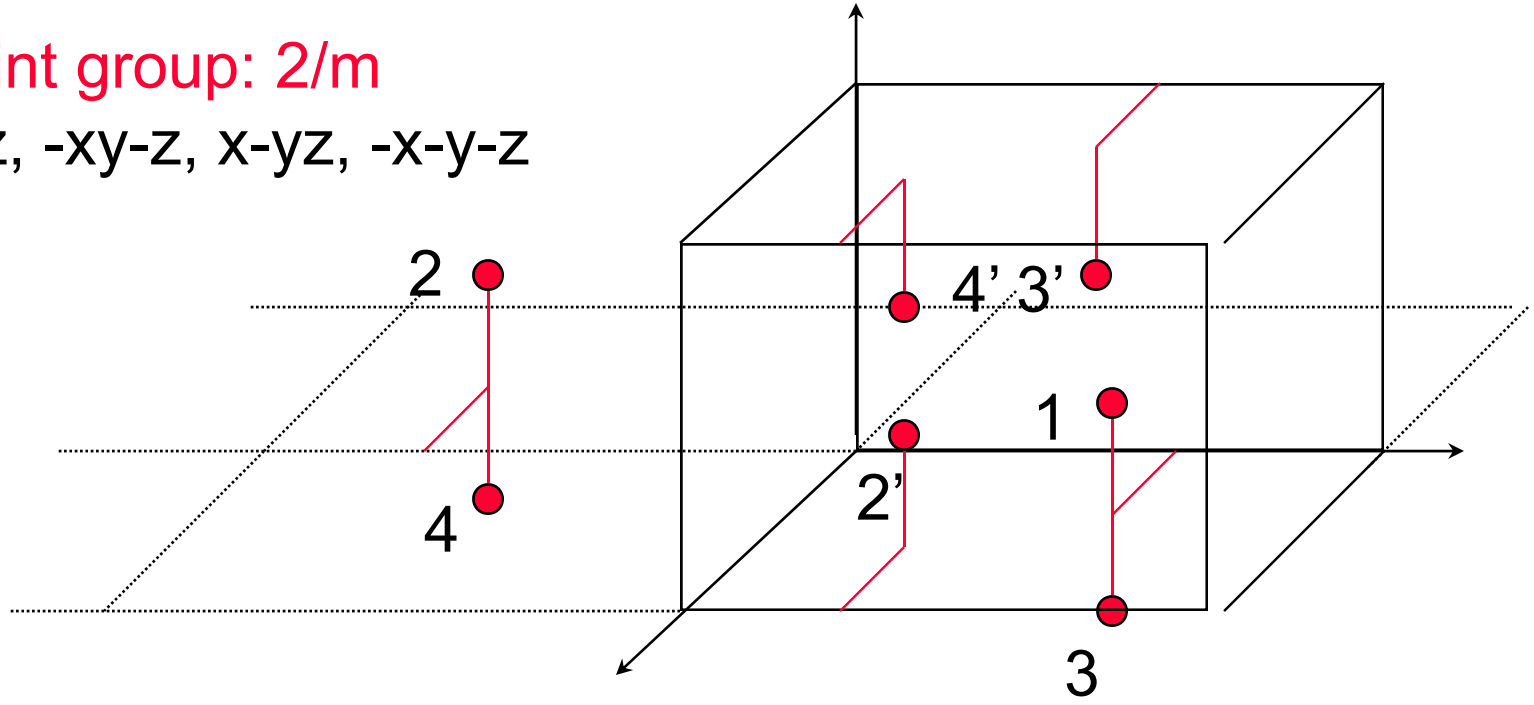
Point group: m

xyz, x-yz



Point group: 2/m

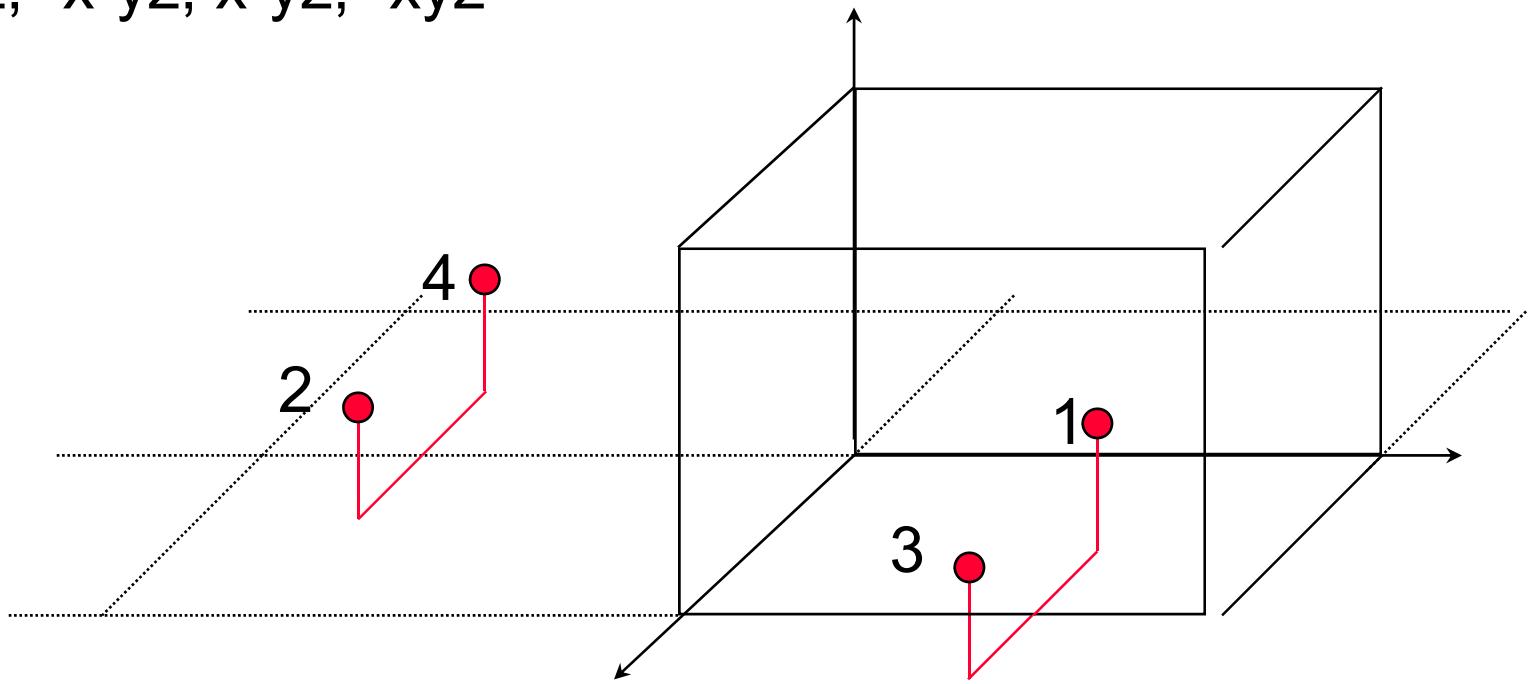
xyz, -xy-z, x-yz, -x-y-z



Orthorhombic Systems

Point group: mm2

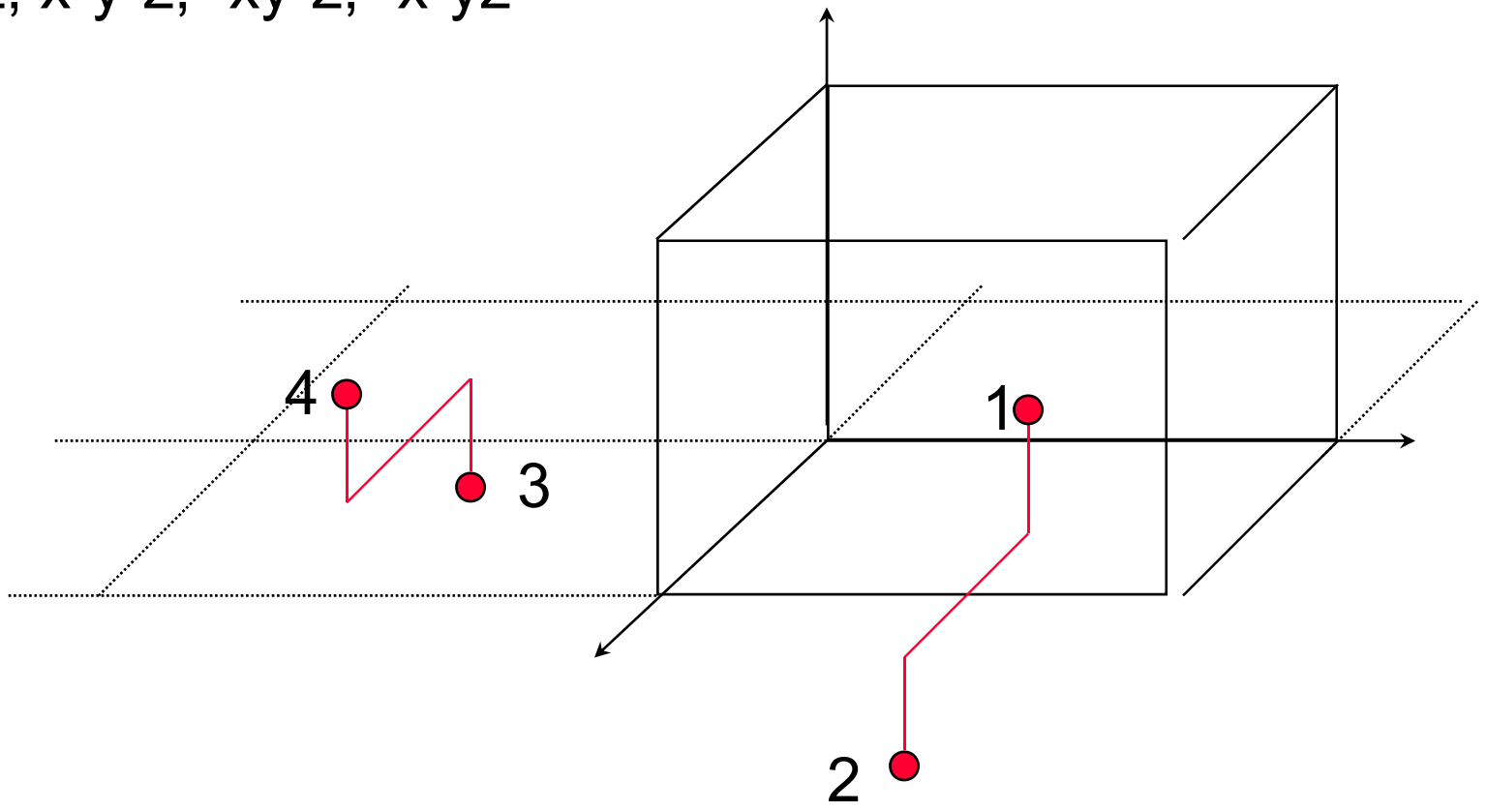
xyz, -x-yz, x-yz, -xyz



Orthorhombic Systems

Point group: 222

xyz, x-y-z, -xy-z, -x-yz

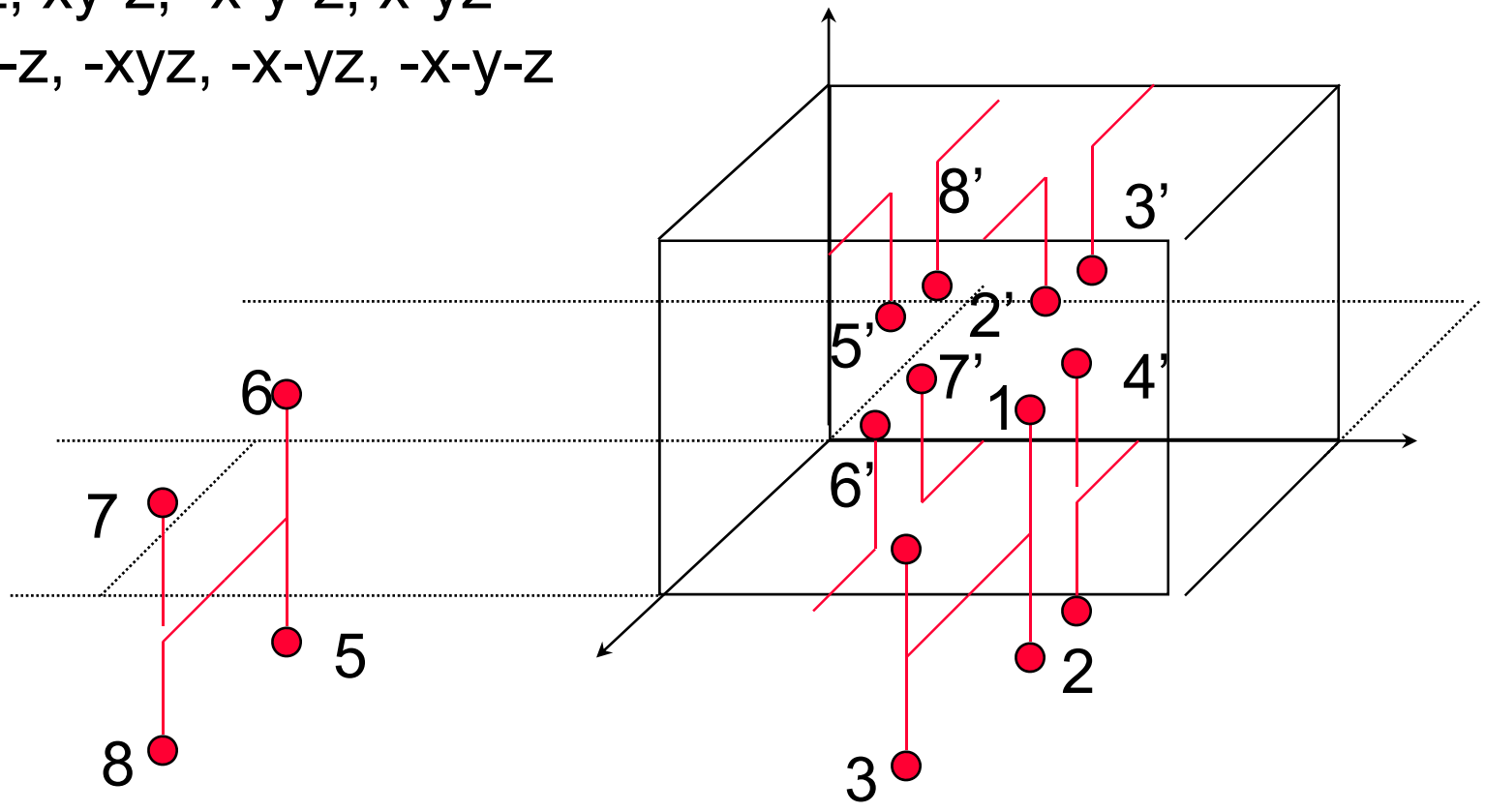


Orthorhombic Systems

Point group: mmm

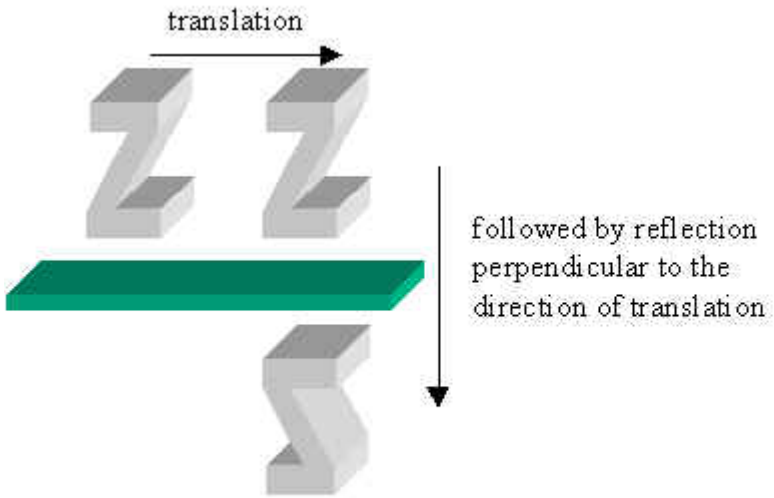
xyz, xy-z, -x-y-z, x-yz

-xy-z, -xyz, -x-yz, -x-y-z

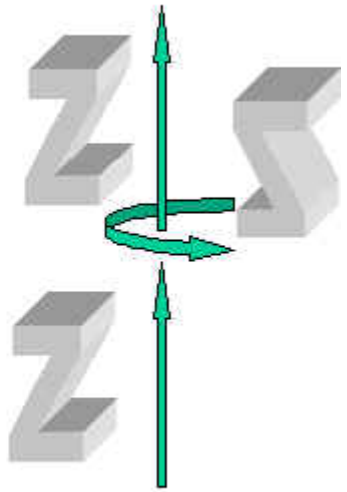


Translational Symmetry in Crystals

There are two further types of symmetry elements/operations that must be taken into consideration when combining point groups and lattices. Both of these operations involve a translational component in addition to either a rotation or a reflection. The symmetry elements are called “screw axes” and “glide planes”.

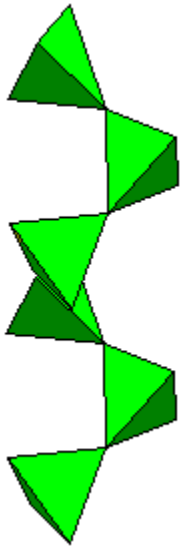


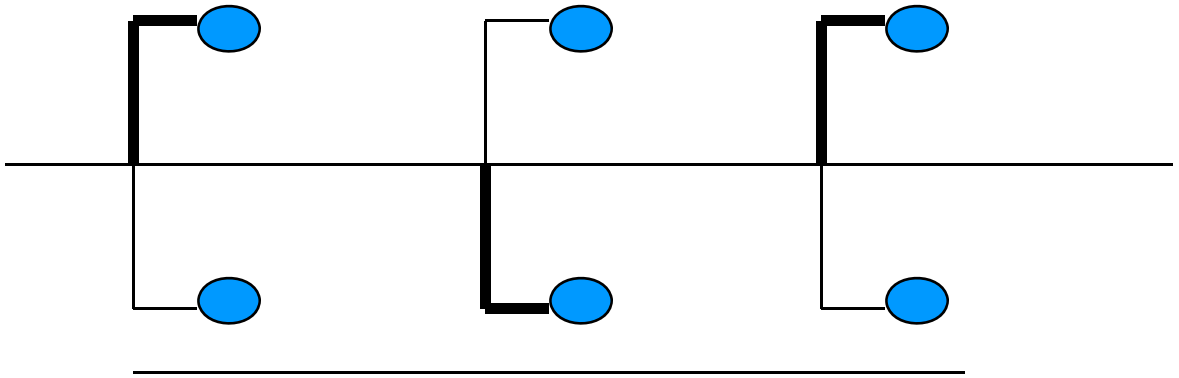
Glide Plane



Twofold screw axis

Screw Axis this symmetry element is given by the symbol n_p where n is the nature of the rotation and the translation is p/n of the cell edge. Thus a two-fold screw axis along b denoted 2_1 take a point xyz to -x, 1/2+y,-z. Remember that positive rotations are counter-clockwise.

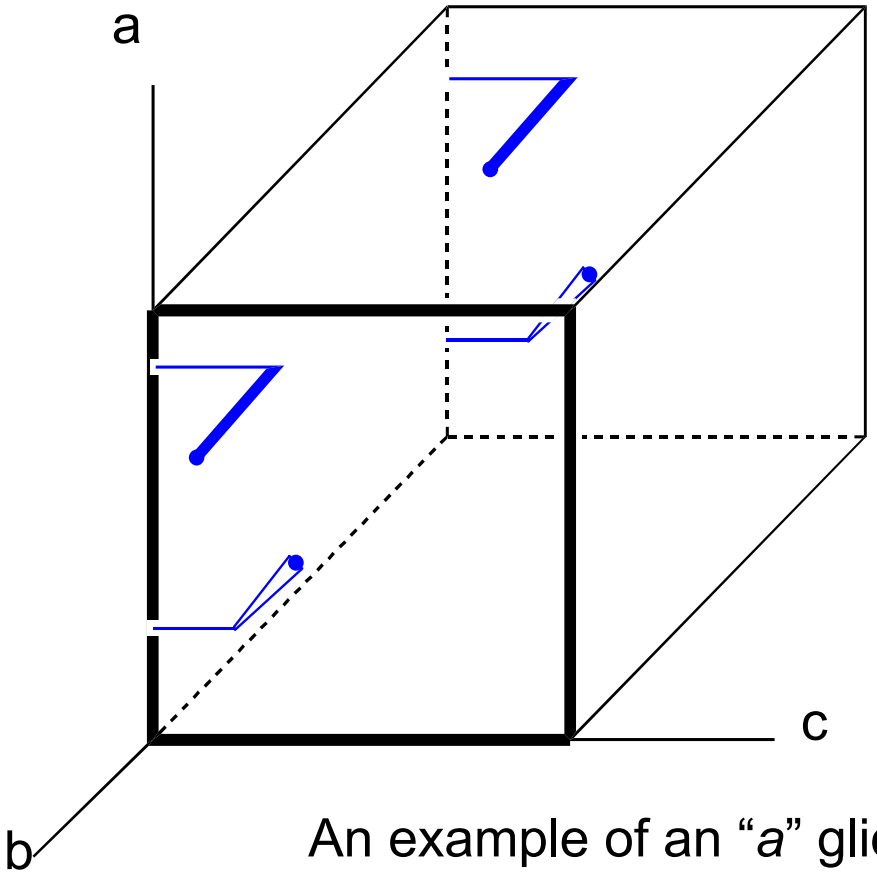




one unit cell length

Note: a 3_2 axis is the mirror image of a 3_1 axis

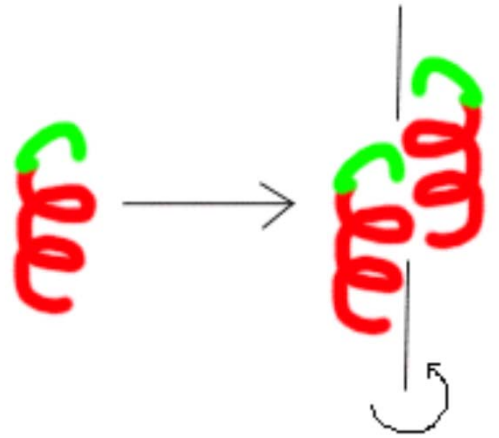
Glide Plane this symmetry element is given by the symbol *a*,*b*,*c*,*n*,or *d* where this represents the reflection in a mirror plane and translation of 1/2 the cell edge. The *n* glide is usually along the diagonal (1/2(a+b)) and the *d* glide is often along the body diagonal (1/4(a+b+c)).



An example of an "*a*" glide plane

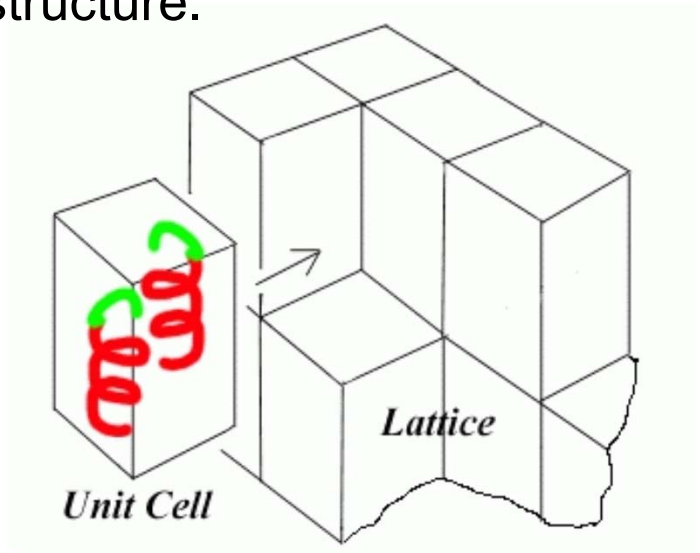
The Asymmetric Unit

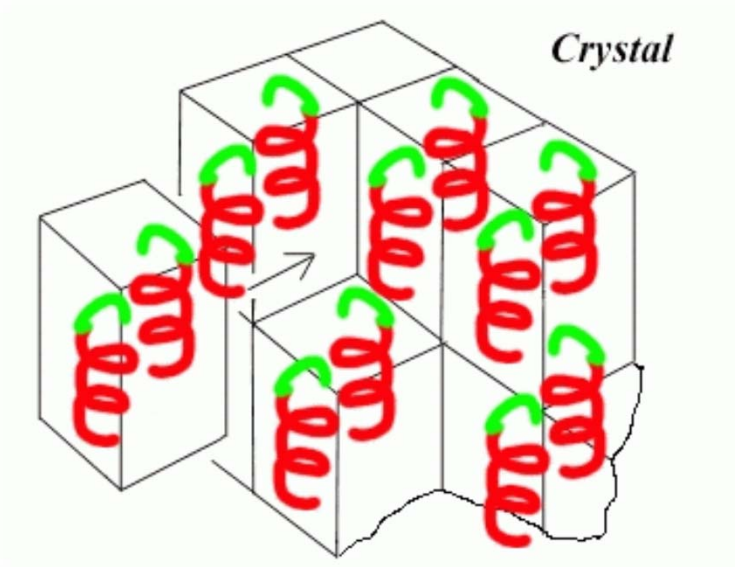
From the preceding treatment, it is apparent that parts of most unit cells are related by symmetry to other parts of the cell. Thus the smallest repeat unit that can be used to construct the entire crystal structure (using both symmetry and translation) is called the *asymmetric unit* (or motif). The **asymmetric unit** can be a single atom, a fraction of a molecule, a molecule, several molecules etc. Determination of the contents of the asymmetric unit thus allows us to reconstruct the crystal structure.



Asymmetric Unit

Unit cell contents





Space Groups

The combination of all the possible crystallographically acceptable point groups with the 14 Bravais lattices (when translational symmetry is also taken into account) provides the 230 *space groups*.

Space groups are typically named using the lattice designation followed by the point group designation (in which mirror planes may be replaced with glide planes and rotation axes may be replaced with screw axes).

Common examples include:
P-1, *P1*, $P2_12_12_1$, *Pnma*, *C2c*, $P2_1/c$, *Ibca, Fm3m, R-3*

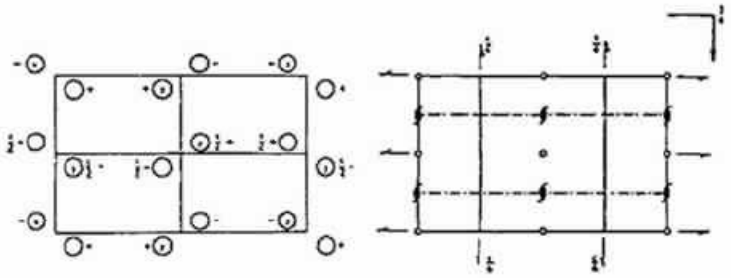
To find out any information you might want about space groups, you should consult the “International Tables for Crystallography, Volume A, Space Group Symmetry," **1996**, Kluwer Academic Publishers. This is generally found in the room adjacent to the diffractometers. Much of the important information can also be found in software applications such as Diamond or WinGX.

Space Group Information

Full Name

Crystal System → Orthorhombic $m\,m\,m$ $P\,2_1/n\,2_1/m\,2_1/a$ No. 62 $Pnma$ D_{2h}^{16} ← Usual Name

General positions (diagram including handedness) →



← Location and type of symmetry elements

Origin at $\bar{1}$

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions	Conditions limiting possible reflections
				General:
8	d	1	x,y,z; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z$; $\bar{x},\frac{1}{2}+y,\bar{z}$; $\frac{1}{2}-x,\bar{y},\frac{1}{2}+z$; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z$; $x,\frac{1}{2}-y,x$; $\frac{1}{2}+x,y,\frac{1}{2}-z$.	hkl: No conditions $0kl$: $k+l=2n$ $h0l$: No conditions $hk0$: $h=2n$ $h00$: $(h=2n)$ $0k0$: $(k=2n)$ $00l$: $(l=2n)$
				Special: as above, plus no extra conditions
4	c	m	$x,\frac{1}{4},z$; $\bar{x},\frac{3}{4},\bar{z}$; $\frac{1}{2}-x,\frac{3}{4},\frac{1}{2}+z$; $\frac{1}{2}+x,\frac{1}{4},\frac{1}{2}-z$.	
4	b	$\bar{1}$	$0,0,\frac{1}{2}$; $0,\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,0$; $\frac{1}{2},\frac{1}{2},0$.	hkl: $h+l=2n$; $k=2n$
4	a	$\bar{1}$	$0,0,0$; $0,\frac{1}{2},0$; $\frac{1}{2},0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.	

← Limiting conditions for observed reflections (this tells us what types of reflections we can see from this space group – more on this later).

Special positions (coordinates) →

Plane groups of special projections →

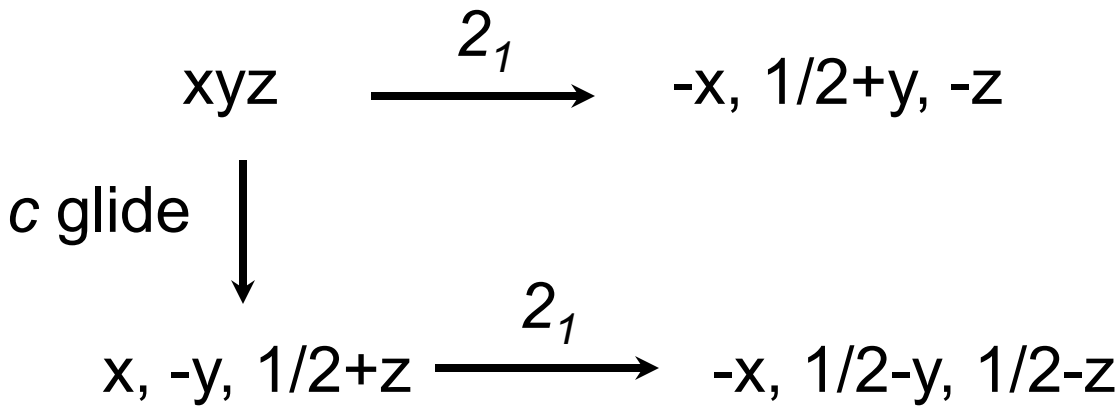
Symmetry of special projections

(001) pgm; $a'=a/2$, $b'=b$ (100) cmm; $b'=b$, $c'=c$ (010) pgg; $c'=c$, $a'=a$

Fig. 5.1. Page 151, Vol. I. reproduced from International Tables for X-Ray Crystallography, 1965 edition (by kind permission of the International Union of Crystallography).

$P2_1/c$ and Symmetry Operators

This is an example of how the equivalent positions are determined for the monoclinic space group *P2₁/c*. Similar treatments can be used to deduce the equivalent positions for any other space group.



xyz
-x,1/2+y,-z
x,-y,1/2+z
-x,1/2-y,1/2-z

shift origin to 0,1/4,1/4

x,1/4+y,1/4+z
-x,3/4+y,1/4-z
x,1/4-y,3/4+z
-x,3/4-y,3/4-z

x,1/4+y,1/4+z

-x,3/4+y,1/4-z

x,1/4-y,3/4+z

-x,3/4-y,3/4-z

subtract 1 from 3/4

Note: the position remains equivalent because these are fractional coordinates.

x,1/4+y,1/4+z

-x,-1/4+y,1/4-z

x,1/4-y,-1/4+z

-x,-1/4-y,-1/4-z

The pairs are related by an inversion center. *-1* or *1*

thus substitute x =X; 1/4+y = Y; 1/4+z = Z

XYZ

-X,1/2+Y,1/2-Z

X,1/2-Y,1/2+Z

-X,-Y,-Z

These are the general equivalent positions in the International Tables. These positions highlight the presence of the center of symmetry and make it the origin of the cell and are thus the most appropriate.

Cell Volume, Density and Z

The final goal of the crystallographic experiment is to determine the arrangement and position of the contents of the unit cell and thus the structure of the crystal. To this point, we have been considering general lattices composed of a single point in the asymmetric unit. Before we examine the effects of the unit cell (asymmetric unit) contents on diffracted X-rays, it is wise to consider one simple method that provides us with insight into the unit cell contents themselves.

The density of the crystal can provide us with much useful information.

$$d \text{ (in g cm}^{-3}) = \text{mass}_{\text{unit cell}} / V_{\text{unit cell}} = (Z)(FW/N_{avo})/V*10^{-24}$$

$$d \approx 1.6605(Z)(FW)/V$$

Where:
FW is the formula weight (not necessarily molecular weight) in g mol^{-1}
Z is the number of formula units in the unit cell (often the number of asymmetric units) – this must be an integer!
N_{avo} is Avogadro's number
V is the unit cell volume in $Å^3$

Cell Volume, Density and Z

For example: A compound L_2PdCl_2 (MW 775) crystallizes from benzene in space group *P2/m* with d = 1.8 g/cc and a unit cell V = 1500 $Å^3$.

Calculating Z we get 2.1 – since this is a bit higher than the integral value, it means that we may have underestimated the formula weight (or have an incorrect density).

Since Z must be and integer (it might be 2.0) see what happens if there is one benzene molecule in the formula unit as well – using a FW of 853, we calculate a Z of 1.9, which is a bit too low.

If we use only ½ of a benzene molecule per formula unit (FW of 814) we get a Z of 2.0.

The observation that this molecule has a Z value of 2 and only 1 benzene molecule in a *P2/m* unit cell has several implications regarding the positions of the atoms in this structure. There are 4 general positions in *P2/m* thus the Pd complexes must be sitting on symmetry elements (relating one half of the molecule to the other) and the benzene must be sitting at a special position of very high symmetry (the intersection of two elements) so that only ¼ of the molecule is in the asymmetric unit.

Cell Volume, Density and Z

Sometimes, the volume and symmetry of the unit cell (in consideration of a reasonable density) provide almost unambiguous information about the location of atoms in a unit cell.

For example, diamond crystals have the cubic space group *Fd-3m* and the length of the cell edge is 3.57Å which provides for a cell of 45.5Å^3. The density of diamond is 3.51 g cm^{-3}, thus a quick calculation of Z gives us a value of 8.0.

Looking at the International Tables, or using the Space Group Tool in WinGX or the space group information in Diamond, you will see that if the carbon atoms were in general positions xyz, there would have to be 192 of them in the unit cell – this is an impossible situation.

In fact, there are only two possible positions that will only generate 8 carbon atoms in the unit cell – so your crystal structure is essentially solved just by using symmetry requirements, cell size and density.