Symmetry & Diffraction

A symmetry element is a movement or operation that leaves an object in a position indistinguishable from its original position.

I. Symmetry in Two Dimensions

A. Point Symmetry Elements (leave at least one point unmoved.)

1. **Mirror** line
   a. reflection through a line
   b. written symbol *m*
   c. graphical symbol is a solid line
2. **Rotation** point
   a. counterclockwise rotation of 360°/*n* about a point
   b. written symbol *n* (an integer number)
   c. graphical symbol is a solid polygon with *n* vertices

   2 = ⬮, 3 = ▲, 4 = ■, 5 = ⬟, 6 = ⬢.
3. Combinations: intersecting mirror lines imply a rotation point and a rotation point acting on a mirror line may generate more mirror lines.

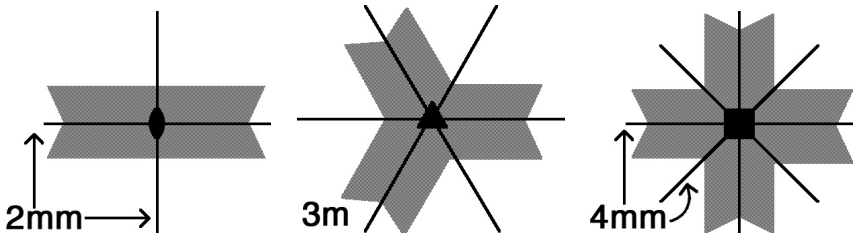
B. **Point Groups** (a set of point symmetry elements which form a mathematical group, i. e., there is an identity, an inverse for every element, and the combination of elements is associative and closed.)

1. We will be concerned only with the "crystallographic" point groups, the point groups which can form translationally repeating patterns:

   1, 2, *m*, 2*mm*, 3, 3*m*, 4, 4*mm*, 6, and 6*mm*.
2. In the general point group name, *nmm*, *n* indicates the rotation point, the first *m* indicates mirror lines containing that point, and the other *m* indicates a second set of mirror lines interleaving the first set. (The mirror lines form two sets if they are not interchanged by the rotation point.) If mirror lines are present, there will be a total of *n* mirror lines.

Point Group Examples.

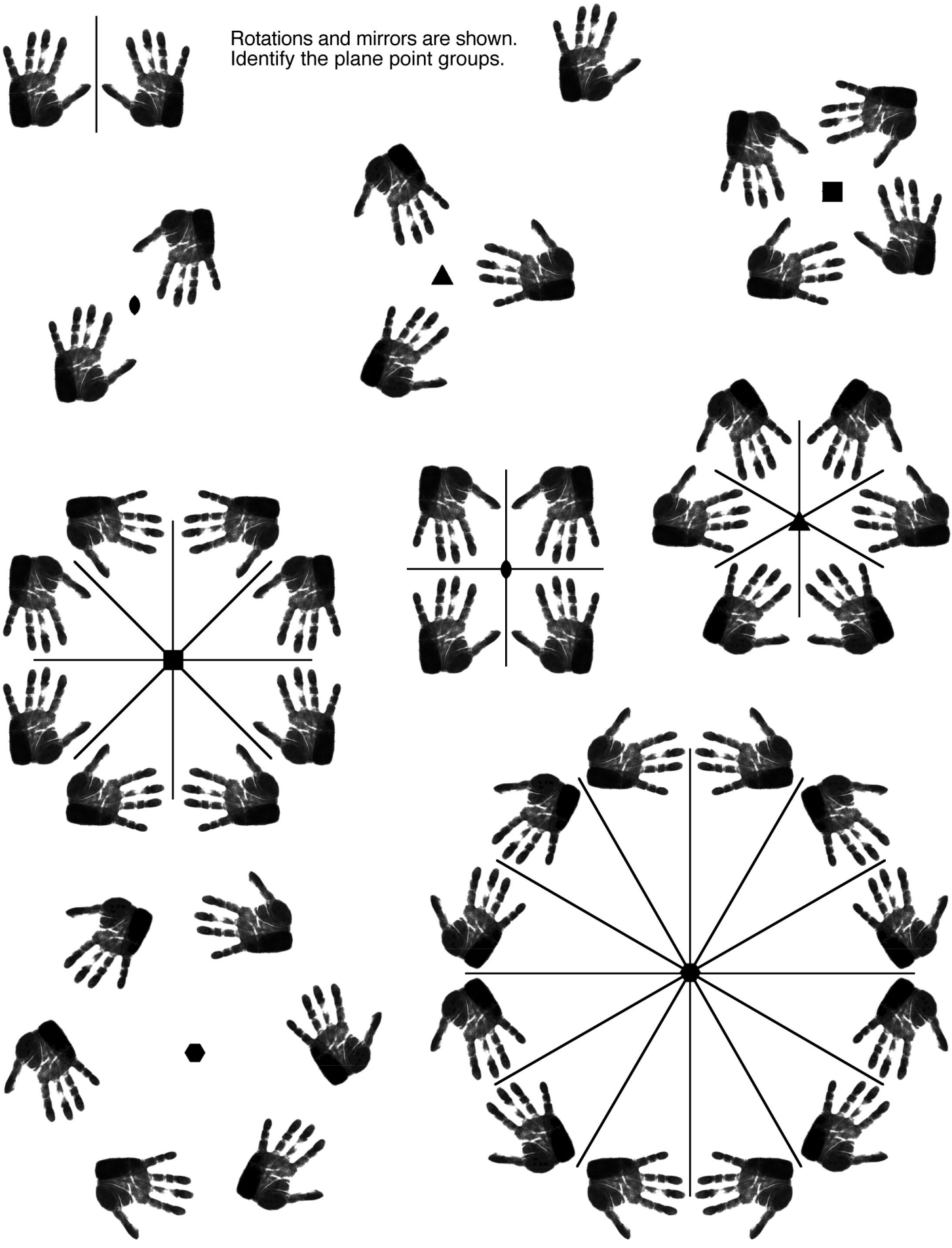
See also page 2.



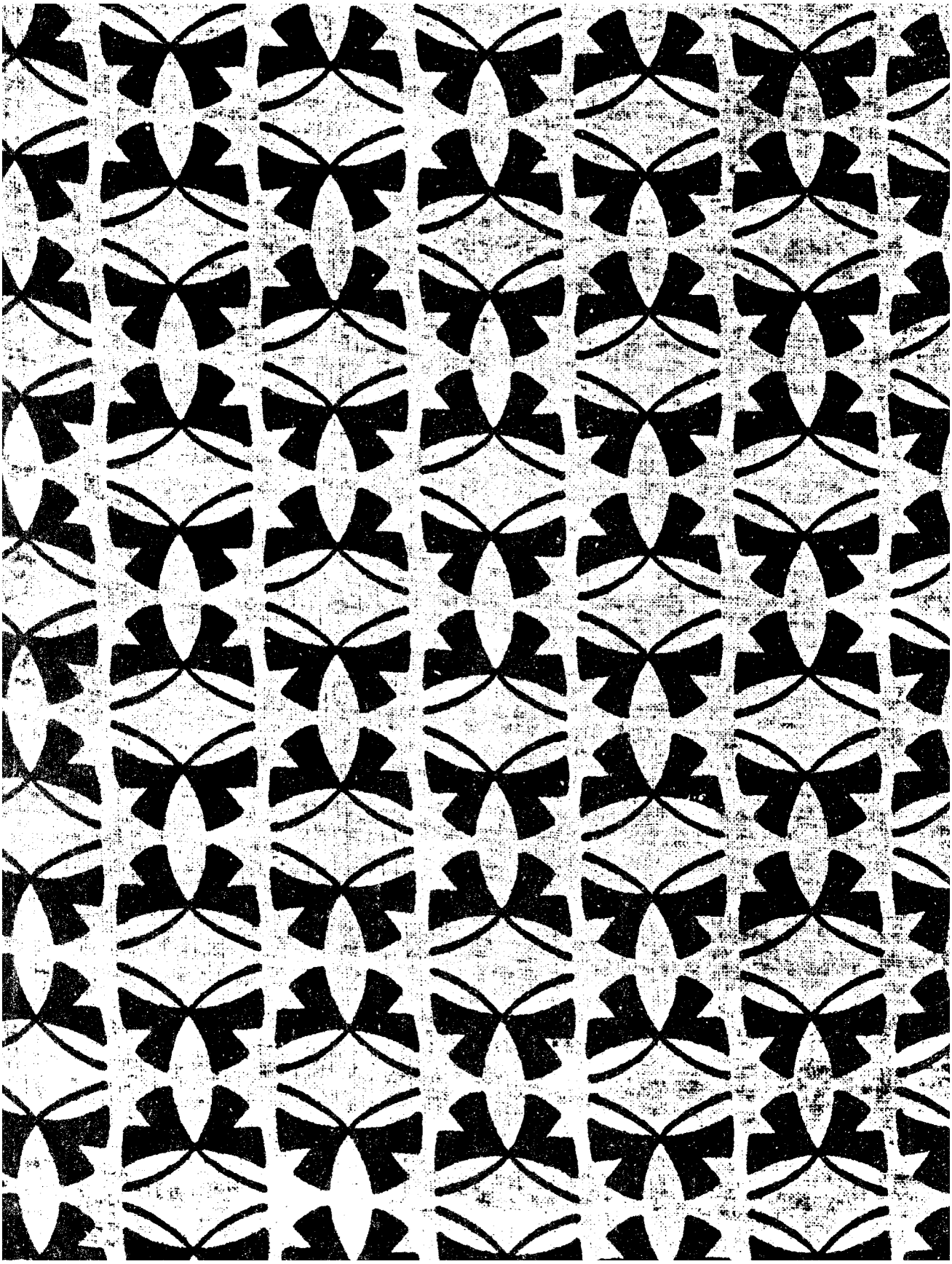
C. **Unit Cell**

1. For a repeating pattern in plane (such as found on page 3), choose one point and mark all identical points. These are **lattice points**, assuming the pattern extends infinitely in all directions.
2. Make a parallelogram with lattice points at the corners. This is a **unit cell**. You can build the whole pattern by duplicating a unit cell and translating in the direction of an edge by the length of the edge.
3. The choice of the unit cell is not unique. There can be lattice points inside the cell or in the middle of edges. A **primitive** cell has lattice points only on the corners; a **centered** cell has lattice points elsewhere.
4. While an infinite number of different unit cells are possible, the convention is to *choose a unit cell related to the symmetry elements* of the pattern. Rotation points should be placed on the cell corners, and mirror or glide lines should be parallel to the cell sides.

Rotations and mirrors are shown.
Identify the plane point groups.

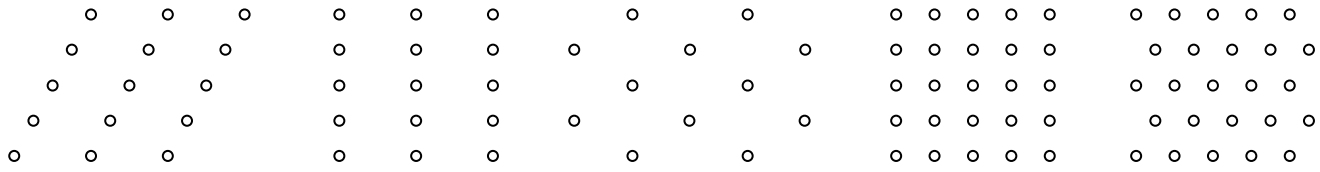


Choose one point and then mark all identical points on this Japanese fabric.



D. **Nets**

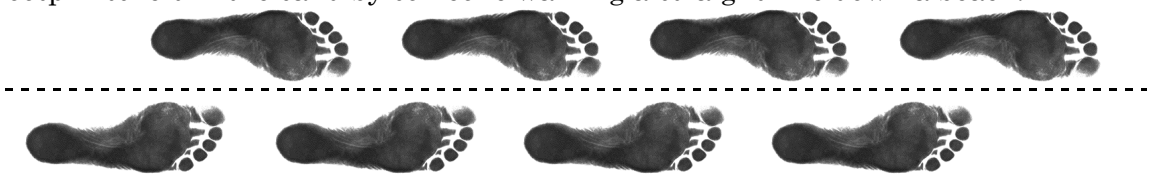
There are five symmetry different types of planar unit cells: oblique parallelogram (unequal sides, angles not 90°), rectangular (unequal sides, angle 90°), rhombohedral (equal sides, angle not 90°), square (equal sides, angles 90°), and hexagonal (equal sides, angles 60° and 120°).



oblique parallelogram | rectangular | rhombohedral (centered rectangular) | square | hexagonal

E. Translational Symmetry Elements

A repeating pattern in a plane may have any of the point symmetry elements as well as a **glide** line. A glide line is a reflection through a line, followed by translation of one-half the repeat distance in a direction parallel to the glide line. The symbol for a glide line is *g*, the graphical symbol is a dashed line, and an example is the footprints left in the sand by someone walking a straight line down a beach.



F. **Plane Groups (Wallpaper patterns)**. Each centering type of each net with each compatible point group with possible replacement of mirrors by glides.

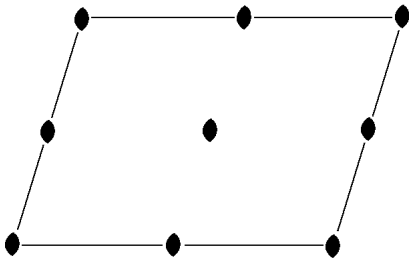
Unit Cell	Point Group	Plane Group Symbol Full	Abbreviated	Symmetry
Oblique (primitive)	1	*p*1		
	2	*p*2		may have 2-fold
Rectangular (primitive and centered)	*m*	*pm*		mirror or glide in one or two directions
		pg		
		cm		
	2*mm*	*p*2*mm*	*pmm*	
		*p*2*mg*	*pmg*	
		*p*2*gg*	*pgg*	
		*c*2*mm*	*cmm*	
Square (primitive)	4	*p*4		4-fold, may have mirror or glide
	4*mm*	*p*4*mm*	*p*4*m*	
		*p*4*mg*	*p*4*g*	
Hexagonal (primitive)	3	*p*3		3-fold with *m* in Δ altitude or Δ sides.
	3*m*	*p*3*m*1		
		*p*31*m*		
	6	*p*6		6-fold with *m* in Δ altitude and sides.
	6*mm*	*p*6*mm*	*p*6*m*	

For diagrams of the symmetry elements in the unit cells, see page 5 or see the plane groups in the *International Tables for X-ray Crystallography*.

Note the difference in line thickness for indicating unit cell edges and mirrors.

*p*1 (Oblique, *p*1)

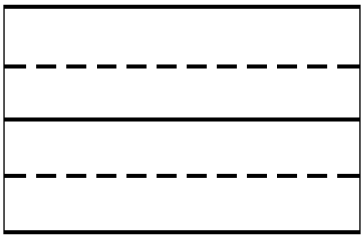
*p*2 (Oblique, *p*211)



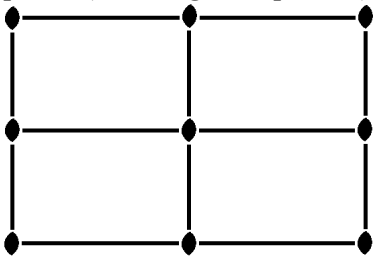
pm (Rectangular, *p*1*m*1)

pg (Rectangular, *p*1*g*1)

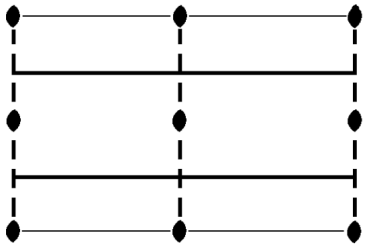
cm (Rectangular, *c*1*m*1)



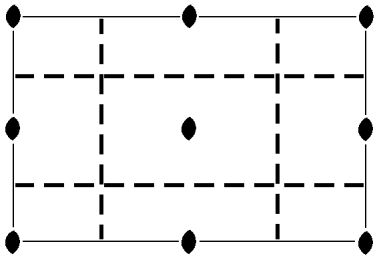
pmm (Rectangular, *p*2*mm*)



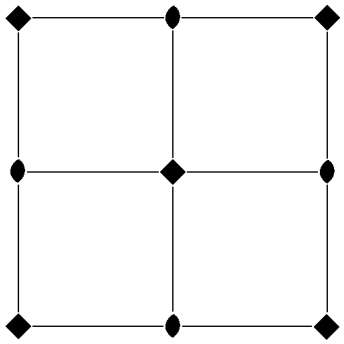
pmg (Rectangular, *p*2*mg*)



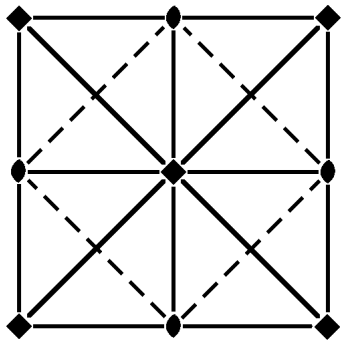
pgg (Rectangular, *p*2*gg*)



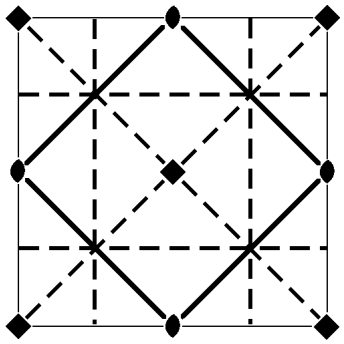
*p*4 (Square, *p*4)



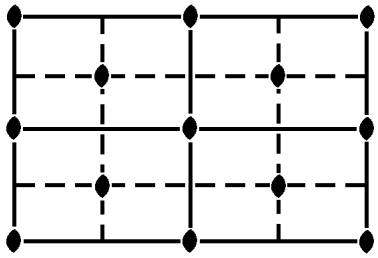
*p*4*m* (Square, *p*4*mm*)



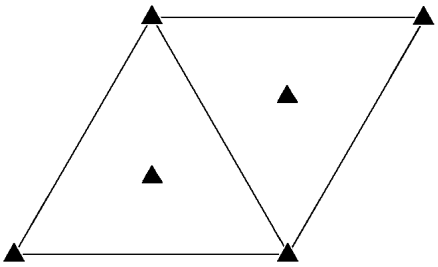
*p*4*g* (Square, *p*4*gm*)



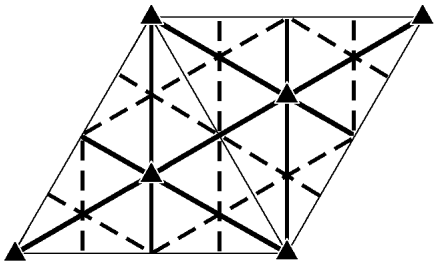
cmm (Rectangular, *c*2*mm*)



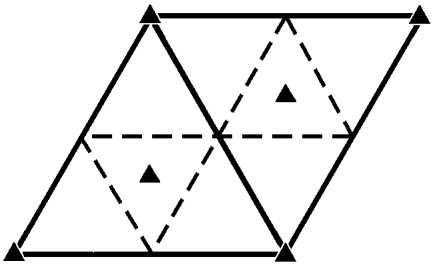
*p*3 (Hexagonal, *p*3)



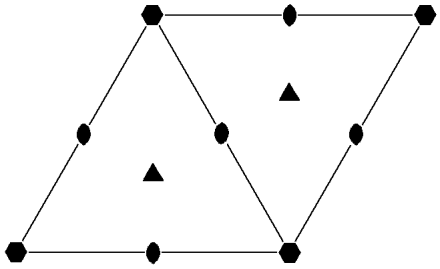
*p*3*m*1 (Hexagonal, *p*3*m*1)



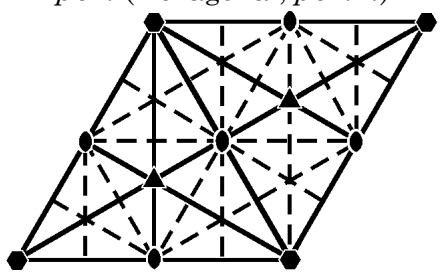
*p*31*m* (Hexagonal, *p*31*m*)



*p*6 (Hexagonal, *p*6)



*p*6*m* (Hexagonal, *p*6*mm*)



II. Symmetry in Three Dimensions

A. Point Symmetry Elements (leave at least one point unmoved)

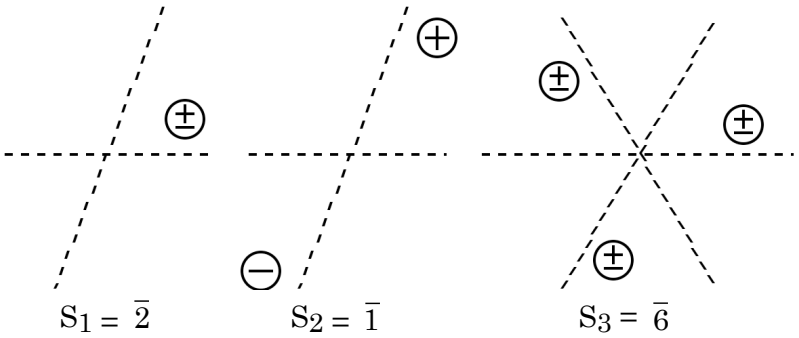
Element	Description	Schoenflies (molecules, quantum chemistry)	Herman-Mauguin (crystallography, geology)
Rotation	Counterclockwise rotation of 360°/n about axis	E, C_2, C_3, C_4	1, 2, 3, 4
Reflection	Reflection through a mirror plane	σ	m
Inversion	All points inverted through center of symmetry	i	$\bar{1}$, "one bar"
Improper Rotation	Rotation of 360°/n followed by reflection through plane perpendicular to the axis	S_1, S_2, S_3, S_4	
	Rotation of 360°/n followed by inversion through a point on the axis		$\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$

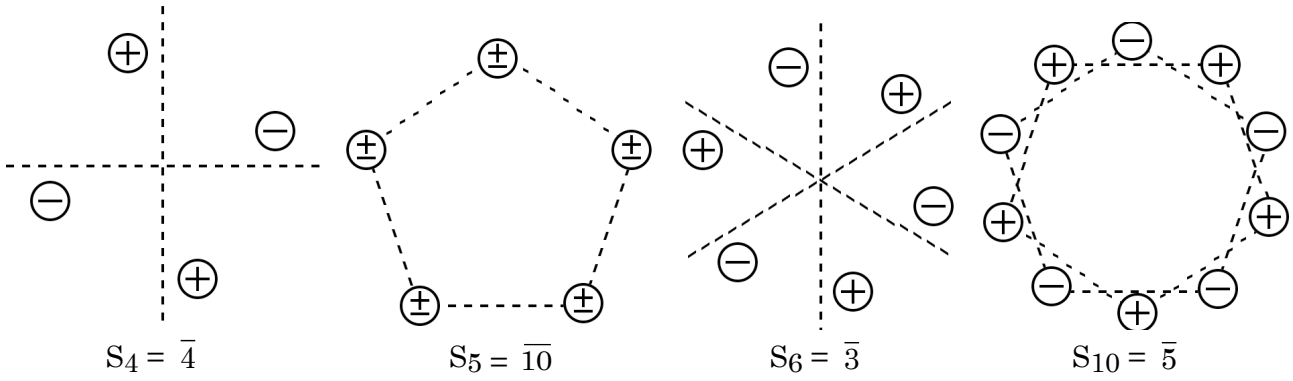
Graphical symbols

$C_2 = 2 =$ 
$C_3 = 3 =$ 
$C_4 = 4 =$ 
$C_6 = 6 =$ 
$\bar{1} = S_2 = i =$
$\bar{2} = S_1 = \sigma = m =$
$\bar{3} = S_6 =$ 
$\bar{4} = S_4 =$ 
$\bar{6} = S_3 =$ 

Comparison of S_n and $\bar{n}$ axes

The two nomenclature systems are easily related for rotation symmetry ($C_n = n$) but they use rather different names for the same improper rotation symmetry:
For odd n, $S_n = \overline{2n}$ and $\bar{n} = S_{2n}$.
$S_n = \bar{n}$ only when n is a multiple of four.


$S_1 = \bar{2}$ $S_2 = \bar{1}$ $S_3 = \bar{6}$


$S_4 = \bar{4}$ $S_5 = \overline{10}$ $S_6 = \bar{3}$ $S_{10} = \bar{5}$

B. **Point groups** (a set of point symmetry elements which form a closed associative mathematical group with identity and inverse)

	Schoenflies	Hermann-Mauguin
1. Rotation axes (360°/n) (optically active for n>1)	C_n	n
2. Mirror plane containing rotation axis (n mirror planes generated)	C_{nv}	nm (n odd, n = 1 is C_s) nmm (n even, second mirror set bisects the first)
3. Rotatory reflection (S_n) Rotatory inversion ($\bar{n}$)	S_n	$\bar{n}$ (n values may be different, $S_2 = \bar{1} = C_i$, $S_3 = \bar{6}$, $S_4 = \bar{4}$, $S_6 = \bar{3}$)
4. Rotation axis with perpendicular mirror plane	C_{nh}	n/m ("/" means perpendicular)
5. n-fold rotation axis with n 2-fold rotation axes perpendicular (optically active)	D_n	$n2$ (n odd) $n22$ (n even, second set of axes bisects the first)
6. n-fold rotation axis with n 2-fold rotation axes perpendicular with mirror planes containing the n-fold axis and bisecting the 2-fold axes *or* rotatory inversion axis in a mirror plane with perpendicular 2-fold axes	D_{nd}	$\bar{n}2m$ (n values may be different: $D_{2d} = \bar{4}2m$, $D_{3d} = \bar{3}2m$)
7. n-fold rotation axis with n 2-fold rotation axes perpendicular with perpendicular mirror plane *or* rotation axis with perpendicular mirror plane and more mirror planes containing the axis	D_{nh}	n/mm (n odd) n/mmm (n even, third set bisects the second set)
8. Cubic point groups, four intersecting 3-fold axes	T T_d T_h O O_h	23 $\bar{4}3m$ (tetrahedral) $m\bar{3}$ 432 $m\bar{3}m$ (octahedral)

C. **Unit Cell**

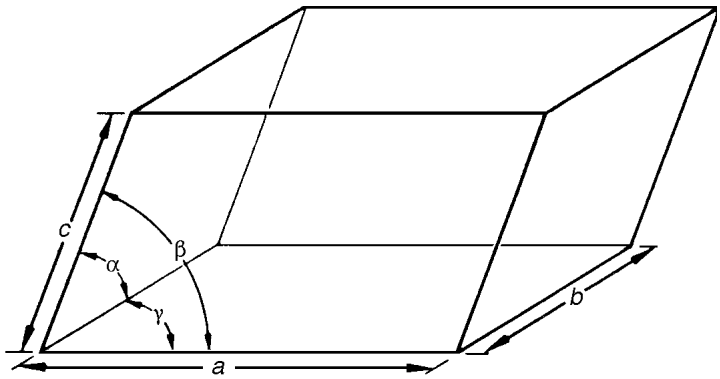
1. For a repeating pattern in space, choose one point and mark all identical points. These are **lattice points**, assuming the pattern extends infinitely in all directions.
2. Make a parallelepiped with lattice points at the corners. This is a **unit cell**. You can build the whole pattern by duplicating a unit cell and *translating in the direction of an edge by the length of the edge.*
3. The choice of the unit cell is not unique. There can be lattice points inside the cell or in the middle of its faces. A **primitive** cell has lattice points only on the corners; a **centered** cell has lattice points elsewhere.
4. While an infinite number of different unit cells are possible, the convention is to *choose a unit cell related to the symmetry elements* of the pattern.

5. Nomenclature

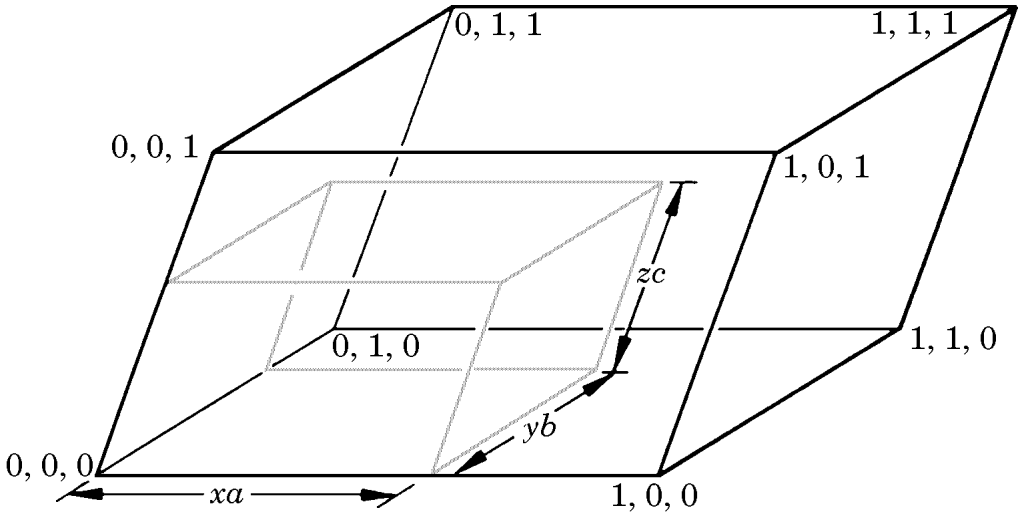
   $\vec{a}$, $\vec{b}$, and $\vec{c}$ are cell edges.

   α, β, and γ are cell angles.

   (α is between $\vec{b}$ and $\vec{c}$,
   β is between $\vec{a}$ and $\vec{c}$, and
   γ is between $\vec{a}$ and $\vec{b}$.)



6. **Fractional coordinates** (x, y, z) refer to xa along $\vec{a}$, yb along $\vec{b}$, zc along $\vec{c}$.



The coordinates of unit cell corners and point x,y,x are shown.

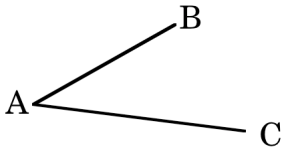
7. Note that in this coordinate system:
   a. Angles between axes are not necessarily 90°.
   b. Basis vectors are not necessarily the same length (1.00 along $\vec{a}$ may represent a different length than 1.00 along $\vec{c}$).
   c. Coordinates differing by an integer are the same (–0.25 = 0.75).

8. **Distance** between two points is calculated from vector dot product $\vec{d} \cdot \vec{d} = |d|^2$

$$d = \sqrt{(\Delta x\ a)^2 + (\Delta y\ b)^2 + (\Delta z\ c)^2 + 2ab\ \Delta x\ \Delta y \cos\gamma + 2ac\ \Delta x\ \Delta z \cos\beta + 2bc\ \Delta y\ \Delta z \cos\alpha}$$

9. **Angle** between three points can be found from law of cosines

$$\angle BAC = \cos^{-1}\left\{\frac{(AB)^2 + (AC)^2 - (BC)^2}{2(AB)(AC)}\right\}$$



$$= \cos^{-1}\left\{\frac{\text{bond}^2 + \text{bond}^2 - \text{nonbond}^2}{2\ \text{bond bond}}\right\}$$

10. **Volume** of the unit cell is

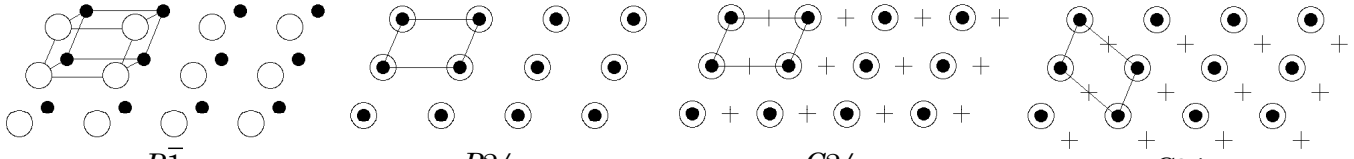
$$V = abc\ \sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma} = abc \text{ if all angles are } 90°.$$

D. **Lattices**

There are 17 different types of three dimensional unit cells. Three dimensional lattices are made by stacking parallel layers of two dimensional nets, either offset or directly over the previous layer. Lower case is used for two dimensional symmetry, and *upper case abbreviations are used for three dimensions*.

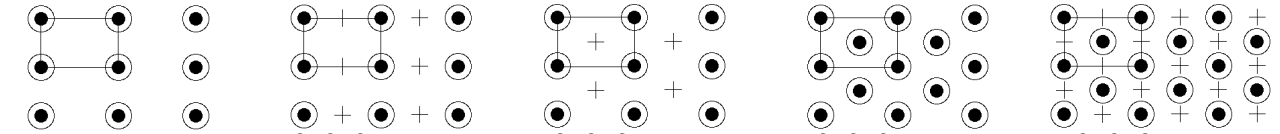
Vertical coordinates in these diagrams: ● at 0, + at 1/2, and ◯ at 1.

1. Lattices based on oblique parallelogram, *p*2, have ⬮ at cell corners, center, and middle of sides.
   a. Stack nets displaced to give triclinic lattice, $P\bar{1}$. **Triclinic** means three cell angles must be specified (no angles are 90°).
   b. Stack ⬮ directly over each other to give monoclinic lattices, *P*2/*m* and *C*2/*m*. *P* is a primitive cell, *C* is centered cell. **Monoclinic** means one cell angle must be specified (two angles are 90°).



$P\bar{1}$ $P2/m$ $C2/m$ $C2/m$

2. Lattices based on rectangle and centered rectangle (rhombohedral), *p*2*mm* and *c*2*mm*, have mirrors in two directions and ⬮ at their intersection. Stack ⬮ directly over each other to give **orthorhombic** (pronounced "ortho" "rhombic") lattice with all angles 90°.



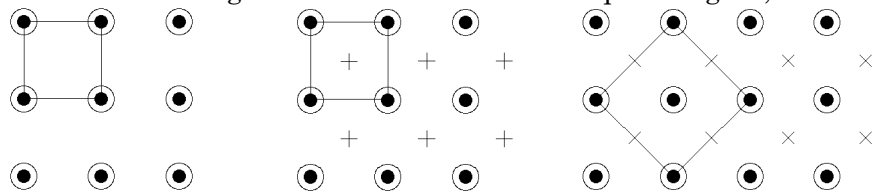
$P\frac{2}{m}\frac{2}{m}\frac{2}{m} = Pmmm$ $C\frac{2}{m}\frac{2}{m}\frac{2}{m} = Cmmm$ $I\frac{2}{m}\frac{2}{m}\frac{2}{m} = Immm$ $C\frac{2}{m}\frac{2}{m}\frac{2}{m} = Cmmm$ $F\frac{2}{m}\frac{2}{m}\frac{2}{m} = Fmmm$

primitive one face centered body centered one face centered all faces centered

3. Lattices based on square, *p*4*mm*, have ■ at cell corners and center.
   a. Stack ■ directly over each other with different spacing than the net to give **tetragonal** lattice with all angles 90° and two axes with equal lengths.

$P\frac{4}{m}\frac{2}{m}\frac{2}{m} = P4/mmm$ $I\frac{4}{m}\frac{2}{m}\frac{2}{m} = I4/mmm$

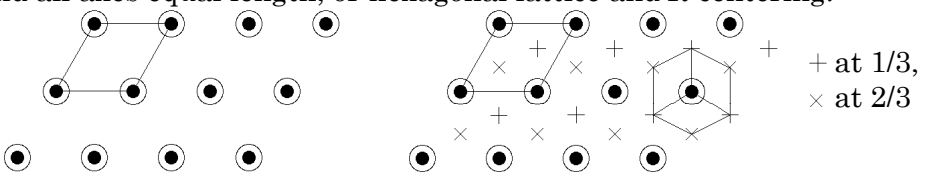
   b. Stack ■ directly over each other with same spacing as the net, to give **cubic** lattice with all angles 90° and all axes with equal lengths, *a*.



$P\frac{4}{m}3\frac{2}{m} = Pm3m$ $I\frac{4}{m}3\frac{2}{m} = Im3m$ $F\frac{4}{m}3\frac{2}{m} = Fm3m$

side $a\sqrt{2}$, × at $\frac{a\sqrt{2}}{2}$.

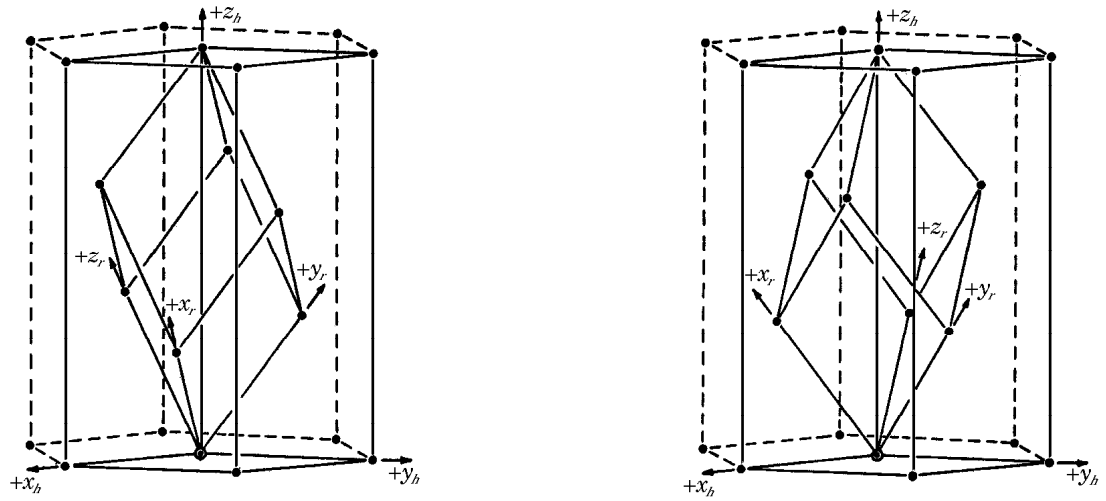
4. Lattices based on hexagonal 120° rhombus, $p6mm$, have ⬢ on corners and ▲ in centers of equilateral triangles which make up the parallelogram.
   a. Stack ⬢ directly over each other to give **hexagonal** lattice with interaxial angles of 90°, 90° and 120° and two axes of equal length.
   b. Stack ▲ directly over each other (takes three layers to get back to the original), to give **rhombohedral** or **trigonal** lattice with all angles equal and all axes equal length, or hexagonal lattice and R centering.



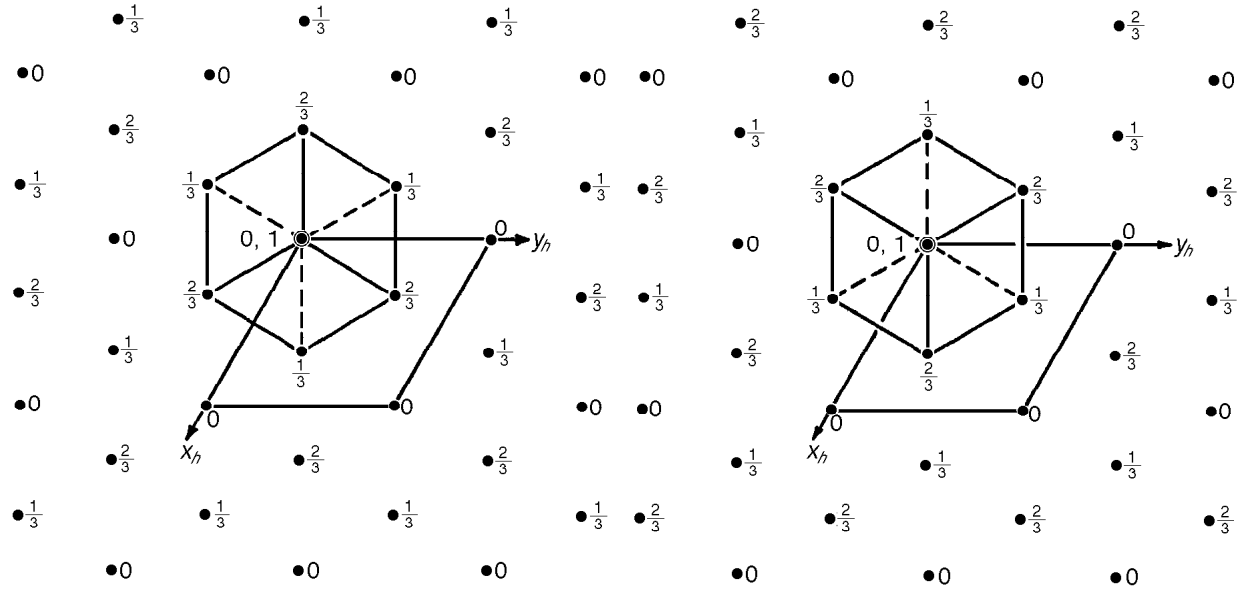
$P\frac{6}{m}\frac{2}{m}\frac{2}{m} = P6/mmm$ $\qquad$ $R\bar{3}m$

Relationship between rhombohedral and hexagonal lattices

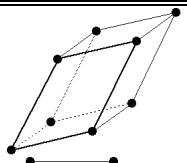
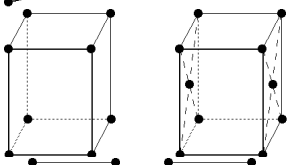
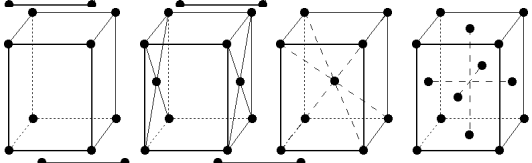
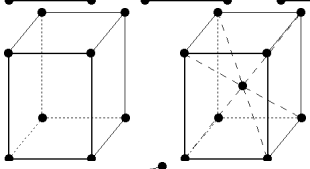
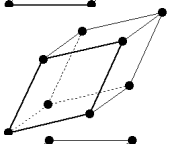
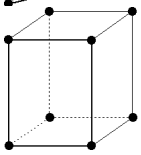
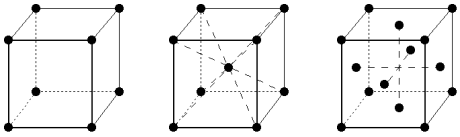
Side view:



Top view:



(----- are lower edges, ——— are upper edges of rhombohedron)

Crystal System	Point Groups	Angle or axes	Lattices
Triclinic	*Possible inversion center:* 1, $\bar{1}$	No restrictions	
Monoclinic	*single twofold and/or mirror:* 2, *m*, 2/*m*	$\alpha = \gamma = 90°$	
Orthorhombic	*Three ⊥twofold and/or mirrors:* 222, *mm*2, *mmm*	$\alpha = \beta = \gamma = 90°$	
Tetragonal	*One fourfold:* 4, $\bar{4}$, 4/*m*, 422, 4*mm*, $\bar{4}$2*m*, 4/*mmm*	$a = b$ $\alpha = \beta = \gamma = 90°$	
Trigonal Rhombohedral	*One threefold:* 3, $\bar{3}$, 32, 3*m*, $\bar{3}$*m*	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	
Hexagonal	*One sixfold:* 6, $\bar{6}$, 6/*m*, 622, 6*mm*, $\bar{6}$2*m*, 6/*mmm*	$a = b$ $\alpha = \beta = 90°$ $\gamma = 120°$	
Cubic	*Four threefold:* 23, *m*$\bar{3}$, 432, $\bar{4}$3*m*, *m*$\bar{3}$*m*	$a = b = c$ $\alpha = \beta = \gamma = 90°$	

5. Lattice points in cell
   a. Unit cell is centered if has lattice points in faces or inside.
      A centered if lattice point in *bc* face.
      B centered if lattice point in *ac* face.
      C centered if lattice point in *ab* face.
      (Centering in only two faces will not give a lattice.)
      F centered if lattice points in all three faces.
      I centered if lattice point in center of cell.
      R centered is rhombohedral centering in hexagonal unit cells.

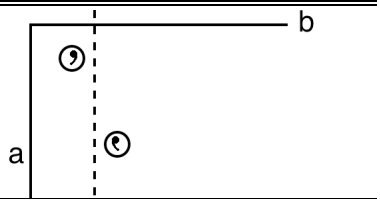
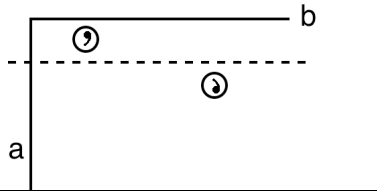
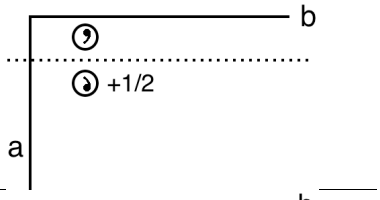
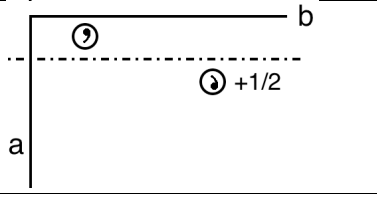
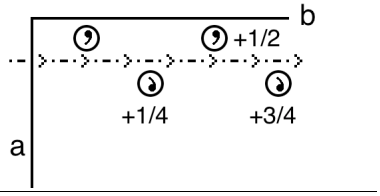
   b. Counting lattice points
      One from 1/8 at each of 8 corners.
      One from *A*, *B*, or *C* centering (1/2 in each of 2 faces).
      One from *I* centering (1 at 1/2, 1/2, 1/2 in center of cell).
      Two from *R* centering (1 each at 1/3, 2/3, 1/3 and 2/3, 1/3, 2/3).
      Three from *F* centering (1/2 in each of 6 faces).

E. Translational Symmetry Elements

	Point Operations			Translation with	
	Reflection	Rotation	Inversion	Reflection	Rotation
1-D	mirror point				
2-D	mirror line	rotation point		glide line	
3-D	mirror plane	rotation axis rotatory reflection	inversion point rotatory inversion	glide plane	screw axis

1. **Glide Planes**

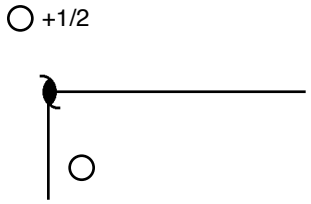
Reflection followed by 1/2 or 1/4 of a unit cell translation in a direction parallel to the glide. The two dimensional symbol is *g*. The three dimensional symbol (*a*, *b*, *c*, *n*, or *d*) identifies the translation direction, either along the $\vec{a}$, $\vec{b}$, or $\vec{c}$ axis, or along a diagonal. Glide plane orientations are indicated by the position in the space group symbol. The first position refers to the plane ⊥ to $\vec{a}$, second to the plane ⊥ to $\vec{b}$, and third to the plane ⊥ to $\vec{c}$. Thus *Pbca* has a *b*-glide ⊥ to $\vec{a}$, a *c*-glide ⊥ to $\vec{b}$, and an *a*-glide ⊥ to $\vec{c}$.

Glide Symbol	Translation	Mirror // to	Mirror ⊥ to	First example
a	a/2	a	b ⇒	
a	a/2	a	c	
b	b/2	b	a ⇒	
b	b/2	b	c	
c	c/2	c	a ⇒	
c	c/2	c	b	
n	(b+c)/2	b and c	a ⇒	
n	(a+c)/2	a and c	b	
n	(a+b)/2	a and b	c	
n	(a+b+c)/2†			
d	(b+c)/4	b and c	a ⇒	
d	(a+c)/4	a and c	b	
d	(a+b)/4	a and b	c	
d	(a+b+c)/4†			

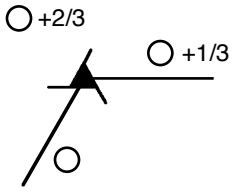
†Only possible for tetragonal and cubic systems

2. **Screw axes**
   a. Rotation of 360°/n about an axis parallel to a unit cell edge, followed by translation of p/n in the direction of that axis (right thumb along translation direction, fingers curl in rotation direction).
   b. Written Symbol, n_p or 2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, and 6_5.
   c. Graphical Symbols

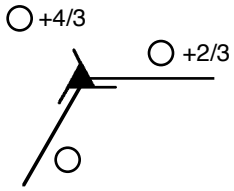
2_1 = 180° rotation then 1/2 cell translation.



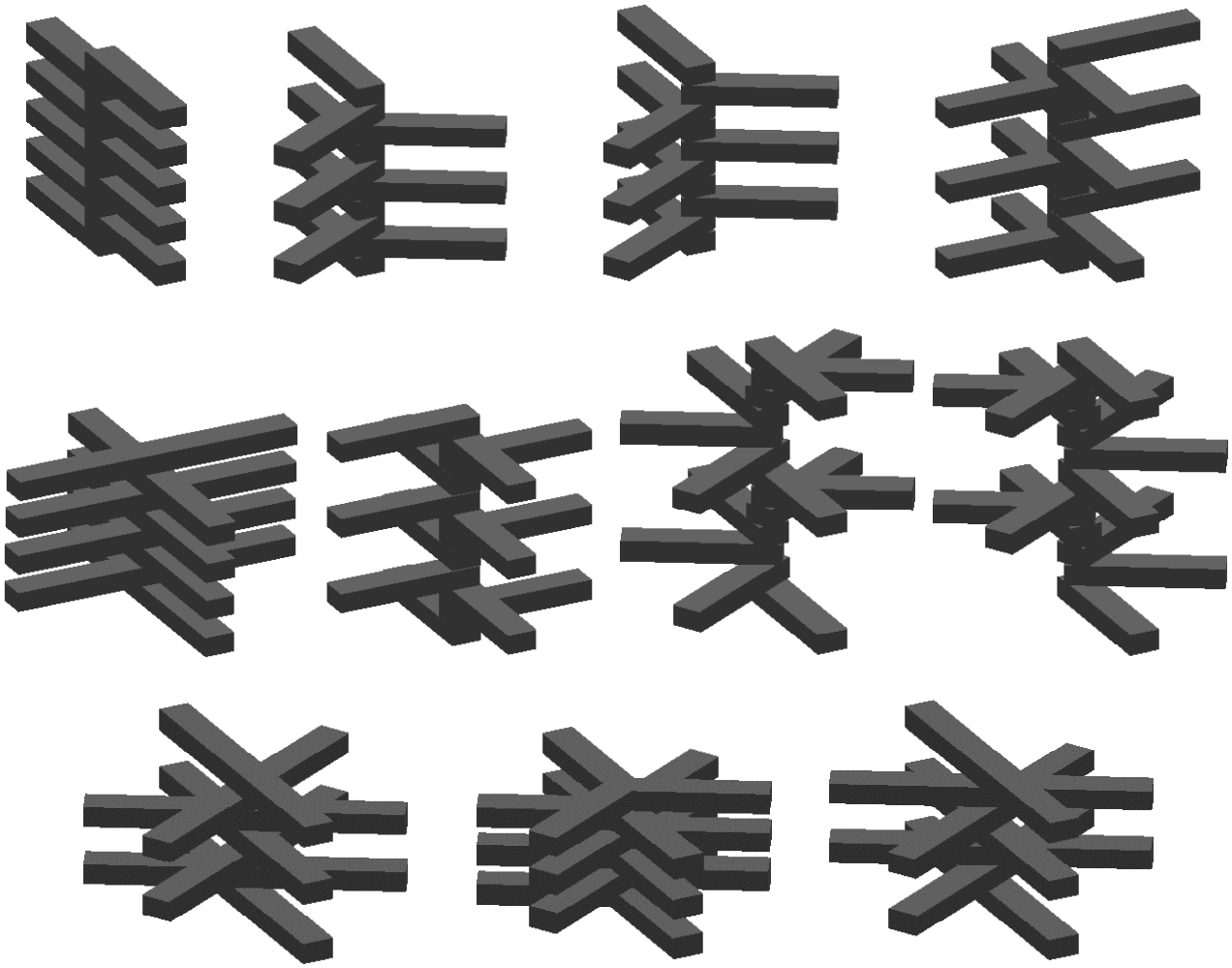
3_1 = 120° rotation then 1/3 cell translation.



3_2 =120° rotation then 2/3 cell translation.



Examples. Can you identify the screw symmetry?



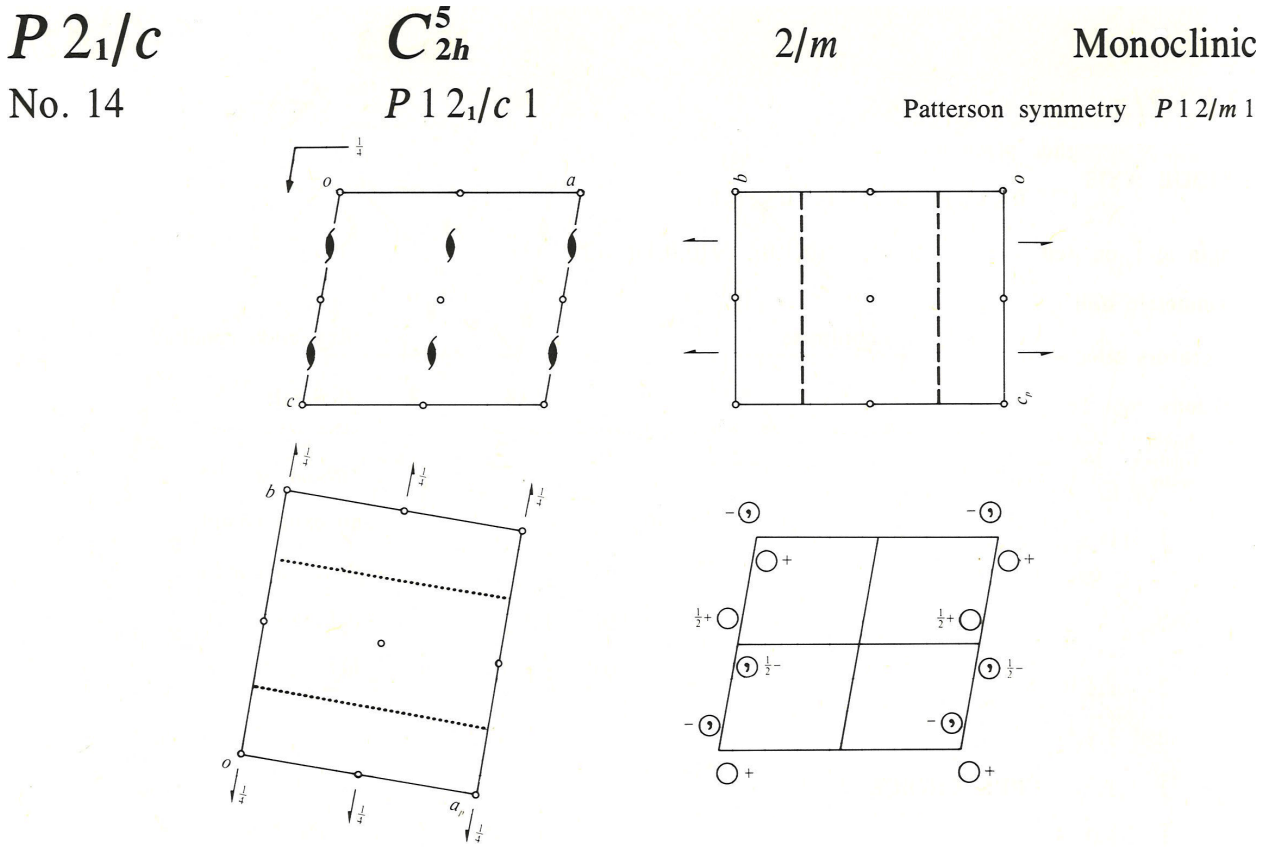
F. **Space Groups**

Each centering type of each lattice with each compatible point group with possible replacement of rotations by screws and/or replacement of mirror planes by glides.

14 Lattices + 32 Point Groups = 230 Space Groups

Triclinic	1	C_1	$P1$						
	$\bar{1}$	C_i	$P\bar{1}$						
Monoclinic	2	C_2	$P2$	$P2_1$	$C2$				
	m	C_s	Pm	Pc	Cm	Cc			
	$2/m$	C_{2h}	$P2/m$	$P2_1/m$	$C2/m$	$P2/c$	$P2_1/c$	$C2/c$	
Orthorhombic	222	D_2	$P222$	$P222_1$	$P2_12_12$	$P2_12_12_1$			
			$C222$	$C222_1$	$F222$	$I222$	$I2_12_12_1$		
	$mm2$	C_{2v}	$Pmm2$	$Pmc2_1$	$Pcc2$	$Pma2$	$Pca2_1$	$Pnc2$	$Pmn2_1$
			$Pba2$	$Pna2_1$	$Pnn2$	$Cmm2$	$Cmc2_1$	$Ccc2$	$Amm2$
			$Abm2$	$Ama2$	$Aba2$	$Fmm2$	$Fdd2$	$Imm2$	$Iba2$ $Ima2$
	mmm	D_{2h}	$Pmmm$	$Pnnn$	$Pccm$	$Pban$	$Pmma$	$Pnna$	$Pmna$
			$Pcca$	$Pbam$	$Pccn$	$Pbcm$	$Pnnm$	$Pmmn$	$Pbcn$
			$Pbca$	$Pnma$	$Cmcm$	$Cmca$	$Cmmm$	$Cccm$	$Cmma$
			$Ccca$	$Fmmm$	$Fddd$	$Immm$	$Ibam$	$Ibca$	$Imma$
Tetragonal	4	C_4	$P4$	$P4_1$	$P4_2$	$P4_3$	$I4$	$I4_1$	
	$\bar{4}$	S_4	$P\bar{4}$	$I\bar{4}$					
	$4/m$	C_{4h}	$P4/m$	$P4_2/m$	$P4/n$	$P4_2/n$	$I4/m$	$I4_1/a$	
	422	D_4	$P422$	$P42_12$	$P4_122$	$P4_12_12$	$P4_222$	$P4_22_12$	
			$P4_322$	$P4_32_12$	$I422$	$I4_122$			
	$4mm$	C_{4v}	$P4mm$	$P4bm$	$P4_2cm$	$P4_2nm$	$P4cc$	$P4nc$	
			$P4_2mc$	$P4_2bc$	$I4mm$	$I4cm$	$I4_1md$	$I4_1cd$	
	$\bar{4}2m$	D_{2d}	$P\bar{4}2m$	$P\bar{4}2c$	$P\bar{4}2_1m$	$P\bar{4}2_1c$	$P\bar{4}m2$	$P\bar{4}c2$	
			$P\bar{4}b2$	$P\bar{4}n2$	$I\bar{4}m2$	$I\bar{4}c2$	$I\bar{4}2m$	$I\bar{4}2d$	
	$4/mmm$	D_{4h}	$P4/mmm$	$P4/mcc$	$P4/nbm$	$P4/nnc$	$P4/mbm$	$P4/mnc$	$P4/nmm$
			$P4/ncc$	$P4_2/mmc$	$P4_2/mcm$	$P4_2/nbc$	$P4_2/nnm$	$P4_2/mbc$	$P4_2/mnm$
			$P4_2/nmc$	$P4_2/ncm$	$I4/mmm$	$I4/mcm$	$I4_1/amd$	$I4_1/acd$	
Trigonal/	3	C_3	$P3$	$P3_1$	$P3_2$	$R3$			
Rhombohedral	$\bar{3}$	S_6	$P\bar{3}$	$R\bar{3}$					
	32	D_3	$P312$	$P321$	$P3_112$	$P3_121$	$P3_212$	$P3_221$	$R32$
	$3m$	C_{3v}	$P3m1$	$P31m$	$P3c1$	$P31c$	$R3m$	$R3c$	
	$\bar{3}m$	D_{3d}	$P\bar{3}1m$	$P\bar{3}1c$	$P\bar{3}m1$	$P\bar{3}c1$	$R\bar{3}m$	$R\bar{3}c$	
Hexagonal	6	C_6	$P6$	$P6_1$	$P6_2$	$P6_3$	$P6_4$	$P6_5$	
	$\bar{6}$	C_{3h}	$P\bar{6}$						
	$6/m$	C_{6h}	$P6/m$	$P6_3/m$					
	622	D_6	$P622$	$P6_122$	$P6_222$	$P6_322$	$P6_422$	$P6_522$	
	$6mm$	C_{6v}	$P6mm$	$P6cc$	$P6_3cm$	$P6_3mc$			
	$\bar{6}2m$	D_{3h}	$P\bar{6}m2$	$P\bar{6}c2$	$P\bar{6}2m$	$P\bar{6}2c$			
	$6/mmm$	D_{6h}	$P6/mmm$	$P6/mcc$	$P6_3/mcm$	$P6_3/mmc$			
Cubic	23	T	$P23$	$F23$	$I23$	$P2_13$	$I2_13$		
	$m\bar{3}$	T_h	$Pm\bar{3}$	$Pn\bar{3}$	$Fm\bar{3}$	$Fd\bar{3}$	$Im\bar{3}$	$Pa\bar{3}$	$Ia\bar{3}$
	432	O	$P432$	$P4_232$	$F432$	$F4_132$	$I432$	$P4_332$	$P4_132$ $I4_132$
	$\bar{4}3m$	T_d	$P\bar{4}3m$	$F\bar{4}3m$	$I\bar{4}3m$	$P\bar{4}3n$	$F\bar{4}3c$	$I\bar{4}3d$	
	$m\bar{3}m$	O_h	$Pm\bar{3}m$	$Pn\bar{3}n$	$Pm\bar{3}n$	$Pn\bar{3}m$	$Fm\bar{3}m$		
			$Fm\bar{3}c$	$Fd\bar{3}m$	$Fd\bar{3}c$	$Im\bar{3}m$	$Ia\bar{3}d$		

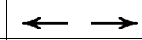
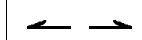
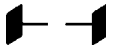
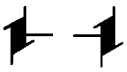
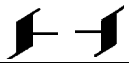
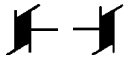
1. **Space group symbol names**. Lattice type (*P*, *A*, *B*, *C*, *F*, *R*, or *I*) followed by information concerning the symmetry in various directions.
   a. Rotation or screw axes are *parallel* to the specified direction. Mirror and glide planes are *perpendicular* to the specified direction. The presence of both is indicated by "/". Example: a primitive cell with a mirror plane perpendicular to a four-fold rotation axis is $P4/m$.
   b. Directions
      i. Triclinic symbols are $P1$ and $P\bar{1}$.
      ii. Monoclinic symbols use one direction that refers to the unique b axis. Examples: $P2$, $P2_1/c$, $C2/m$
      iii. Orthorhombic symbols use three directions that refer to the crystal axes, a, b, and c. Examples: $Pmmm$, $P2_12_12$, $Pbca$
      iv. Tetragonal symbols use three directions. The first direction refers to the unique c axis, the second direction to the a and b axes (they are symmetry equivalent), and the third direction to the ab bisectors. Examples: $P4/mmm$, $I4cm$, $P42_12$
      v. Trigonal and hexagonal symbols use three directions. The first direction refers to the c axis, the second direction to the a and b axes and the ab bisectors, and the third direction to the bisectors of the second group. Examples: $P312$, $P321$
      vi. Cubic symbols use three directions. The first direction refers to the a, b, and c axes, the second direction refers to the body diagonals (this will always be 3 or $\bar{3}$), and the third direction refers to the face diagonals.
2. Space group diagrams in the *International Tables*



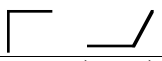
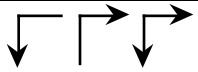
a. Symmetry elements. The origin is indicated by *o*, and axes are labeled *a*, *b*, *c*.

b. Equivalent positions. ○ is a right handed molecule, ⓩ is a left handed molecule related by a mirror, glide, or inversion center. "+" and "–" refer to the height above or below the page. Given one ○, the remaining ○ and ⓩ are generated by the symmetry elements.

c. **Symmetry Axis Symbols**

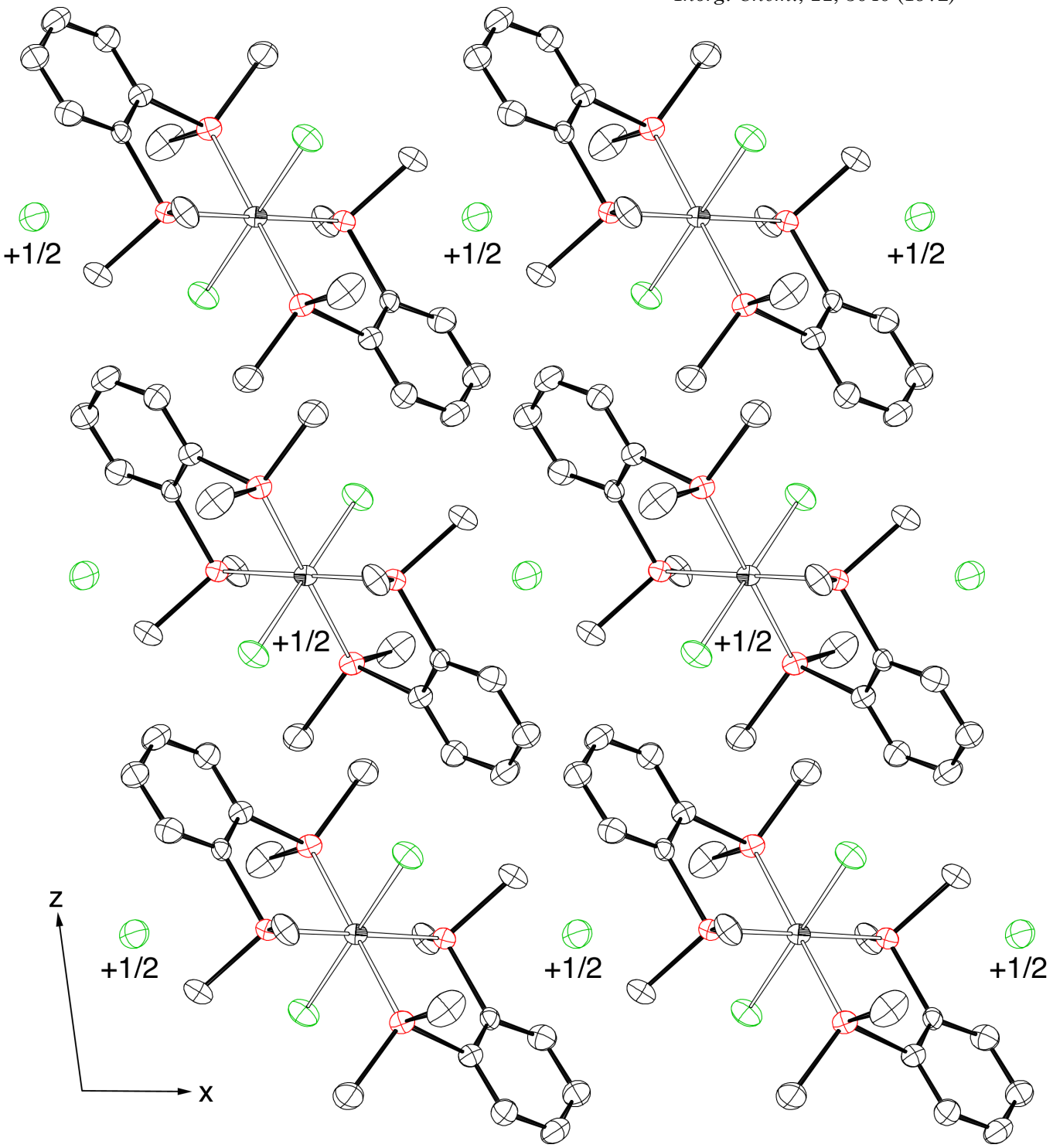
Symmetry	Normal to paper	Parallel to paper	Screw translation	Symmetry	Normal to paper	Screw translation
1				3		
$\bar{1}$				3_1		1/3
2				3_2		2/3
2_1			1/2	$\bar{3}$		
$2/m$				6		
$2_1/m$			1/2	6_1		1/6
4				6_2		2/6
4_1			1/4	6_3		3/6
4_2			2/4	6_4		4/6
4_3			3/4	6_5		5/6
$\bar{4}$				$\bar{6}$		
$4/m$				$6/m$		
$4_2/m$			1/2	$6_3/m$		1/2

d. **Symmetry Plane Symbols**

Symmetry	Plane Normal to drawing plane	Plane Parallel to drawing plane	Glide translation
m mirror			none
a, *b*, *c* // glide			*a*/2, *b*/2, or *c*/2 // to drawing plane (arrow direction)
a, *b*, *c* ⊥ glide			*a*/2, *b*/2, or *c*/2 ⊥ to drawing plane
n net diagonal // and ⊥ glide			(*a*+*b*)/2 or (*b*+*c*)/2 or (*c*+*a*)/2 or (*a*+*b*+*c*)/2; 1/2 cell // and 1/2 cell ⊥ to drawing plane (arrow direction)
d diamond glide			(*a*±*b*)/4 or (*b*±*c*)/4 or (*c*±*a*)/4 or (*a*±*b*±*c*)/4; 1/4 cell // and 1/4 cell ⊥ to drawing plane (arrow direction)

3. Both $[Ni(diars)_2Cl_2]Cl$ and $[Co(diars)_2Cl_2]Cl$, where diars is *o*-$(As(CH_3)_2)_2C_6H_4$, crystallize in space group $P2_1/c$. Hydrogen atoms are not shown. Ions with 1/2 next to them are half a unit cell higher in *y* then their counterparts.

Inorg. Chem., **11**, 3040 (1972)



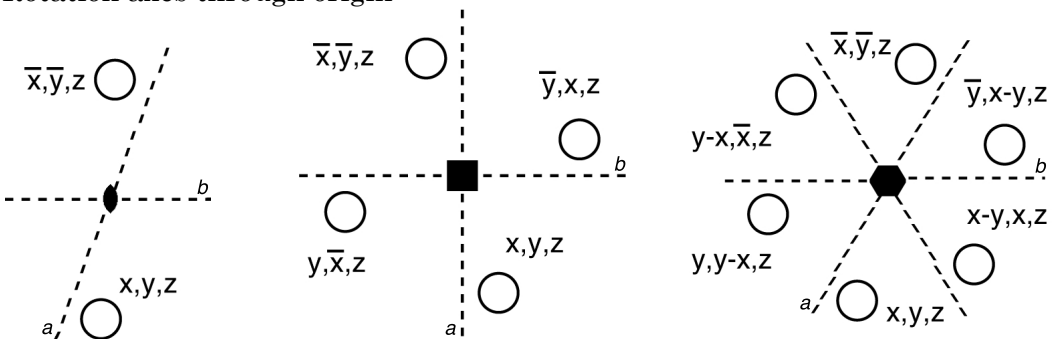
a. Locate and identify the symmetry elements of the space group.

b. What is the minimum number of atoms whose positions must be known for this space group and structure, in order to know the entire structure? This asymmetric unit is represented by ◯ in the equivalent position diagram.

III. **Symmetry Equivalent Positions**

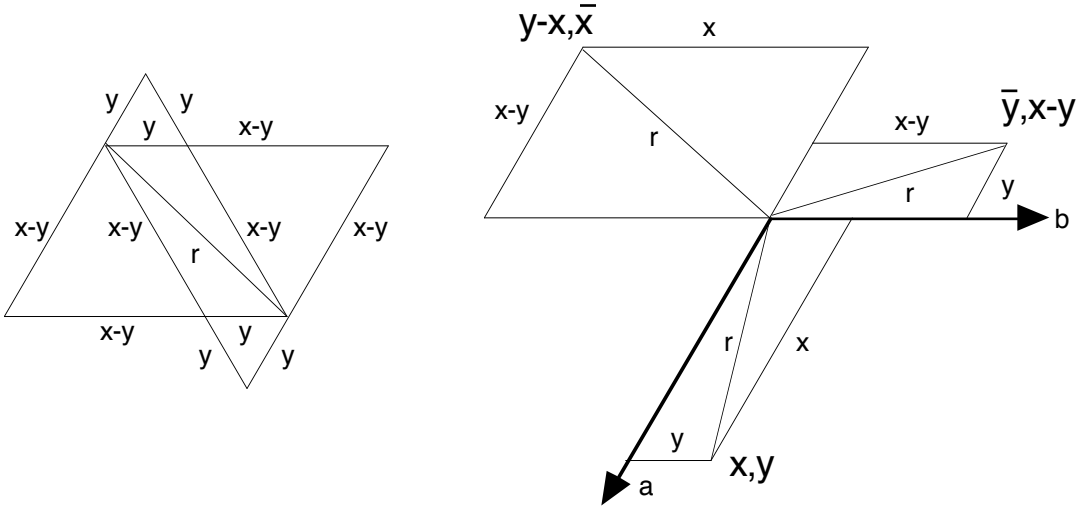
(Equivalent positions are points generated from *x, y, z* by symmetry operations.)

A. Rotation axes through origin

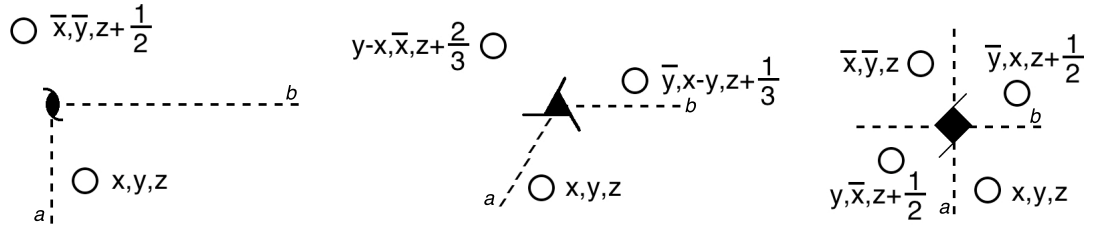


2-fold 4-fold 6-fold

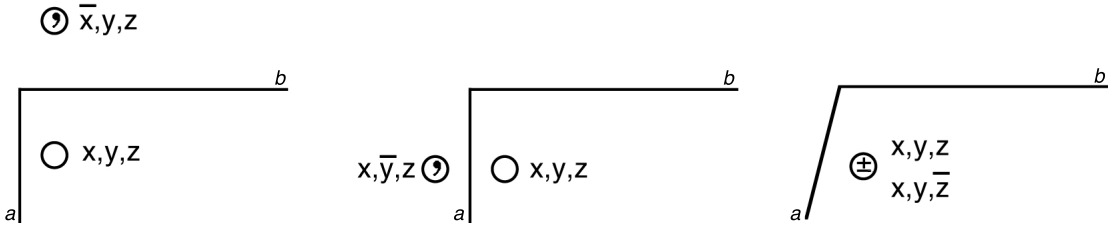
To verify the 3-fold and 6-fold rotation positions, take a parallelogram with 60° and 120° angles. Define the sides as *x* and *x*–*y*. Add some equilateral triangles with side *y* to make more parallelograms. Define the common diagonal as *r*. Move the parallelograms to the coordinate system. The 6-fold rotation positions can be derived by applying a 2-fold rotation to the 3-fold equivalent positions.



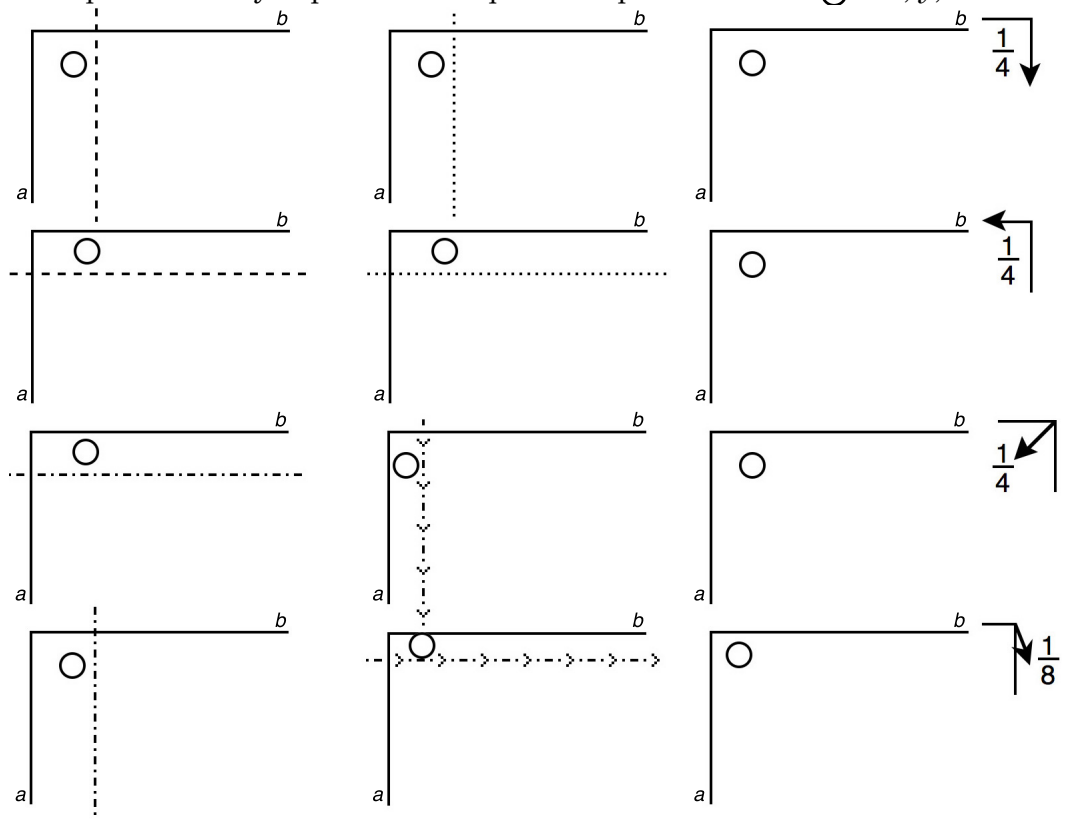
B. Screw axes through origin



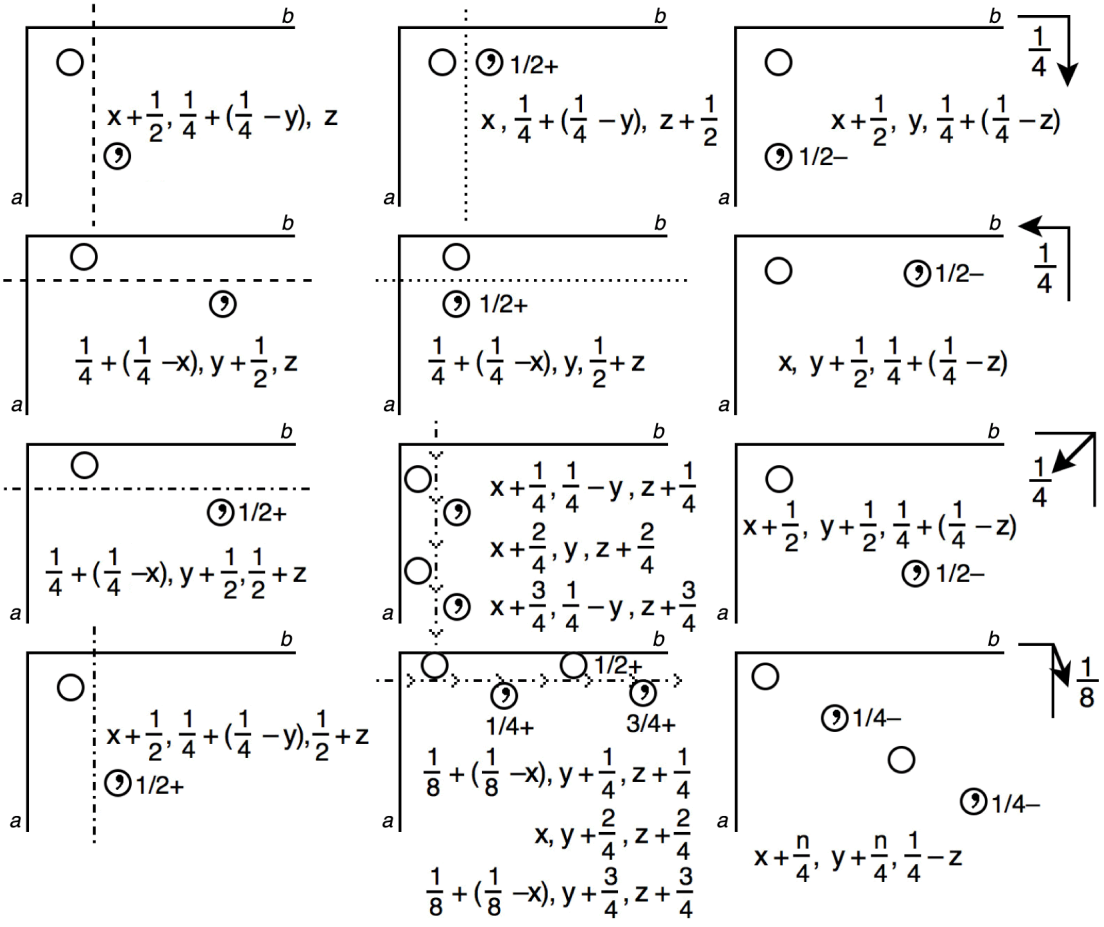
C. Mirror plane through origin and perpendicular to *a* (left), *b* (center) or *c* (right)



C. Glide planes. Can you predict the equivalent positions from ○ at *x*, *y*, *z*?



Answers:

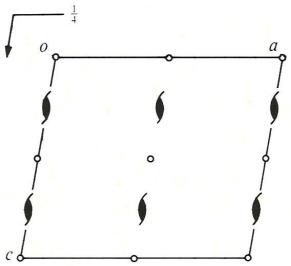


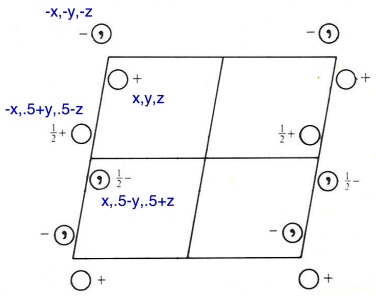
F. Equivalent Positions and the *International Tables*

1. Coordinates of the equivalent positions are given under the diagrams.
2. When a point x, y, z lies on a symmetry element, the number of generated equivalent positions will be reduced. The point symmetry of these "special" positions are also given.

$P\,2_1/c$ $\quad C_{2h}^5$ $\quad 2/m$ $\quad$ Monoclinic

No. 14 $\quad P\,1\,2_1/c\,1$ $\quad$ Patterson symmetry $P\,1\,2/m\,1$



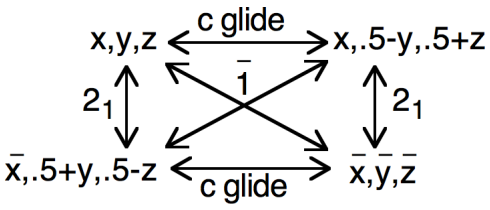


Positions
Multiplicity, Wyckoff letter, Site symmetry

Coordinates

4	e	1	(1) x,y,z	(2) $\bar{x},\bar{y},\bar{z}$	(3) $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$	(4) $x,\frac{1}{2}-y,\frac{1}{2}+z$
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$	
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$	

} special positions



3. Practice using equivalent positions

a. If an atom has coordinates 0.123, 0.795, 0.468 in space group $P2_1/c$, what are the coordinates of the equivalent positions that are *inside* the unit cell?

x,y,z	0.123,	0.795, 0.468
$\bar{x},\bar{y},\bar{z}$	–0.123,	–0.795, –0.468 ⇒ 0.877, 0.205, 0.532
$\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$	–0.123,	1.295, 0.032 ⇒ 0.877, 0.295, 0.032
$x,\frac{1}{2}-y,\frac{1}{2}+z$	0.123,	–0.295, 0.968 ⇒ 0.123, 0.705, 0.968

b. If an atom has coordinates 0, 0, 0 in space group $P2_1/c$, what are the coordinates of the equivalent atoms inside the unit cell?

This atom sits on a center of symmetry (special position type a in the Wyckoff numbering) and there will only be two such atoms in the unit cell, having coordinates 0, 0, 0 and 0, 1/2, 1/2. Note that using the general positions generates only these same two locations.

c. What is the point group of the metal in the structure on page 17?

The structure has $P2_1/c$ symmetry and the metal is located at 0, 0, 0 which has point group $\bar{1}$ or C_i (type a in the Wyckoff numbering).

d. If an atom has coordinates 0.123, 0.795, 0.468 in space group *Cmm*2 (below), how many equivalent atoms are in the unit cell? General positions in *Cmm*2 (type *f* in the Wyckoff numbering) have 8 equivalent positions.

e. What are the coordinates for these atoms? For centered cells, additional lattice points are present other than 0, 0, 0. These lattice points are listed above the general positions. Add the centering coordinates to the equivalent position coordinates for a complete list. In this case, the centering requires the arrangement around 1/2, 1/2, 0 to be the same as that around 0, 0, 0.

x,y,z = 0.123, 0.795, 0.468 $\quad \frac{1}{2}+x,\frac{1}{2}+y,z$ = 0.623, 1.295, 0.468

$\bar{x},\bar{y},z$ = –0.123, –0.795, 0.468 $\quad \frac{1}{2}-x,\frac{1}{2}-y,z$ = 0.377, –0.295, 0.468

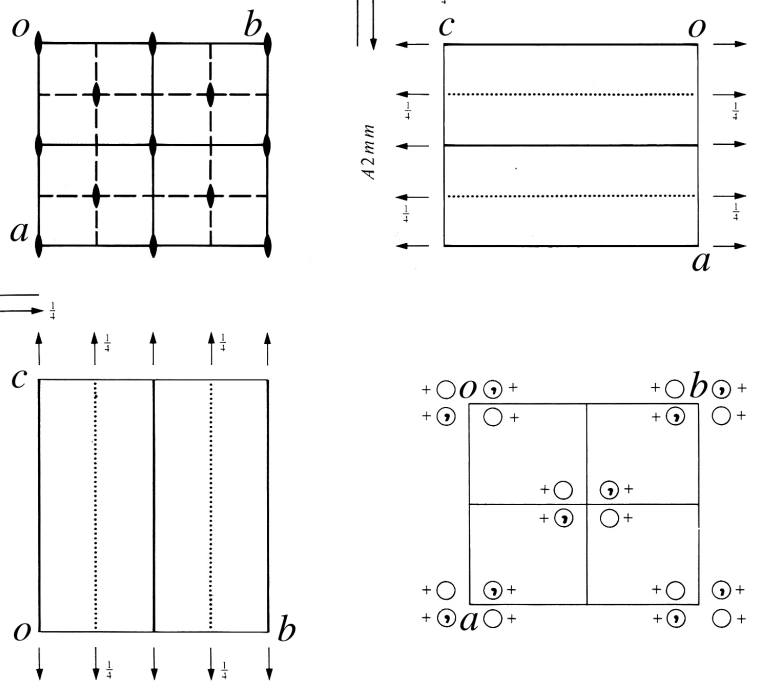
$x,\bar{y},z$ = –0.123, 0.795, 0.468 $\quad \frac{1}{2}-x,\frac{1}{2}+y,z$ = –0.123, 1.295, 0.468

$\bar{x},y,z$ = 0.123, –0.795, 0.468 $\quad \frac{1}{2}+x,\frac{1}{2}-y,z$ = 0.623, –0.295, 0.468

C m m 2 C_{2v}^{11} *m m 2* Orthorhombic

No. 35 *C m m 2*

Patterson symmetry *C m m m*



Positions Multiplicity, Wyckoff letter, Site symmetry			Coordinates (0,0,0)+	$(\frac{1}{2},\frac{1}{2},0)$+
8	*f*	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$ (3) $x,\bar{y},z$ (4) $\bar{x},y,z$
4	*e*	*m*	$0,y,z$	$0,\bar{y},z$
4	*d*	*m*	$x,0,z$	$\bar{x},0,z$
4	*c*	2	$\frac{1}{4},\frac{1}{4},z$	$\frac{1}{4},\frac{3}{4},z$
2	*b*	*mm2*	$0,\frac{1}{2},z$	
2	*a*	*mm2*	$0,0,z$	

G. Matrix Representations of equivalent positions. "Row into column" multiplication. "Bar" over number, e.g. $\bar{x}$, means negative number.

identity

$$\begin{Bmatrix}1&0&0\\0&1&0\\0&0&1\end{Bmatrix}\begin{Bmatrix}x\\y\\z\end{Bmatrix}=\begin{Bmatrix}1x+0y+0z\\0x+1y+0z\\0x+0y+1z\end{Bmatrix}=\begin{Bmatrix}x\\y\\z\end{Bmatrix}$$

2-fold parallel to a at 0,0

$$\begin{Bmatrix}1&0&0\\0&-1&0\\0&0&-1\end{Bmatrix}\begin{Bmatrix}x\\y\\z\end{Bmatrix}=\begin{Bmatrix}1x+0y+0z\\0x-1y+0z\\0x+0y-1z\end{Bmatrix}=\begin{Bmatrix}x\\\bar{y}\\\bar{z}\end{Bmatrix}$$

m perpendicular to a at 0

$$\begin{Bmatrix}-1&0&0\\0&1&0\\0&0&1\end{Bmatrix}\begin{Bmatrix}x\\y\\z\end{Bmatrix}=\begin{Bmatrix}-x+0y+0z\\0x+1y+0z\\0x+0y+1z\end{Bmatrix}=\begin{Bmatrix}\bar{x}\\y\\z\end{Bmatrix}$$

3-fold parallel to a at 0,0

$$\begin{Bmatrix}0&-1&0\\1&-1&0\\0&0&1\end{Bmatrix}\begin{Bmatrix}x\\y\\z\end{Bmatrix}=\begin{Bmatrix}0x-1y+0z\\1x-1y+0z\\0x+0y+1z\end{Bmatrix}=\begin{Bmatrix}\bar{y}\\x-y\\z\end{Bmatrix}$$

b glide perpendicular to c at 0

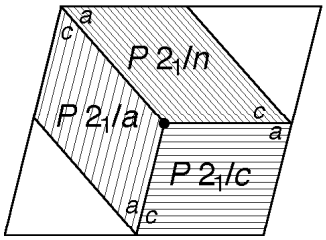
$$\begin{Bmatrix}0\\.5\\0\end{Bmatrix}+\begin{bmatrix}1&0&0\\0&1&0\\0&0&-1\end{bmatrix}\begin{Bmatrix}x\\y\\z\end{Bmatrix}=\begin{Bmatrix}x\\.5+y\\\bar{z}\end{Bmatrix}$$

2_1 parallel to a at 0,0

$$\begin{Bmatrix}.5\\0\\0\end{Bmatrix}+\begin{bmatrix}1&0&0\\0&-1&0\\0&0&-1\end{bmatrix}\begin{Bmatrix}x\\y\\z\end{Bmatrix}=\begin{Bmatrix}.5+x\\\bar{y}\\\bar{z}\end{Bmatrix}$$

H. You may occasionally come across an altered setting that is not in the tables. These can be simply derived by an exchange of axes. For example, $P2_1/c$, $P2_1/a$, and $P2_1/n$ are all the same symmetry; they differ only by how the axes are named.

$P2_1/c$	$x,y,z;$	$\bar{x},\bar{y},\bar{z};$	$-x,\frac{1}{2}+y,\frac{1}{2}-z;$	$x,\frac{1}{2}-y,\frac{1}{2}+z;$
$P2_1/a$	$x,y,z;$	$\bar{x},\bar{y},\bar{z};$	$\frac{1}{2}-x,\frac{1}{2}+y,-z;$	$\frac{1}{2}+x,\frac{1}{2}-y,z;$
$P2_1/n$	$x,y,z;$	$\bar{x},\bar{y},\bar{z};$	$\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z;$	$\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z;$



I. Density and special positions

1. NaCl crystallizes in space group $Fm\bar{3}m$ (next page) with cell dimensions 5.640 Å. If the density is 2.164 g/mL, can any atoms lie in general positions? If not, on which special positions do the atoms lie?

$$\frac{z\ (23.0+35.5)\text{ grams}}{6.02\times10^{23}(5.64\times10^{-8}\text{cm})^3}=\frac{2.164\text{ g}}{\text{cm}^3}$$ which gives $z = 4.00$

According to the density, there are 4 Na and 4 Cl per unit cell (and not the 192 required for a general position). One sits on special position a and the other on special position b; both have $m\bar{3}m$ or O_h coordination.

2. CaF_2 also crystallizes in space group $Fm\bar{3}m$, with cell dimensions 5.463 Å. If the density is 3.163 g/mL, on which equivalent positions do the atoms lie?

$$\frac{z\ (40.1+2(19.0))\text{ grams}}{6.02\times10^{23}(5.463\times10^{-8}\text{cm})^3}=\frac{3.163\text{ g}}{\text{cm}^3}$$ which gives $z = 3.98$

The 8 F in the unit cell must be position c with $\bar{4}3m$ or T_d coordination. The 4 Ca are either position types a or b with $m\bar{3}m$ or O_h coordination.

$Fm\bar{3}m$ O_h^5 $m\,\bar{3}\,m$ Cubic

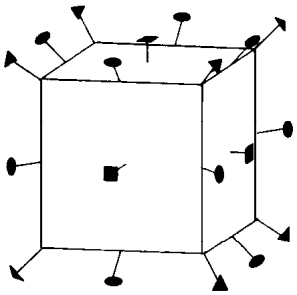
No. 225 $F\,4/m\;\bar{3}\;2/m$

Positions

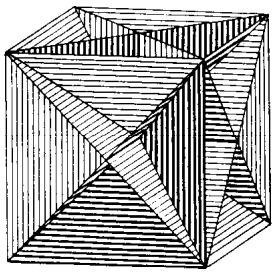
Multiplicity, Wyckoff letter, Site symmetry

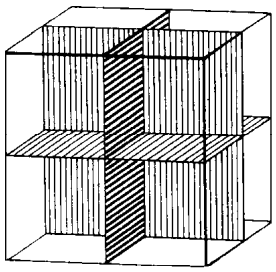
Coordinates

			(0,0,0)+	(0,$\frac{1}{2}$,$\frac{1}{2}$)+	($\frac{1}{2}$,0,$\frac{1}{2}$)+	($\frac{1}{2}$,$\frac{1}{2}$,0)+		
192	*l*	1	(1) *x*,*y*,*z*	(2) *z*,*x*,*y*	(3) *y*,*z*,*x*	(4) *x*,*z*,*y*	(5) *y*,*x*,*z*	(6) *z*,*y*,*x*
			(7) *x*,$\bar{y}$,$\bar{z}$	(8) *z*,$\bar{x}$,$\bar{y}$	(9) *y*,$\bar{z}$,$\bar{x}$	(10) *x*,$\bar{z}$,$\bar{y}$	(11) *y*,$\bar{x}$,$\bar{z}$	(12) *z*,$\bar{y}$,$\bar{x}$
			(13) $\bar{x}$,*y*,$\bar{z}$	(14) $\bar{z}$,*x*,$\bar{y}$	(15) $\bar{y}$,*z*,$\bar{x}$	(16) $\bar{x}$,*z*,$\bar{y}$	(17) $\bar{y}$,*x*,$\bar{z}$	(18) $\bar{z}$,*y*,$\bar{x}$
			(19) $\bar{x}$,$\bar{y}$,*z*	(20) $\bar{z}$,$\bar{x}$,*y*	(21) $\bar{y}$,$\bar{z}$,*x*	(22) $\bar{x}$,$\bar{z}$,*y*	(23) $\bar{y}$,$\bar{x}$,*z*	(24) $\bar{z}$,$\bar{y}$,*x*
			(25) $\bar{x}$,$\bar{y}$,$\bar{z}$	(26) $\bar{z}$,$\bar{x}$,$\bar{y}$	(27) $\bar{y}$,$\bar{z}$,$\bar{x}$	(28) $\bar{x}$,$\bar{z}$,$\bar{y}$	(29) $\bar{y}$,$\bar{x}$,$\bar{z}$	(30) $\bar{z}$,$\bar{y}$,$\bar{x}$
			(31) $\bar{x}$,*y*,*z*	(32) $\bar{z}$,*x*,*y*	(33) $\bar{y}$,*z*,*x*	(34) $\bar{x}$,*z*,*y*	(35) $\bar{y}$,*x*,*z*	(36) $\bar{z}$,*y*,*x*
			(37) *x*,$\bar{y}$,*z*	(38) *z*,$\bar{x}$,*y*	(39) *y*,$\bar{z}$,*x*	(40) *x*,$\bar{z}$,*y*	(41) *y*,$\bar{x}$,*z*	(42) *z*,$\bar{y}$,*x*
			(43) *x*,*y*,$\bar{z}$	(44) *z*,*x*,$\bar{y}$	(45) *y*,*z*,$\bar{x}$	(46) *x*,*z*,$\bar{y}$	(47) *y*,*x*,$\bar{z}$	(48) *z*,*y*,$\bar{x}$
96	*k*	*m*	*x*,*x*,*z*	*z*,*x*,*x*	*x*,*z*,*x*	$\bar{x}$,$\bar{x}$,$\bar{z}$	$\bar{z}$,$\bar{x}$,$\bar{x}$	$\bar{x}$,$\bar{z}$,$\bar{x}$
			x,$\bar{x}$,$\bar{z}$	*z*,$\bar{x}$,$\bar{x}$	*x*,$\bar{z}$,$\bar{x}$	$\bar{x}$,*x*,*z*	$\bar{z}$,*x*,*x*	$\bar{x}$,*z*,*x*
			$\bar{x}$,*x*,$\bar{z}$	$\bar{z}$,*x*,$\bar{x}$	$\bar{x}$,*z*,$\bar{x}$	*x*,$\bar{x}$,*z*	*z*,$\bar{x}$,*x*	*x*,$\bar{z}$,*x*
			$\bar{x}$,$\bar{x}$,*z*	$\bar{z}$,$\bar{x}$,*x*	$\bar{x}$,$\bar{z}$,*x*	*x*,*x*,$\bar{z}$	*z*,*x*,$\bar{x}$	*x*,*z*,$\bar{x}$
96	*j*	*m*	0,*y*,*z*	*z*,0,*y*	*y*,*z*,0	0,*z*,*y*	*y*,0,*z*	*z*,*y*,0
			0,$\bar{y}$,$\bar{z}$	$\bar{z}$,0,$\bar{y}$	$\bar{y}$,$\bar{z}$,0	0,$\bar{z}$,$\bar{y}$	$\bar{y}$,0,$\bar{z}$	$\bar{z}$,$\bar{y}$,0
			0,*y*,$\bar{z}$	$\bar{z}$,0,*y*	*y*,$\bar{z}$,0	0,$\bar{z}$,*y*	*y*,0,$\bar{z}$	$\bar{z}$,*y*,0
			0,$\bar{y}$,*z*	*z*,0,$\bar{y}$	$\bar{y}$,*z*,0	0,*z*,$\bar{y}$	$\bar{y}$,0,*z*	*z*,$\bar{y}$,0
48	*i*	*mm2*	$\frac{1}{2}$,*x*,*x*	*x*,$\frac{1}{2}$,*x*	*x*,*x*,$\frac{1}{2}$	$\frac{1}{2}$,*x*,$\bar{x}$	$\bar{x}$,$\frac{1}{2}$,*x*	*x*,$\bar{x}$,$\frac{1}{2}$
			$\frac{1}{2}$,$\bar{x}$,$\bar{x}$	$\bar{x}$,$\frac{1}{2}$,$\bar{x}$	$\bar{x}$,$\bar{x}$,$\frac{1}{2}$	$\frac{1}{2}$,$\bar{x}$,*x*	*x*,$\frac{1}{2}$,$\bar{x}$	$\bar{x}$,*x*,$\frac{1}{2}$
48	*h*	*mm2*	0,*x*,*x*	*x*,0,*x*	*x*,*x*,0	0,*x*,$\bar{x}$	$\bar{x}$,0,*x*	$\bar{x}$,*x*,0
			0,$\bar{x}$,$\bar{x}$	$\bar{x}$,0,$\bar{x}$	$\bar{x}$,$\bar{x}$,0	0,$\bar{x}$,*x*	*x*,0,$\bar{x}$	$\bar{x}$,*x*,0
48	*g*	*2mm*	*x*,$\frac{1}{4}$,$\frac{1}{4}$	$\frac{1}{4}$,*x*,$\frac{1}{4}$	$\frac{1}{4}$,$\frac{1}{4}$,*x*	*x*,$\frac{1}{4}$,$\frac{3}{4}$	$\frac{3}{4}$,*x*,$\frac{1}{4}$	$\frac{1}{4}$,$\frac{3}{4}$,*x*
			$\bar{x}$,$\frac{1}{4}$,$\frac{1}{4}$	$\frac{1}{4}$,$\bar{x}$,$\frac{1}{4}$	$\frac{1}{4}$,$\frac{1}{4}$,$\bar{x}$	$\bar{x}$,$\frac{1}{4}$,$\frac{3}{4}$	$\frac{3}{4}$,$\bar{x}$,$\frac{1}{4}$	$\frac{1}{4}$,$\frac{3}{4}$,$\bar{x}$
32	*f*	3*m*	*x*,*x*,*x*	*x*,$\bar{x}$,$\bar{x}$	$\bar{x}$,*x*,$\bar{x}$	$\bar{x}$,$\bar{x}$,*x*		
			$\bar{x}$,$\bar{x}$,$\bar{x}$	$\bar{x}$,*x*,*x*	*x*,$\bar{x}$,*x*	*x*,*x*,$\bar{x}$		
24	*e*	4*mm*	*x*,0,0	0,*x*,0	0,0,*x*	$\bar{x}$,0,0	0,$\bar{x}$,0	0,0,$\bar{x}$
24	*d*	*mmm*	0,$\frac{1}{4}$,$\frac{1}{4}$	$\frac{1}{4}$,0,$\frac{1}{4}$	$\frac{1}{4}$,$\frac{1}{4}$,0	0,$\frac{1}{4}$,$\frac{3}{4}$	$\frac{3}{4}$,0,$\frac{1}{4}$	$\frac{1}{4}$,$\frac{3}{4}$,0
8	*c*	$\bar{4}3m$	$\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$	$\frac{1}{4}$,$\frac{3}{4}$,$\frac{3}{4}$				
4	*b*	$m\bar{3}m$	$\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$					
4	*a*	$m\bar{3}m$	0,0,0					



Cubic axes





Cubic planes

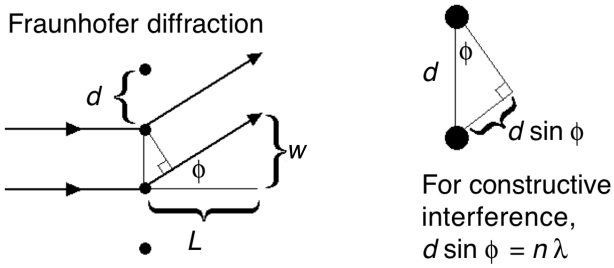
3. ZnS (zinc blende) crystallizes in space group $F\bar{4}3m$ with cell dimensions 5.429 Å. If the density is 4.092 g/mL, what are the positions of the atoms?

IV. **Diffraction**

The phenomenon of interference has many forms and applications. For example, we can use diffraction to build a spectrometer, or read the pits on a compact disk, or determine the molecular structure of a solid.

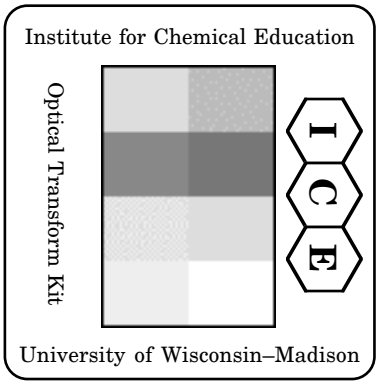
A. Diffraction in Two Dimensions

1. When light interacts with an ordered two-dimensional array of wave scattering centers, each center behaves as its own point source of light. The light from these centers interferes to form a pattern of light, a diffraction pattern known as Fraunhofer diffraction. The nature of this diffraction pattern can be calculated mathematically by knowing the pattern of the scattering centers; conversely, the pattern of the scattering centers may be elucidated by studying the diffraction pattern.

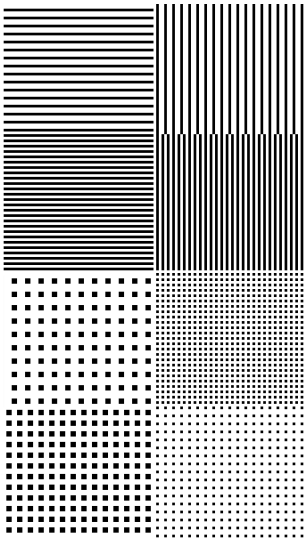


Fraunhofer diffraction from a two-dimensional array depends on the wavelength and array spacing.

2. **Obtain a Discovery Optical Transform Slide**. The features on the slide are a little less than a millimeter apart and hence too close for our eye to resolve, but the densities of features in the different regions of the slide can be perceived. When the slide is oriented with ICE on the right side, the patterns on the slide will be as shown in the magnified figure. The lines in the upper portion might represent chains of atoms (a polymer) and the squares in the lower portion might represent atoms of different size.



Discovery Slide



Discovery Slide Patterns (magnified)

Either shine a laser beam through the upper right corner of the slide and onto a screen or look through that corner of a slide at a laser spot aimed at a wall. **Caution! Do not look directly into the beam.**

Do you see a single laser spot (the beam passes right through), vertical lines (the slide is projected), or some other array?

We will take *w*, the spacing between the "spots" on the wall, as our observable. How does w depend on

d, the distance between the "atoms" on the slide?

L, the distance to the wall?

λ, the wavelength of light (labeled on each laser light source)?

For each combination of *w*, *d*, *L*, and λ, keep two variables constant and determine whether the remaining two variables are directly or inversely related.

a. Keep *d* and λ constant. Use a red laser pointer and try the full length of the room, half the length of the room and a quarter the length of the room for *L*. If the laser and slide are moved closer to the wall to change *L*, what happens to *w*? Are *L* and *w* directly or inversely related?

b. Keep *L* and λ constant. Use a red laser pointer and pick two similar arrays on the slide for comparison (horizontal lines, vertical lines or the sequence of 4 square arrays). If the spacing *d* between features on the slide is reduced, what happens to *w*? Are *d* and *w* directly or inversely related?

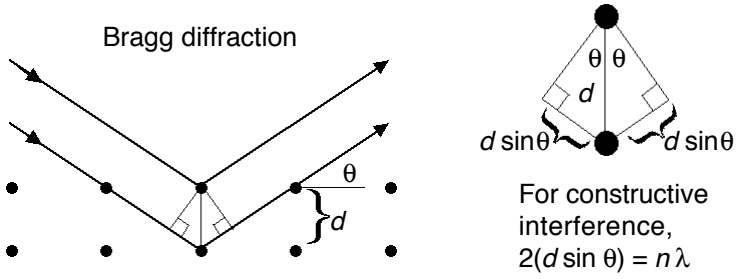
c. Keep *d* and *L* constant. If you use a red, a green, and a blue laser to vary λ, what happens to *w*? The λ of the color is labeled on each laser light source. Are λ and *w* directly or inversely related?

d. Keep *d* and *L* constant. Look through the slide at a point source of white light (such as a miniMaglite). Each spot breaks into the full visible spectrum. Which color is diffracted the most? Which color is diffracted the least? Are λ and *w* directly or inversely related?

e. Combine your four variables into one equation. Since $w/L = \tan \phi = \sin \phi / \cos \phi$, and $\cos \phi \approx 1$ for the small diffraction angles observed in this experiment, does your equation match the Fraunhofer equation, $n \lambda = d \sin \phi$?

B. Diffraction in Three Dimensions

1. **Bragg diffraction** from a three dimensional array of atoms or ions is similar to the two dimensional Fraunhofer diffraction. Beams of x-rays are shown striking two atoms, one directly above another. The atoms are assumed to be in parallel planes, along with many other atoms. In order for the two beams to be in phase and reinforce each other, their path lengths must differ by a whole number of wavelengths, $n\lambda$, where n is an integer. If this is not the case, the beams will be out of phase and cancel each other. Applying trigonometry reveals that the difference in path length between the two beams is $2(d \sin \theta)$, where d is the distance between the atomic planes and θ is the angle between the incident (or reflected) x-ray beam and the plane of atoms. Constructive interference occurs and a diffraction spot is observed when the Bragg condition is satisfied: $2(d \sin \theta) = n\lambda$. When the wavelength of radiation is known and the scattering angle is measured, it is possible to calculate d, the distance between the scattering atoms. X-ray diffraction yields important information about the distances between planes of atoms and dimensions of the unit cell.

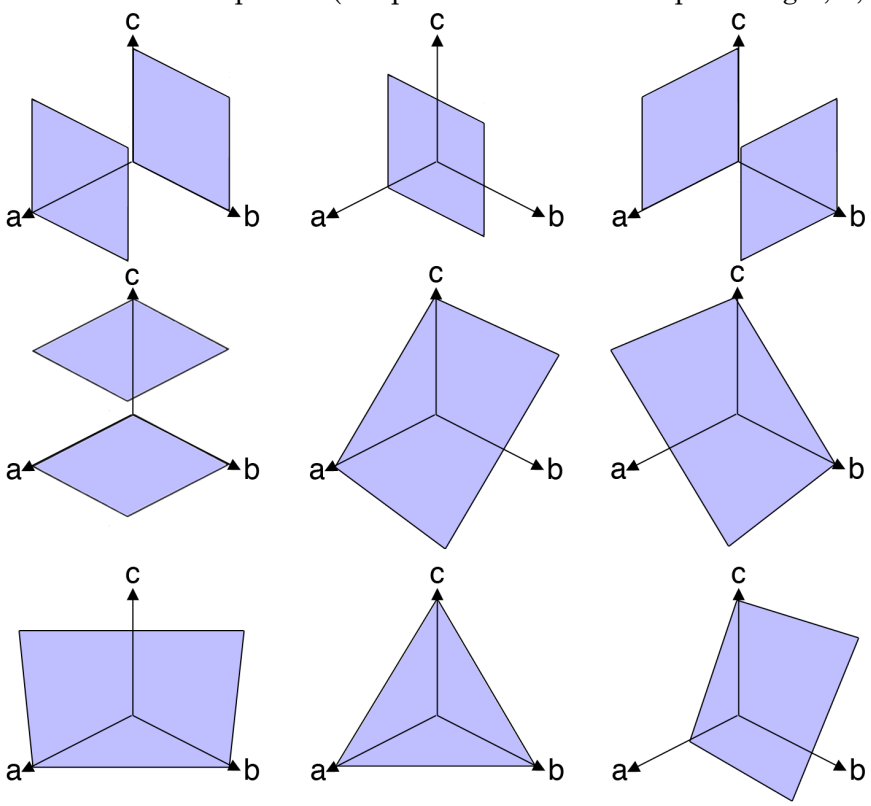


Bragg diffraction from a three-dimensional array depends on the wavelength and array spacing. The angle between the continuation of the incoming beam and the diffracted beam is 2θ.

Scattering from layers of parallel planes $hx + ky + lz = 1$, where x, y, and z are fractional coordinates, yields the Bragg equation, $2d \sin \theta = n \lambda$, where d is the distance between planes hkl and θ is the incident angle. hkl are the Miller indices of the plane (the indices are the reciprocals of the intercepts along a, b, and c), as well as the coordinates of the diffraction ray.

2. **Miller indices**. Name these hkl planes (reciprocals of the intercepts along a, b, and c)

Cuts a at 1, cuts b and c at ∞, so (100)



Plane hkl cuts a into h divisions, b into k divisions, and c into l divisions (where a, b, c are the unit cell axes). There is a phase difference of 2π between reflections from planes of any given set of parallel hkl. Thus a unit translation along an axis has a phase difference of $2\pi h$, $2\pi k$ or $2\pi l$ respectively. For an atom located at fractional coordinates x,y,z, the phase difference from the origin is thus $2\pi hx$, $2\pi ky$, and $2\pi lz$ respectively, for a total phase difference of $\delta = 2\pi (hx + ky + lz)$. Each set of planes can give rise to a diffraction peak.

Cubic $$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal $$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Orthorhombic $$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Hexagonal $$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2}$$

Monoclinic $$\frac{1}{d_{hkl}^2} = \frac{1}{\sin^2\beta}\left[\frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right]$$

Triclinic $$\frac{1}{d_{hkl}^2} = \frac{1}{V^2}\left[h^2 b^2 c^2 \sin^2\alpha + k^2 a^2 c^2 \sin^2\beta + l^2 a^2 b^2 \sin^2\gamma\right.$$

$$+2hkabc^2\left(\cos\alpha\cos\beta-\cos\gamma\right)+2kla^2bc\left(\cos\beta\cos\gamma-\cos\alpha\right)+2hlab^2c\left(\cos\alpha\cos\gamma-\cos\beta\right)\Big]$$

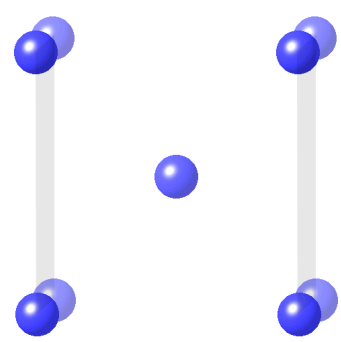
3. **Space group extinctions** are predicted for translational symmetry elements (centering, glides, and screws). For example, consider a C centered cell where the point x, y, z is equivalent to point x+1/2, y+1/2, z.

$\exp[2\pi i(hx+ky+lz)] + \exp[2\pi i(hx+ky+lz+\frac{h+k}{2})] = 0$ when $(h+k)$ is odd;

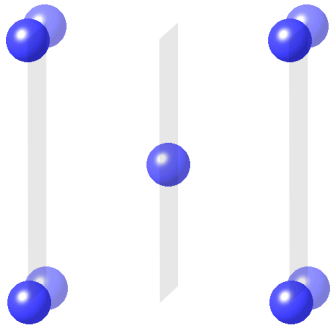
$= 2\exp[2\pi i(hx+ky+lz)]$ when (h+k) is even since $\cos(x) = \cos(x+2\pi) = -\cos(x+\pi)$
$\sin(x) = \sin(x+2\pi) = -\sin(x+\pi)$

All peaks with $h+k$ odd have zero intensity and peaks with $h+k$ even have double intensity! Another example is when there is a set of planes with the same atoms halfway between hkl that will diffract out of phase. In this case peak hkl will also not be observed.

Body Centered Cubic

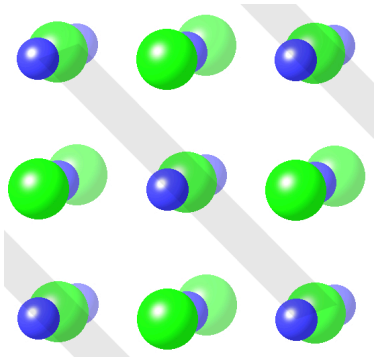


100 will not be observed

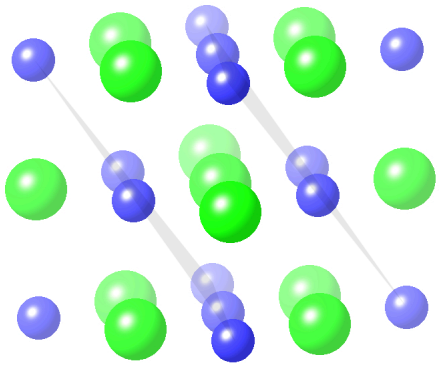


200 will be observed

NaCl structure



110 will not be observed



111 will be observed

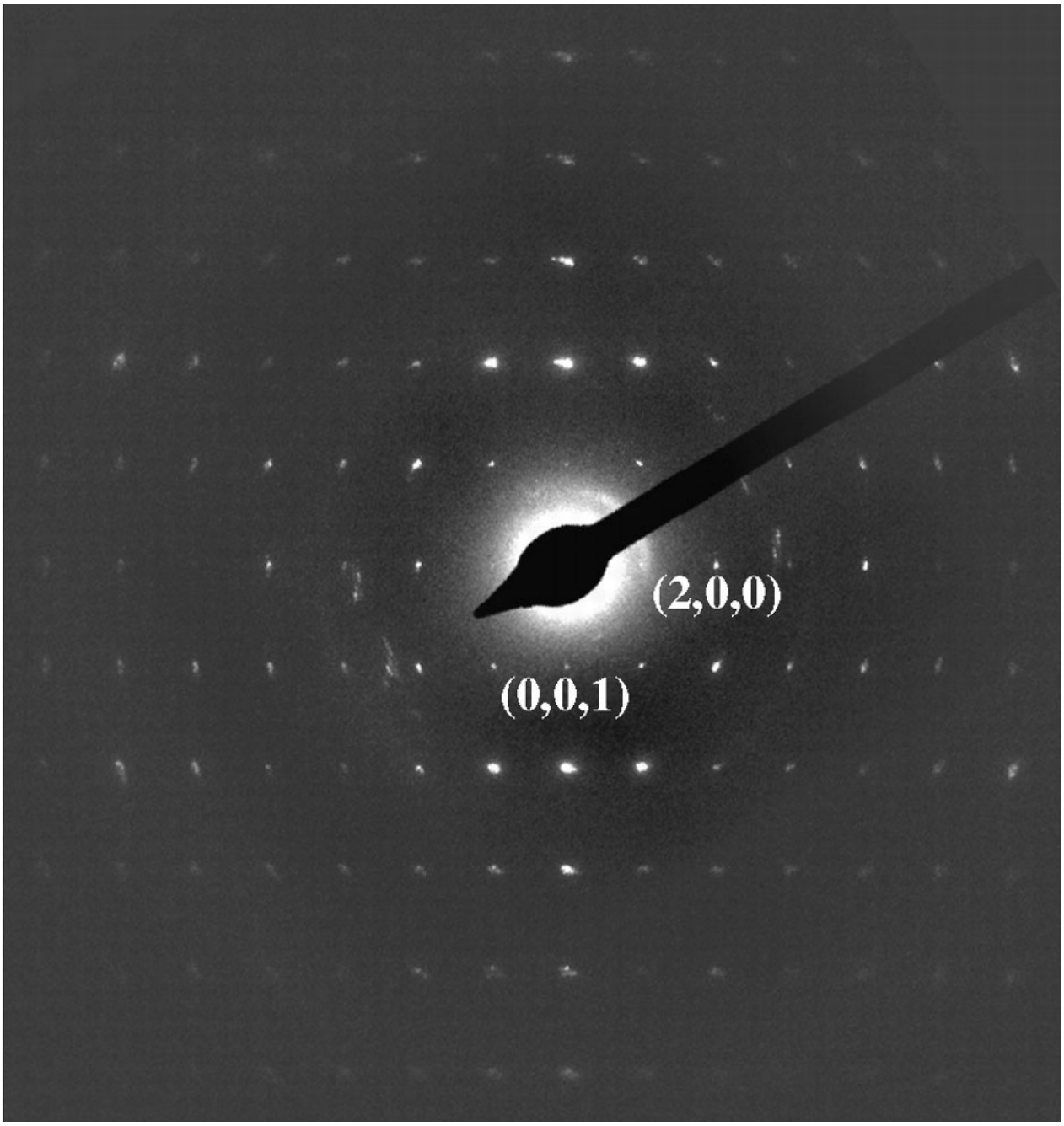
Observed Peaks

Primitive Cubic:	100, 110, 111, 200, 210, 211…
Body-Centered Cubic:	110, 200, 211, 220, 310, 222… ($h + k + l$ is even)
Face-Centered Cubic:	111, 200, 220, 311, 222, 400… (h, k, l either all odd or all even)

The International Tables list the space group reflection conditions for all the space groups. For example, space group $P2_1/c$ requires only $hk0$: $h = 2n$ and $h00$: $h = 2n$ while the higher symmetry $Fm\bar{3}m$ requires many more reflection conditions.

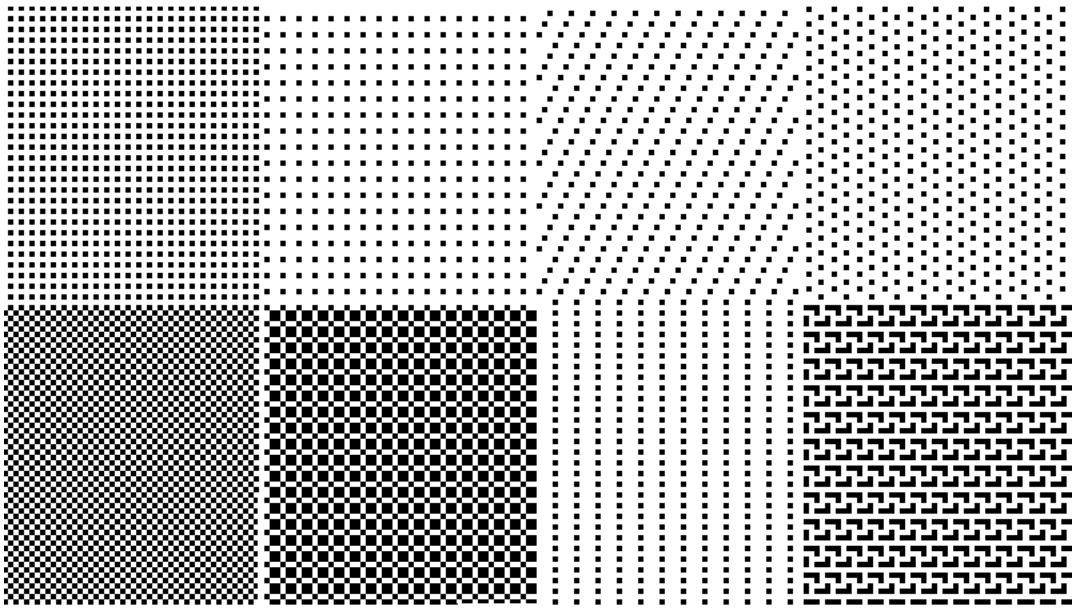
hkl: $h + k$, $h + l$, $k + l = 2n$.
$0kl$: k, $l = 2n$ and $h0l$: h, $l = 2n$ and $hk0$: h, $k = 2n$.
hhl: $h + l = 2n$ and hkk: $h + k = 2n$ and hkh: $h + k = 2n$.
$h00$: $h = 2n$ and $0k0$: $k = 2n$ and $00l$: $l = 2n$.
unless an atom is located on special position which adds hkl: $h = 2n$ and $k = 2n$ *and* $l = 2n$.

4. **Information from X-ray Diffraction Patterns**
   a. *hkl positions* depend on the *hkl* planes (and thus depend only on the *lattice*). The positions allow determination of the cell dimensions and the crystal system.
   b. *hkl intensities* depend on what is in the lattice (scattering factors), where the atoms are located (fractional coordinates), and the symmetry (space group). The zero intensity peaks ("extinctions" or "absent reflections") allow determination of the space group. The intensities of the remaining peaks allow determination of the structure (the *x,y,z* positions of the atoms).



Single crystal electron diffraction of anhydrous cholesterol.
http://www.jlr.org/content/46/5/942/F4.expansion.html

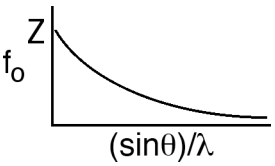
Unit Cell Slide



What happens when you add the same atom to the center of the unit cell?
What happens when you add a different atom to the center of the unit cell?
What happens to the pattern if you tip the rectangle?
What happens if the pattern has glide symmetry?

5. **Scattering factors**

For spherical atoms, their x-ray scattering ability is a function only of the type of atom (number of electrons) and sin θ/λ (where θ is the Bragg angle and λ is the x-ray wavelength). The scale is defined such that the scattering factor is the atomic number, Z, for $(\sin\theta)/\lambda = 0$. Their low x-ray scattering power makes hydrogen atoms difficult to see in the presence of heavy atoms (like transition metals).



Thermal vibrations of an atom change its scattering power. Since the electron cloud is more spread out, the scattering power drops off more rapidly,

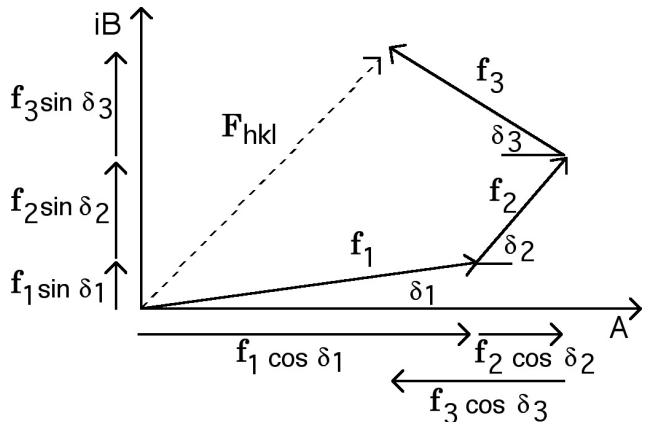
$$f = f_o \exp \frac{-B}{4d^2}$$

where B is a refined parameter = $8\ \pi^2\ \mu^2$ (μ^2 is the mean squared amplitude of isotropic vibration) and d is the interplanar spacing. Since the formula for d contains 6 terms,

$$d_{hkl} = V\ [h^2\ b^2\ c^2 \sin^2\alpha + k^2\ a^2\ c^2 \sin^2\beta + l^2\ a^2\ b^2 \sin^2\gamma + 2h\ l\ a\ b^2 c\ (\cos\alpha\ \cos\gamma - \cos\beta)$$
$$+ 2\ h\ k\ a\ b\ c^2\ (\cos\alpha\ \cos\beta - \cos\gamma) + 2\ k\ l\ a^2\ b\ c\ (\cos\beta\ \cos\gamma - \cos\alpha)]^{-1/2},$$

a more general anisotropic temperature factor expression has a coefficient for each of the 6 terms as a refined parameter: B11, B22, B33, B12, B13, B23. Several different anisotropic expressions are used commonly. The 6 components are plotted as an ellipsoid (See ORTEP).

Scattering factors from each atom are summed together in a **structure factor**, F_{hkl}. The structure factor is the resultant of j waves scattered in the direction of reflection hkl by the j atoms in the unit cell. Each of these waves has an amplitude f_j that depends on the scattering ability of the element and a phase δ_j with respect to the wave scattered by hypothetical electrons at the origin of the cell.



$$|F_{hkl}| = \sqrt{A^2 + B^2}$$

$$= \sqrt{[\sum_j f_j \cos\delta_j]^2 + [\sum_j f_j \sin\delta_j]^2}$$

where j is summed over the atoms in the unit cell.

Substituting in for δ the phase difference that depends on the fractional coordinates yields:

$$|F_{hkl}| = \sqrt{[\sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j)]^2 + [\sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)]^2}$$

or in complex form (since the length of vector r = a + *i*b is $|r| = \sqrt{a^2 + b^2}$),

$$F_{hkl} = \sum f_i \cos 2\pi(hx_i + ky_i + lz_i) + i \sum f_i \sin 2\pi(hx_i + ky_i + lz_i)$$

$$F_{hkl} = \sum f_i \exp[2\pi i(hx_i + ky_i + lz_i)]$$

This is the theoretical quantity, also known as F_{calc} that predicts the structure factors from the position of all the atoms.

6. **Solving a diffraction structure**

We now have $F_{hkl} = \sum f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$, the structure factor with both phase and amplitude, in terms of the fractional atomic coordinates. The fourier transform is

$$\rho_{xyz} = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} \exp[-2\pi i\,(hx + ky + lz)],$$

the electron density at point *x*, *y*, *z* based on the structure factors.

Thus to find the structure (electron density, ρ_{xyz}), we need F_{hkl}; to find F_{hkl} all we need are the coordinates of the atoms. If this seems circular, it may be because it *is* circular. The problem is that our scaled experimental observations $I_{hkl} = |F_{obs}|^2$. We need the magnitude and the phase, but can only find the magnitude $|F_{obs}|$ in $F_{hkl} = |F_{obs}| \cos\alpha + i\,|F_{obs}| \sin\alpha$. Since α is the phase, this is known as the phase problem.

In practice, we *guess an answer* and calculate F_{hkl}. The phases of the calculated structure are then assigned to the observed amplitude for the reflection. The electron density can then be calculated, and slightly altered coordinates obtained. The technique of least squares refinement is used to minimize deviations. While there may be many unknowns (three positional parameters and six thermal parameters for each atom), there are usually thousands of intensity data to fit. A measure of success in the agreement between F_{obs} and F_{hkl} is the "R factor."

$$R = \frac{\sum |F_{obs}| - |F_{calc}|}{\sum |F_{obs}|}$$

A good R-factor for a small molecule would be <0.05 and a good R-factor for a protein structure might be <0.2

Direct methods involve guessing the signs of a few strong reflections and using probability to predict the others. If enough are correct, the structure is apparent in the electron density map. These mathematical methods were developed by Hauptman and Karle, who received the 1985 Nobel Prize in chemistry for their work.

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