Structure and Symmetry

22.14 – Intro to Nuclear Materials
February 5, 2015

Scanned images, unless cited, are from Allen & Thomas, "The Structure of Materials," 1999.

Crystallography – The Common Language of Materials Science

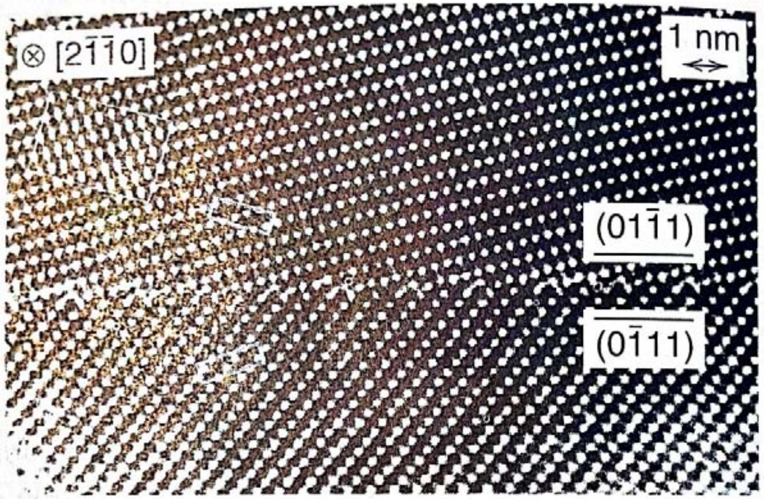


Figure 5.63 High-resolution transmission electron micrograph showing high-angle grain boundary in alumina, Al_2O_3. This particular boundary is a tilt boundary, with 35.2° misorientation about common [2 $\bar{1}$ $\bar{1}$ 0] direction (Kleebe, 1993, p. 365).

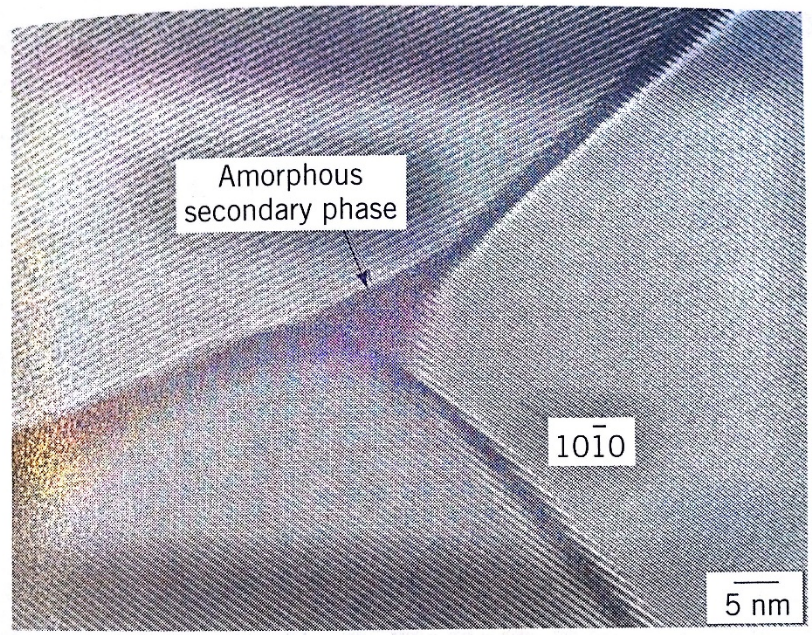
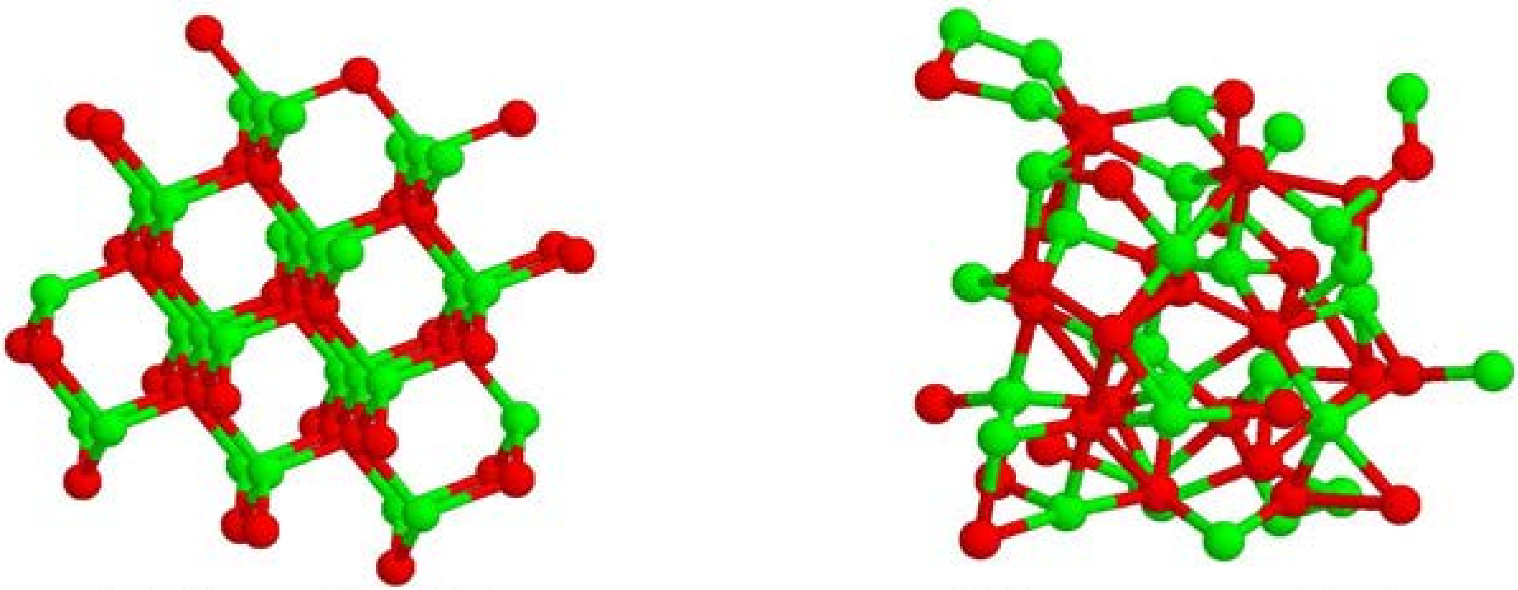


Figure 5.64 High-resolution transmission electron micrograph of grain edge in sintered, reaction-bonded silicon nitride, Si_3N_4. Grain edge is wetted by amorphous phase (Kleebe, 1993, p. 365).

Crystalline vs. Amorphous

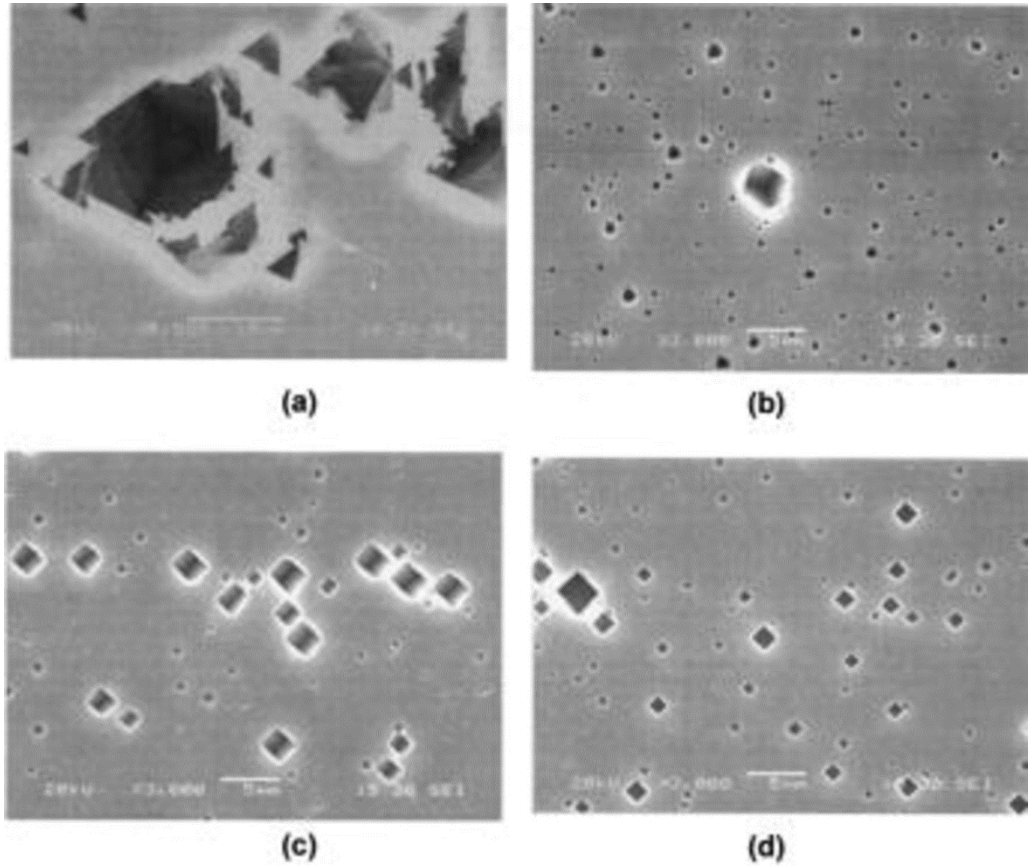
The difference is long-range order, and *symmetry*



(a) Crystalline InP (b) Amorphous InP

http://physics.anu.edu.au/eme/research/amorphous.php

Symmetry Evident in Materials

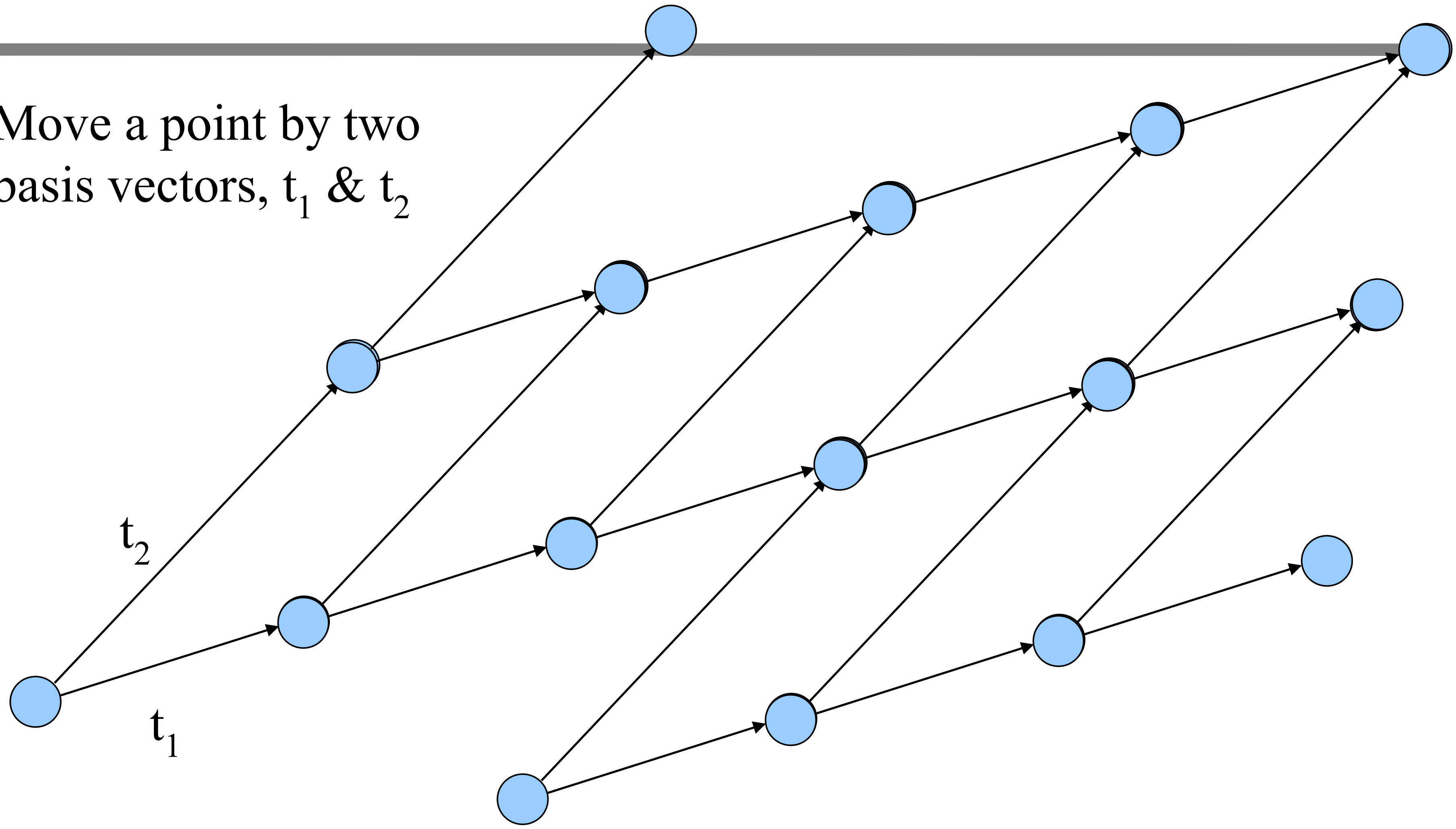


Etch pits in single crystal aluminum

Source: J. H. Seob, J.-H. Ryuc, D. N. Lee. "Formation of Crystallographic Etch Pits during AC Etching of Aluminum." ***J. Electrochem Soc.*****, 150(9):B433-B438 (2003).**

Simplest Operation: Translation

Move a point by two basis vectors, t_1 & t_2



Higher Symmetry

Place restrictions on t_1 and t_2, and the angle between them.

How many combinations can you think of?

Choosing Unit Cells

Draw a cell that does the following:

- Contains fewest number of atoms
- Has angles closest to 90 degrees
- Exhibits the most symmetry

Try with different plane groups in class

Choosing Unit Cells Example

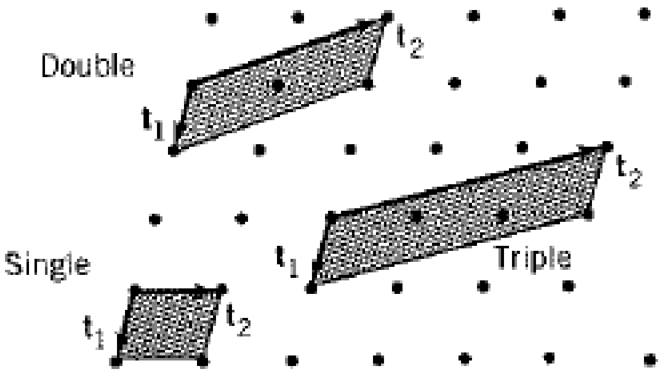
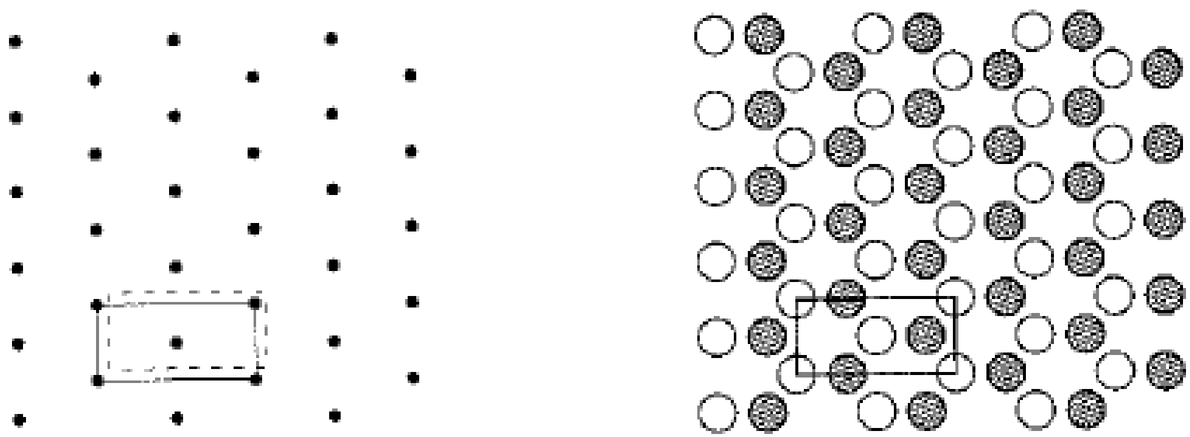
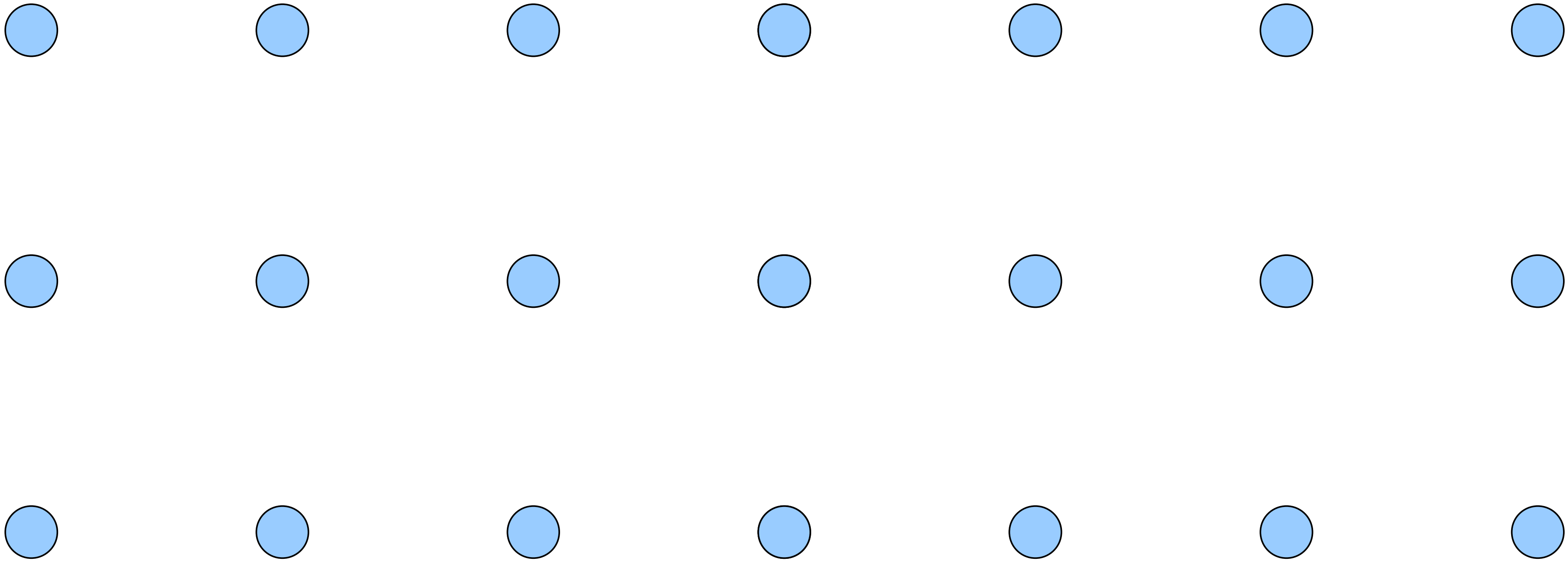


Figure 3.4 Illustration of procedure for outlining primitive, double, and triple cells. Note that basis vectors have been chosen such that angle γ is obtuse.

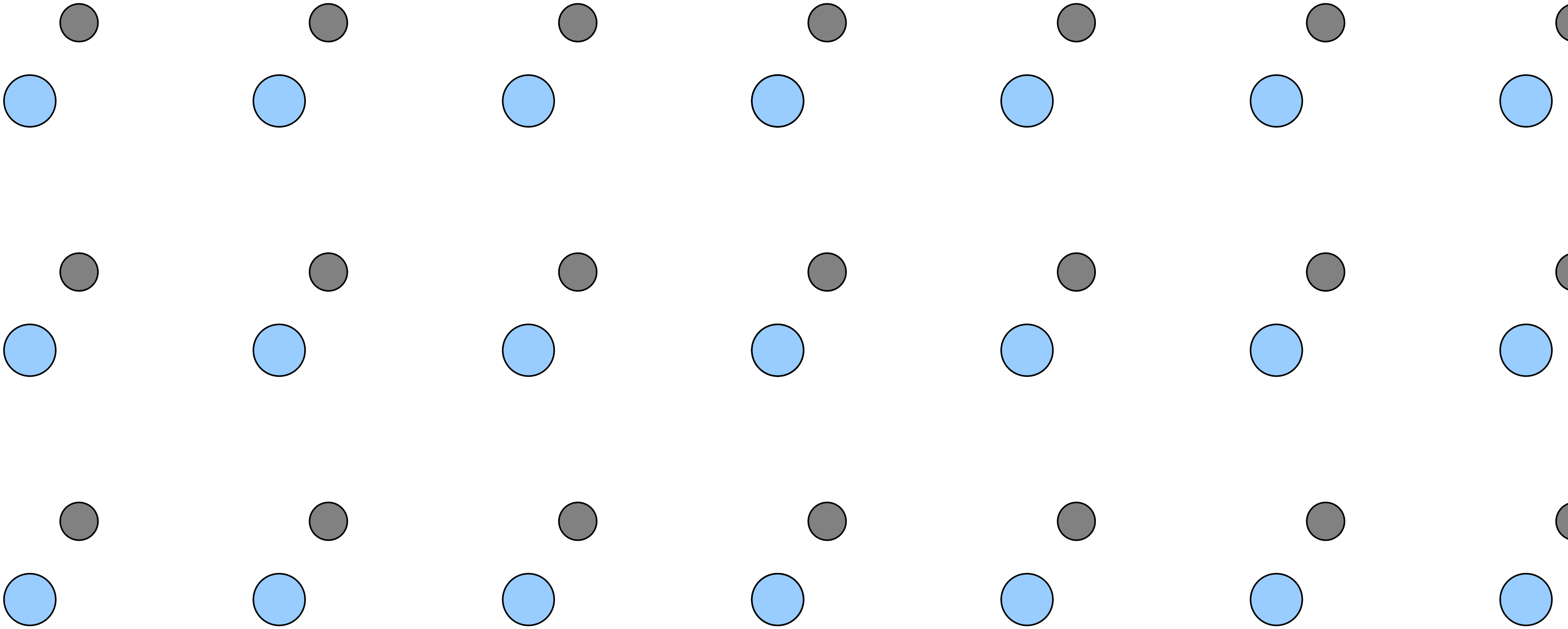


(a) (b)

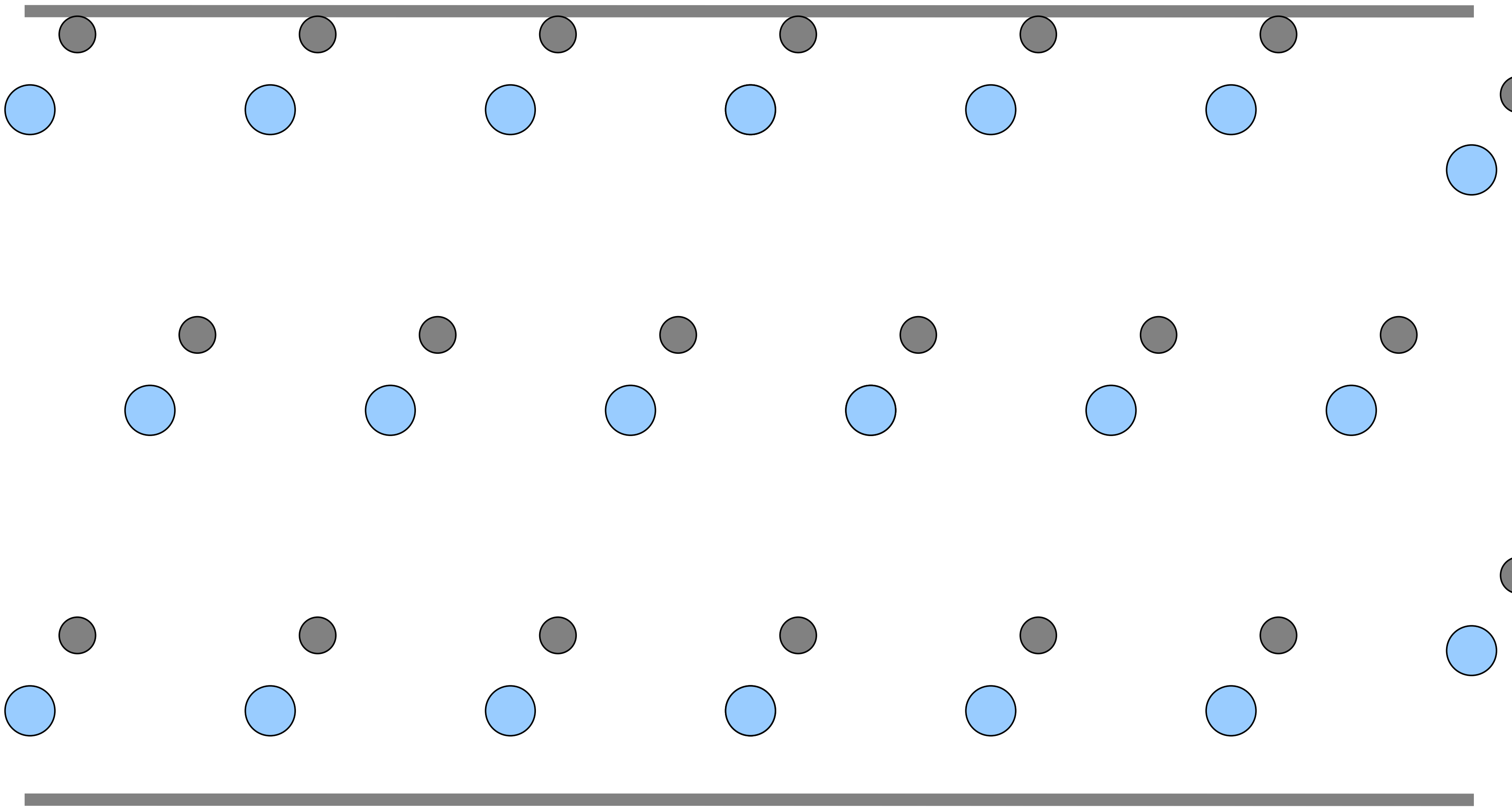
Choosing Unit Cells



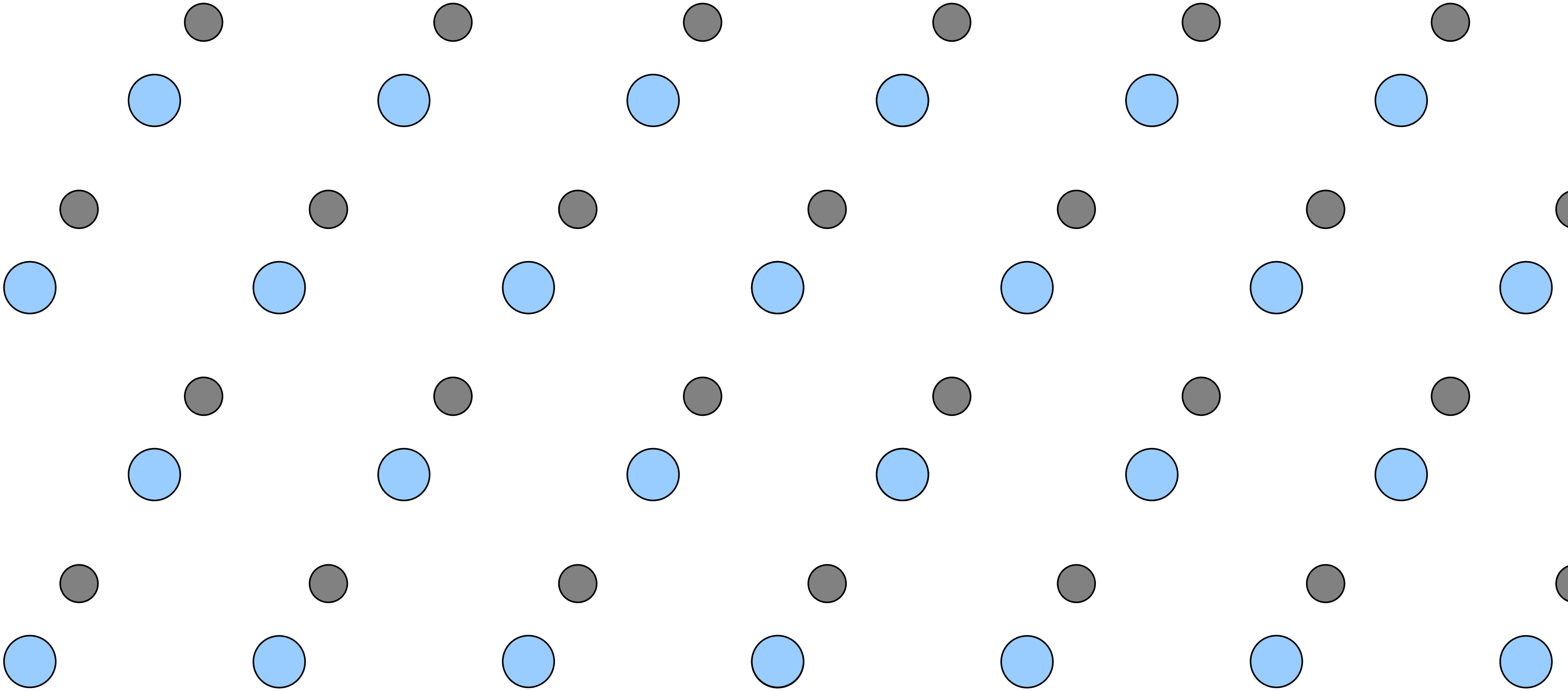
Choosing Unit Cells



Choosing Unit Cells

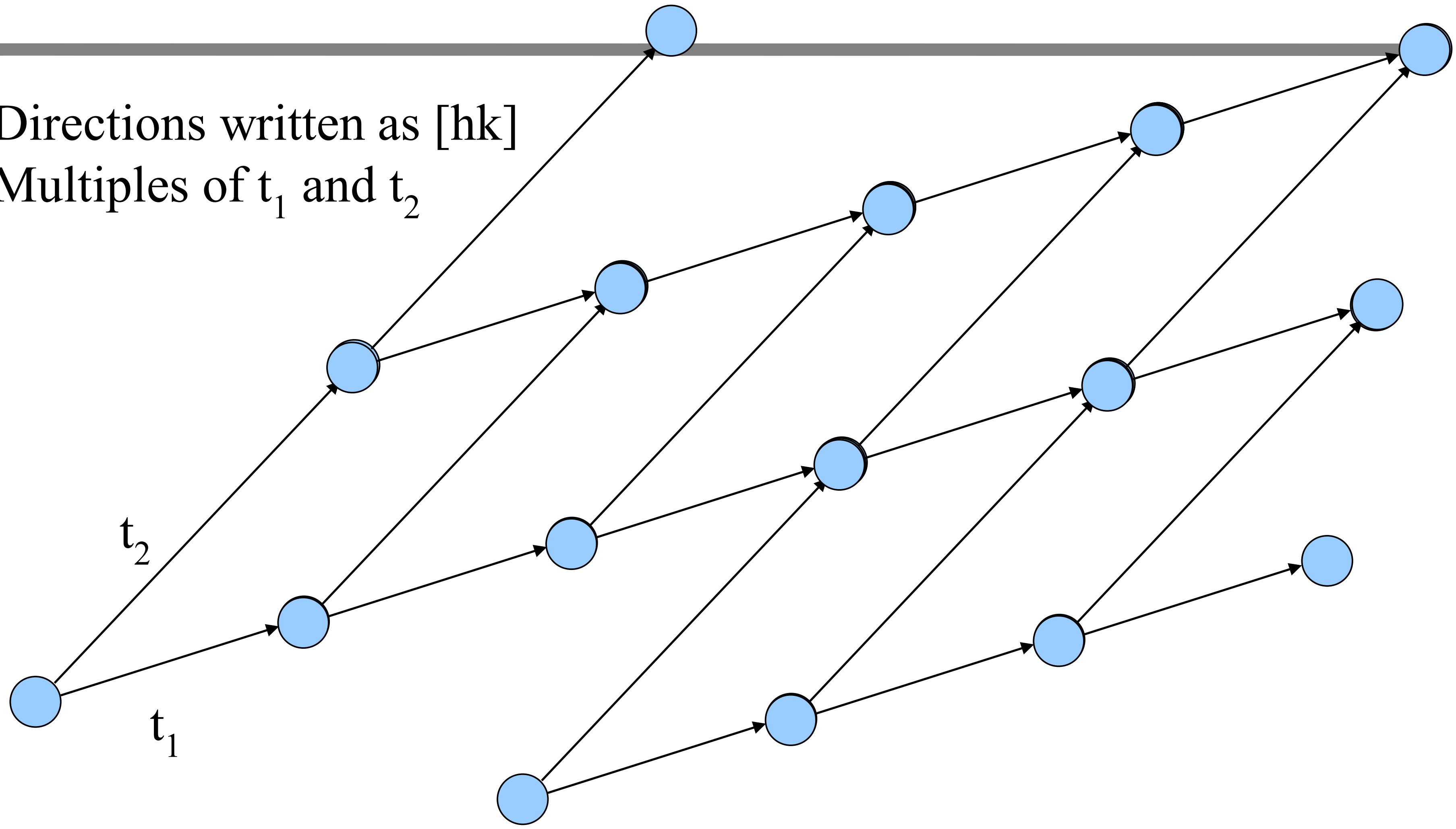


Choosing Unit Cells



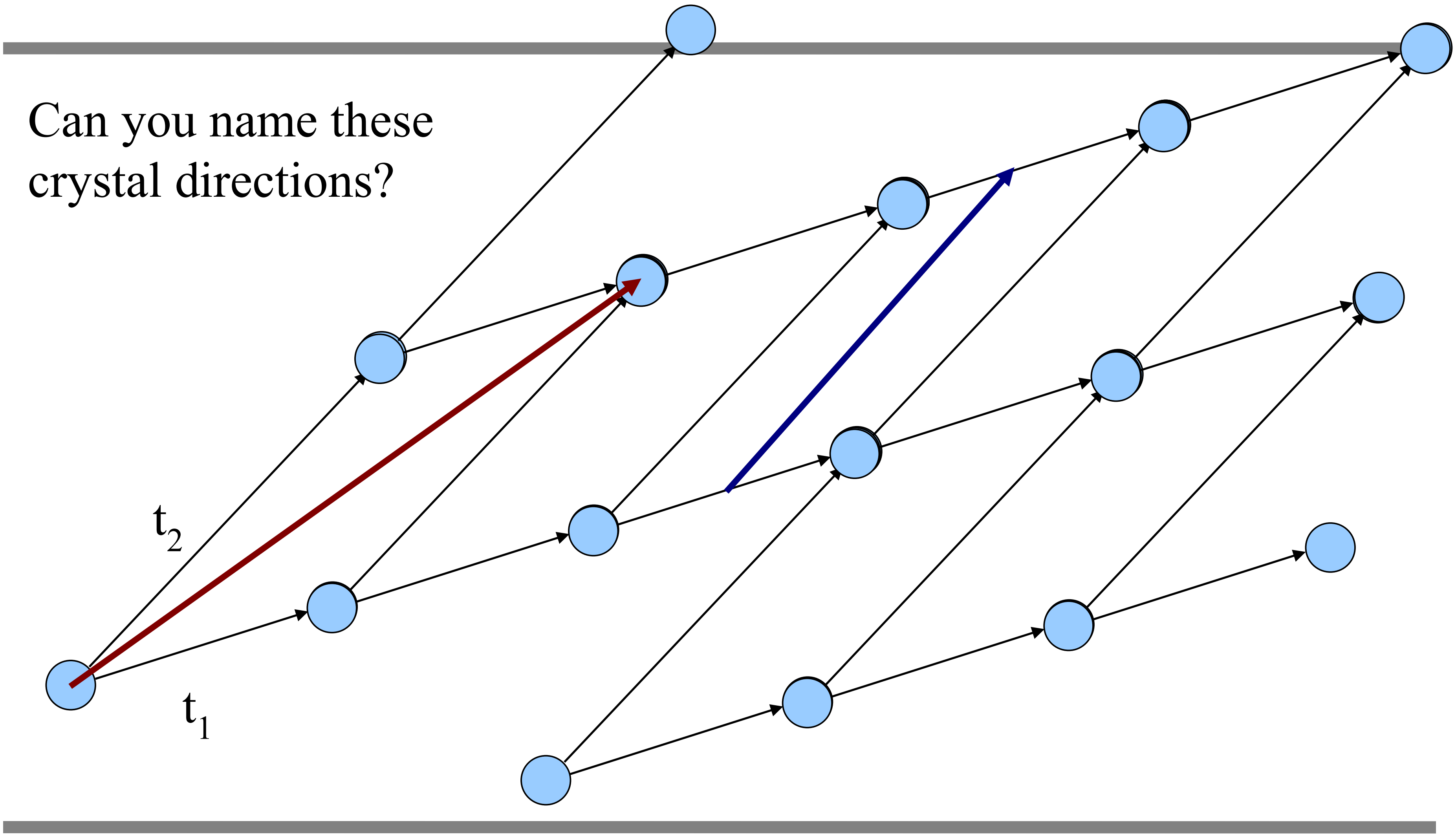
Miller Indices

Directions written as [hk]
Multiples of t_1 and t_2



Miller Indices

Can you name these crystal directions?



Symmetry Operators in 2D

Rotational

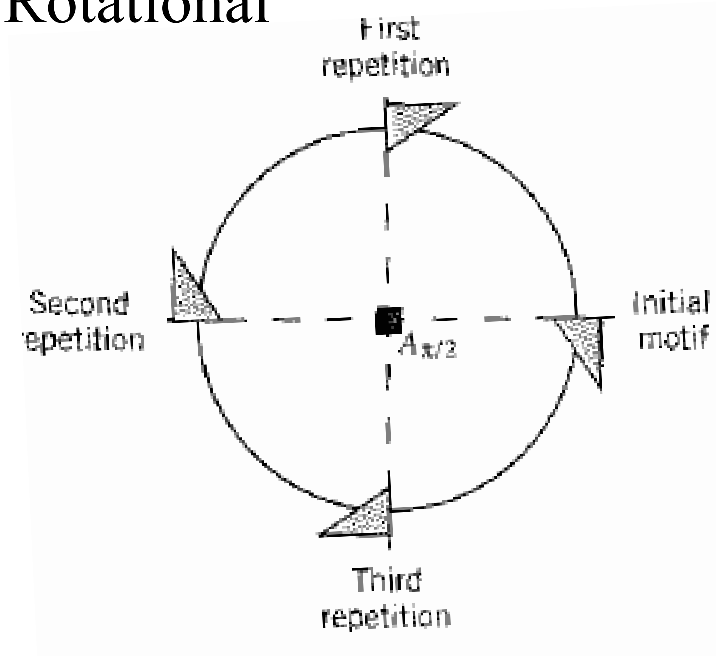


Figure 3.10 Operation of fourfold axis of rotational symmetry $A_{\pi/2}$.

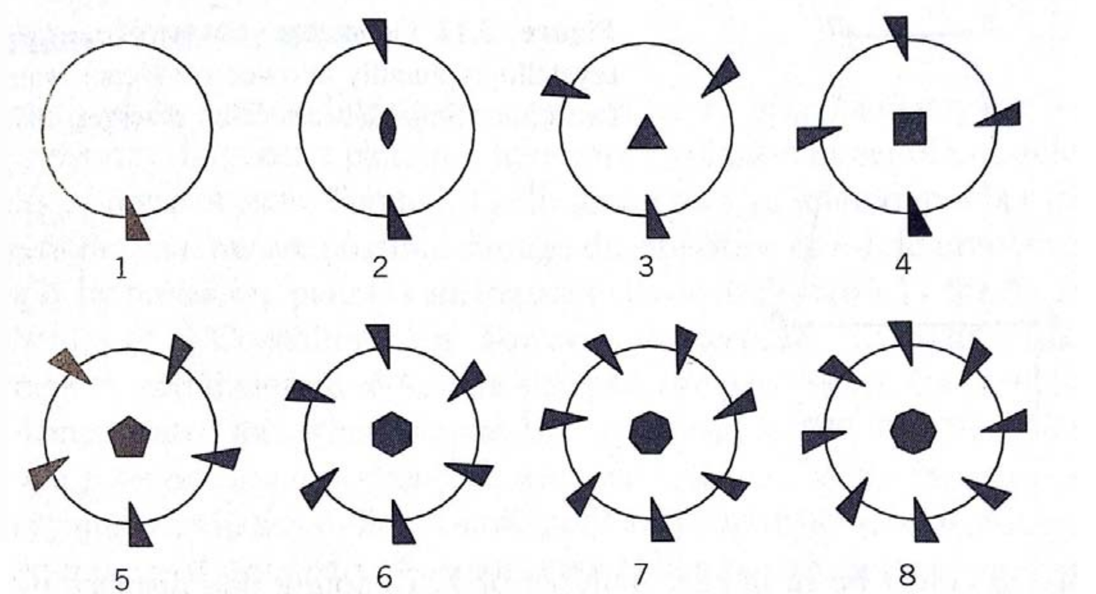
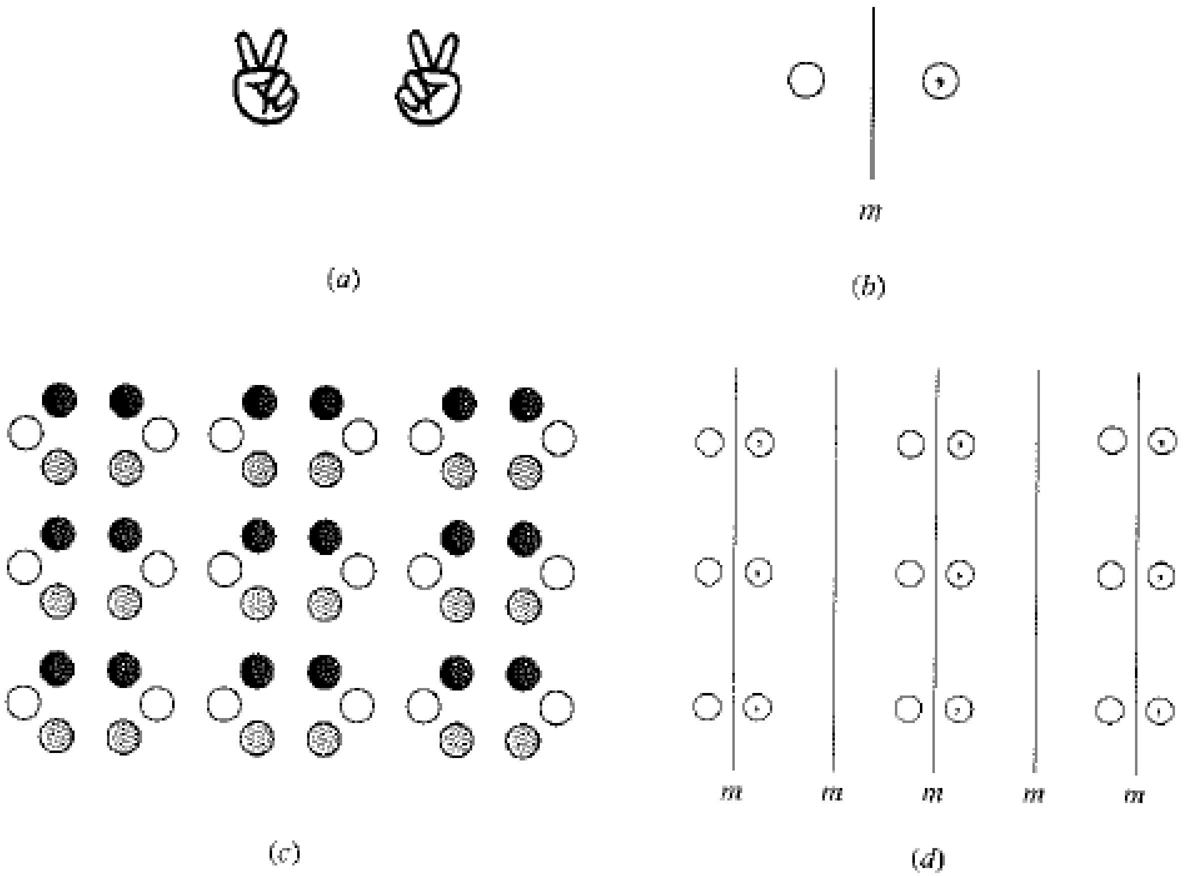


Figure 3.11 Patterns produced by various proper rotation axes.

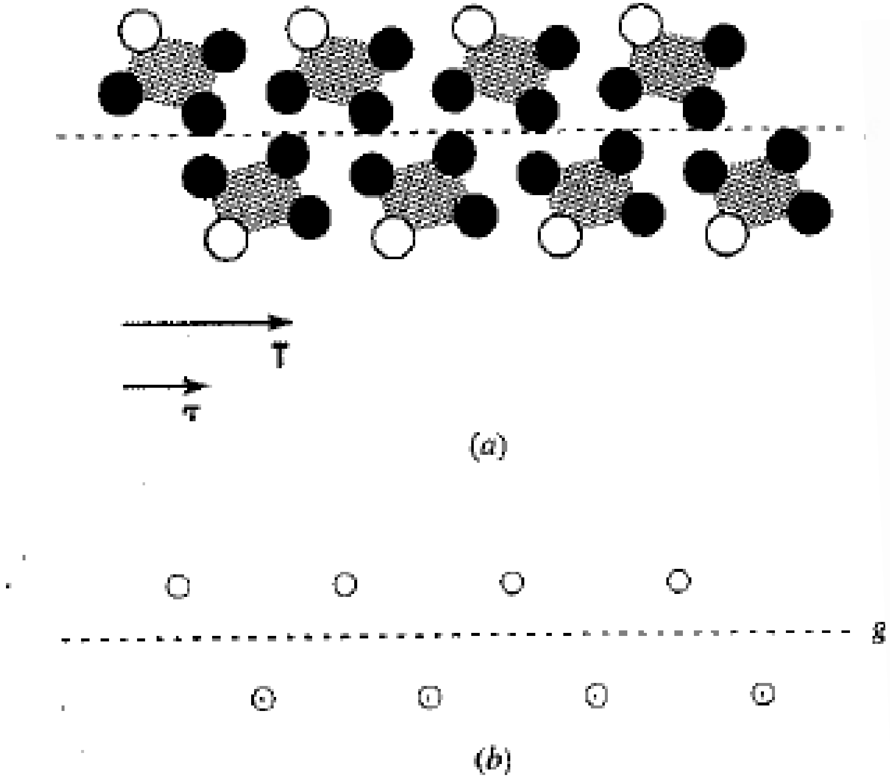
Symmetry Operators in 2D

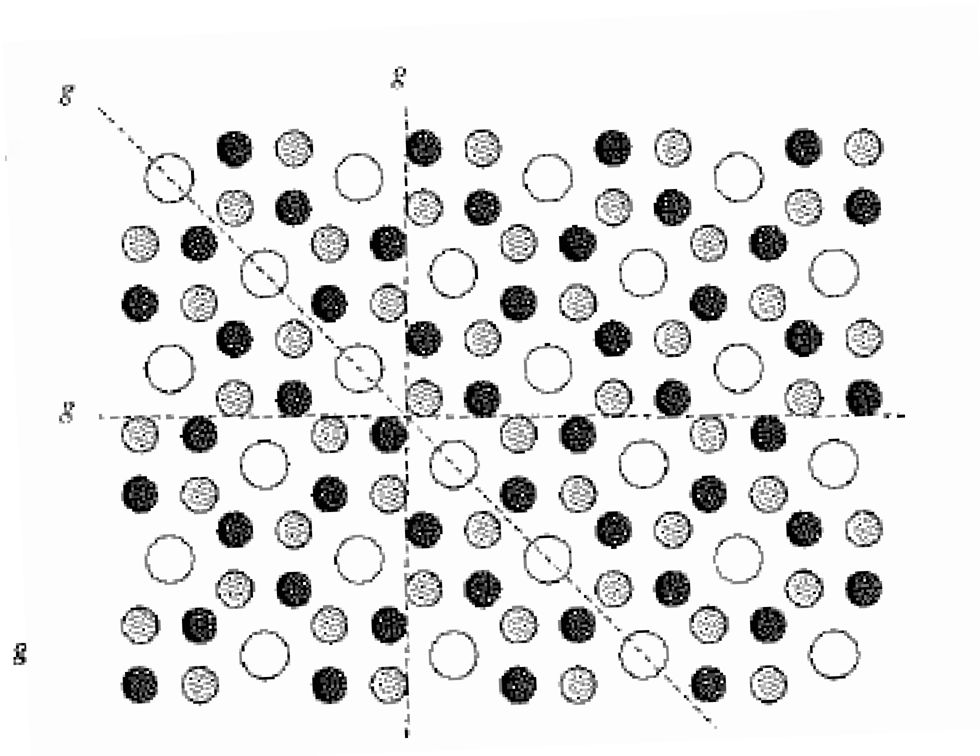
Mirror



Symmetry Operators in 2D

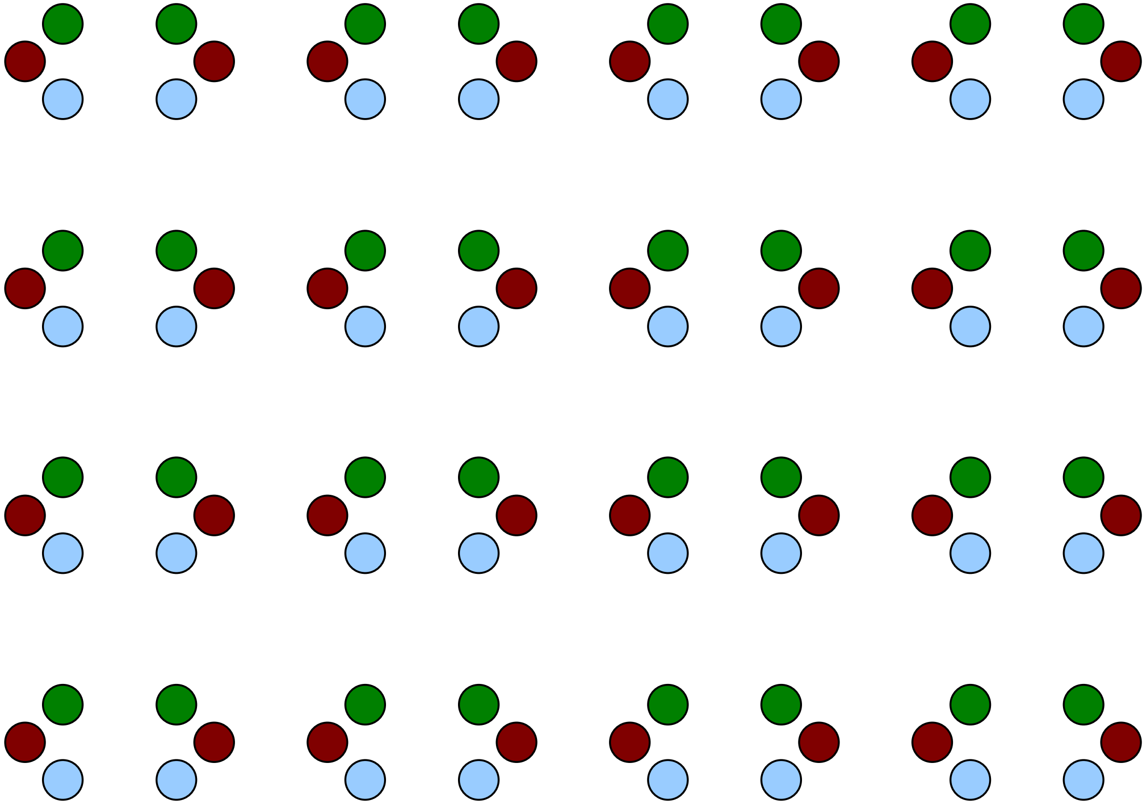
Glide





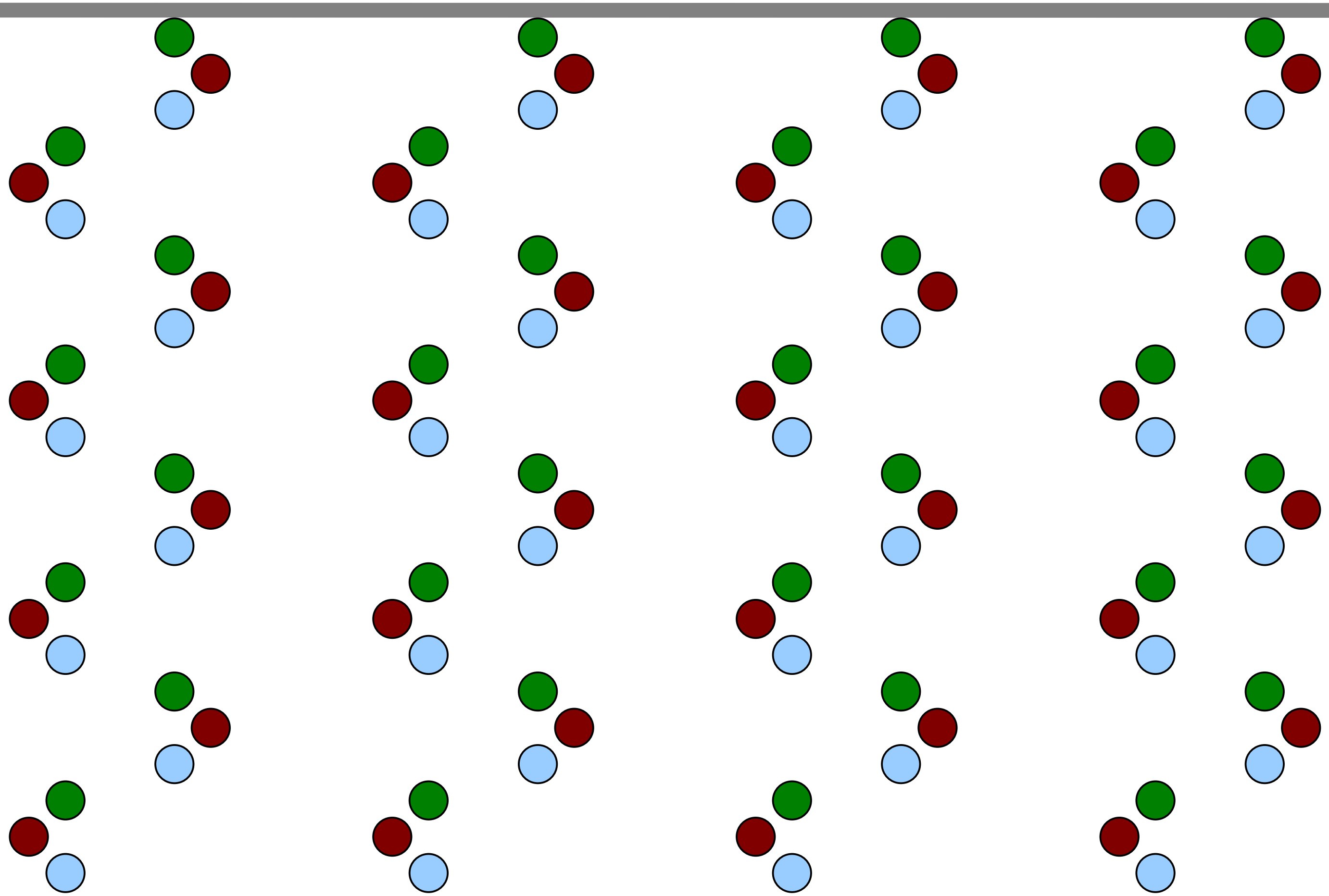
Symmetry Operators in 2D

Mirror

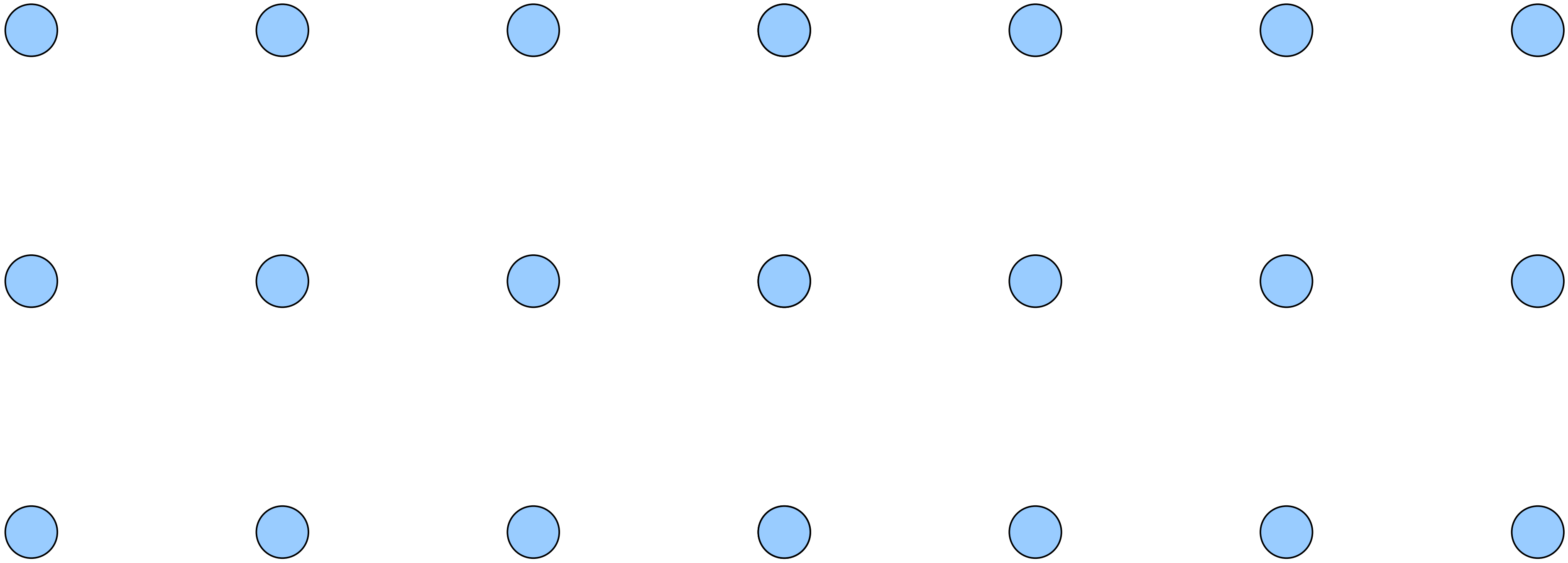


Symmetry Operators in 2D

Glide



Square Lattice Symmetry



Moving to 3D

Four new symmetry operators

- Inversion
- Rotoinversion (rotation & inversion)
- Rotoreflection (rotation & reflection)
- Screw axes (rotation & translation)

Inversion

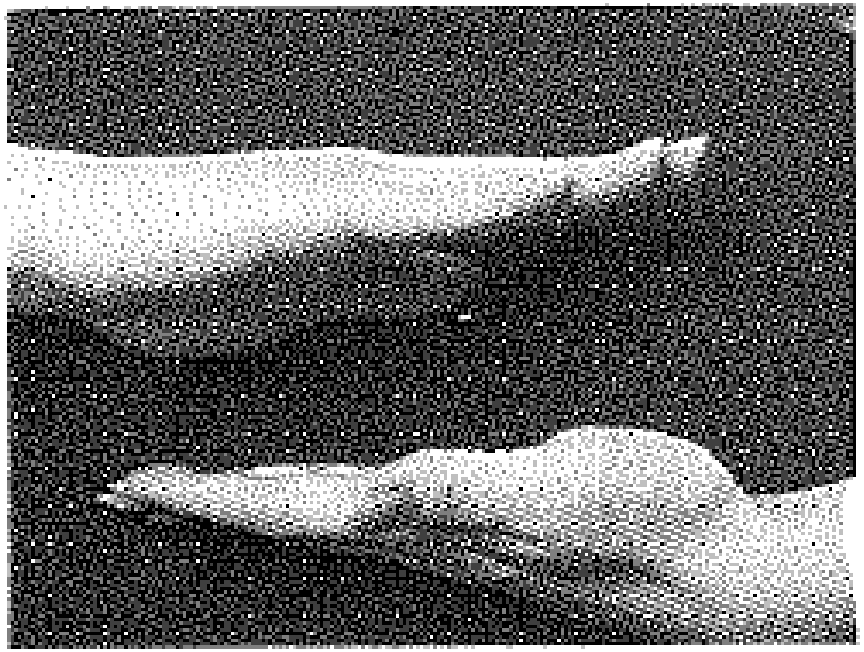


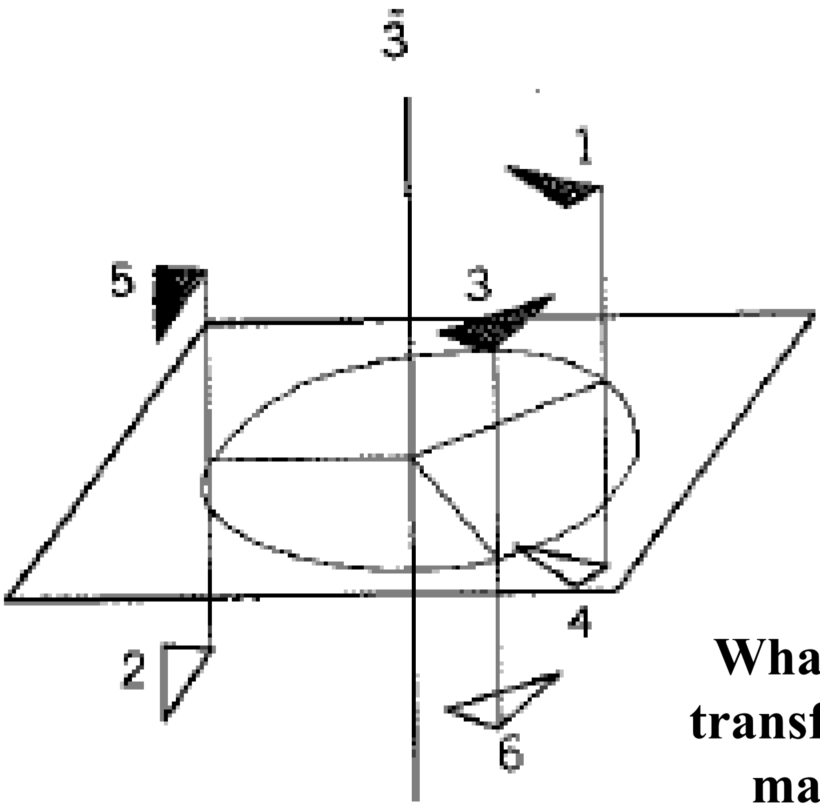
Figure 3.33 An inversion center is created between right and left hands when they are positioned as illustrated.

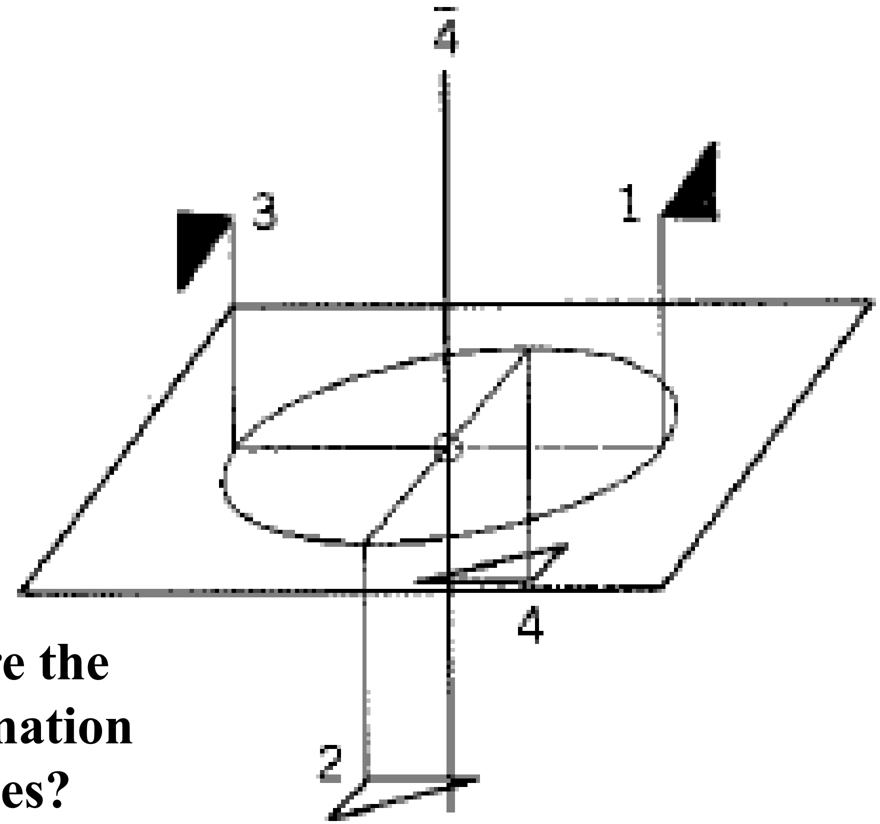
New coordinates

$$\begin{bmatrix} h' \\ k' \\ l' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} h \\ k \\ l \end{bmatrix} = \begin{bmatrix} -h \\ -k \\ -l \end{bmatrix}$$

Transformation matrix **Old coordinates**

Rotoreflection & Rotoinversion





What are the transformation matrices?

Screw Axes

Rotation followed by translation

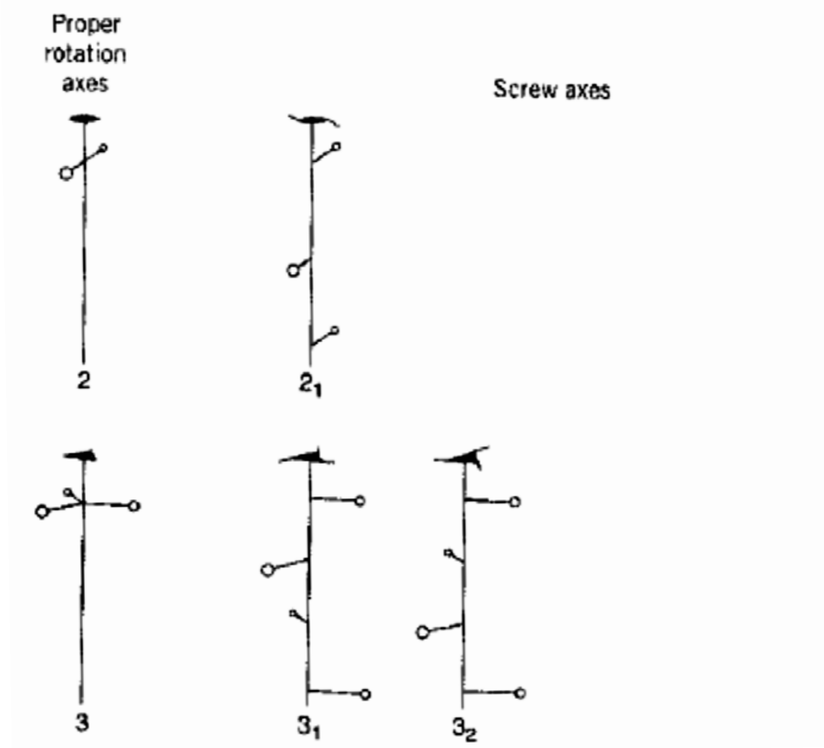


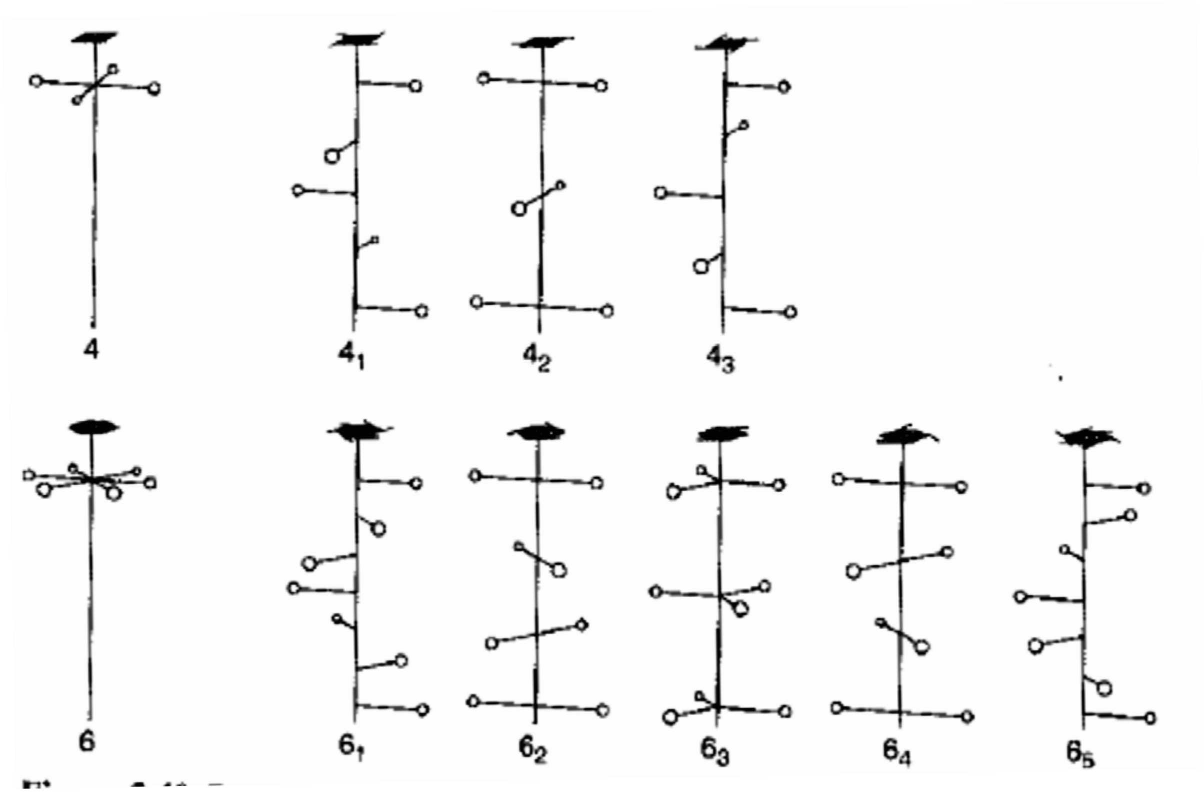
Table 3.3 Allowed Crystallographic Screw Axes

n	Components	Proper Rotation Axes	The Eleven Permissible Crystallographic Screw Axes				
1	α	0 (or 2π)					
	τ	0 (or $\mathbf{T}_{\parallel}$)					
	Designation	1					
2	α	π	π				
	τ	0	$\frac{1}{2}\mathbf{T}_{\parallel}$				
	Designation	2	2_1				
3	α	$\frac{2}{3}\pi$	$\frac{2}{3}\pi$	$\frac{2}{3}\pi$			
	τ	0	$\frac{1}{3}\mathbf{T}_{\parallel}$	$\frac{2}{3}\mathbf{T}_{\parallel}$			
	Designation	3	3_1	3_2			
4	α	$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	$\frac{1}{2}\pi$		
	τ	0	$\frac{1}{4}\mathbf{T}_{\parallel}$	$\frac{2}{4}\mathbf{T}_{\parallel}$	$\frac{3}{4}\mathbf{T}_{\parallel}$		
	Designation	4	4_1	4_2	4_3		
6	α	$\frac{1}{3}\pi$	$\frac{1}{3}\pi$	$\frac{1}{3}\pi$	$\frac{1}{3}\pi$	$\frac{1}{3}\pi$	$\frac{1}{3}\pi$
	τ	0	$\frac{1}{6}\mathbf{T}_{\parallel}$	$\frac{2}{6}\mathbf{T}_{\parallel}$	$\frac{3}{6}\mathbf{T}_{\parallel}$	$\frac{4}{6}\mathbf{T}_{\parallel}$	$\frac{5}{6}\mathbf{T}_{\parallel}$
	Designation	6	6_1	6_2	6_3	6_4	6_5

Source: Buerger, 1978, p. 204.

Screw Axes

Rotation followed by translation



Generalized Rotation Matrix

$$R = \begin{bmatrix} \cos\theta + u_x^2(1-\cos\theta) & u_x u_y(1-\cos\theta) - u_z\sin\theta & u_x u_z(1-\cos\theta) + u_y\sin\theta \\ u_y u_x(1-\cos\theta) + u_z\sin\theta & \cos\theta + u_y^2(1-\cos\theta) & u_y u_z(1-\cos\theta) - u_x\sin\theta \\ u_z u_x(1-\cos\theta) - u_y\sin\theta & u_z u_y(1-\cos\theta) + u_x\sin\theta & \cos\theta + u_z^2(1-\cos\theta) \end{bmatrix}$$

Or more concisely:

$$R = \cos\theta \mathbf{I} + \sin\theta [\mathbf{u}]_\times + (1-\cos\theta)\mathbf{u}\otimes\mathbf{u},$$

Where (u_x, u_y, u_z) is a unit vector

Miller Indices in 3D

Directions – [hkl]

Families of directions – <hkl>

Planes – (hkl)

Families of planes – {hkl}

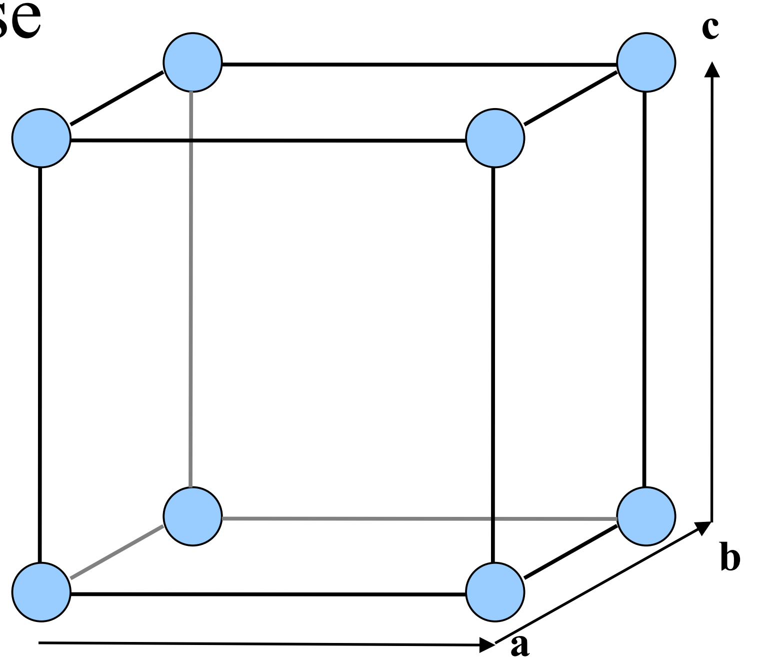
Explore Some Examples

Done in class, using Crystalmaker

Miller Indices – Lattice Parameter

Here, a=b =c

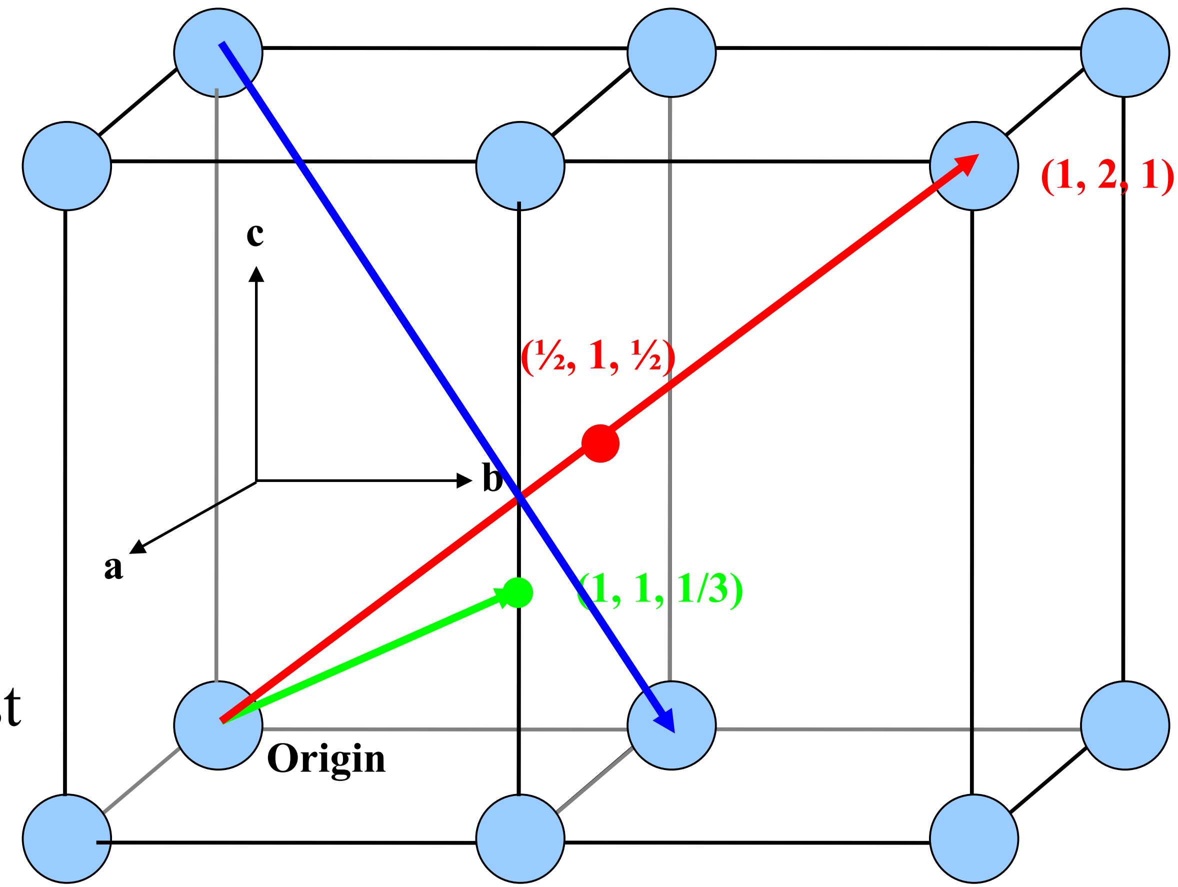
– Not always the case



Miller Indices – Directions

Drawing directions inside unit cell:

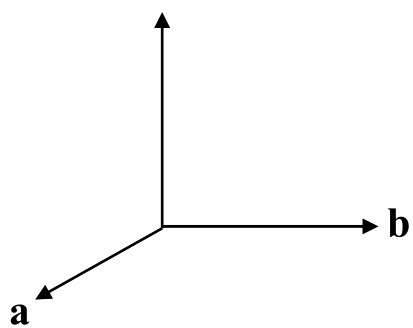
- [121]
- [01$\bar{1}$] ($\bar{1}$ means negative
- [331]
    - Divide so largest index = 1 to get intercepts

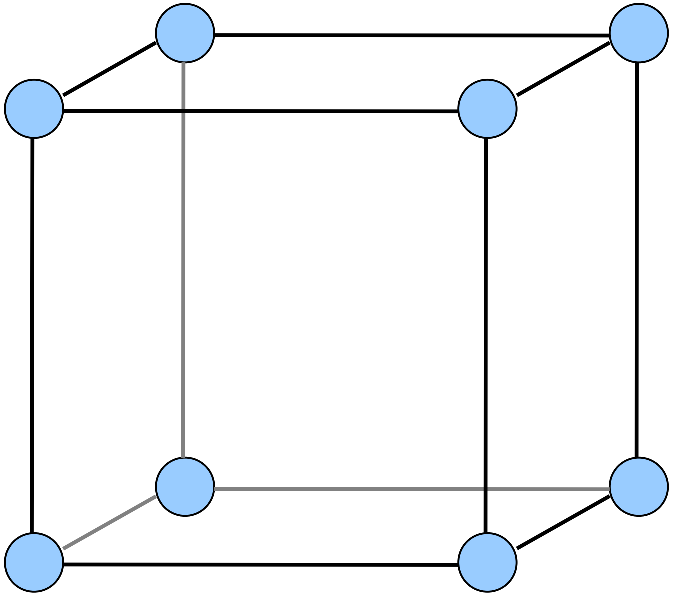


Miller Indices – Direction Examples

Draw the following directions:

- [001]
- $[00\bar{1}]$
- [250]
- $[1\bar{1}1]$
- [441]
- [632]
- [633]

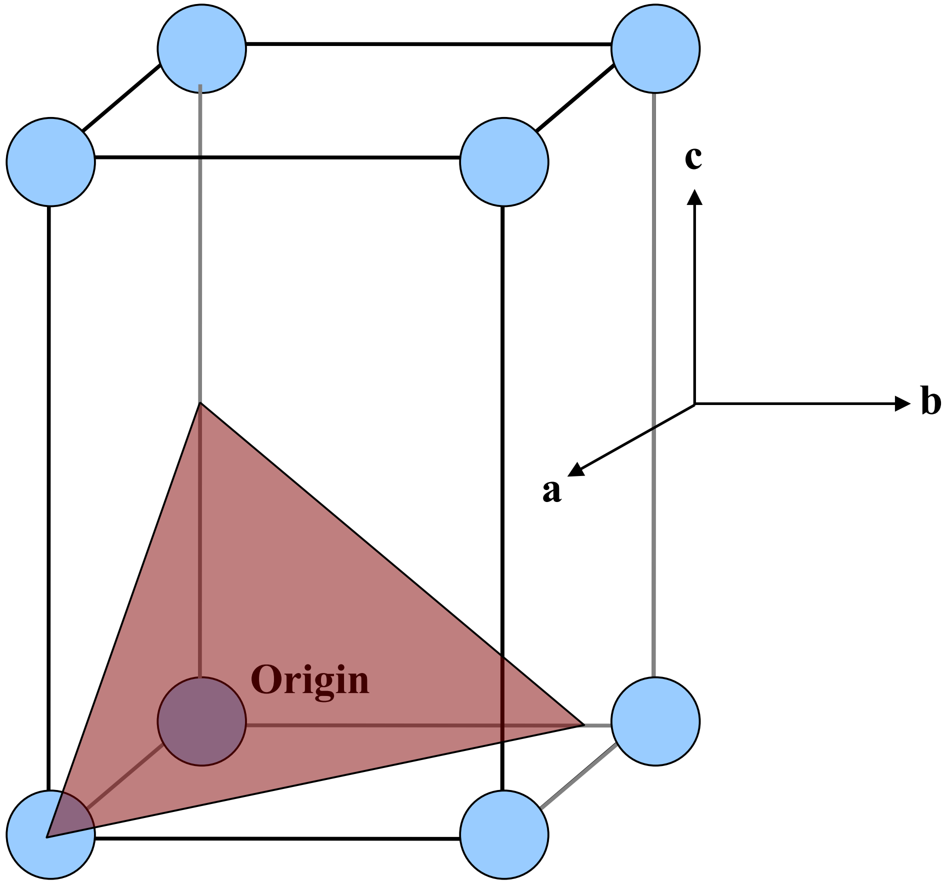




Miller Indices – Planes

Example:

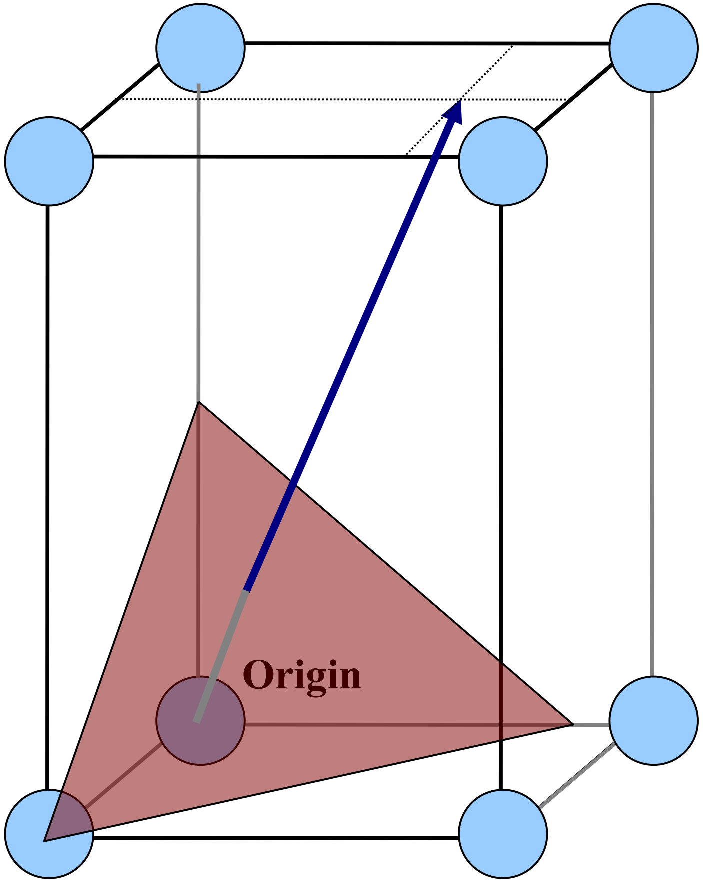
- **(234)**
  - Take reciprocals of indices (½, 1/3, ¼)
  - Multiply so largest index is one (1, 2/3, ½)
  - These are the plane intercepts on lattice axes

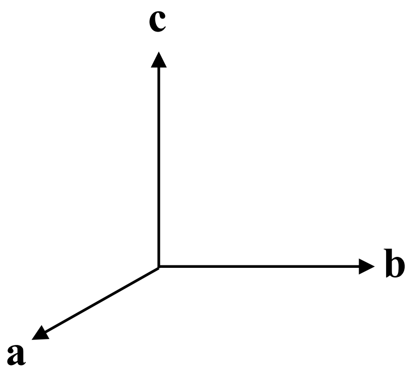


Miller Indices – Directions and Planes

Example:

- (234)
- [234]

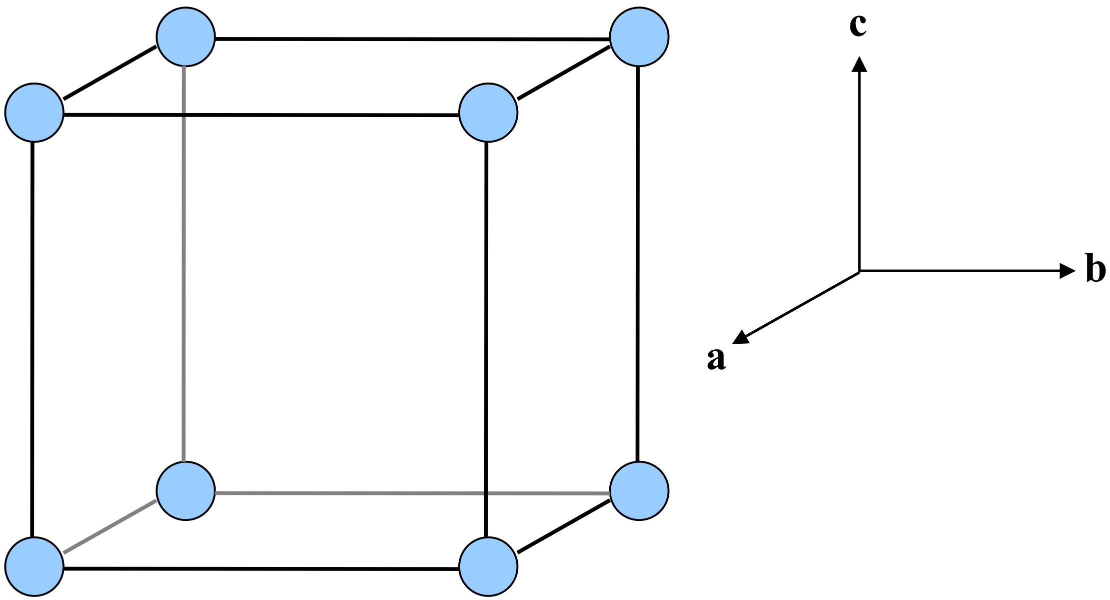




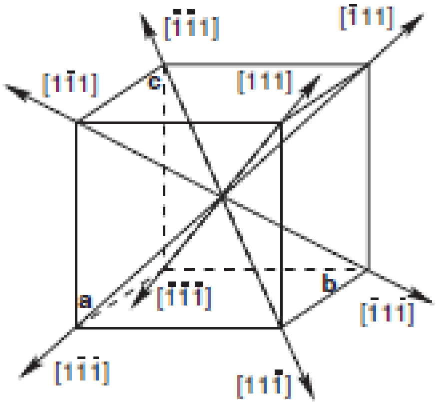
Miller Indices – Plane Examples

Draw the following planes:

- (001)
- (001)
- (251)
- (111)
- (441)
- (632)
- (633)



Families of Directions & Planes



Family of [111] directions

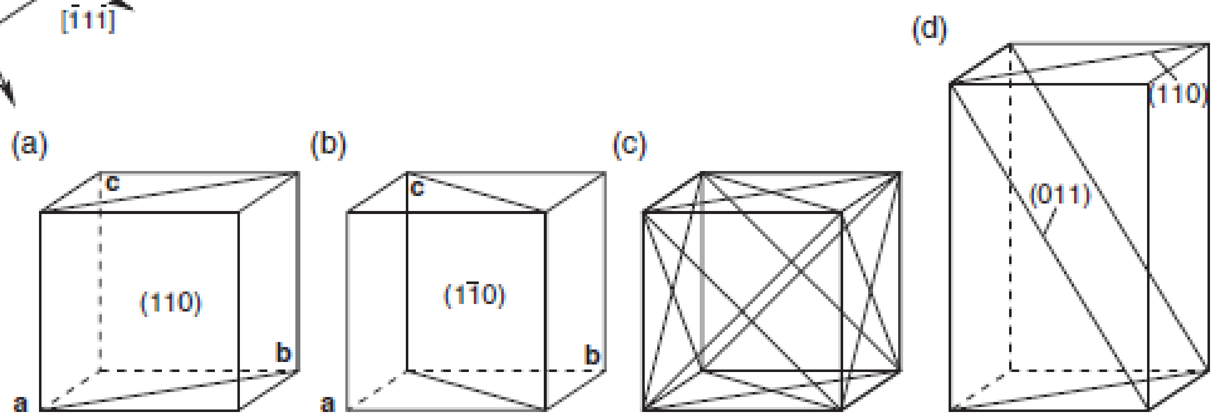
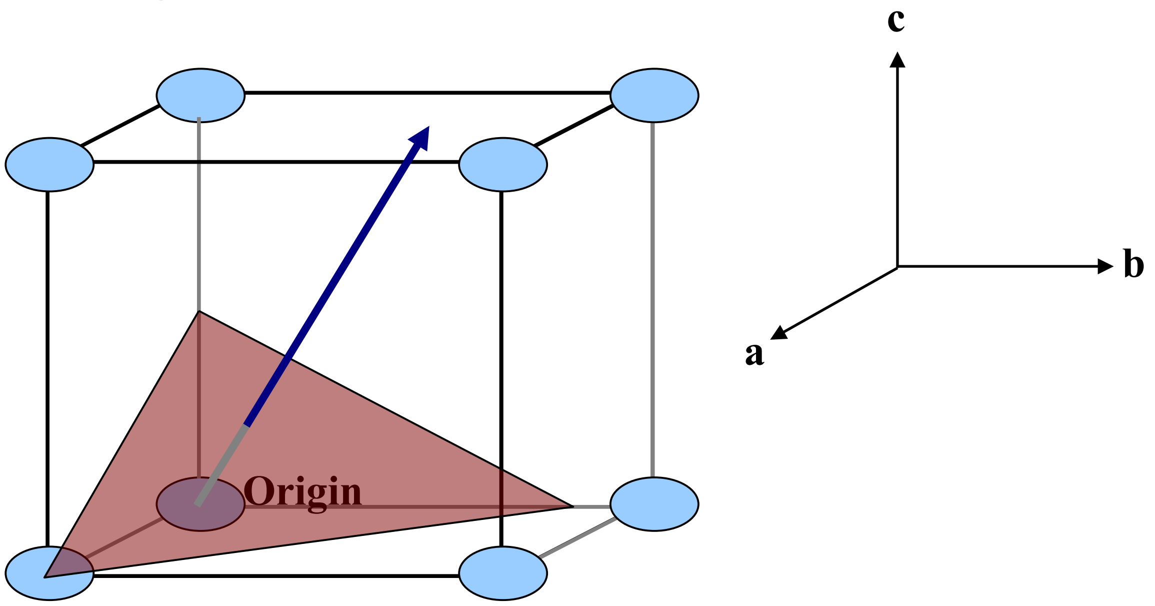


Figure 5.4 Equivalence of the {110} planes in a cubic crystal; in (d) the lattice is tetragonally distorted, and the (110) and (101) planes are no longer equivalent.

Miller Indices – Directions and Planes

In a cubic lattice directions are normal to planes. Example:

- (234)
- [234]

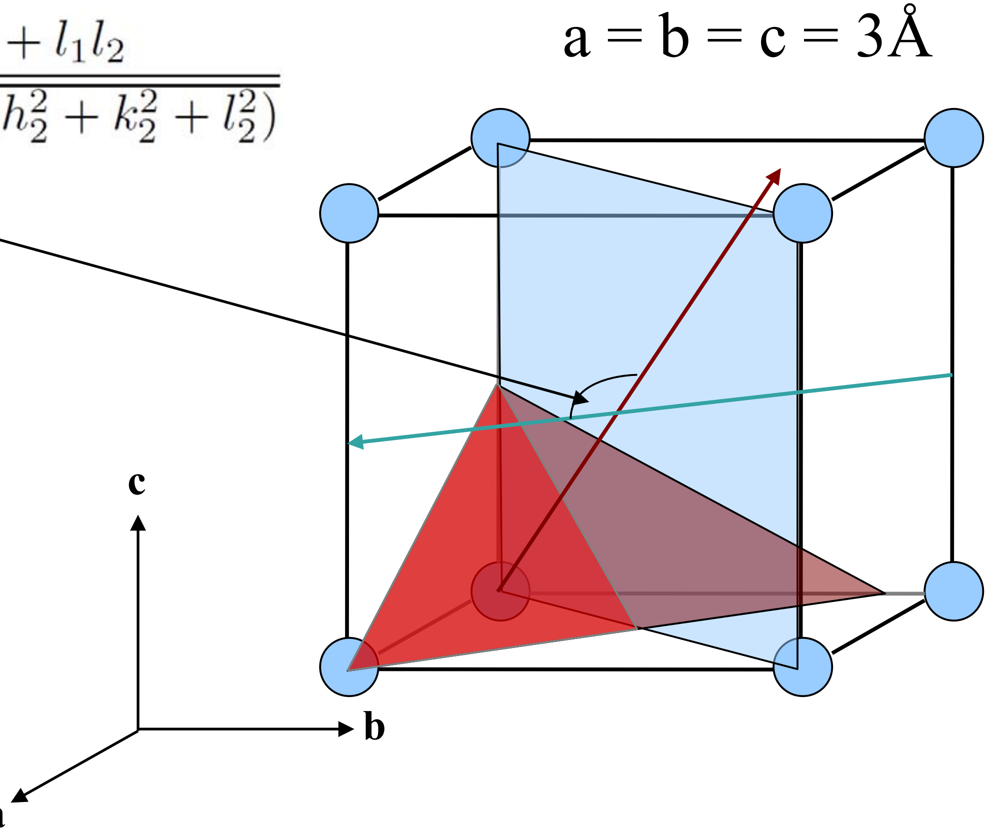


Miller Indices – Angle Between Planes in a Cubic Lattice

$$cos\,(\phi) = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)}\sqrt{(h_2^2 + k_2^2 + l_2^2)}}$$

Example:

- (234)
- (110)
  - **97.55 degrees**



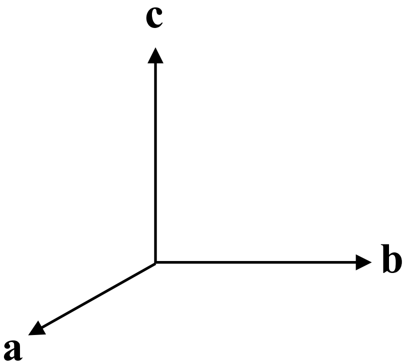
Miller Indices – Angle Between Planes in a Non-Cubic Lattice

<u>Multiply vectors by lattice constants</u>

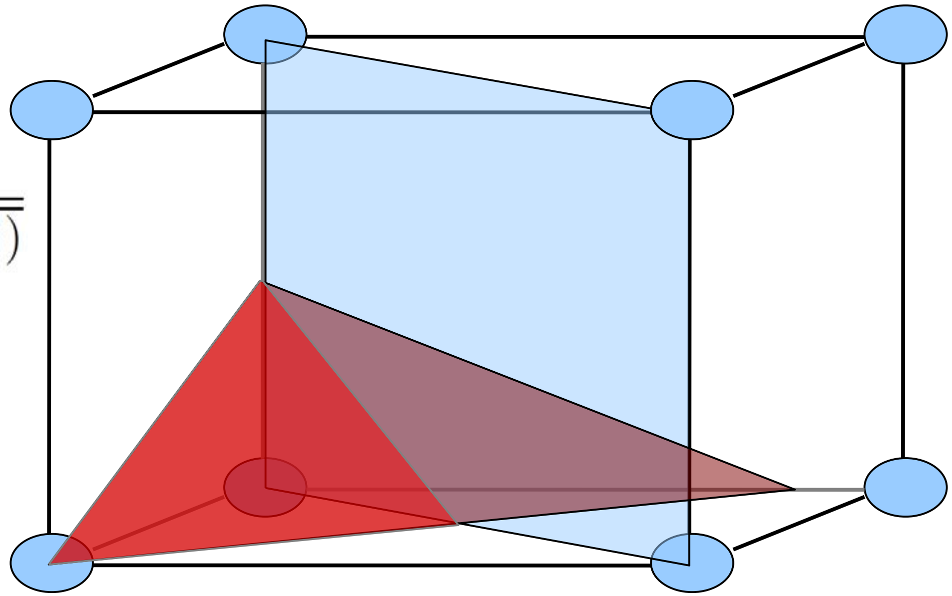
$$cos\left(\phi\right) = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)}\sqrt{(h_2^2 + k_2^2 + l_2^2)}}$$

Example:

- (234)
- (110)
  - **108.44 degrees**



a = c = 3Å, b = 5Å



Miller Indices – Directions Common to Planes

Direction [uvw] common to planes $(h_1k_1l_1)$ and $h_2k_2l_2)$:

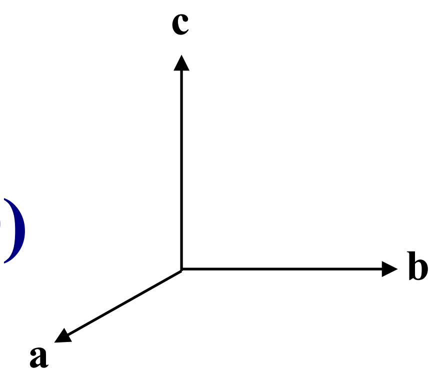
$$u = k_1 l_2 - l_1 k_2 \qquad v = l_1 h_2 - h_1 l_2 \qquad w = h_1 k_2 - k_1 h_2$$

Check the *Weiss Zone Law*:

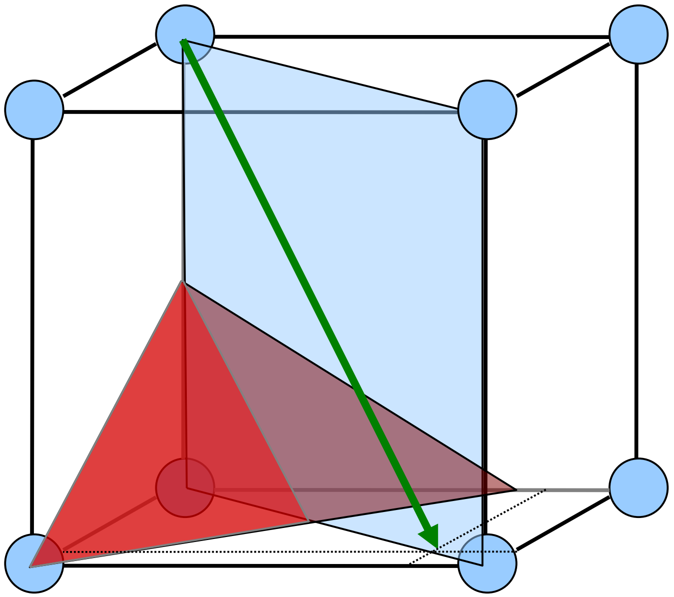
$$hu + kv + lw = 0$$

Example:

- (234) and (110)
  - [4,4,5]



a = b = c = 3Å



Bravais Lattices

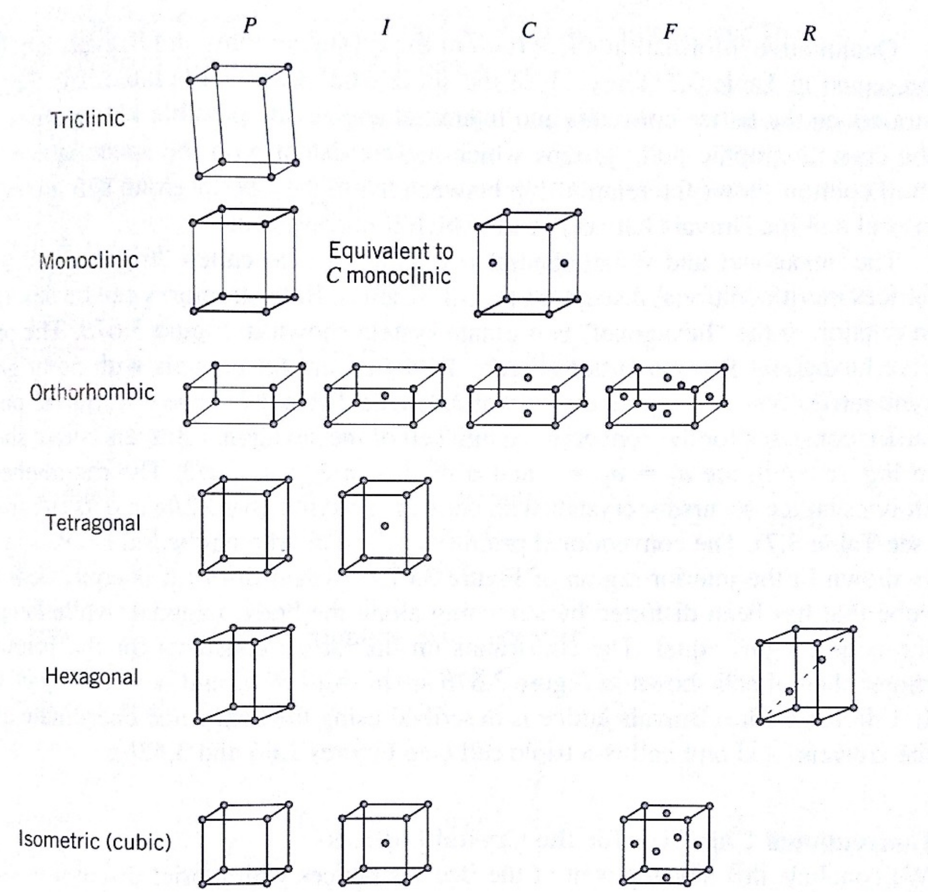


Figure 3.66 The fourteen Bravais lattices and the six crystal systems.

1) Characterize these systems in terms of a, b, c, and angles

2) Why is body-centered monoclinic equivalent to base-centered monoclinic?

Packing Fraction

This slide intentionally left blank...

done in class!

Space Groups

Unique combinations of symmetry, denoted by certain symbols

Find them in:

The Int'l Tables for Crystallography

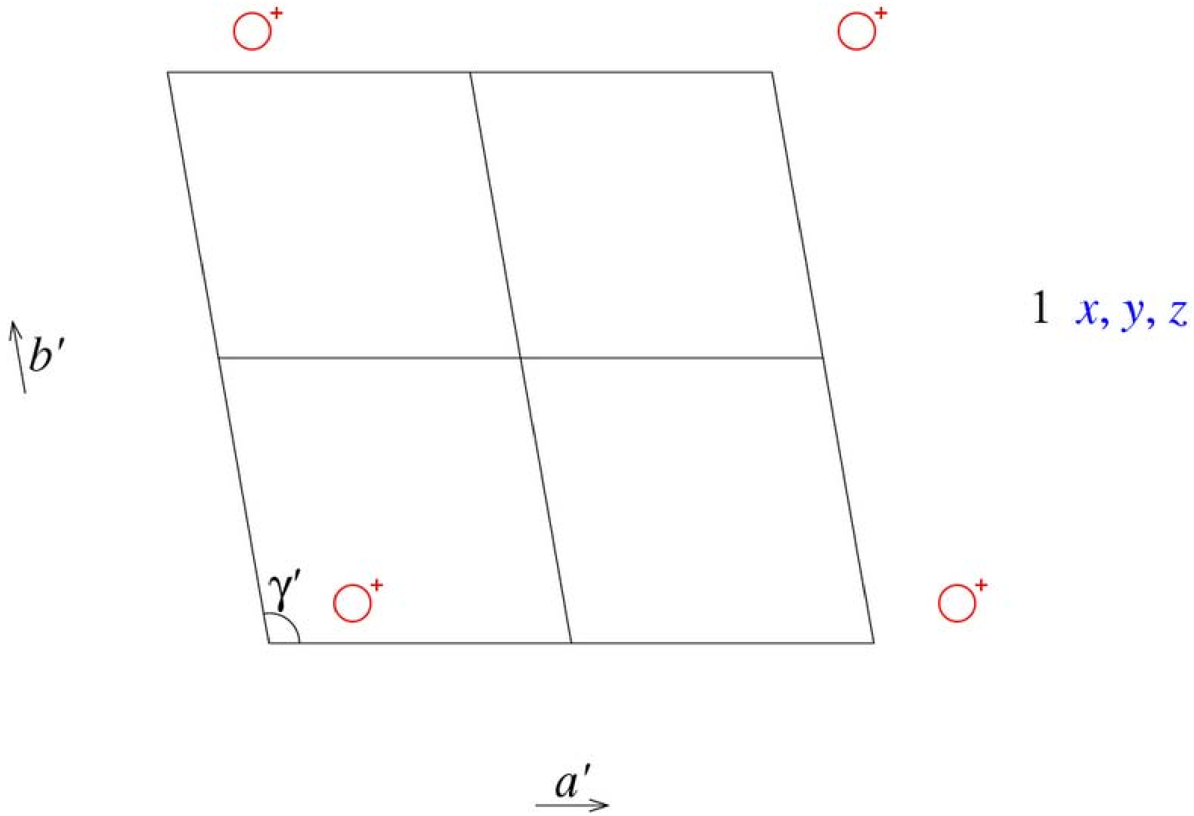
http://it.iucr.org/

Or for free at the University College of London:

http://img.chem.ucl.ac.uk/sgp/large/sgp.htm

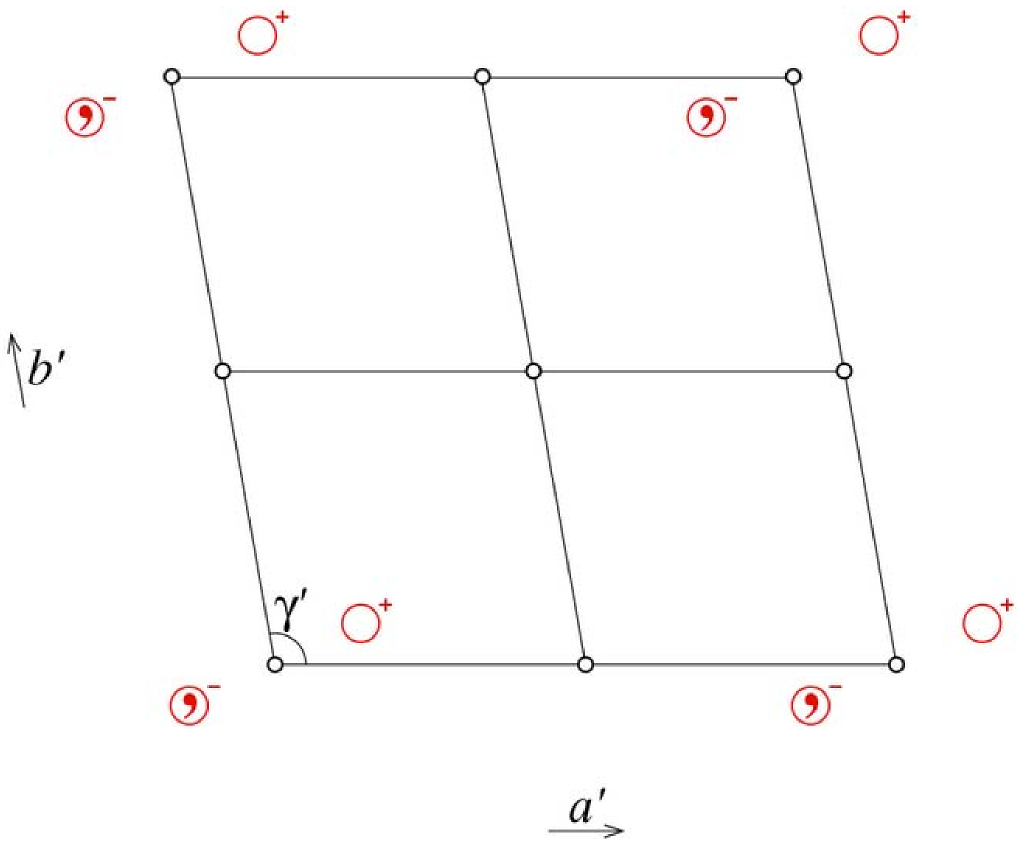
Example: Triclinic (P1)

http://img.chem.ucl.ac.uk/sgp/large/sgp.htm



Example: Triclinic ($P\bar{1}$)

http://img.chem.ucl.ac.uk/sgp/large/sgp.htm



1 x, y, z

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

Example Space Groups

http://img.chem.ucl.ac.uk/sgp/large/sgp.htm

178. $P\ 6_1\ 2\ 2$	179. $P\ 6_5\ 2\ 2$	180. $P\ 6_2\ 2\ 2$	181. $P\ 6_4\ 2\ 2$	182. $P\ 6_3\ 2\ 2$
183. $P\ 6\ m\ m$	184. $P\ 6\ c\ c$	185. $P\ 6_3\ c\ m$	186. $P\ 6_3\ m\ c$	187. $P\ \text{-}6\ m\ 2$
188. $P\ \text{-}6\ c\ 2$	189. $P\ \text{-}6\ 2\ m$	190. $P\ \text{-}6\ 2\ c$	191. $P\ 6\ /\ m\ m\ m$	192. $P\ 6\ /\ m\ c\ c$
193. $P\ 6_3\ /\ m\ c\ m$	194. $P\ 6_3\ /\ m\ m\ c$			

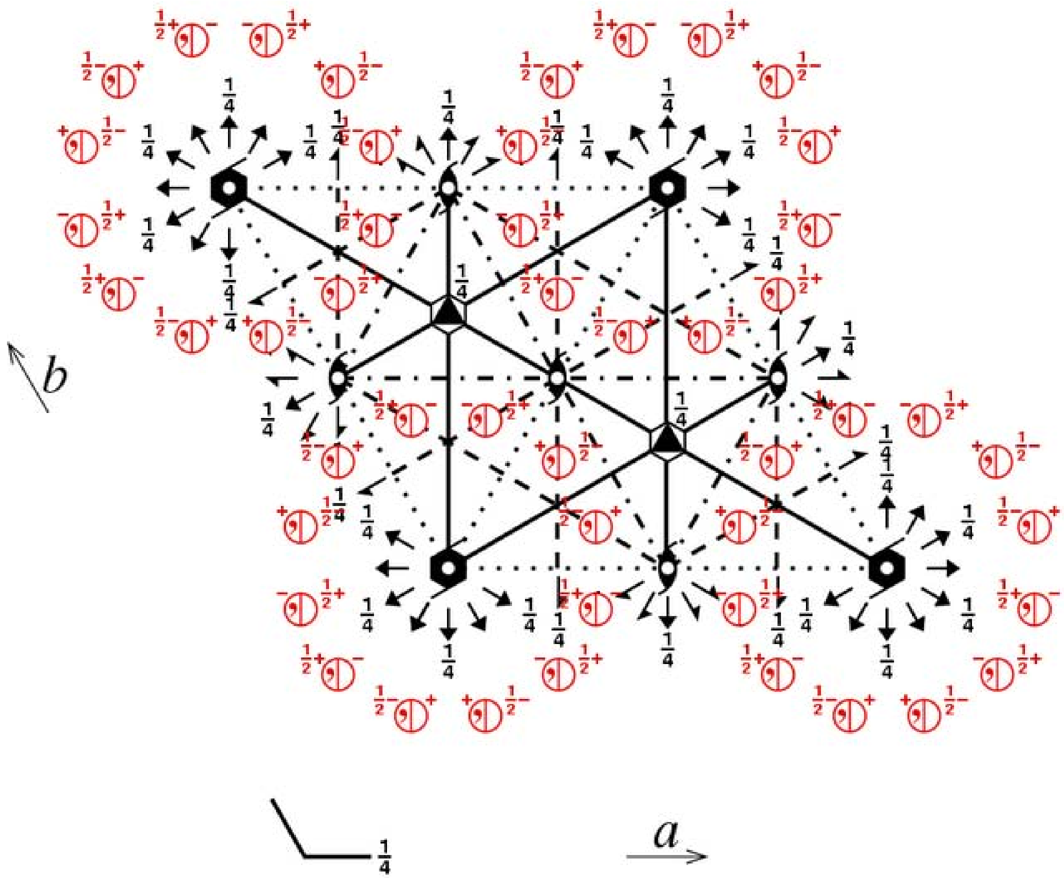
Cubic

195. $P\ 2\ 3$	196. $F\ 2\ 3$	197. $I\ 2\ 3$	198. $P\ 2_1\ 3$	199. $I\ 2_1\ 3$
200. $P\ m\ \text{-}3$	201. $P\ n\ \text{-}3$	202. $F\ m\ \text{-}3$	203. $F\ d\ \text{-}3$	204. $I\ m\ \text{-}3$
205. $P\ a\ \text{-}3$	206. $I\ a\ \text{-}3$	207. $P\ 4\ 3\ 2$	208. $P\ 4_2\ 3\ 2$	209. $F\ 4\ 3\ 2$
210. $F\ 4_1\ 3\ 2$	211. $I\ 4\ 3\ 2$	212. $P\ 4_3\ 3\ 2$	213. $P\ 4_1\ 3\ 2$	214. $I\ 4_1\ 3\ 2$
215. $P\ \text{-}4\ 3\ m$	216. $F\ \text{-}4\ 3\ m$	217. $I\ \text{-}4\ 3\ m$	218. $P\ \text{-}4\ 3\ n$	219. $F\ \text{-}4\ 3\ c$

http://img.chem.ucl.ac.uk/sgp/large/sgp.htm

$P6_3/mmc$

$P6_3/mmc$ *$P\,6_3/m\;2/m\;2/c$* *$6/mmm$* No. 194



1 x, y, z
2 $\bar{y}, x-y, z$
3 $\bar{x}+y, \bar{x}, z$
4 $\bar{x}, \bar{y}, \frac{1}{2}+z$
5 $x-y, x, \frac{1}{2}+z$
6 $y, \bar{x}+y, \frac{1}{2}+z$
7 $\bar{y}, \bar{x}, z$
8 $\bar{x}+y, y, z$
9 $x, x-y, z$
10 $y, x, \frac{1}{2}+z$
11 $x-y, \bar{y}, \frac{1}{2}+z$
12 $\bar{x}, \bar{x}+y, \frac{1}{2}+z$
13 $\bar{x}, \bar{y}, \bar{z}$
14 $y, \bar{x}+y, \bar{z}$
15 $x-y, x, \bar{z}$
16 $x, y, \frac{1}{2}-z$
17 $\bar{x}+y, \bar{x}, \frac{1}{2}-z$
18 $\bar{y}, x-y, \frac{1}{2}-z$
19 $y, x, \bar{z}$
20 $x-y, \bar{y}, \bar{z}$
21 $\bar{x}, \bar{x}+y, \bar{z}$
22 $\bar{y}, \bar{x}, \frac{1}{2}-z$
23 $\bar{x}+y, y, \frac{1}{2}-z$
24 $x, x-y, \frac{1}{2}-z$

Example Space Groups

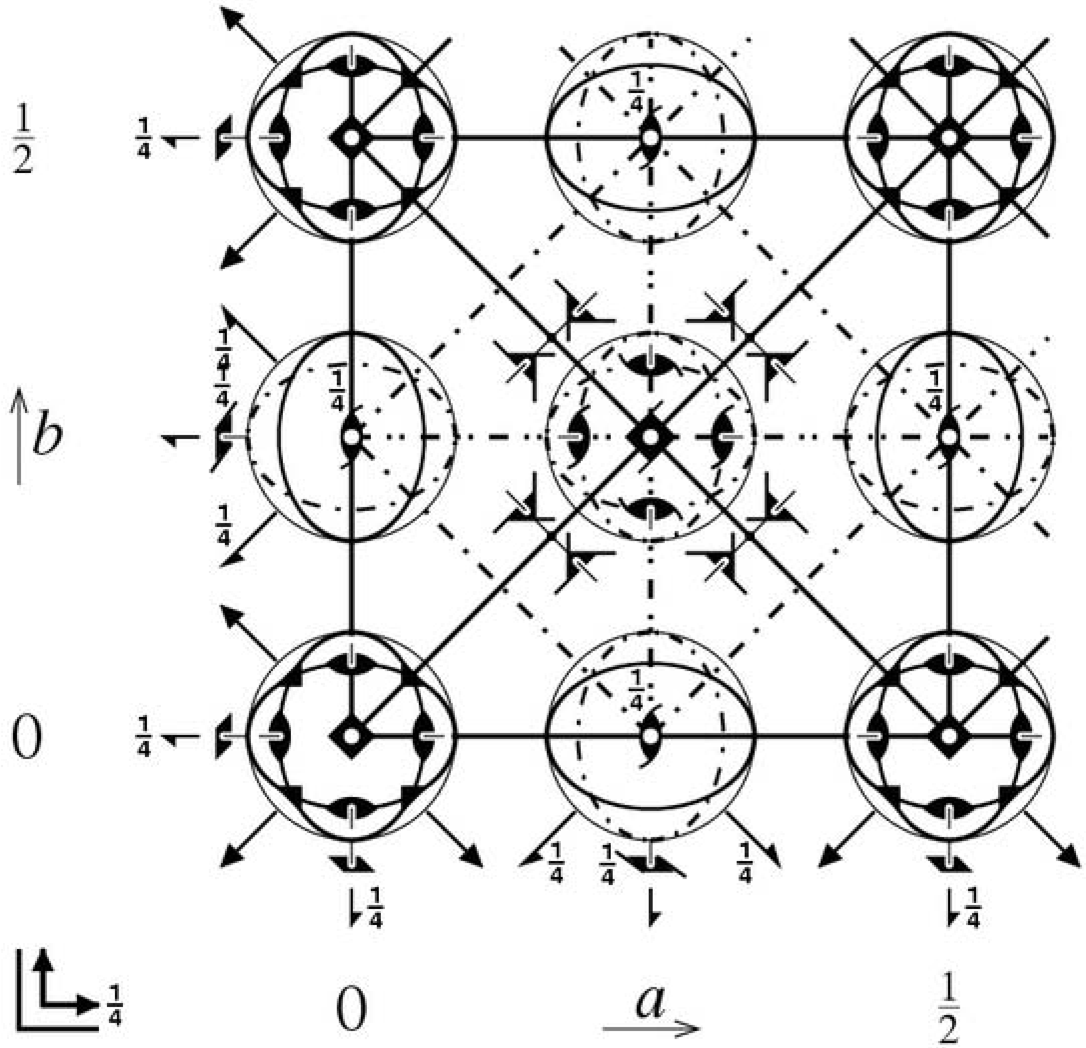
http://img.chem.ucl.ac.uk/sgp/large/sgp.htm

188. P -6 c 2	189. P -6 2 m	190. P -6 2 c	191. P 6 / m m m	192. P 6 / m c c
193. P 6_3 / m c m	194. P 6_3 / m m c			

Cubic

195. P 2 3	196. F 2 3	197. I 2 3	198. P 2_1 3	199. I 2_1 3
200. P m -3	201. P n -3	202. F m -3	203. F d -3	204. I m -3
205. P a -3	206. I a -3	207. P 4 3 2	208. P 4_2 3 2	209. F 4 3 2
210. F 4_1 3 2	211. I 4 3 2	212. P 4_3 3 2	213. P 4_1 3 2	214. I 4_1 3 2
215. P -4 3 m	216. F -4 3 m	217. I -4 3 m	218. P -4 3 n	219. F -4 3 c
220. I -4 3 d	221. P m -3 m	222. P n -3 n	223. P m -3 n	224. P n -3 m
225. F m -3 m	226. F m -3 c	227. F d -3 m	228. F d -3 c	229. I m -3 m
230. I a -3 d				

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



1	x, y, z	25	$\bar{x}, \bar{y}, \bar{z}$
2	$x, \bar{y}, \bar{z}$	26	$\bar{x}, y, z$
3	$\bar{x}, y, \bar{z}$	27	$x, \bar{y}, z$
4	$\bar{x}, \bar{y}, z$	28	$x, y, \bar{z}$
5	z, x, y	29	$\bar{z}, \bar{x}, \bar{y}$
6	$\bar{z}, \bar{x}, y$	30	$z, x, \bar{y}$
7	$z, \bar{x}, \bar{y}$	31	$\bar{z}, x, y$
8	$\bar{z}, x, \bar{y}$	32	$z, \bar{x}, y$
9	y, z, x	33	$\bar{y}, \bar{z}, \bar{x}$
10	$\bar{y}, z, \bar{x}$	34	$y, \bar{z}, x$
11	$\bar{y}, \bar{z}, x$	35	$y, z, \bar{x}$
12	$y, \bar{z}, \bar{x}$	36	$\bar{y}, z, x$
13	$x, \bar{z}, y$	37	$\bar{x}, z, \bar{y}$
14	$x, z, \bar{y}$	38	$\bar{x}, \bar{z}, y$
15	$\bar{x}, \bar{z}, \bar{y}$	39	x, z, y
16	$\bar{x}, z, y$	40	$x, \bar{z}, \bar{y}$
17	$z, y, \bar{x}$	41	$\bar{z}, \bar{y}, x$
18	$\bar{z}, y, x$	42	$z, \bar{y}, \bar{x}$
19	$\bar{z}, \bar{y}, \bar{x}$	43	z, y, x
20	$z, \bar{y}, x$	44	$\bar{z}, y, \bar{x}$
21	$\bar{y}, x, z$	45	$y, \bar{x}, \bar{z}$
22	$y, \bar{x}, z$	46	$\bar{y}, x, \bar{z}$
23	$\bar{y}, \bar{x}, \bar{z}$	47	y, x, z
24	$y, x, \bar{z}$	48	$\bar{y}, \bar{x}, z$

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

rsity of London.

Explore Some Examples

Done in class, using Crystalmaker