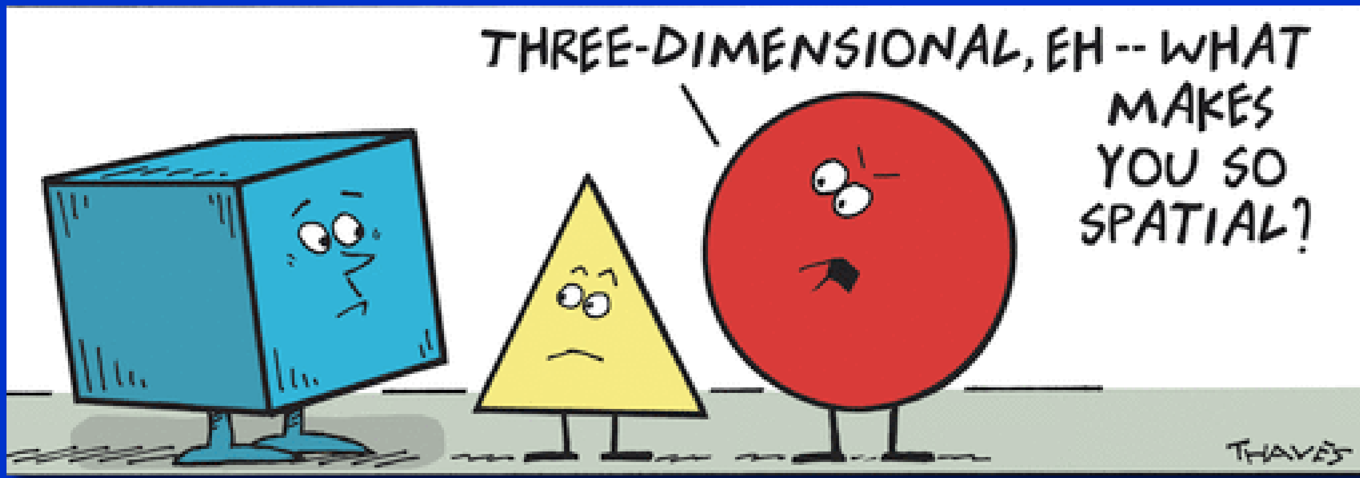


Basic Crystallography for X-ray Diffraction

Earle Ryba

What's this weird thing in the database??? → P63/mcm (193)

orthor

ic

I cubi

2nd sett

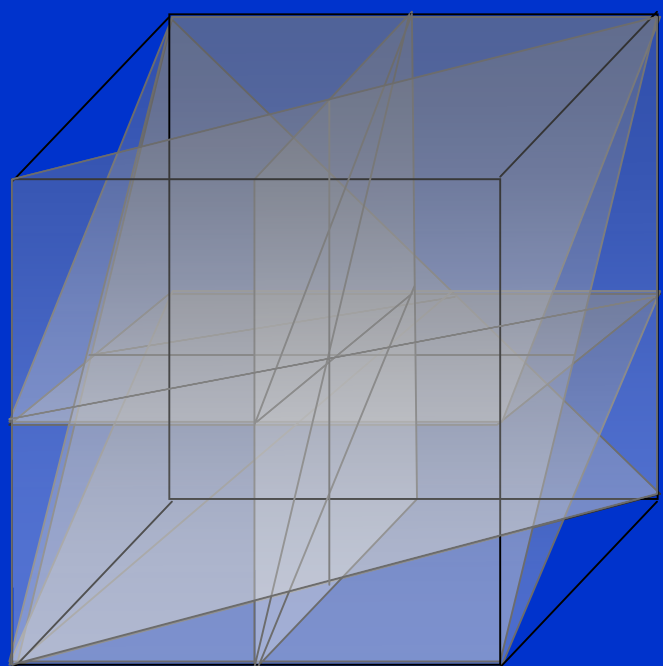
Miller indices

[220]

Bravais latti

Wyckoff positions

And what are these guys???



In X-ray diffraction, use repetition of atom arrangement to get diffraction pattern

Repetition = Symmetry

Repetition = Symmetry

Types of repetition:

Rotation
Translation

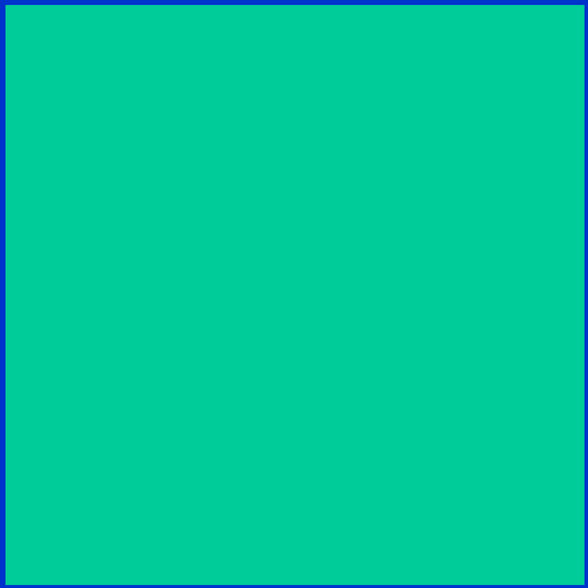
Rotation

What is rotational symmetry?

I can rotate this object

rotate

Please close your eyes while I rotate (maybe) this object

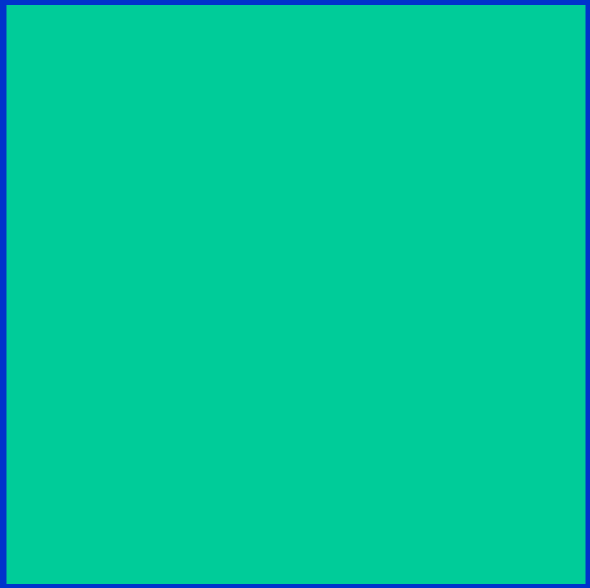


rotate

Did I rotate it?

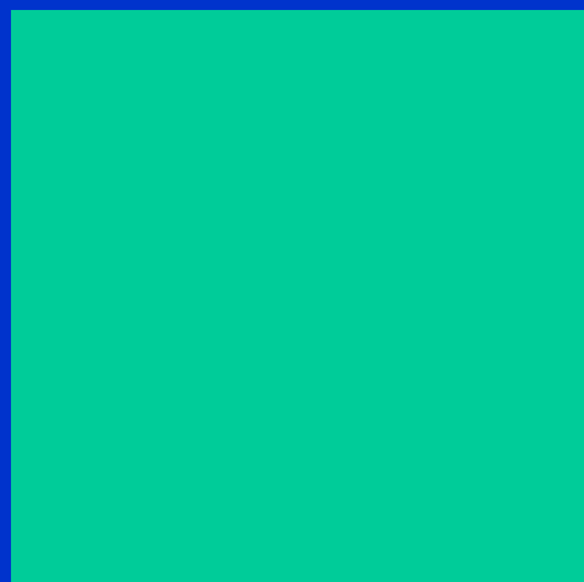
rotate

The object is obviously symmetric…it has symmetry



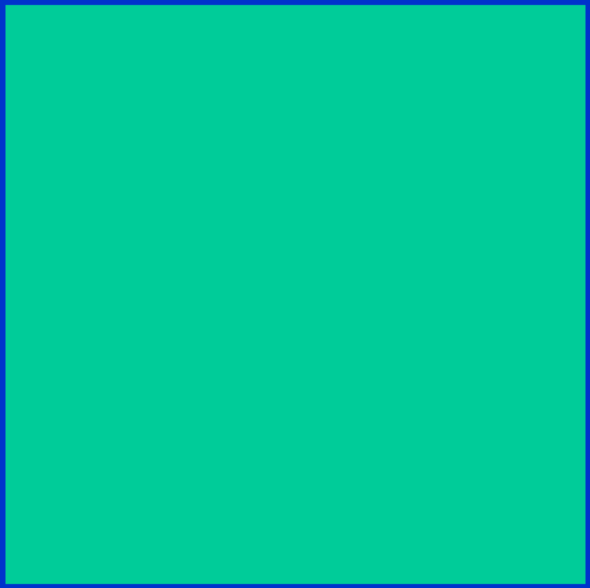
The object is obviously symmetric…it has symmetry

Can be rotated 90° w/o detection

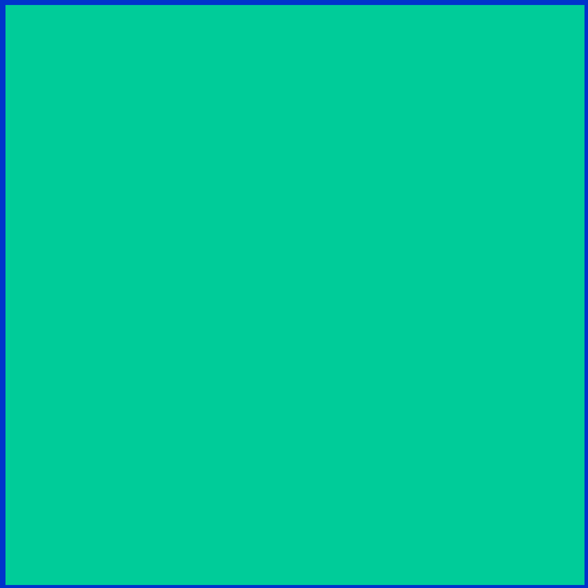


…………so symmetry is really

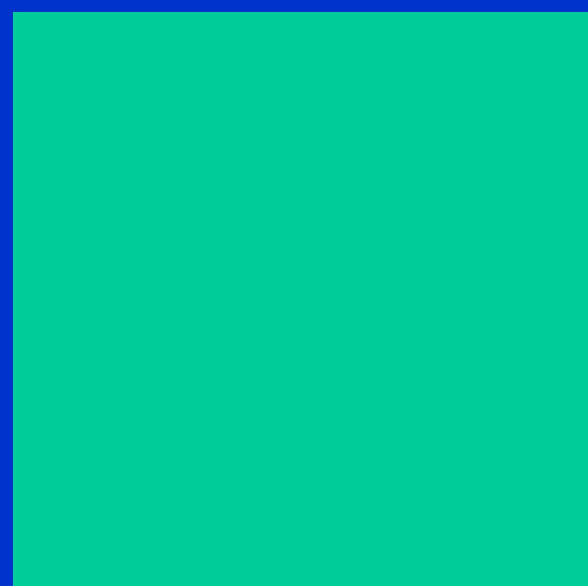
doing nothing



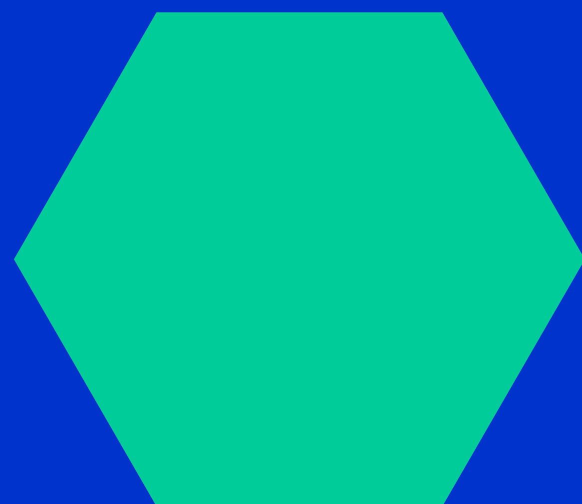
Symmetry is doing nothing - or at least doing something so that it looks like nothing was done!



What kind of symmetry does this object have?



Another example:



And another:

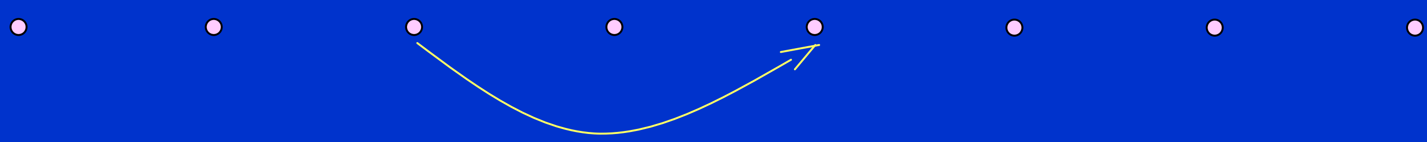
What about translation?

Same as rotation

What about translation?

Same as rotation

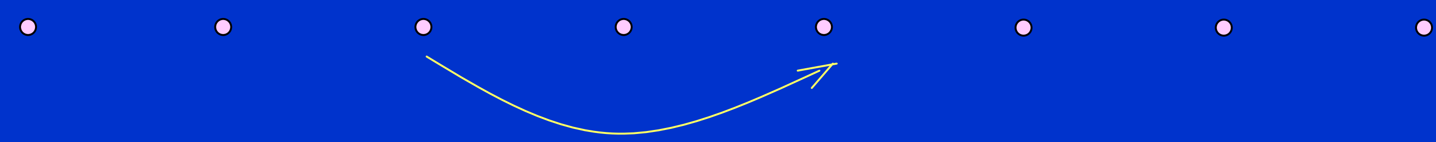
Ex: one dimensional array of points



What about translation?

Same as rotation

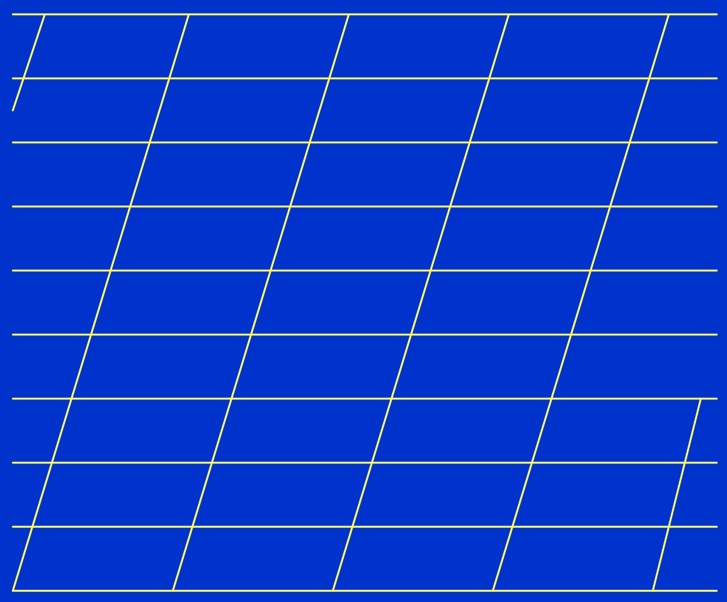
Ex: one dimensional array of points



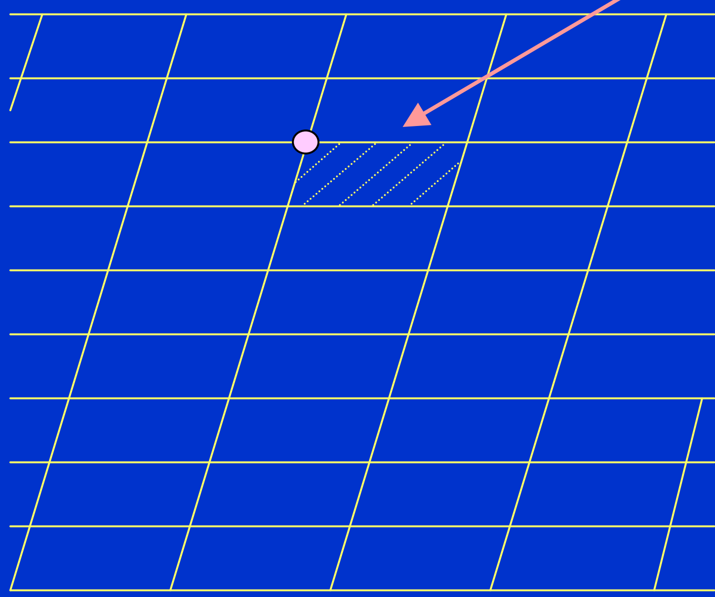
Translations are restricted to only certain values to get symmetry (periodicity)

2D translations

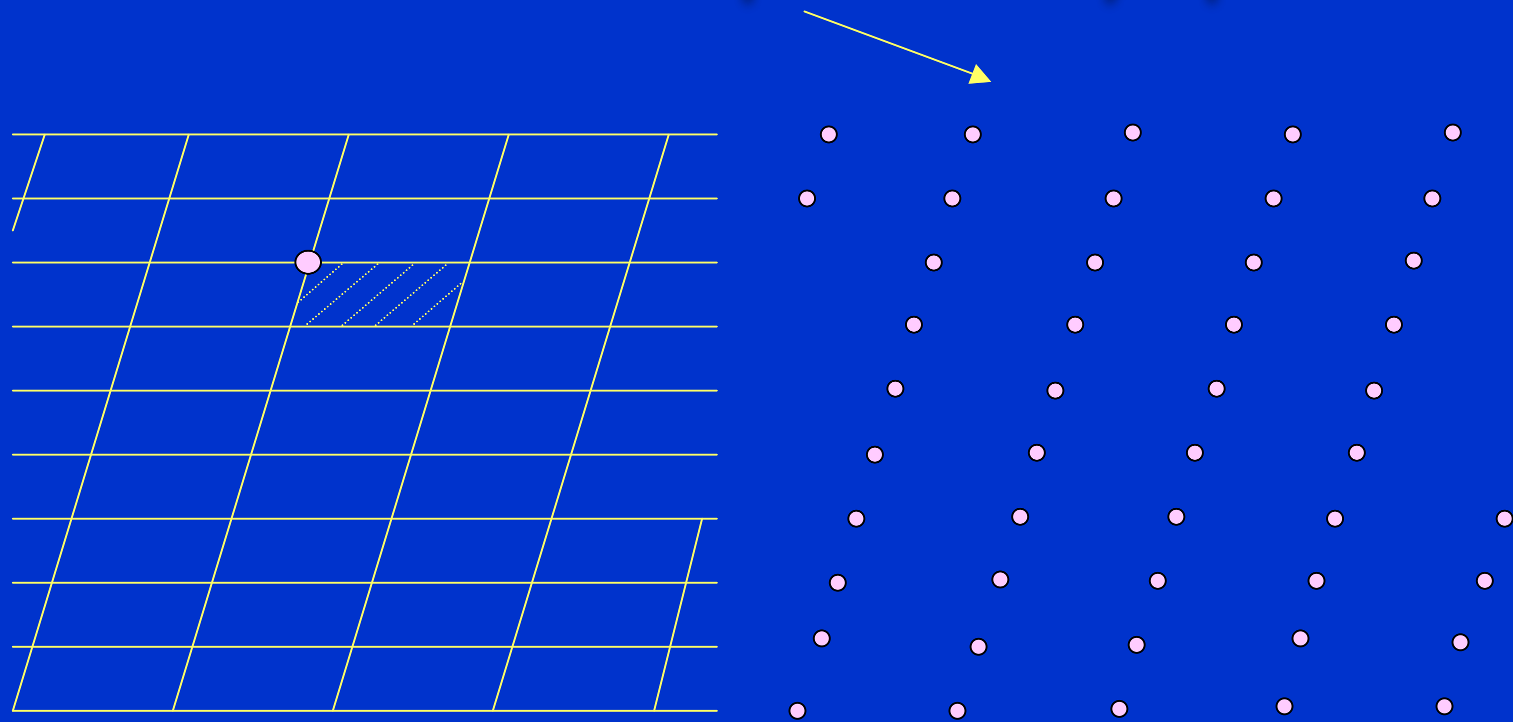
Example



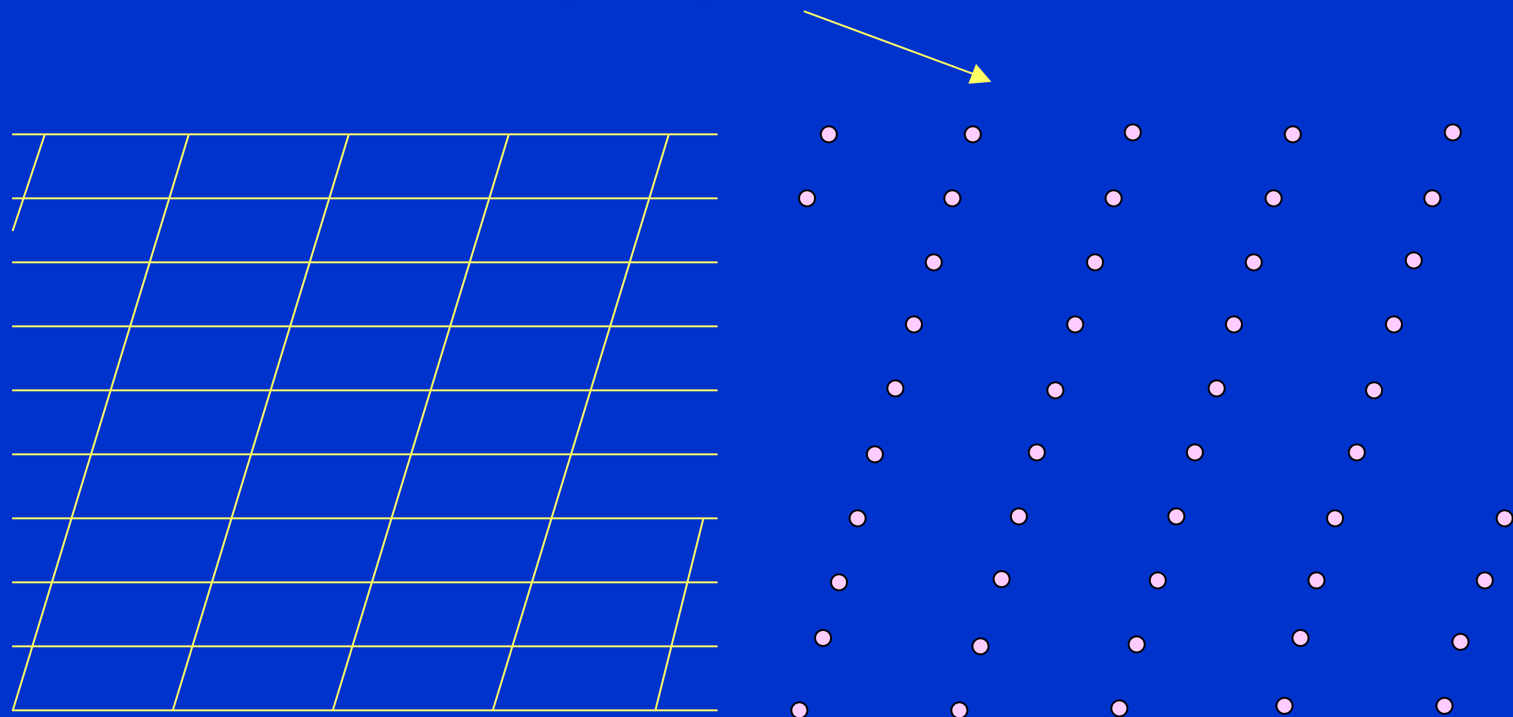
This block can be represented by a point



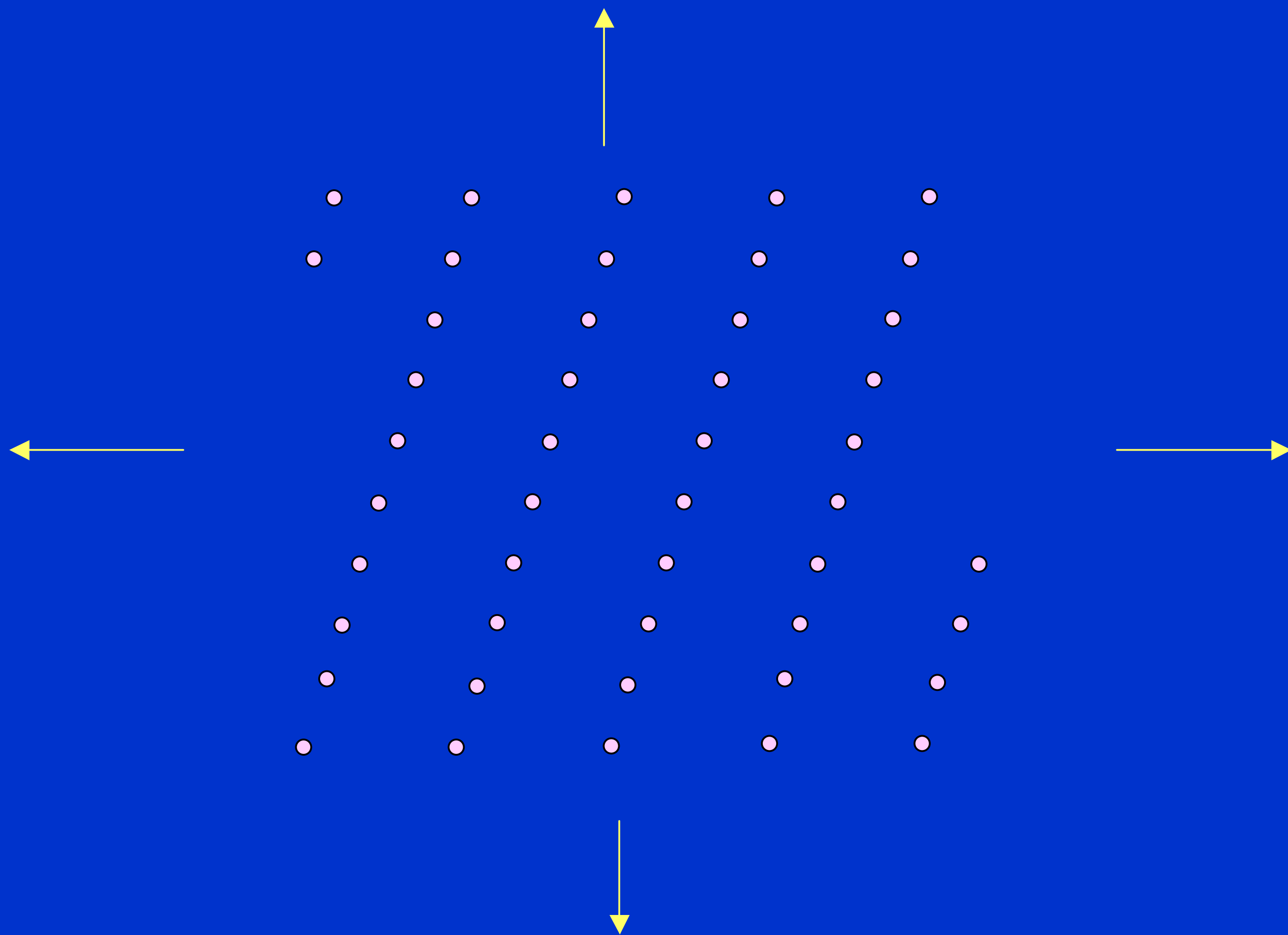
Each block is represented by a point



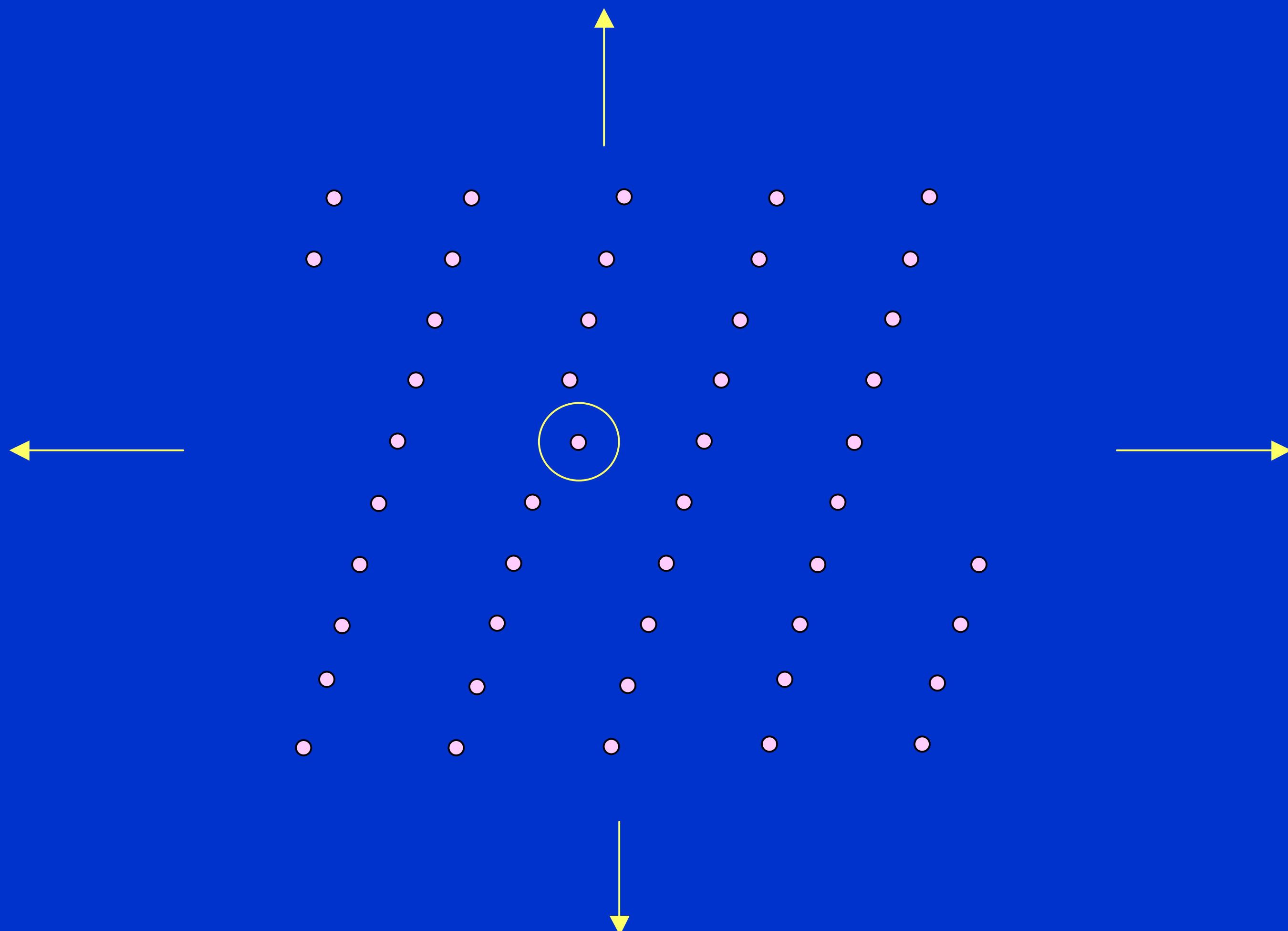
This array of points is a LATTICE



Lattice - infinite, perfectly periodic array of points in a space

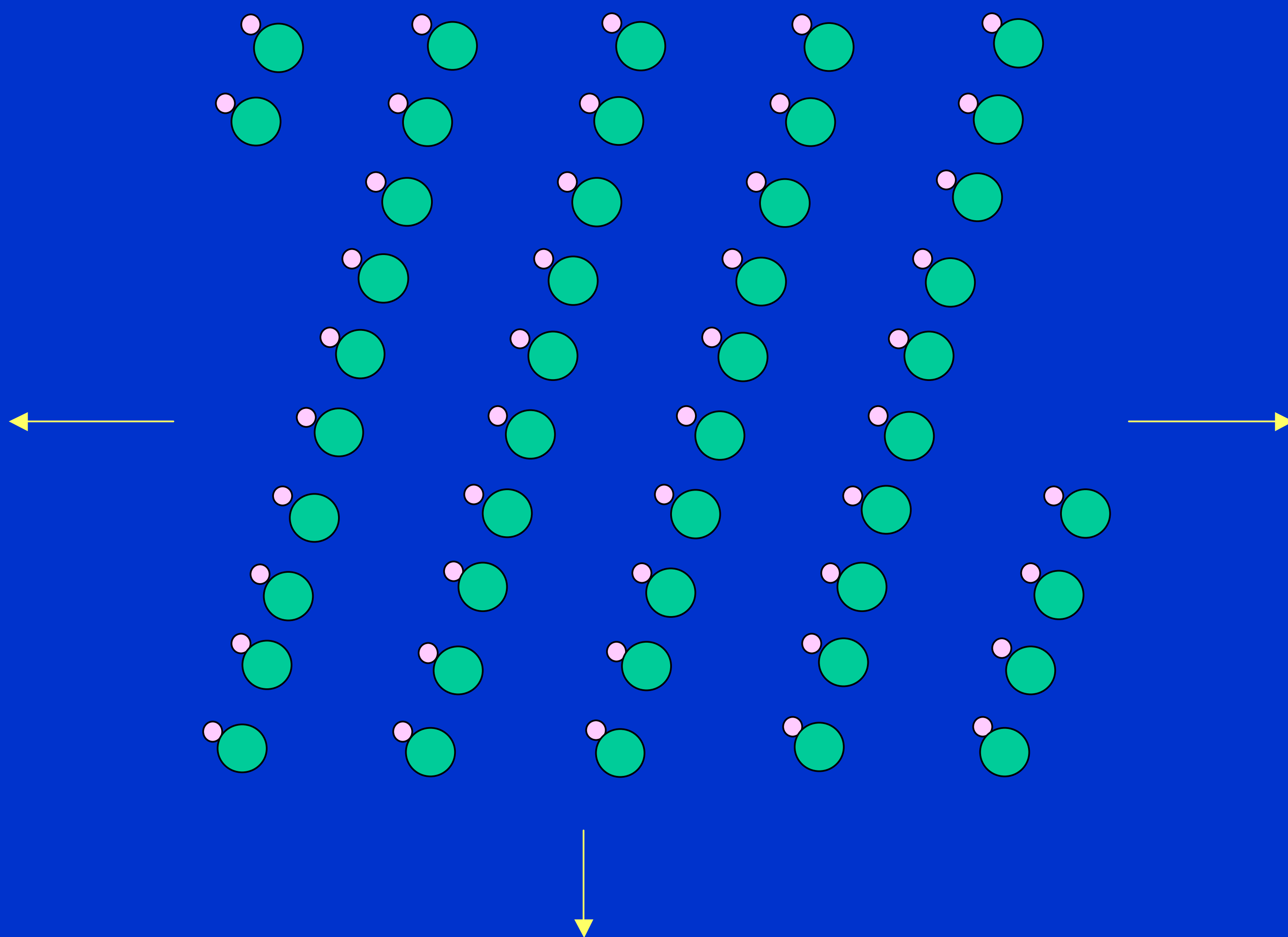


Not a lattice:



Not a lattice - becuz not just points

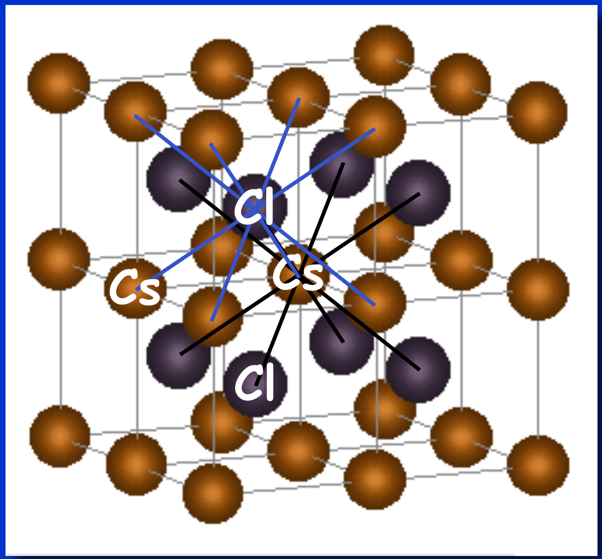
....some kind of STRUCTURE



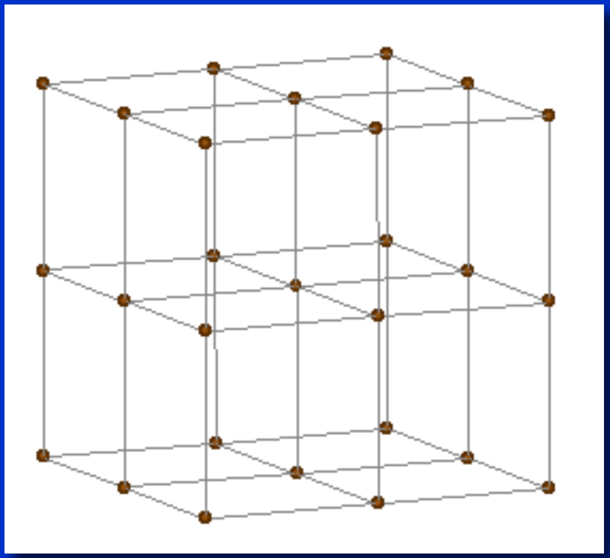
Lattice - infinite, perfectly periodic array of points in a space

each point has identical surroundings

use this as test for lattice points



CsCl structure



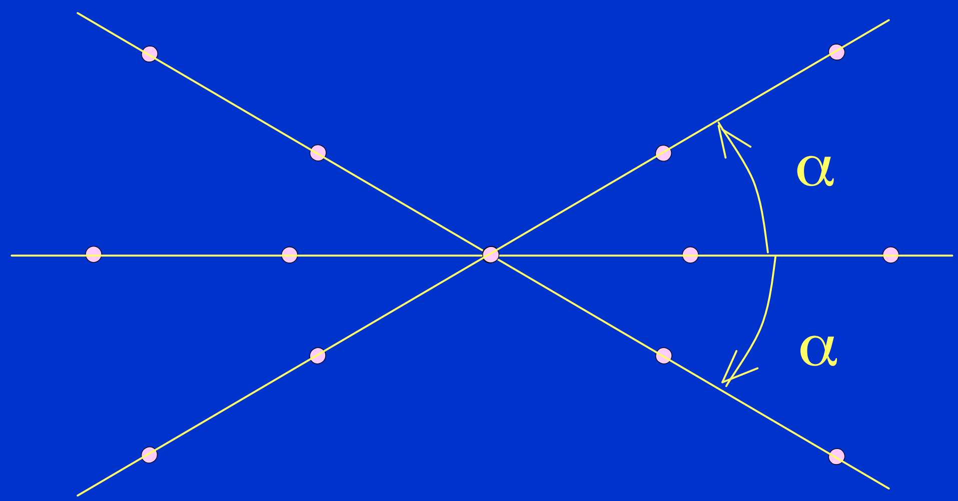
lattice points

Combining periodicity and rotational symmetry

What types of rotational symmetry allowed?

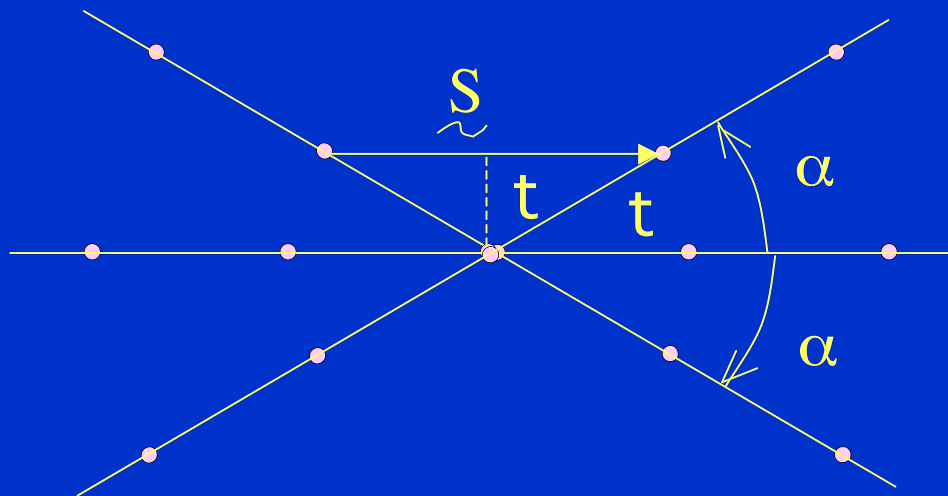
Combining periodicity and rotational symmetry

Suppose periodic row of points is rotated through $\pm\,\alpha$:

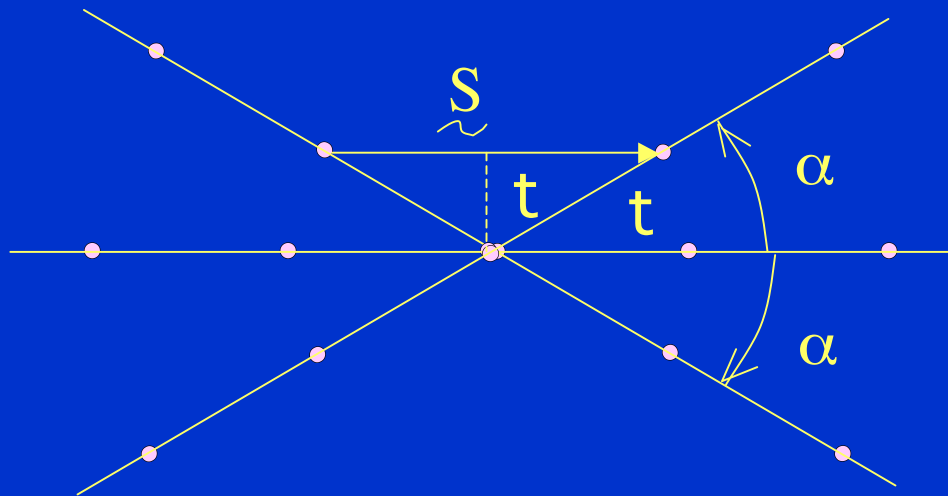


Combining periodicity and rotational symmetry

To maintain periodicity,



vector $\underset{\sim}{S}$ = an integer x basis translation $\underset{\sim}{t}$



vector $\underset{\sim}{S}$ = an integer x basis translation $\underset{\sim}{t}$

$$t \cos\alpha = S/2 = mt/2$$

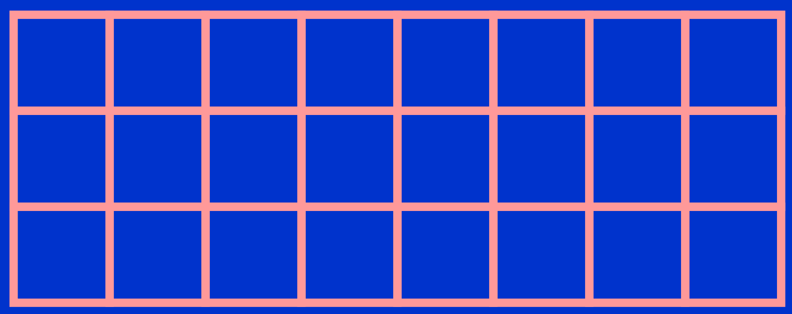
m	cos α	α		axis
2	1	0	2 π	1
1	1/2	π/3	5π/3	6
0	0	π/2	3π/2	4
-1	-1/2	2π/3	4π/3	3
-2	-1	- π	π	2

m	$\cos\alpha$	α		axis
2	1	0	π	1
1	1/2	$\pi/3$	$5\pi/3$	6
0	0	$\pi/2$	$3\pi/2$	4
-1	-1/2	$2\pi/3$	$4\pi/3$	3
-2	-1	$-\pi$	$-\pi$	2

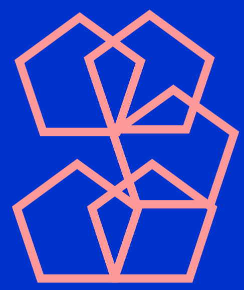
Only rotation axes consistent with lattice periodicity in 2-D or 3-D

What about 5-fold axes?

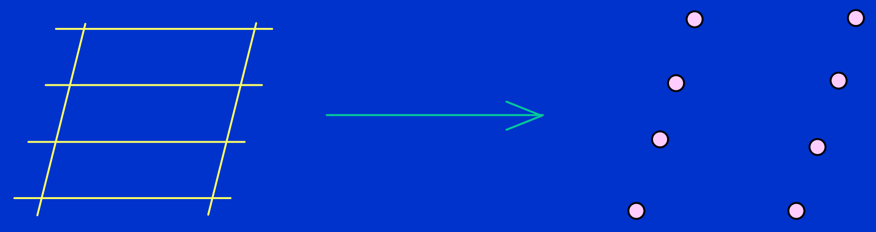
Can fill space OK with square (4-fold) by translating



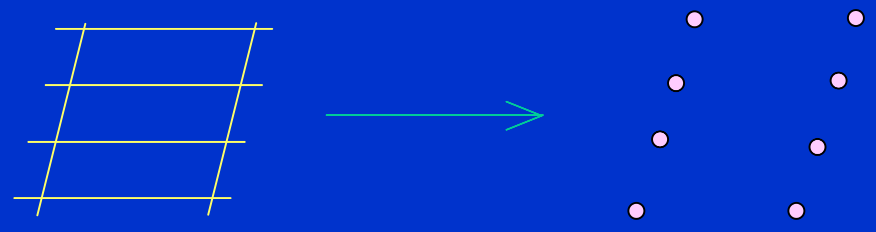
But with pentagon (5-fold)…….



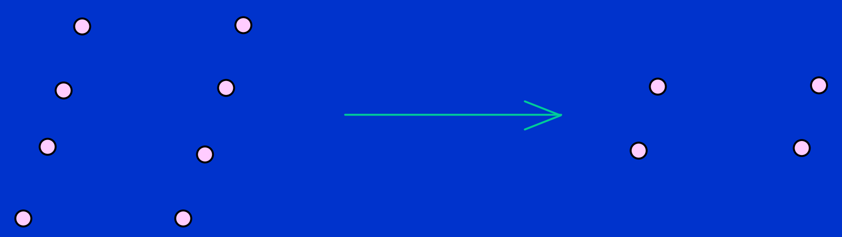
We abstracted points from the block shape:



We abstracted points from the block shape:

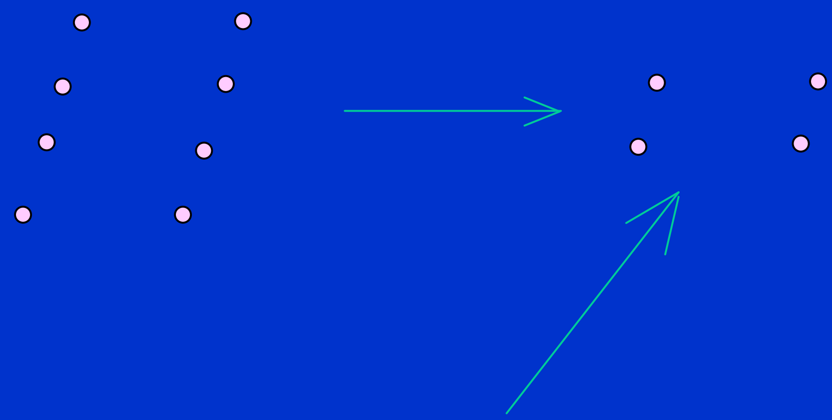


Now we abstract further:



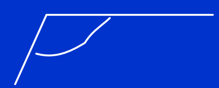
(every block is identical)

Now we abstract further:



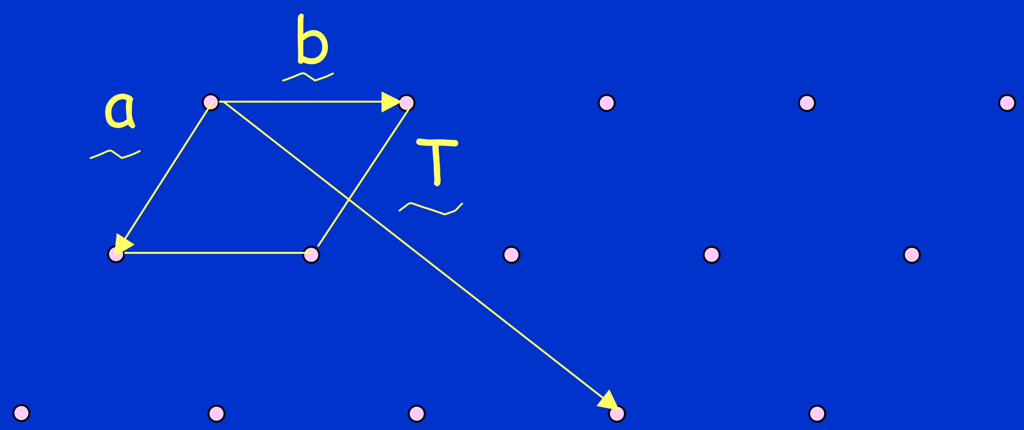
This is a UNIT CELL

Represented by two lengths and an angle



…….or, alternatively, by two vectors

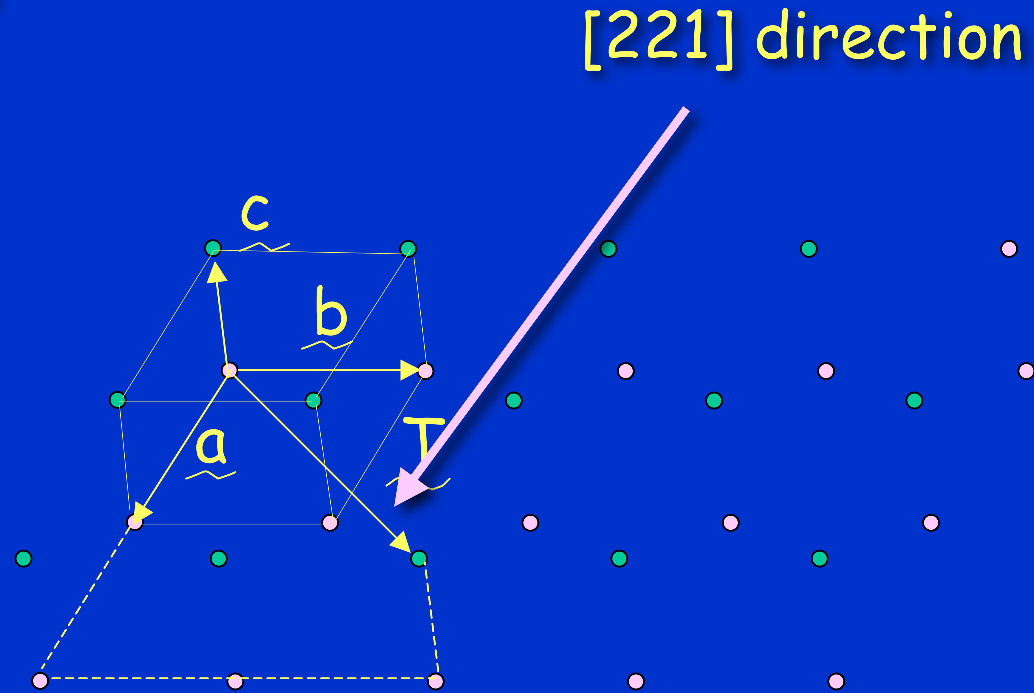
Basis vectors and unit cells



$$\underset{\sim}{T} = t_a \underset{\sim}{a} + t_b \underset{\sim}{b}$$

$\underset{\sim}{a}$ and $\underset{\sim}{b}$ are the basis vectors for the lattice

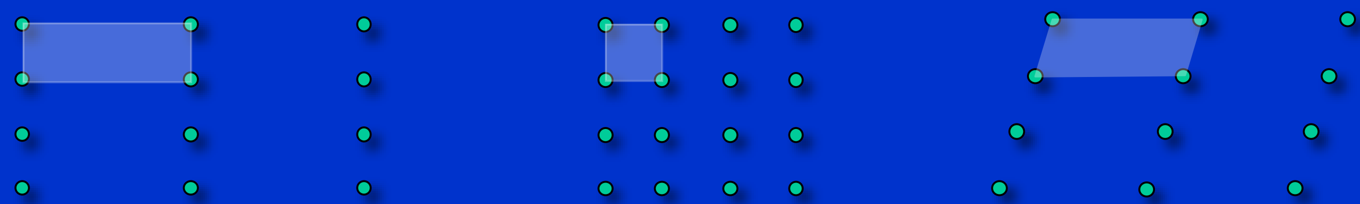
In 3-D:



$$\underset{\sim}{T} = t_a \underset{\sim}{a} + t_b \underset{\sim}{b} + t_c \underset{\sim}{c}$$

$\underset{\sim}{a}$, $\underset{\sim}{b}$, and $\underset{\sim}{c}$ are the basis vectors for the 3-D lattice

Different types of lattices



Lattices classified into crystal systems according to shape of unit cell (symmetry)

In 3-D

Lengths a, b, c & angles α, β, γ are the lattice parameters

Crystal systems

System	Interaxial Angles	Axes
Triclinic	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$a \neq b \neq c$
Monoclinic	$\alpha = \gamma = 90^\circ \neq \beta$	$a \neq b \neq c$
Orthorhombic	$\alpha = \beta = \gamma = 90^\circ$	$a \neq b \neq c$
Tetragonal	$\alpha = \beta = \gamma = 90^\circ$	$a = b \neq c$
Cubic	$\alpha = \beta = \gamma = 90^\circ$	$a = b = c$
Hexagonal	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	$a = b \neq c$
Trigonal	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	$a = b \neq c$

Symmetry characteristics of the crystal systems

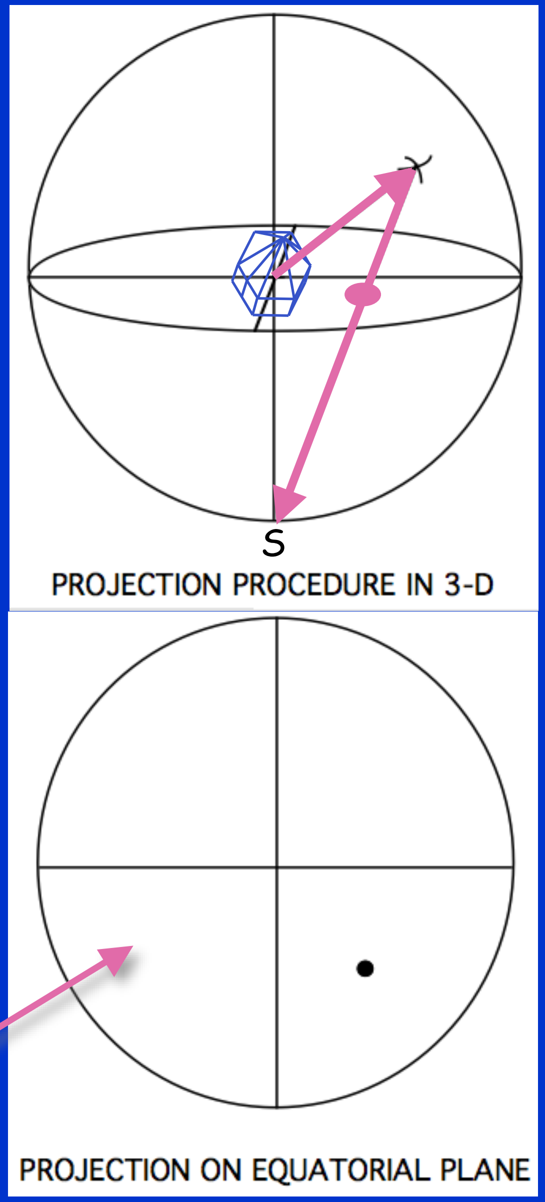
System	Minimum symmetry
Triclinic	1 or $\bar{1}$
Monoclinic	2 or $\bar{2}$
Orthorhombic	three 2s or $\bar{2}$s
Tetragonal	4 or $\bar{4}$
Cubic	four 3s or $\bar{3}$s
Hexagonal	6 or $\bar{6}$
Trigonal	3 or $\bar{3}$

Stereographic projections

Show or represent 3-D object in 2-D

Procedure:

1. Place object at center of sphere
2. From sphere center, draw line representing some feature of object out to intersect sphere
3. Connect point to N or S pole of sphere. Where sphere passes through equatorial plane, mark projected point
4. Show equatorial plane in 2-D – this is stereographic projection



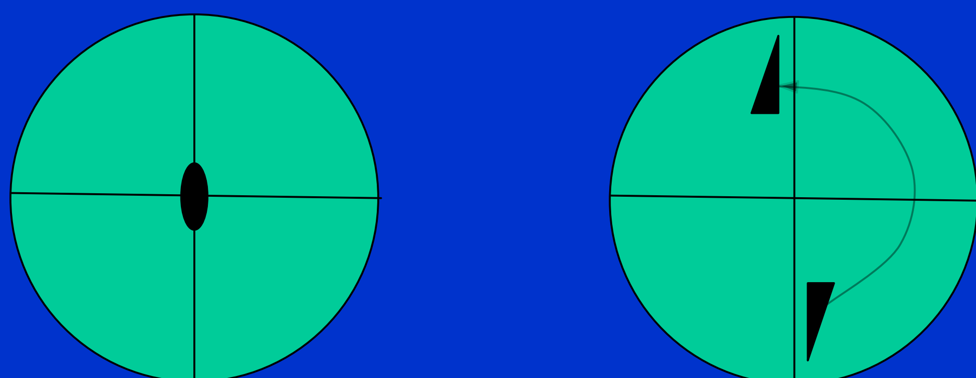
Stereographic projections of symmetry groups

Types of pure rotation symmetry

Rotation 1, 2, 3, 4, 6

Rotoinversion $\bar{1}$ (= i), $\bar{2}$ (= m), $\bar{3}$, $\bar{4}$, $\bar{6}$

Draw point group diagrams (stereographic projections)



symmetry elements　　　　equivalent points

Stereographic projections of symmetry groups

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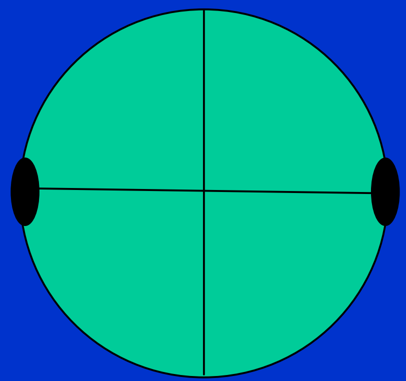
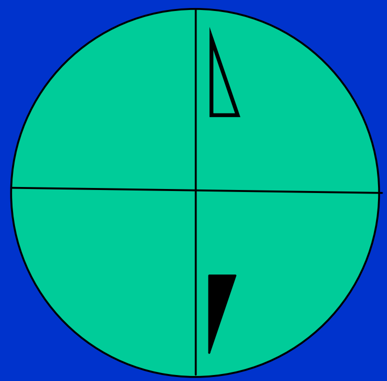


symmetry elements



equivalent points

Stereographic projections of symmetry groups

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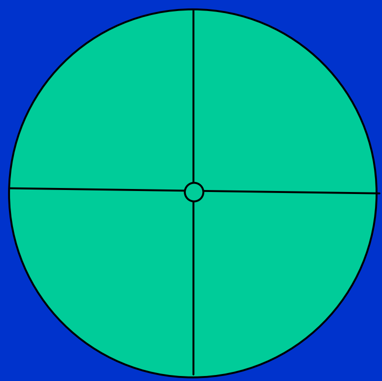
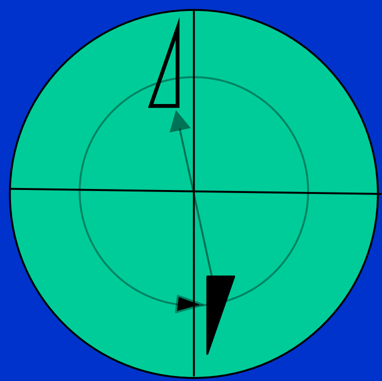


symmetry elements



equivalent points

Stereographic projections of symmetry groups

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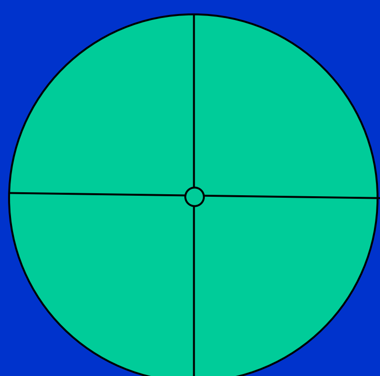
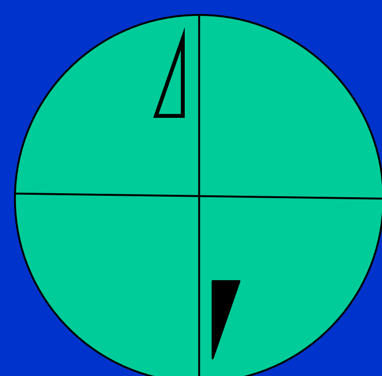


symmetry elements



equivalent points

All objects, structures with *i* symmetry are centric

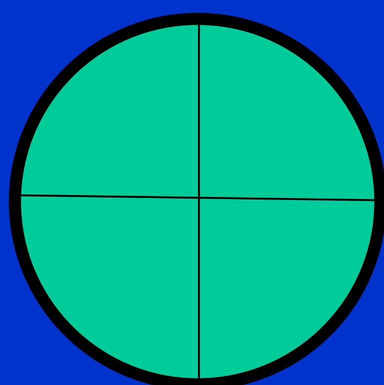
Stereographic projections of symmetry groups

Types of pure rotation symmetry

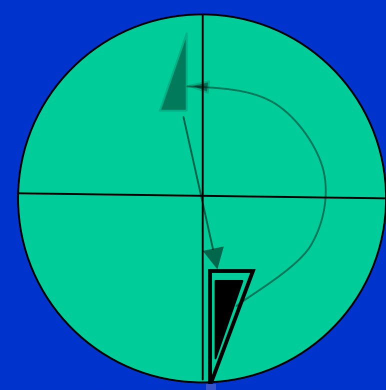
Rotation 1, 2, 3, 4, 6

Rotoinversion $\bar{1}$ (= i), $\bar{2}$ (= m), $\bar{3}$, $\bar{4}$, $\bar{6}$

Draw point group diagrams (stereographic projections)



symmetry elements



equivalent points

Stereographic projections of symmetry groups

Types of pure rotation symmetry

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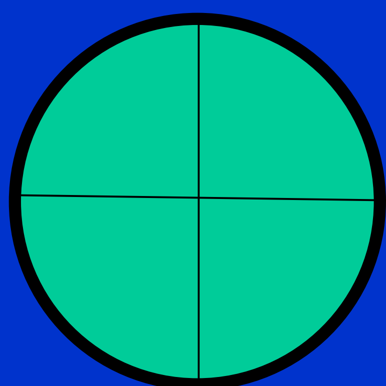
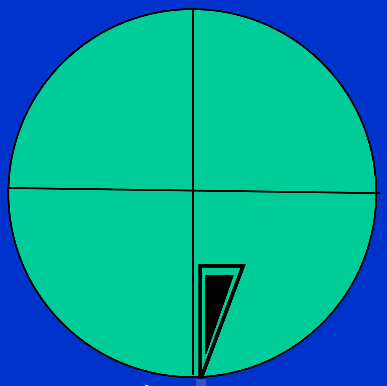


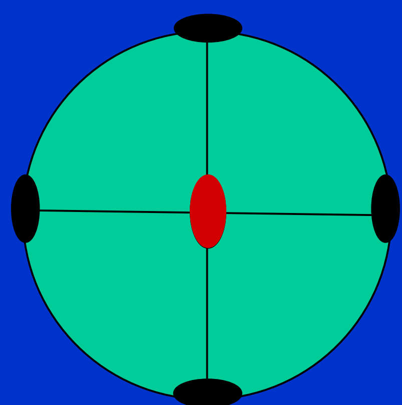
symmetry elements



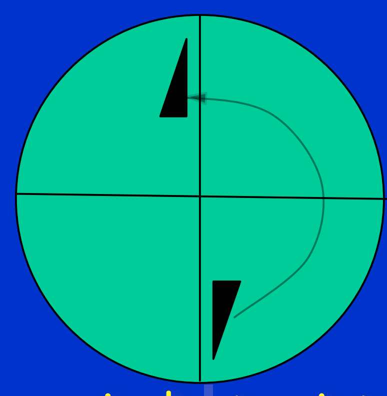
equivalent points

Stereographic projections of symmetry groups

More than one rotation axis - point group 222



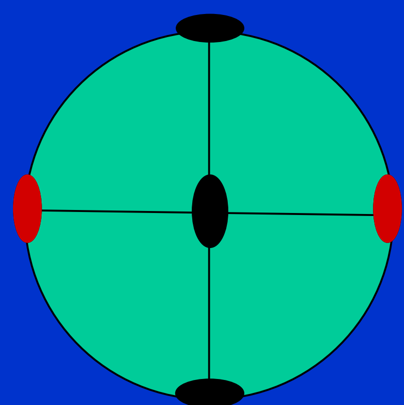
symmetry elements



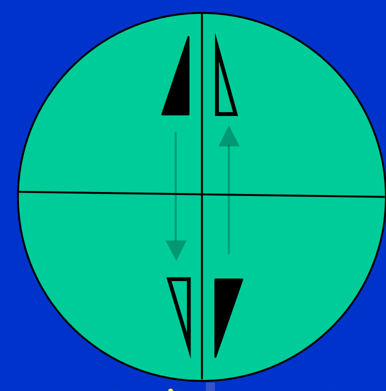
equivalent points

Stereographic projections of symmetry groups

More than one rotation axis - point group 222



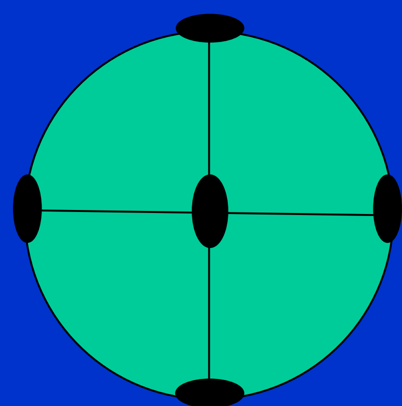
symmetry elements



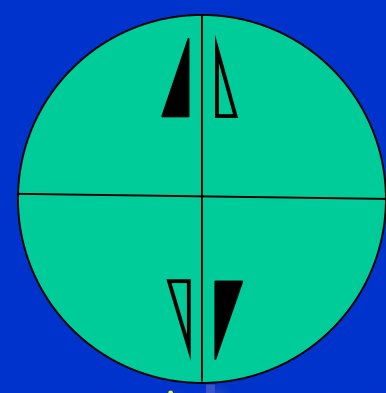
equivalent points

Stereographic projections of symmetry groups

More than one rotation axis - point group 222



symmetry elements

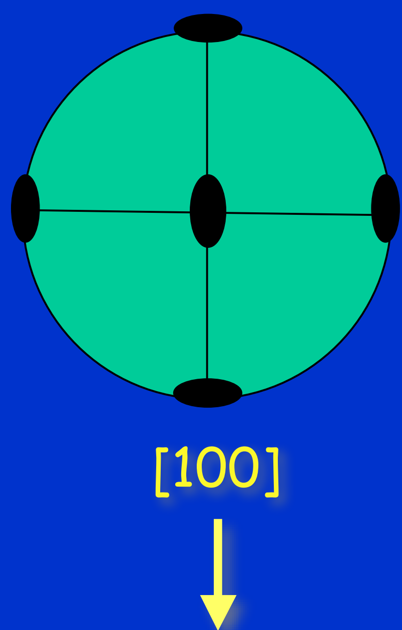


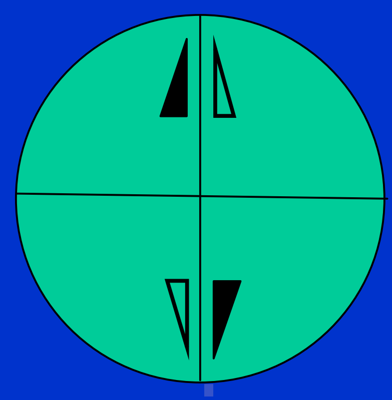
equivalent points

orthorhombic

Stereographic projections of symmetry groups

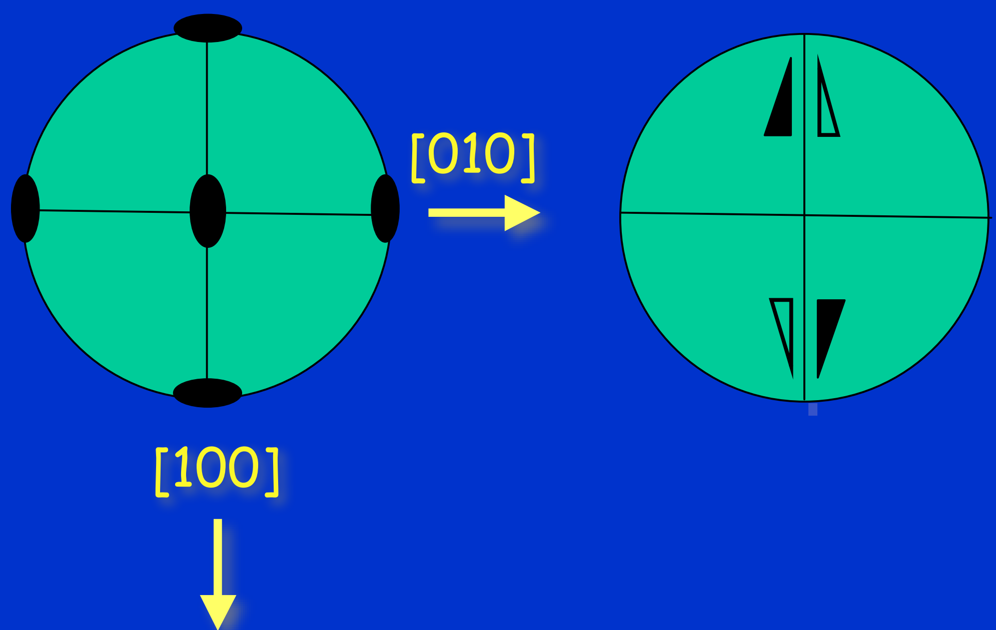
More than one rotation axis - point group $\boxed{2}22$





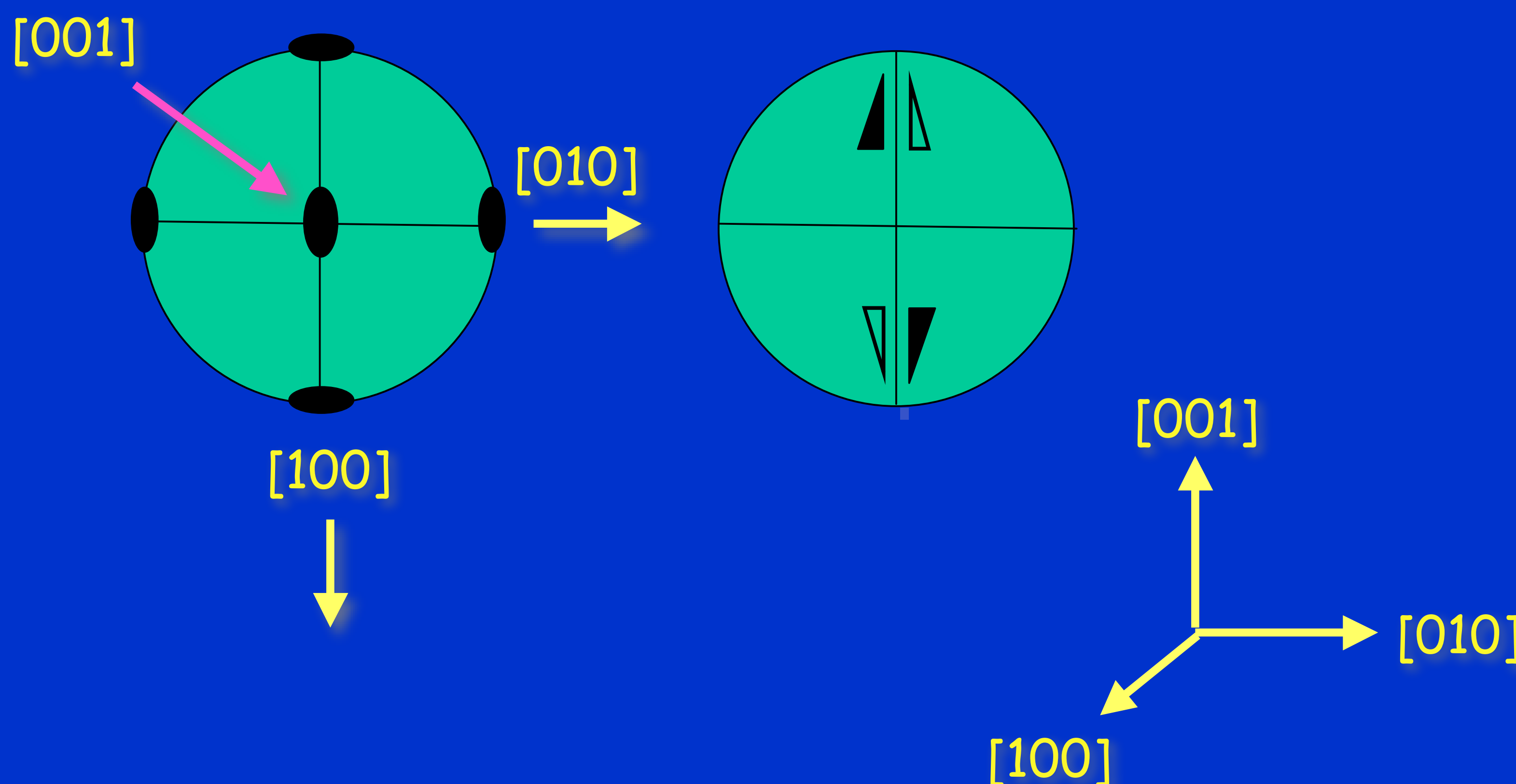
Stereographic projections of symmetry groups

More than one rotation axis - point group 222



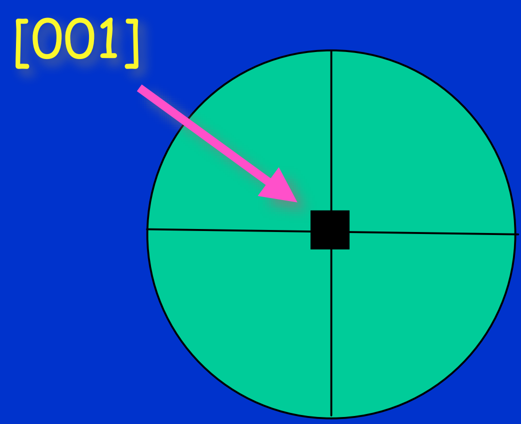
Stereographic projections of symmetry groups

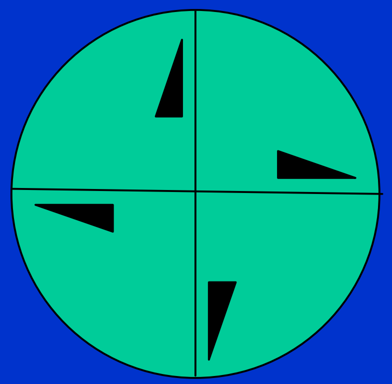
More than one rotation axis - point group 22$\boxed{2}$



Stereographic projections of symmetry groups

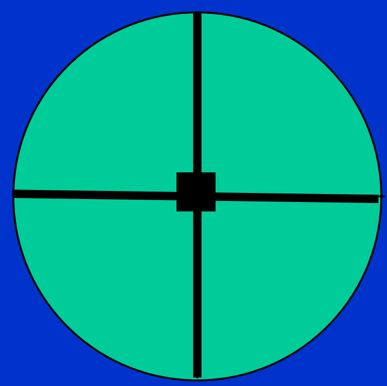
Rotation + mirrors - point group 4mm



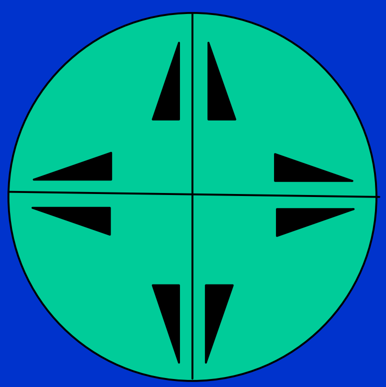


Stereographic projections of symmetry groups

Rotation + mirrors - point group 4mm

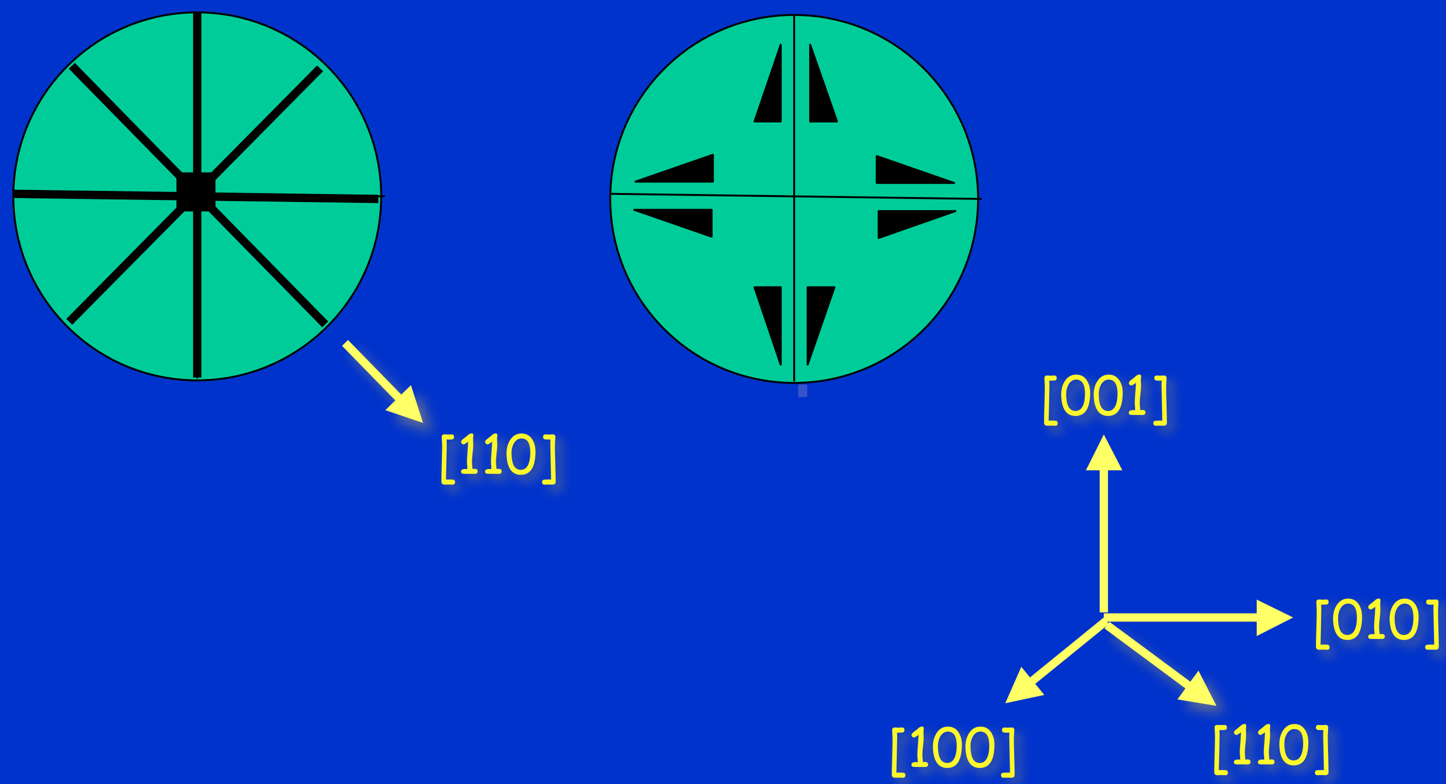


[100]



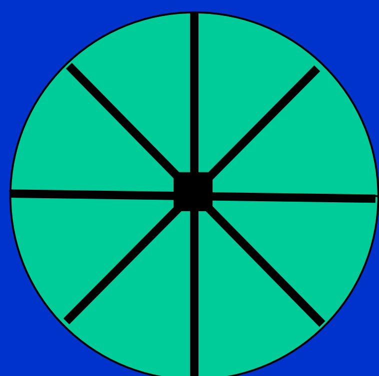
Stereographic projections of symmetry groups

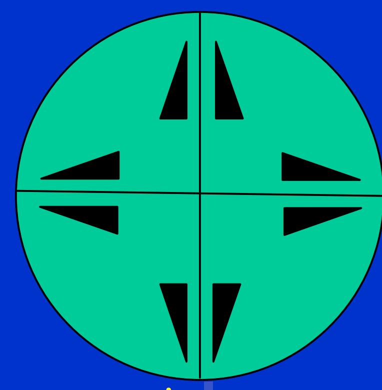
Rotation + mirrors - point group 4mm



Stereographic projections of symmetry groups

Rotation + mirrors - point group 4mm

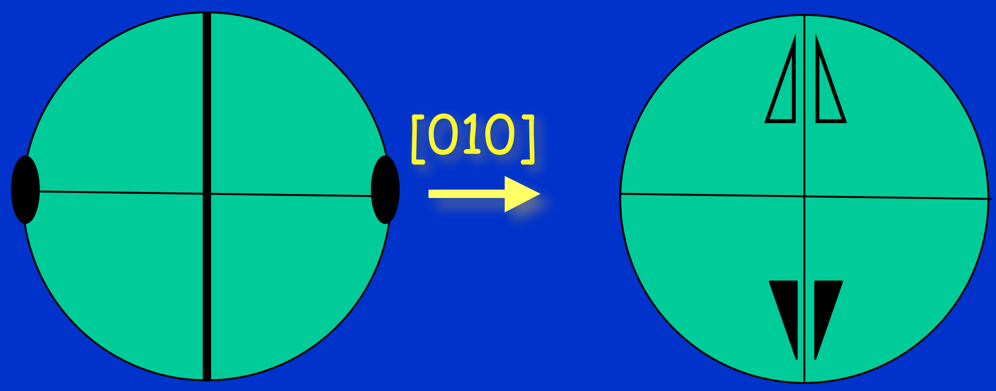




tetragonal

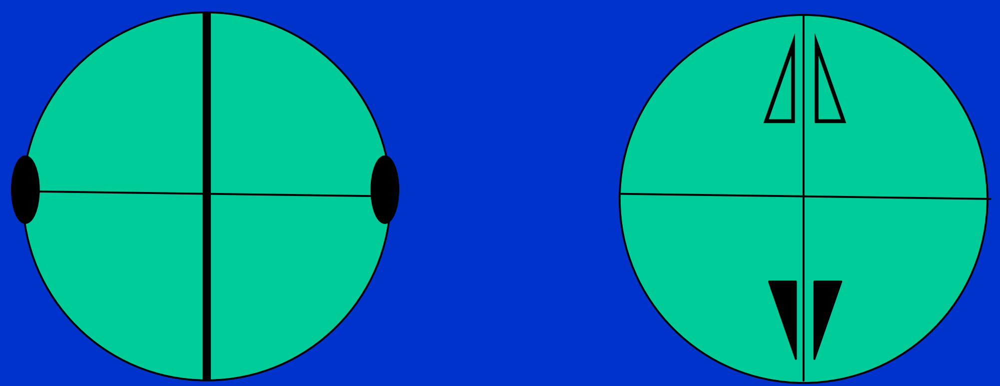
Stereographic projections of symmetry groups

Rotation + mirrors - point group 2/m



Stereographic projections of symmetry groups

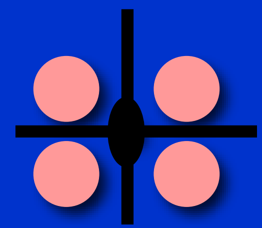
Rotation + mirrors - point group 2/m



symmetry elements equivalent points

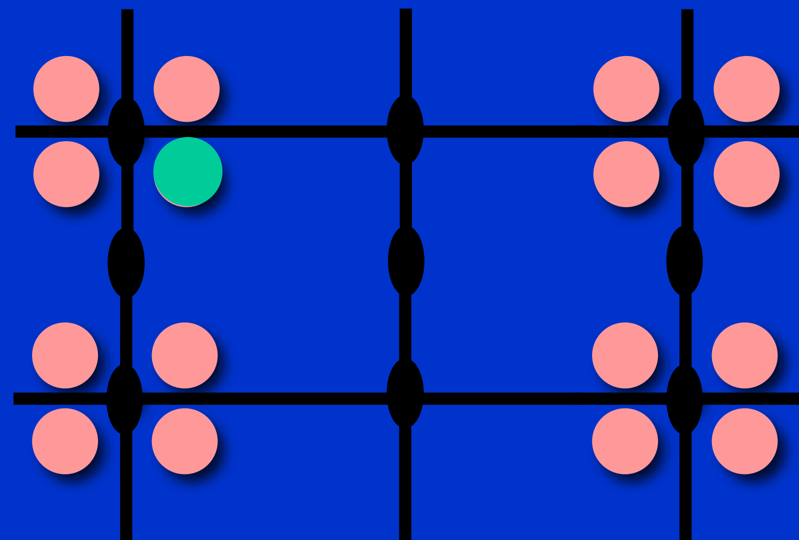
monoclinic

Combining point groups with Bravais lattices
to form crystal
(need consider only one unit cell)



A space group is formed (3-D) - Pmm2

Combining point groups with Bravais lattices to form crystal (need consider only one unit cell)

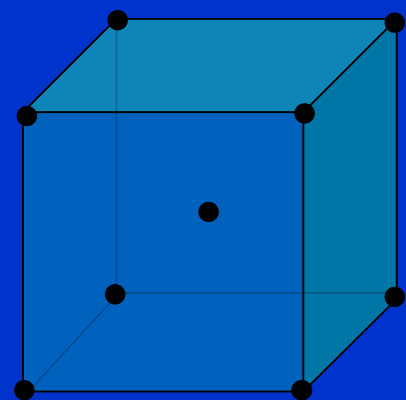


Note: if coordinates (x,y,z) of one atom known, then, because of symmetry, all other atom coordinates known

Choosing unit cells in a lattice

Sometimes, a good unit cell has more than one lattice point

3-D example:

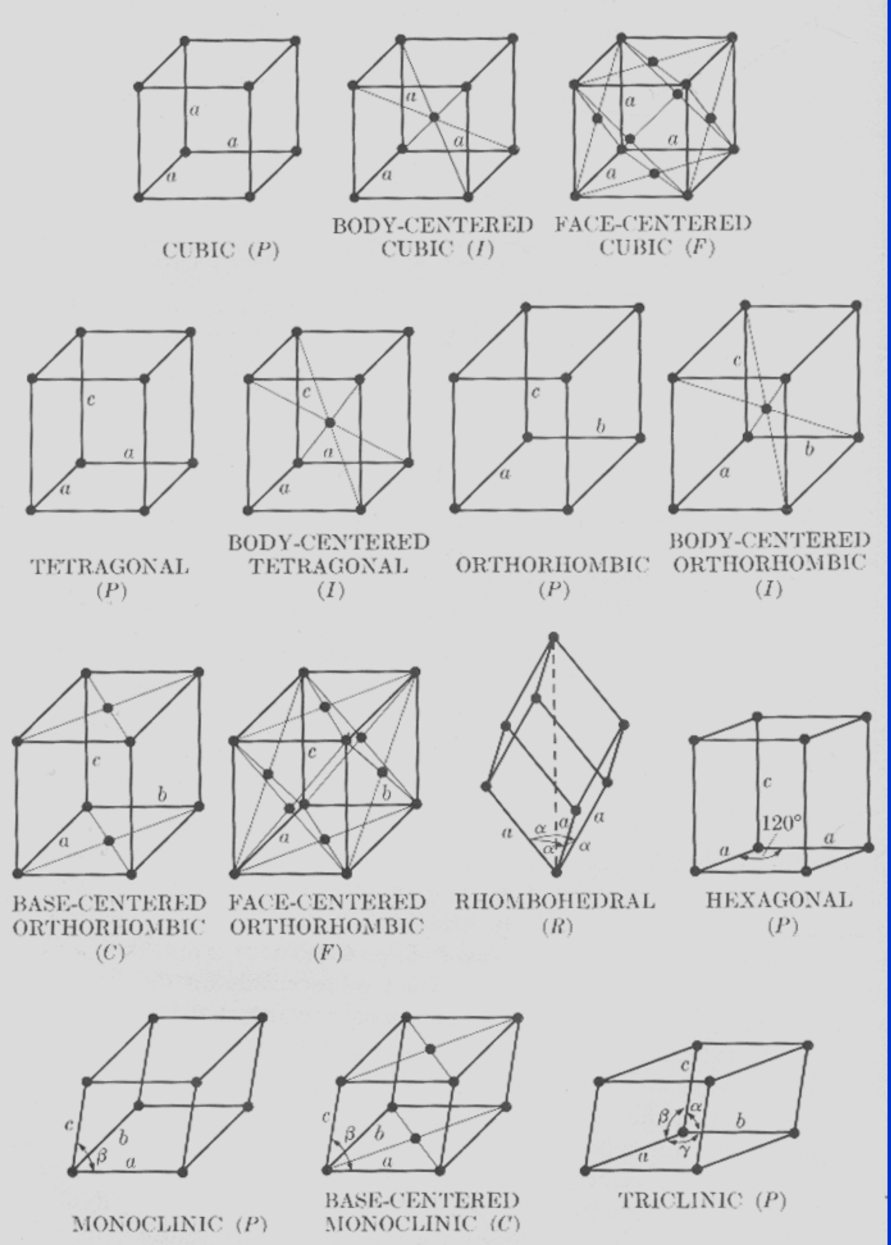


body-centered cubic (bcc, or I cubic)
(two lattice pts./cell)
The primitive unit cell is not a cube

Within each crystal system, different types of centering consistent with symmetry

System	Allowed centering
Triclinic	P (primitive)
Monoclinic	P, I (innerzentiert)
Orthorhombic	P, I, F (flächenzentiert), A (end centered)
Tetragonal	P, I
Cubic	P, I, F
Hexagonal	P
Trigonal	P, R (rhombohedral centered)

The 14 Bravais lattices



The fourteen Bravais lattices.

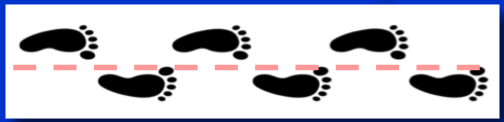
230 space groups (see Int'l Tables for Crystallography, Vol. A)

Combine 32 point groups (rotational symmetry) with

a. 14 Bravais lattices (translational symmetry)

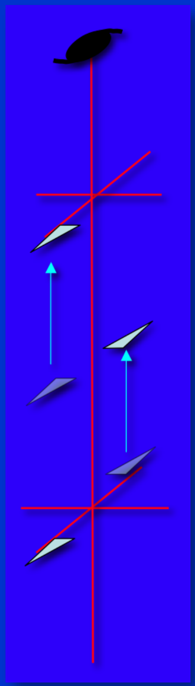
b. glide planes (rotational + translational symmetry) -

a, b, c, n, d, e

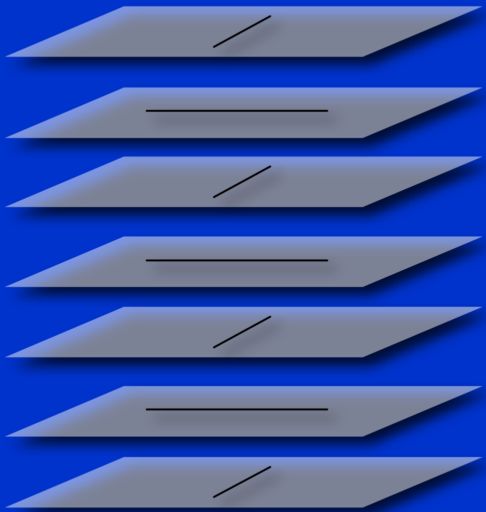


c. screw axes (rotational + translational symmetry) -

2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5



Screw axis example - 4_2



Space groups

Combine all types of translational
and rotational symmetry operations
(230 possible combinations)

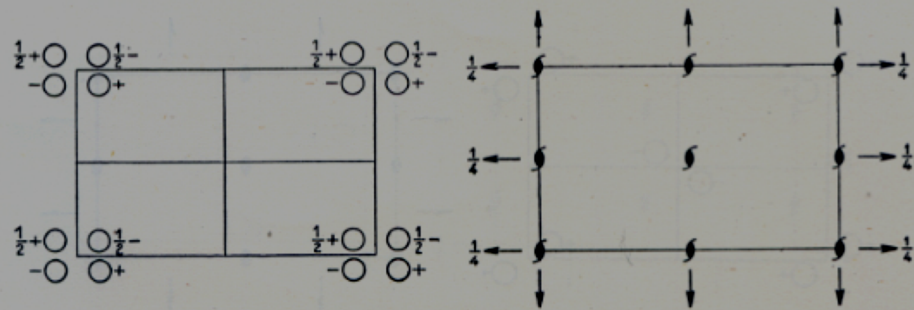
Some examples:

P 4mm (tetragonal)
P 6/m (hexagonal)
I 23 (cubic)
F 4/m $\bar{3}$ 2/m (cubic)
P $2_1 2_1 2_1$ (orthorhombic)
P 6_3/mmc (hexagonal)

screw axis

glide plane

Orthorhombic 222 $P\,2\,2\,2_1$ No. 17 $P\,2\,2\,2_1$ D_2^2



Origin at 212_1

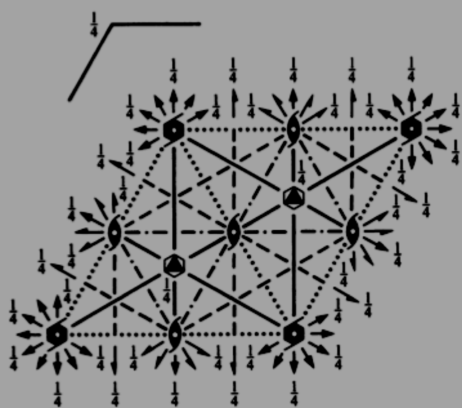
Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions	Conditions limiting possible reflections
				General:
4	e	1	$x,y,z;\ \ x,\bar{y},\bar{z};\ \ \bar{x},\bar{y},\tfrac{1}{2}+z;\ \ \bar{x},y,\tfrac{1}{2}-z.$	hkl: $0kl$: $h0l$: $hk0$: $h00$: $0k0$: No conditions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

Symmetry of special projections

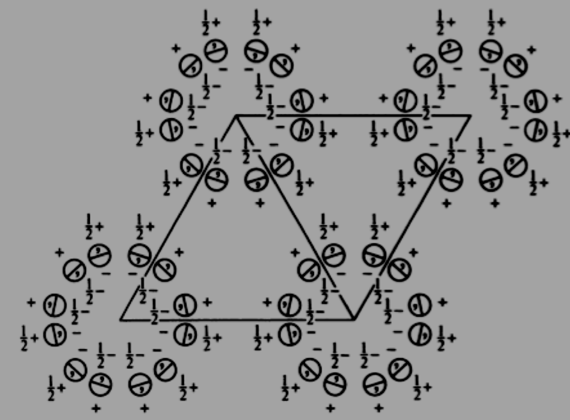
(001) pmm; $a'=a,\ b'=b$ (100) pgm; $b'=b,\ c'=c$ (010) pmg; $c'=c,\ a'=a$

No. 194 $P\ 6_3/m\ 2/m\ 2/c$

Patterson symmetry $P6/mmm$



For $\bar{1}$ and $\bar{6}$ see $P6_3/m$ (No. 176)



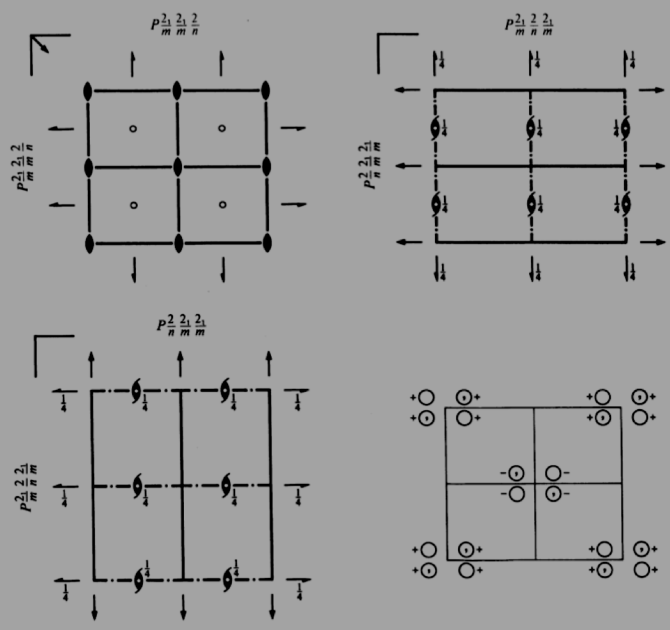
Origin at centre ($\bar{3}m1$) at $\bar{3}2/mc$

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates	Reflection conditions
				General:
24	l	1	(1) x,y,z (2) $\bar{y},x-y,z$ (3) $\bar{x}+y,\bar{x},z$ (4) $\bar{x},\bar{y},z+\frac{1}{2}$ (5) $y,\bar{x}+y,z+\frac{1}{2}$ (6) $x-y,x,z+\frac{1}{2}$ (7) $y,x,\bar{z}$ (8) $x-y,\bar{y},\bar{z}$ (9) $\bar{x},\bar{x}+y,\bar{z}$ (10) $\bar{y},\bar{x},\bar{z}+\frac{1}{2}$ (11) $\bar{x}+y,y,\bar{z}+\frac{1}{2}$ (12) $x,x-y,\bar{z}+\frac{1}{2}$ (13) $\bar{x},\bar{y},\bar{z}$ (14) $y,\bar{x}+y,\bar{z}$ (15) $x-y,x,\bar{z}$ (16) $x,y,\bar{z}+\frac{1}{2}$ (17) $\bar{y},x-y,\bar{z}+\frac{1}{2}$ (18) $\bar{x}+y,\bar{x},\bar{z}+\frac{1}{2}$ (19) $\bar{y},\bar{x},z$ (20) $\bar{x}+y,y,z$ (21) $x,x-y,z$ (22) $y,x,z+\frac{1}{2}$ (23) $x-y,\bar{y},z+\frac{1}{2}$ (24) $\bar{x},\bar{x}+y,z+\frac{1}{2}$	$hh\overline{2h}l$: $l=2n$ $000l$: $l=2n$
				Special: as above, plus
12	k	$.m.$	$x,2x,z$ $2\bar{x},\bar{x},z$ $x,\bar{x},z$ $\bar{x},2\bar{x},z+\frac{1}{2}$ $2x,x,z+\frac{1}{2}$ $\bar{x},x,z+\frac{1}{2}$ $2x,x,\bar{z}$ $\bar{x},2\bar{x},\bar{z}$ $\bar{x},x,\bar{z}$ $2\bar{x},\bar{x},\bar{z}+\frac{1}{2}$ $x,2x,\bar{z}+\frac{1}{2}$ $x,\bar{x},\bar{z}+\frac{1}{2}$	no extra conditions
12	j	$m..$	$x,y,\frac{1}{4}$ $\bar{y},x-y,\frac{1}{4}$ $\bar{x}+y,\bar{x},\frac{1}{4}$ $\bar{x},\bar{y},\frac{3}{4}$ $y,\bar{x}+y,\frac{3}{4}$ $x-y,x,\frac{3}{4}$ $y,x,\frac{3}{4}$ $x-y,\bar{y},\frac{3}{4}$ $\bar{x},\bar{x}+y,\frac{3}{4}$ $\bar{y},\bar{x},\frac{1}{4}$ $\bar{x}+y,y,\frac{1}{4}$ $x,x-y,\frac{1}{4}$	no extra conditions
12	i	$.2.$	$x,0,0$ $0,x,0$ $\bar{x},\bar{x},0$ $\bar{x},0,\frac{1}{2}$ $0,\bar{x},\frac{1}{2}$ $x,x,\frac{1}{2}$ $\bar{x},0,0$ $0,\bar{x},0$ $x,x,0$ $x,0,\frac{1}{2}$ $0,x,\frac{1}{2}$ $\bar{x},\bar{x},\frac{1}{2}$	$hkil$: $l=2n$
6	h	$mm2$	$x,2x,\frac{1}{4}$ $2\bar{x},\bar{x},\frac{1}{4}$ $x,\bar{x},\frac{1}{4}$ $\bar{x},2\bar{x},\frac{3}{4}$ $2x,x,\frac{3}{4}$ $\bar{x},x,\frac{3}{4}$	no extra conditions
6	g	$.2/m.$	$\frac{1}{2},0,0$ $0,\frac{1}{2},0$ $\frac{1}{2},\frac{1}{2},0$ $\frac{1}{2},0,\frac{1}{2}$ $0,\frac{1}{2},\frac{1}{2}$ $\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$hkil$: $l=2n$
4	f	$3m.$	$\frac{1}{3},\frac{2}{3},z$ $\frac{2}{3},\frac{1}{3},z+\frac{1}{2}$ $\frac{2}{3},\frac{1}{3},\bar{z}$ $\frac{1}{3},\frac{2}{3},\bar{z}+\frac{1}{2}$	$hkil$: $l=2n$ or $h-k=3n+1$ or $h-k=3n+2$
4	e	$3m.$	$0,0,z$ $0,0,z+\frac{1}{2}$ $0,0,\bar{z}$ $0,0,\bar{z}+\frac{1}{2}$	$hkil$: $l=2n$
2	d	$\bar{6}m2$	$\frac{1}{3},\frac{2}{3},\frac{3}{4}$ $\frac{2}{3},\frac{1}{3},\frac{1}{4}$	$hkil$: $l=2n$ or $h-k=3n+1$ or $h-k=3n+2$
2	c	$\bar{6}m2$	$\frac{1}{3},\frac{2}{3},\frac{1}{4}$ $\frac{2}{3},\frac{1}{3},\frac{3}{4}$	
2	b	$\bar{6}m2$	$0,0,\frac{1}{4}$ $0,0,\frac{3}{4}$	$hkil$: $l=2n$
2	a	$\bar{3}m.$	$0,0,0$ $0,0,\frac{1}{2}$	$hkil$: $l=2n$

No. 59 $P\ 2_1/m\ 2_1/m\ 2/n$ Patterson symmetry $Pmmm$

ORIGIN CHOICE 1



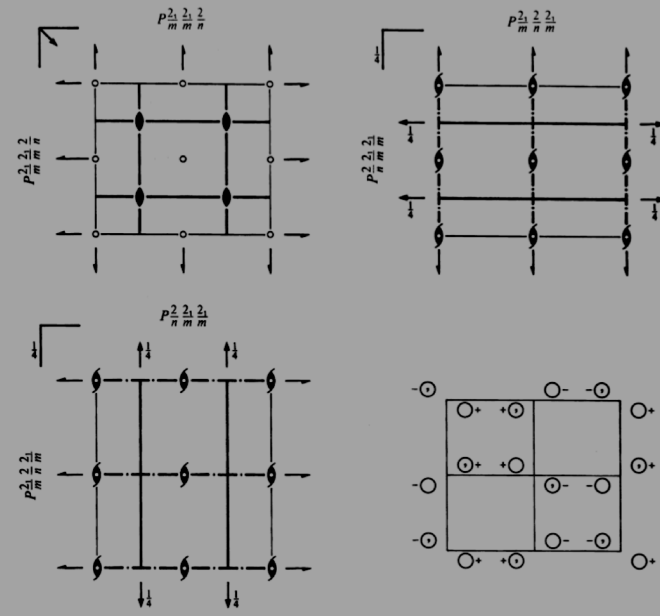
Origin at $mm2/n$, at $\frac{1}{4},\frac{1}{4},0$ from $\bar{1}$

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
8	g	1	(1) x,y,z (5) $\bar{x}+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$	(2) $\bar{x},\bar{y},z$ (6) $x+\frac{1}{2},y+\frac{1}{2},\bar{z}$	(3) $\bar{x}+\frac{1}{2},y+\frac{1}{2},\bar{z}$ (7) $x,\bar{y},z$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$ (8) $\bar{x},y,z$	$hk0$: $h+k=2n$ $h00$: $h=2n$ $0k0$: $k=2n$
							Special: as above, plus
4	f	$.m.$	$x,0,z$	$\bar{x},0,z$	$\bar{x}+\frac{1}{2},\frac{1}{2},\bar{z}$	$x+\frac{1}{2},\frac{1}{2},\bar{z}$	no extra conditions
4	e	$m..$	$0,y,z$	$0,\bar{y},z$	$\frac{1}{2},y+\frac{1}{2},\bar{z}$	$\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$	no extra conditions
4	d	$\bar{1}$	$\frac{1}{4},\frac{1}{4},\frac{1}{2}$	$\frac{3}{4},\frac{3}{4},\frac{1}{2}$	$\frac{1}{4},\frac{3}{4},\frac{1}{2}$	$\frac{3}{4},\frac{1}{4},\frac{1}{2}$	hkl : $h,k=2n$
4	c	$\bar{1}$	$\frac{1}{4},\frac{1}{4},0$	$\frac{3}{4},\frac{3}{4},0$	$\frac{1}{4},\frac{3}{4},0$	$\frac{3}{4},\frac{1}{4},0$	hkl : $h,k=2n$
2	b	$mm2$	$0,\frac{1}{2},z$	$\frac{1}{2},0,\bar{z}$			no extra conditions
2	a	$mm2$	$0,0,z$	$\frac{1}{2},\frac{1}{2},\bar{z}$			no extra conditions

No. 59 $P\ 2_1/m\ 2_1/m\ 2/n$ Patterson symmetry $Pmmm$

ORIGIN CHOICE 2



Origin at $\bar{1}$ at 2_12_1n, at $-\frac{1}{4},-\frac{1}{4},0$ from $mm2$

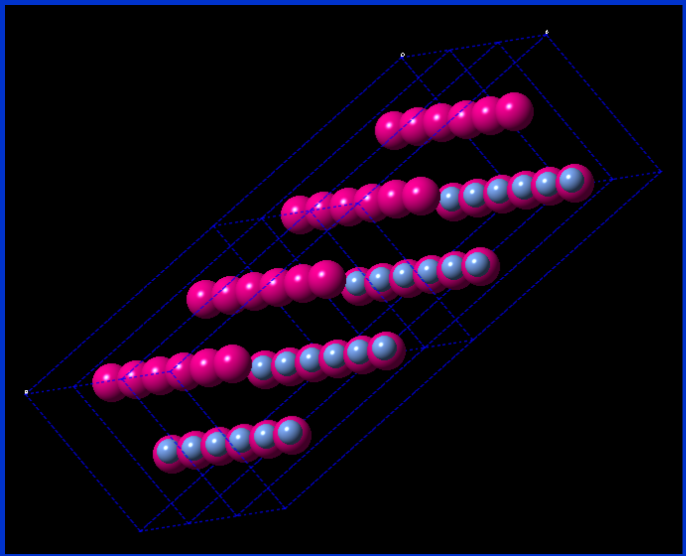
Positions

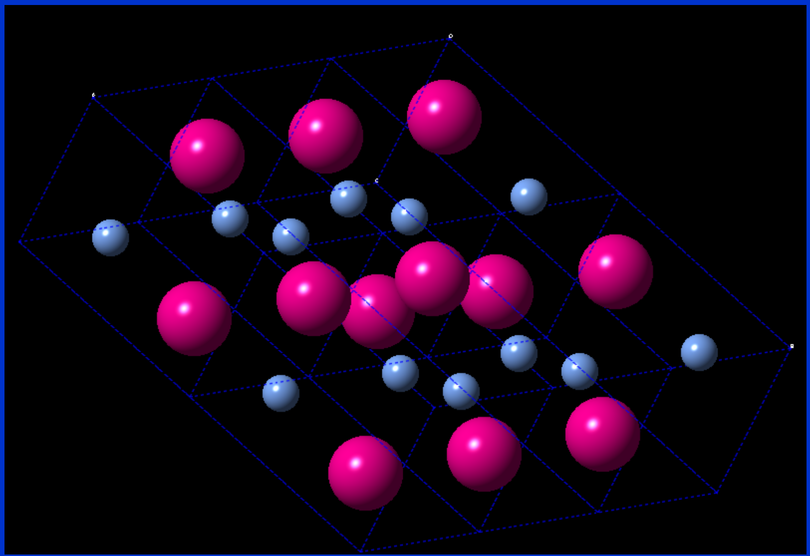
Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
8	g	1	(1) x,y,z (5) $\bar{x},\bar{y},\bar{z}$	(2) $\bar{x}+\frac{1}{2},\bar{y}+\frac{1}{2},z$ (6) $x+\frac{1}{2},y+\frac{1}{2},\bar{z}$	(3) $\bar{x},y+\frac{1}{2},\bar{z}$ (7) $x,\bar{y}+\frac{1}{2},z$	(4) $x+\frac{1}{2},\bar{y},\bar{z}$ (8) $\bar{x}+\frac{1}{2},y,z$	$hk0$: $h+k=2n$ $h00$: $h=2n$ $0k0$: $k=2n$
							Special: as above, plus
4	f	$.m.$	$x,\frac{1}{4},z$	$\bar{x}+\frac{1}{2},\frac{1}{4},z$	$\bar{x},\frac{3}{4},\bar{z}$	$x+\frac{1}{2},\frac{3}{4},\bar{z}$	no extra conditions
4	e	$m..$	$\frac{1}{4},y,z$	$\frac{1}{4},\bar{y}+\frac{1}{2},z$	$\frac{3}{4},y+\frac{1}{2},\bar{z}$	$\frac{3}{4},\bar{y},\bar{z}$	no extra conditions
4	d	$\bar{1}$	$0,0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$	hkl : $h,k=2n$
4	c	$\bar{1}$	$0,0,0$	$\frac{1}{2},\frac{1}{2},0$	$0,\frac{1}{2},0$	$\frac{1}{2},0,0$	hkl : $h,k=2n$
2	b	$mm2$	$\frac{1}{4},\frac{3}{4},z$	$\frac{3}{4},\frac{1}{4},\bar{z}$			no extra conditions
2	a	$mm2$	$\frac{1}{4},\frac{1}{4},z$	$\frac{3}{4},\frac{3}{4},\bar{z}$			no extra conditions

CrN:

Pmmn a = 2.9698, b = 4.1318, c = 2.8796 Å

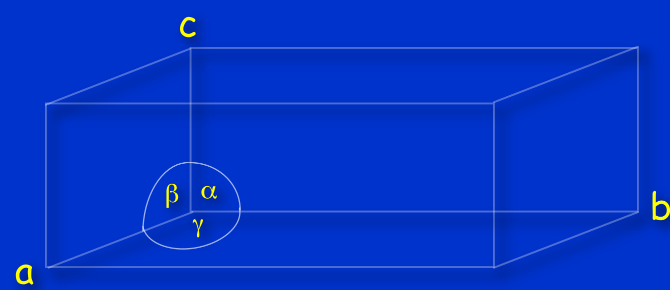
Cr in 2a, z = 0.24 N in 2b, z = 0.26





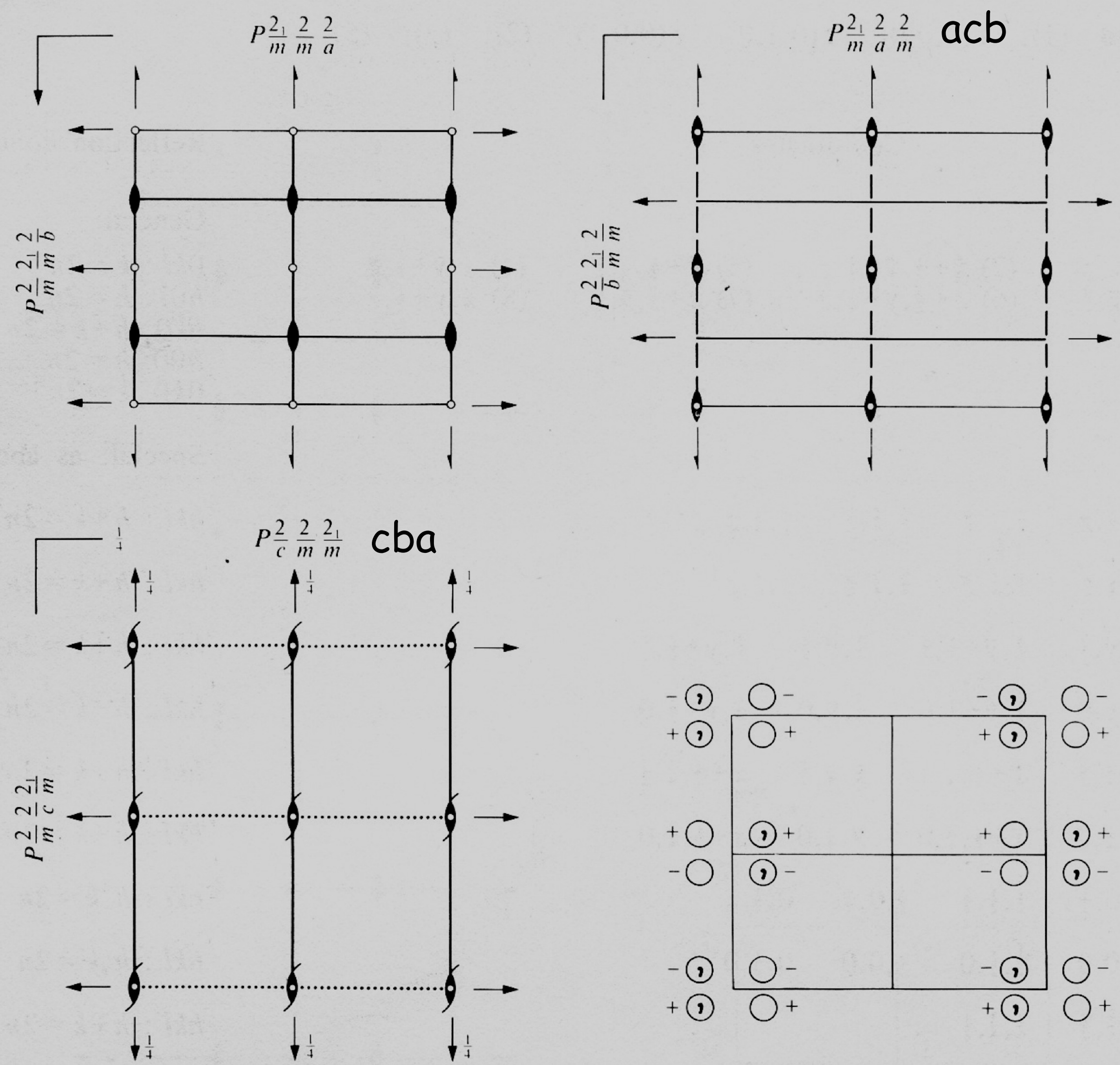
Axes settings

Unit cells can be chosen various ways - particularly, a problem in monoclinic & orthorhombic



$Pmma$ D_{2h}^{5} mmm Orthorhombic

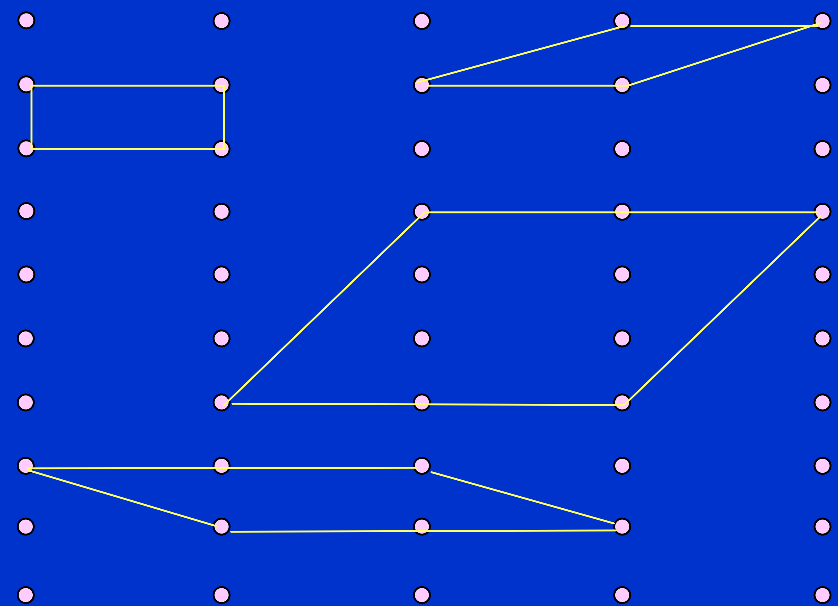
No. 51 $P\,2_1/m\,2/m\,2/a$ Patterson symmetry $Pmmm$



Example from a database

- Authors list compd as Ibam
- Database interchanged b and c, lists space group as Ibma
- Ibma not possible combination of symmetry operations
- Interchanging b and c gives Icma

For given lattice, infinite number of unit cells possible:



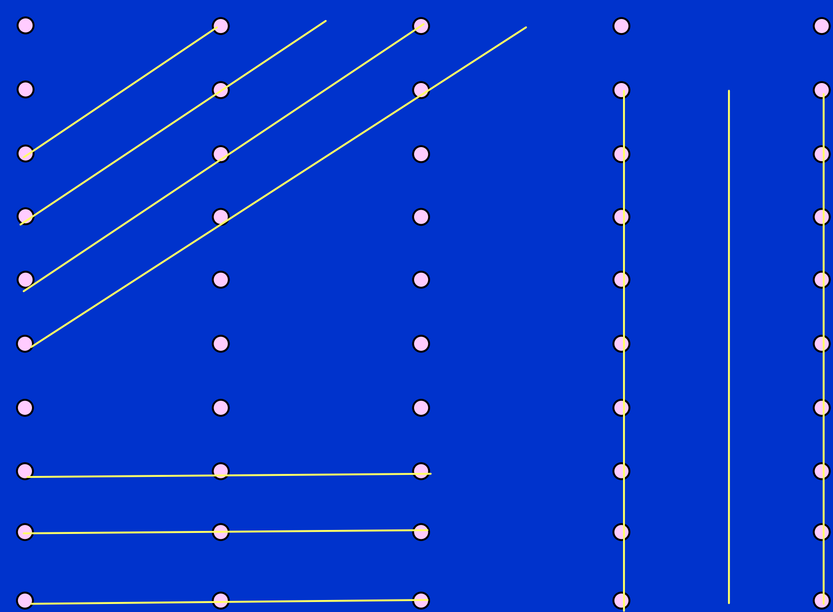
When choosing unit cell, pick:

Simplest, smallest
Right angles, if possible
Cell shape consistent with symmetry

Must be a parallelepiped

When cell chosen, everything is fixed for lattice.

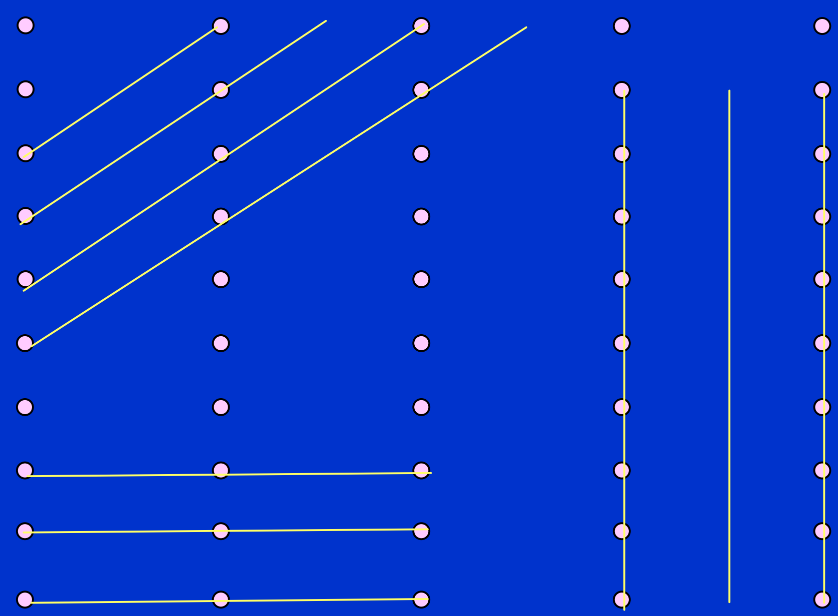
For ex., diffracting planes



Infinite number of sets of reflecting planes

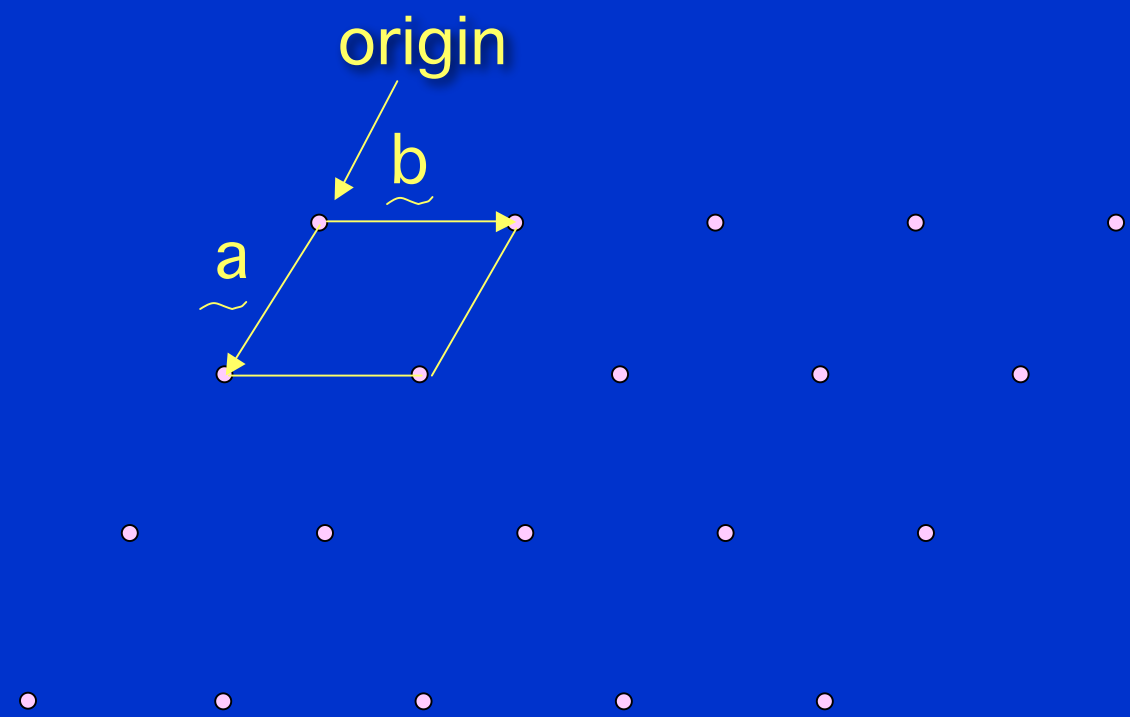
Keep track by giving them names - Miller indices

(hkl)



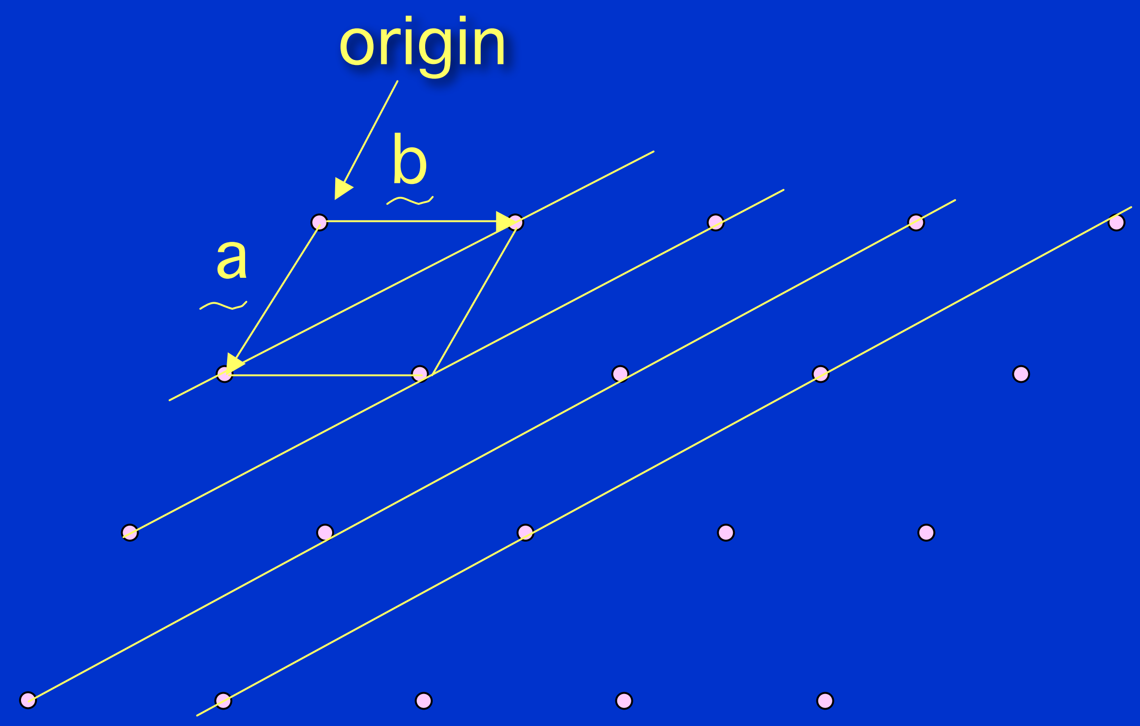
Miller indices (hkl)

Choose cell, cell origin, cell axes:



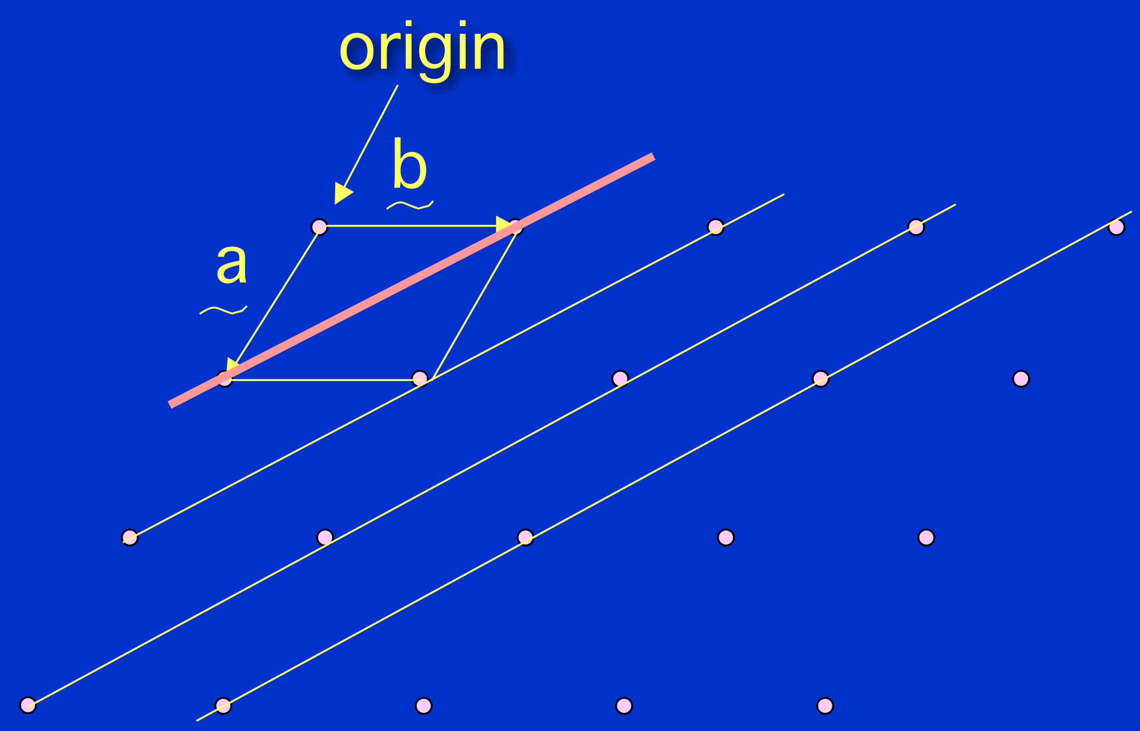
Miller indices (hkl)

Choose cell, cell origin, cell axes
Draw set of planes of interest:



Miller indices (hkl)

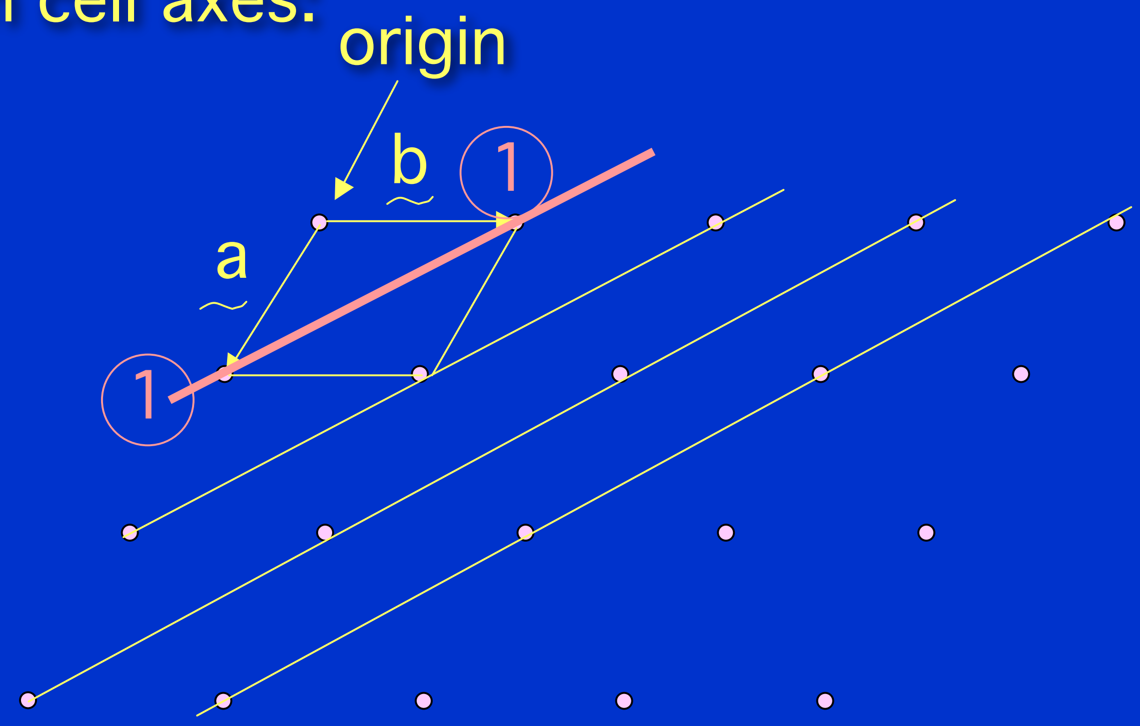
Choose cell, cell origin, cell axes
Draw set of planes of interest
Choose plane nearest origin:



Miller indices (hkl)

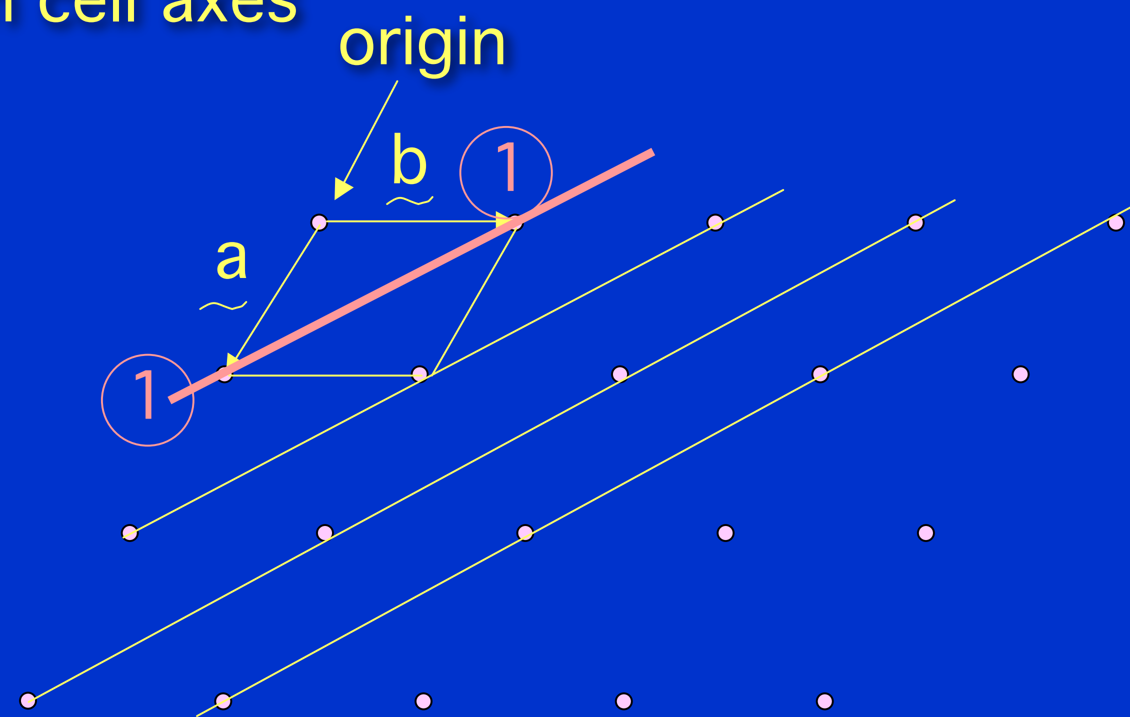
Choose cell, cell origin, cell axes
Draw set of planes of interest
Choose plane nearest origin
Find intercepts on cell axes:

1,1,∞



Miller indices (hkl)

Choose cell, cell origin, cell axes
Draw set of planes of interest
Choose plane nearest origin
Find intercepts on cell axes



1,1,∞

Invert these
to get (hkl)

(110)

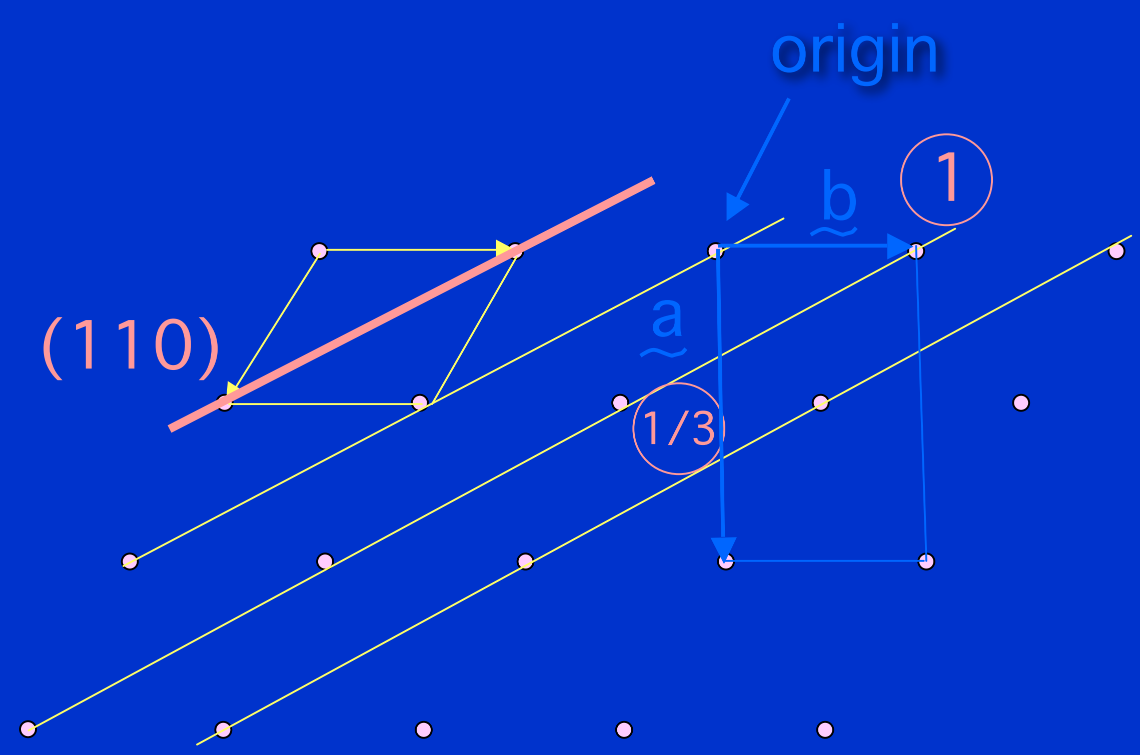
Miller indices (hkl)

If cell is chosen differently, Miller indices change

1/3,1,∞

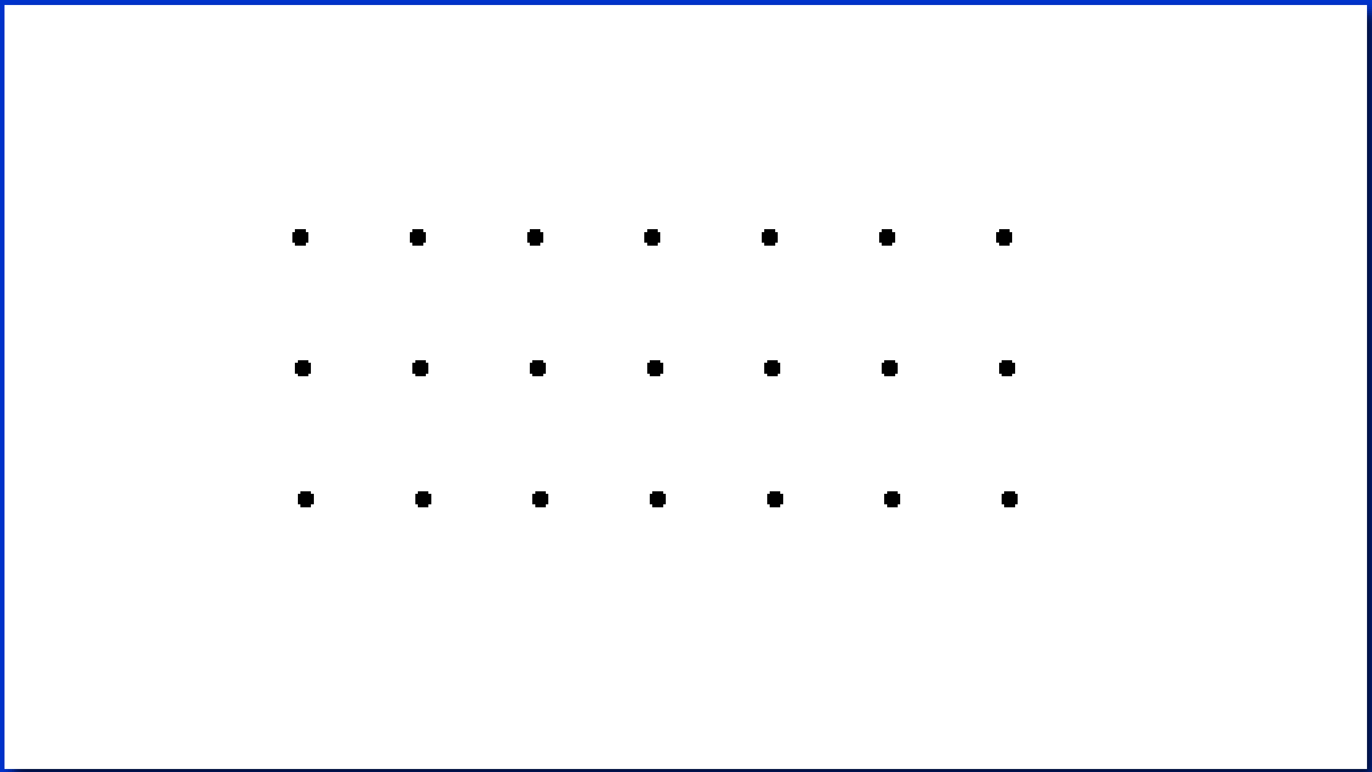
Inverting

(310)



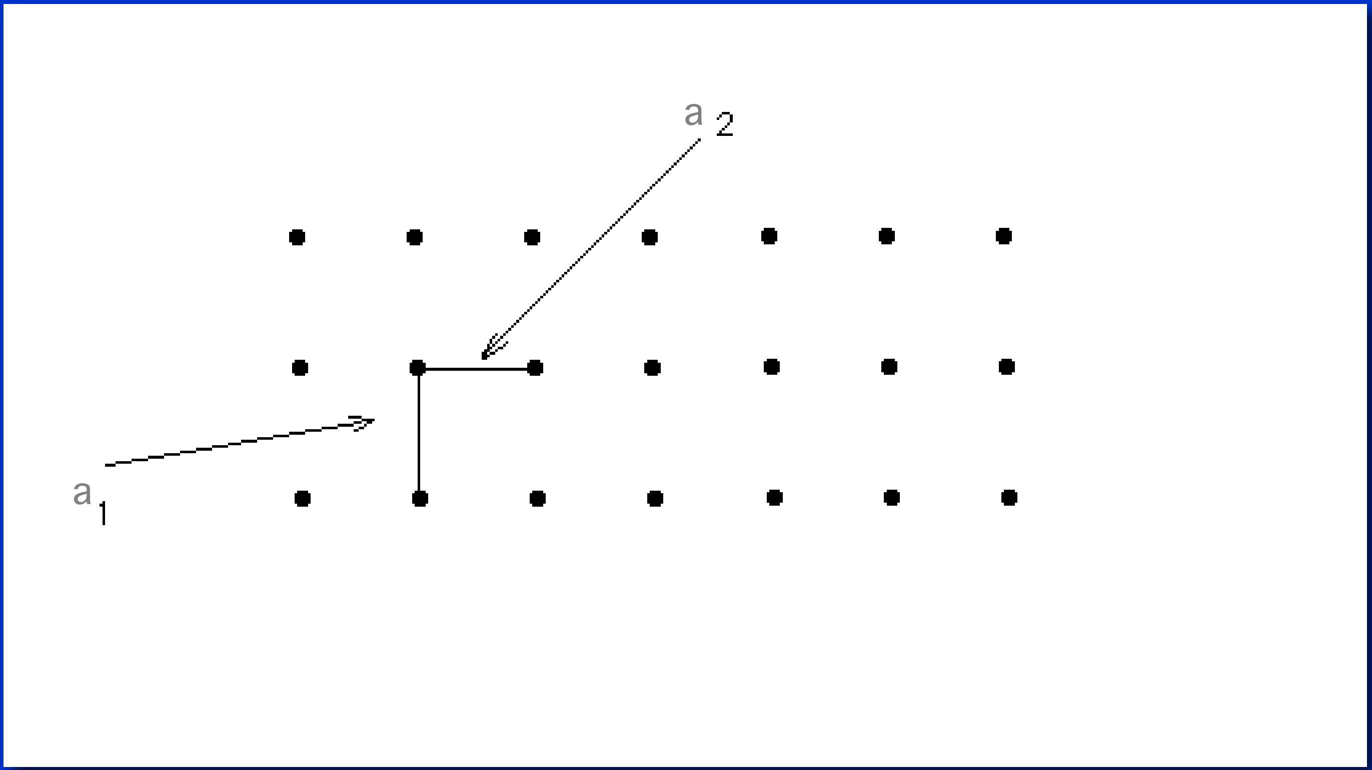
Reciprocal lattice

Real space lattice



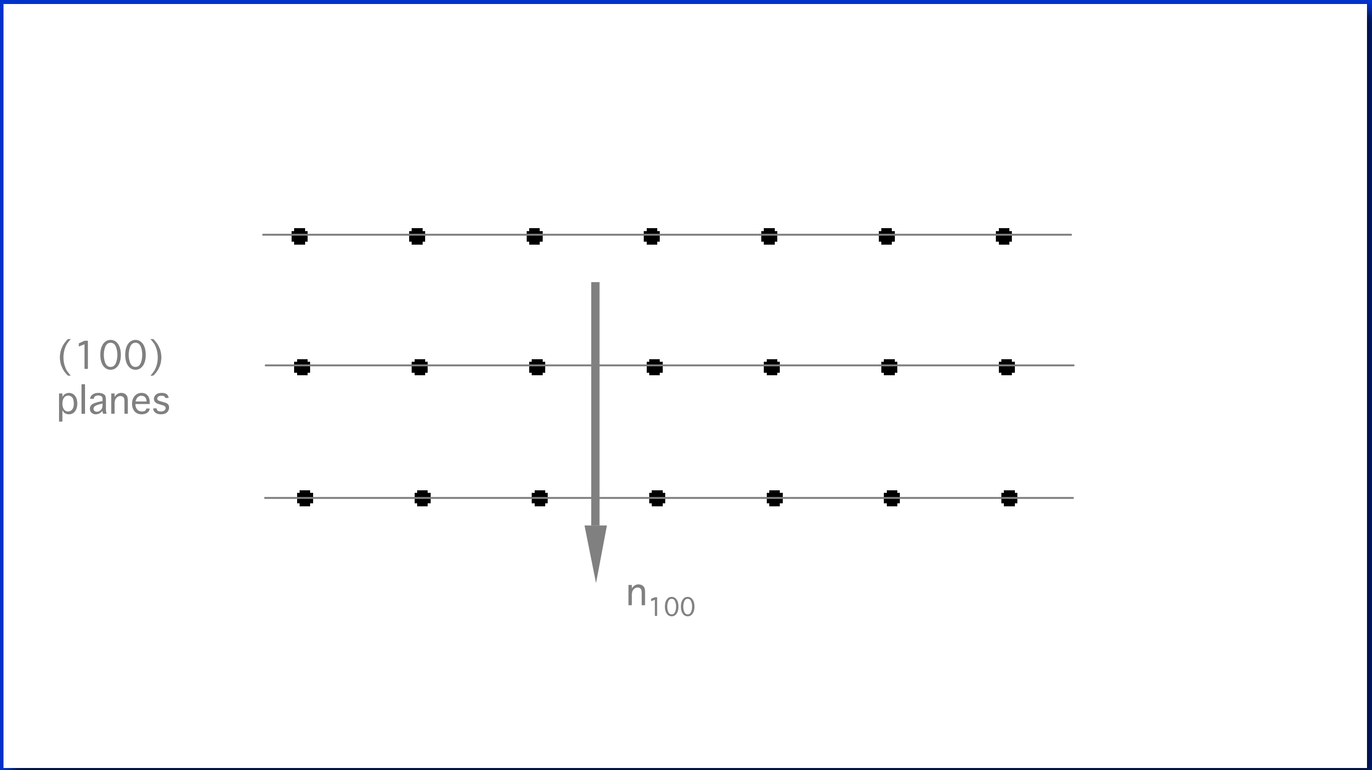
Reciprocal lattice

Real space lattice - basis vectors



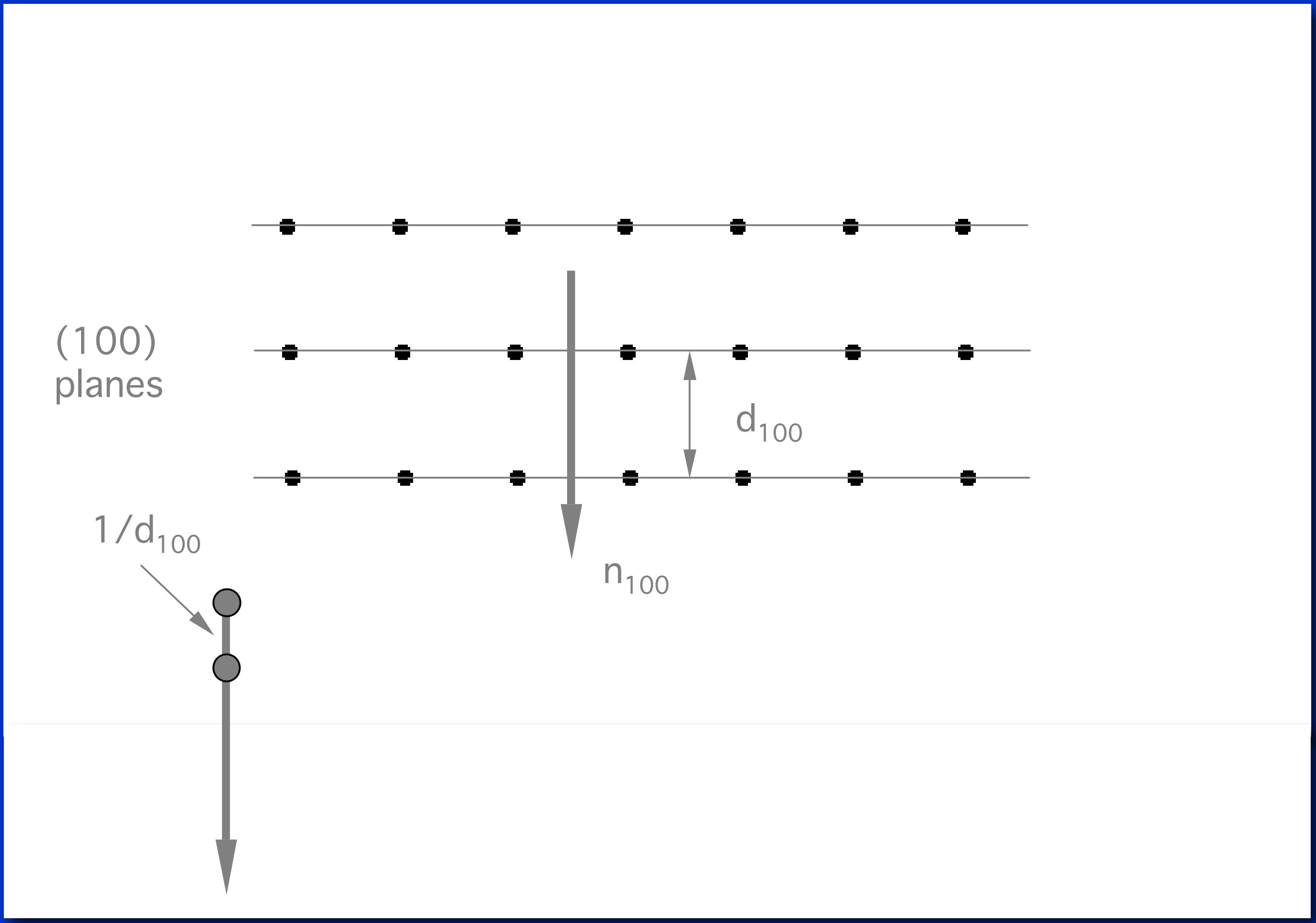
Reciprocal lattice

Real space lattice - choose set of planes



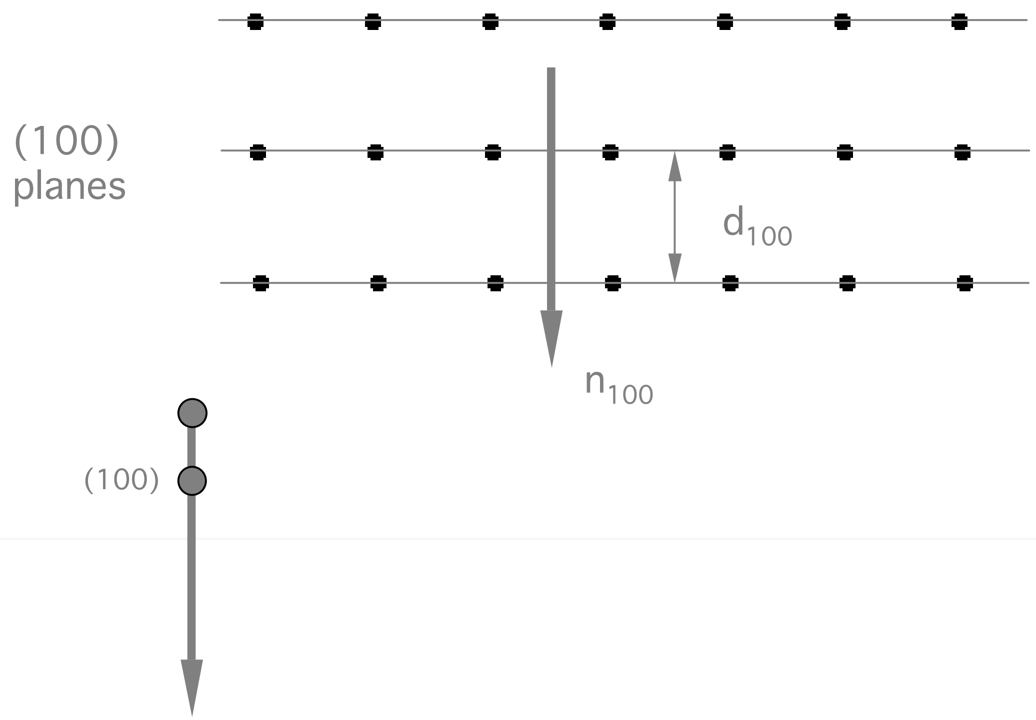
Reciprocal lattice

Real space lattice - interplanar spacing d



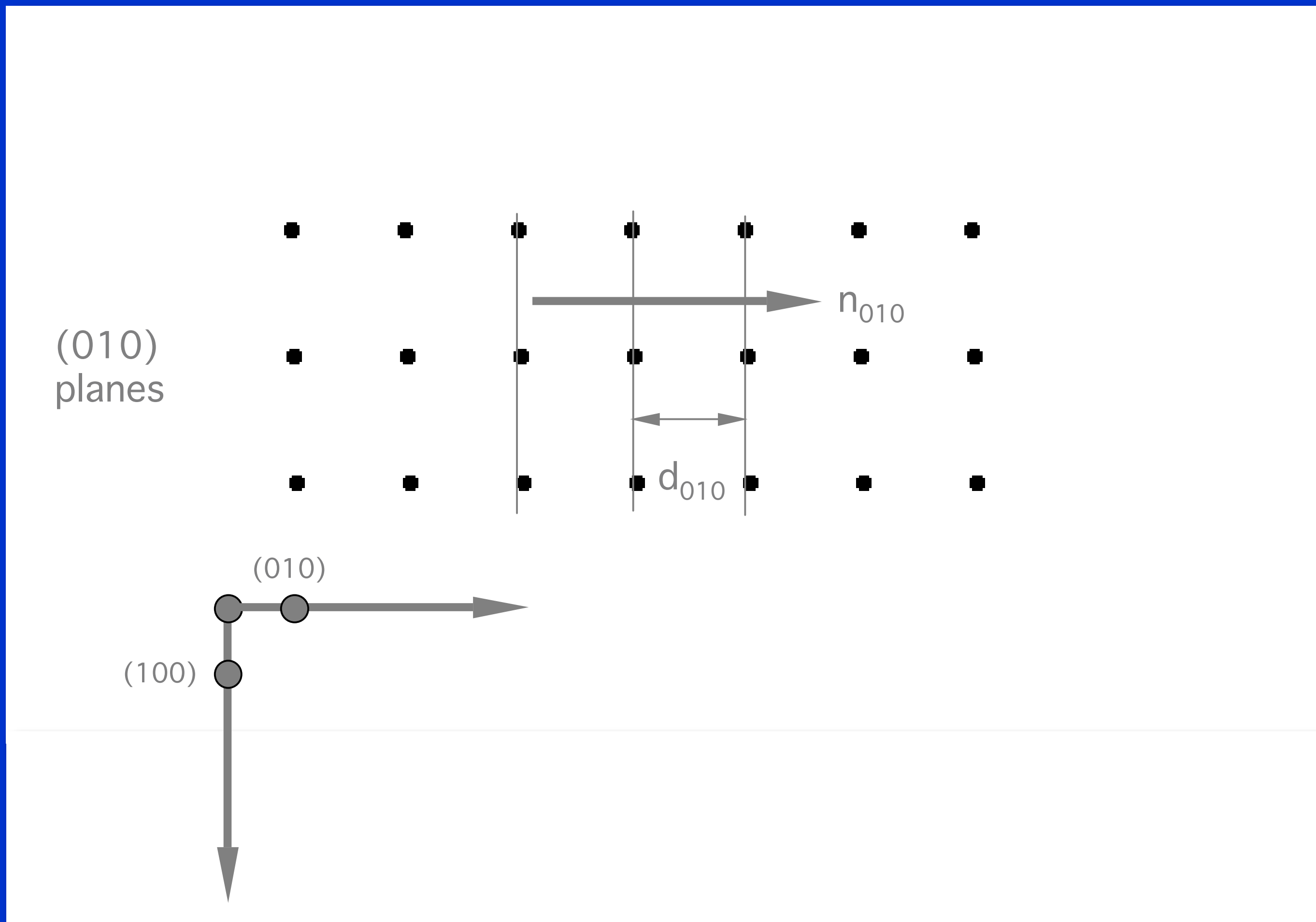
Reciprocal lattice

Real space lattice —> the (100) recip lattice pt



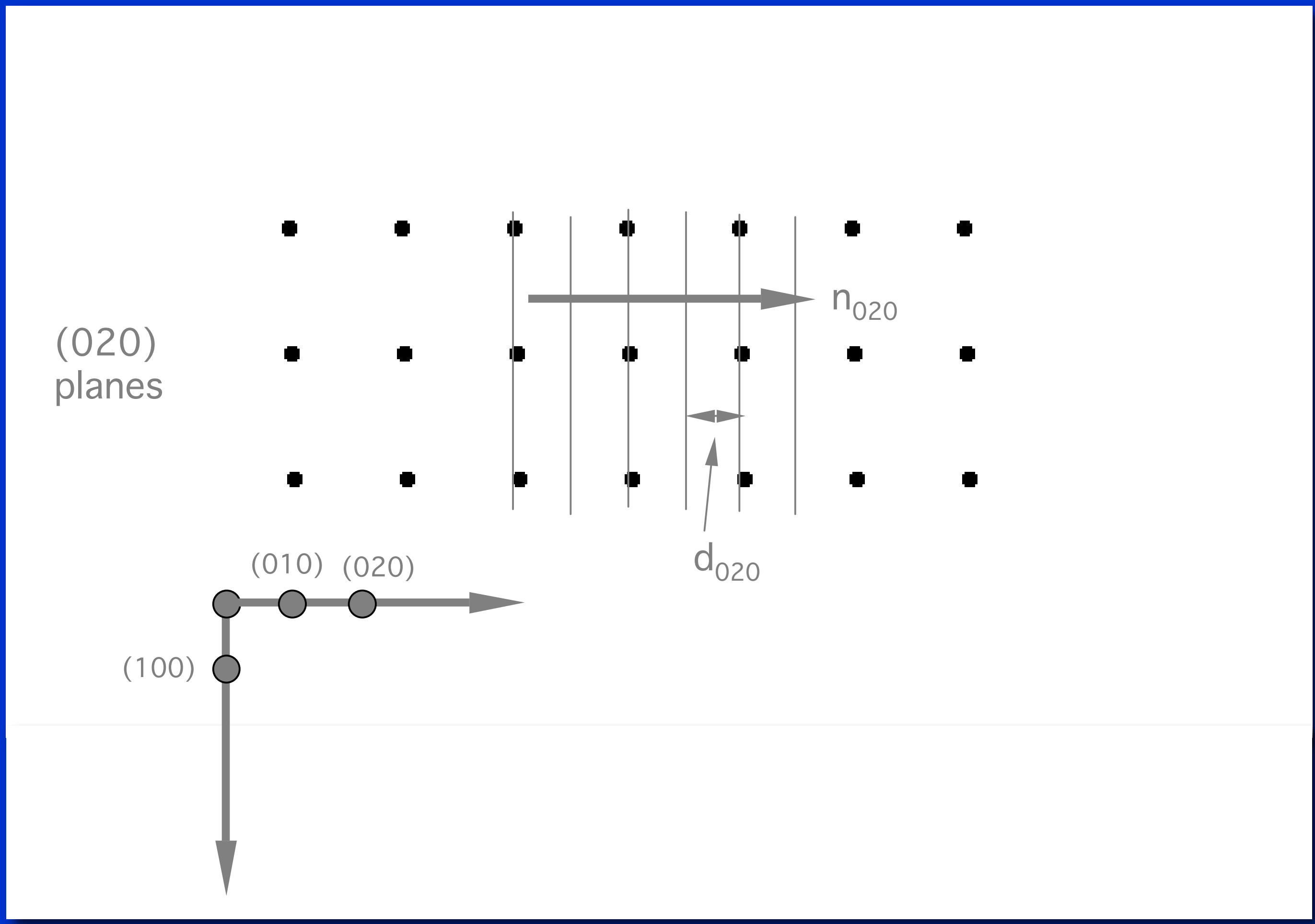
Reciprocal lattice

The (010) recip lattice pt



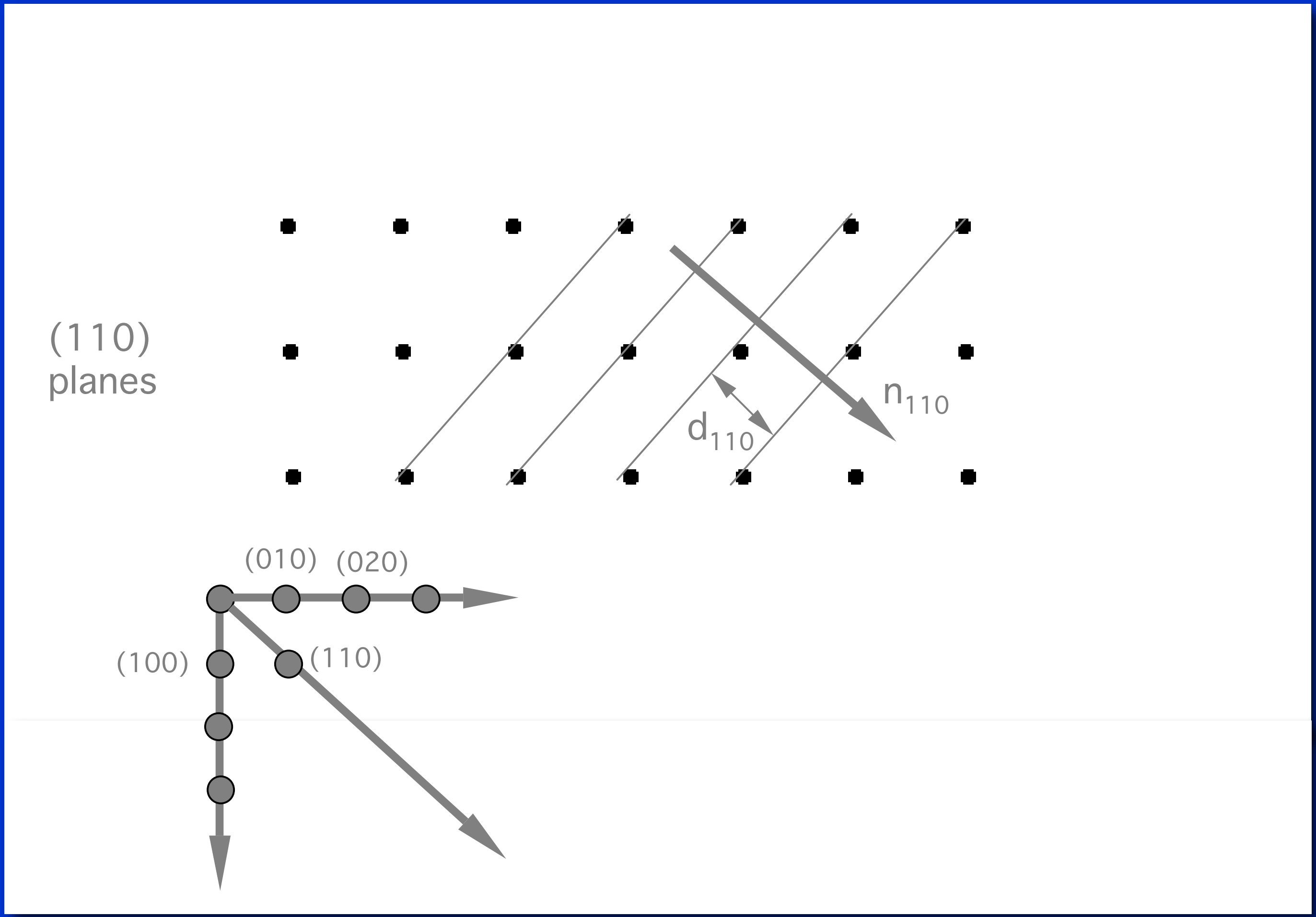
Reciprocal lattice

The (020) recip lattice pt



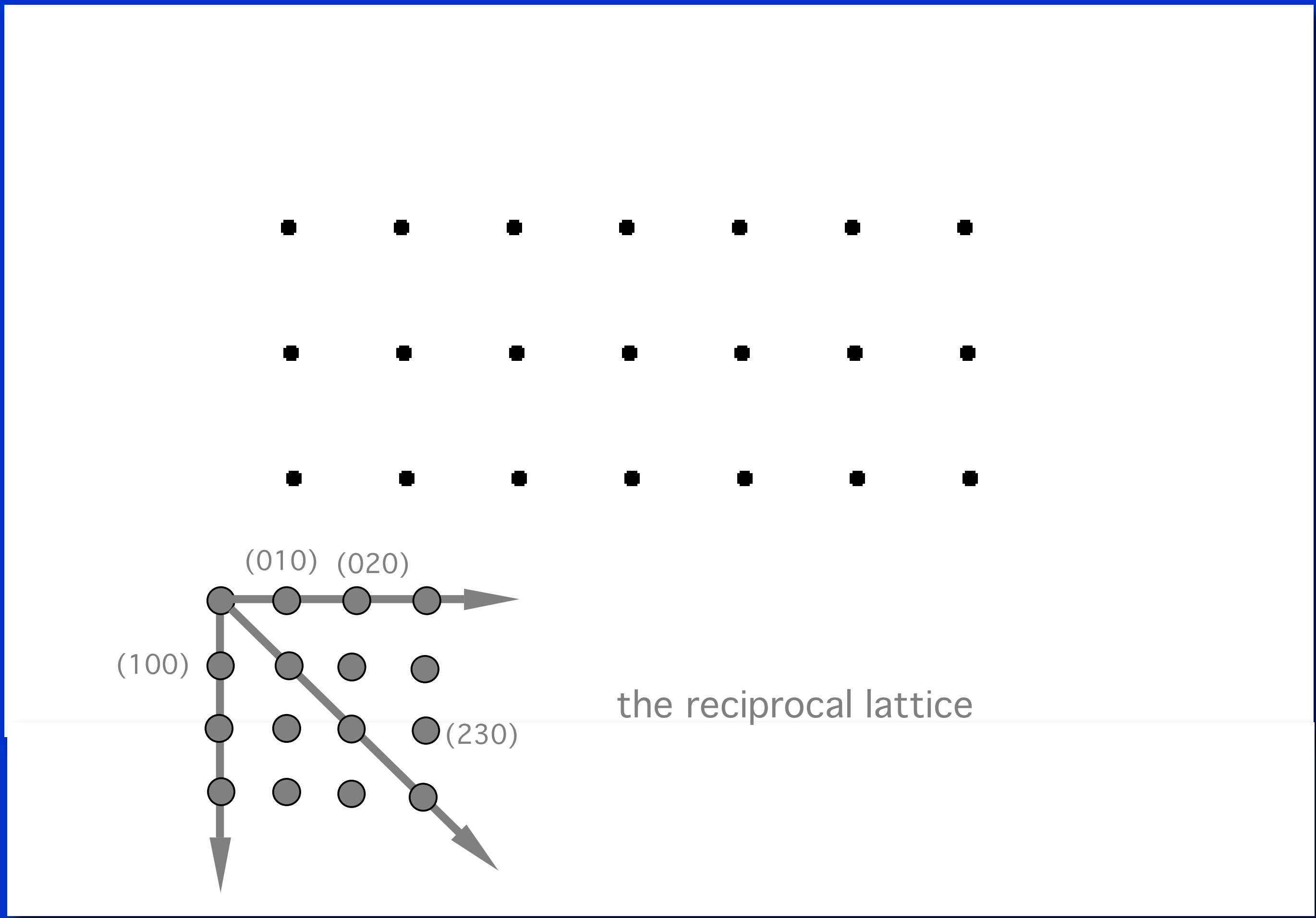
Reciprocal lattice

The (110) recip lattice pt



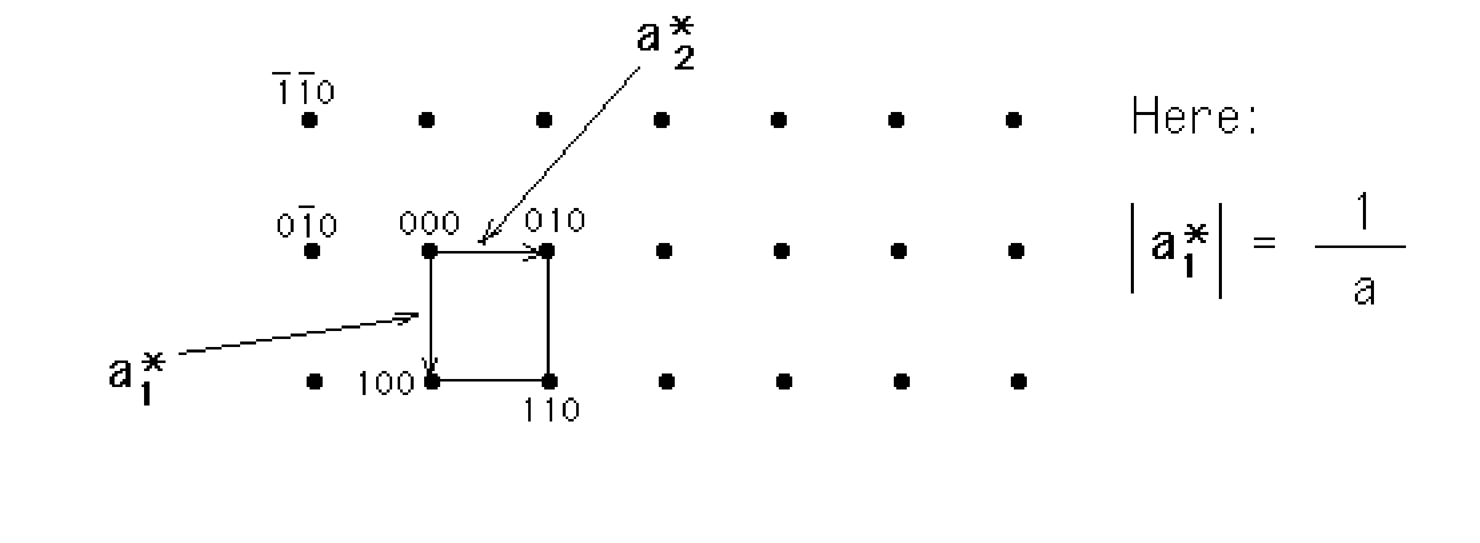
Reciprocal lattice

Still more recip lattice pts



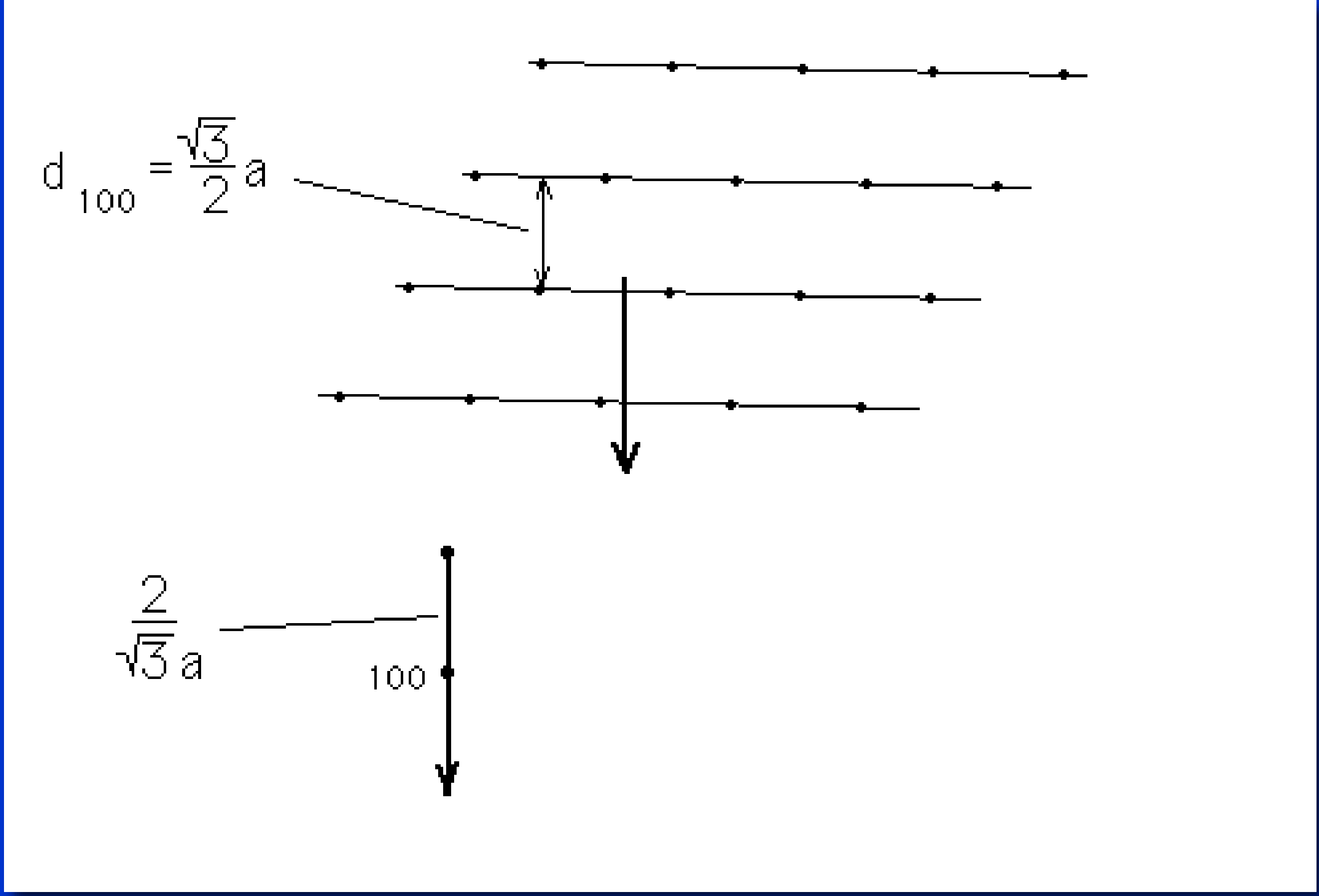
Reciprocal lattice

Recip lattice notation



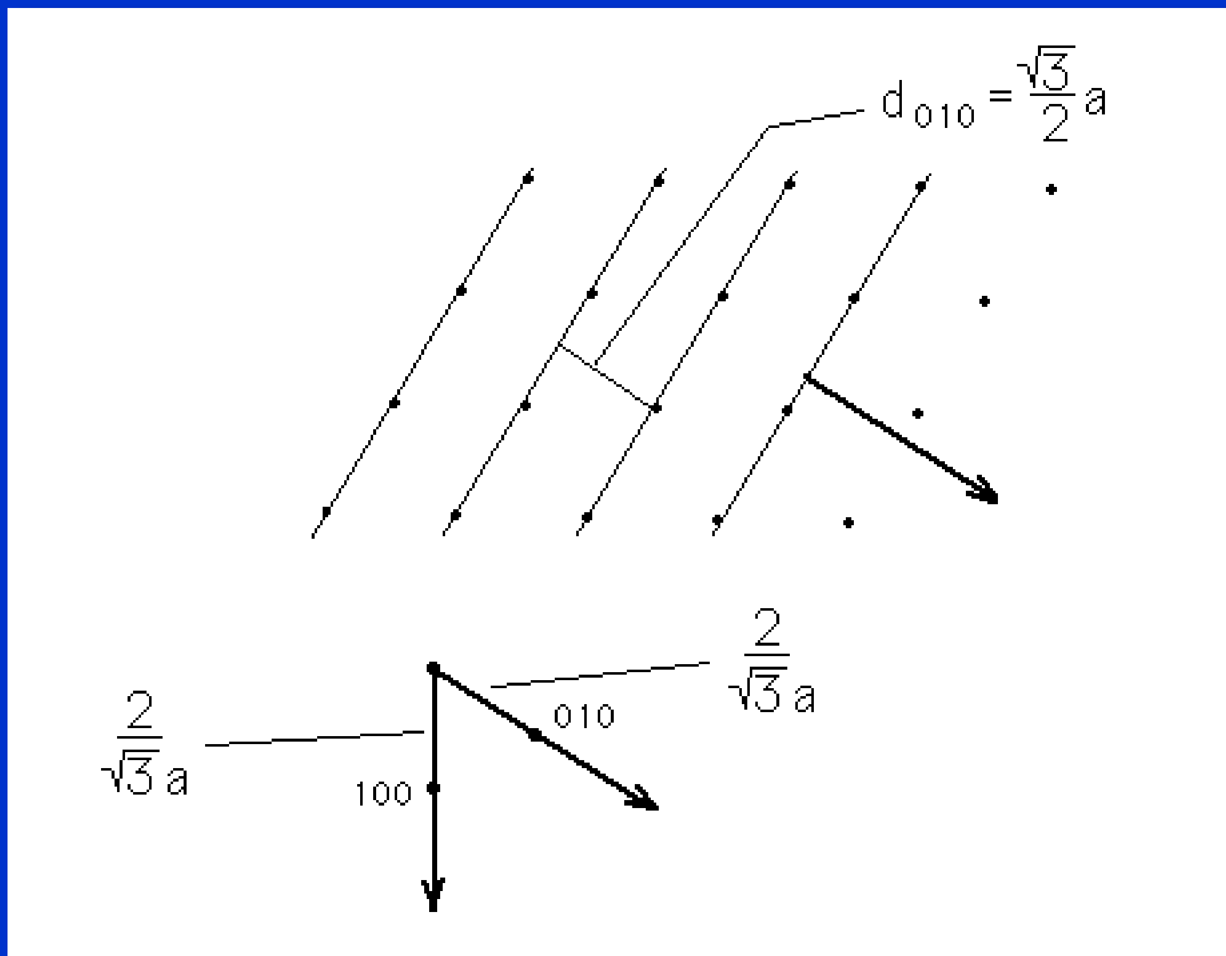
Reciprocal lattice

Hexagonal real space lattice



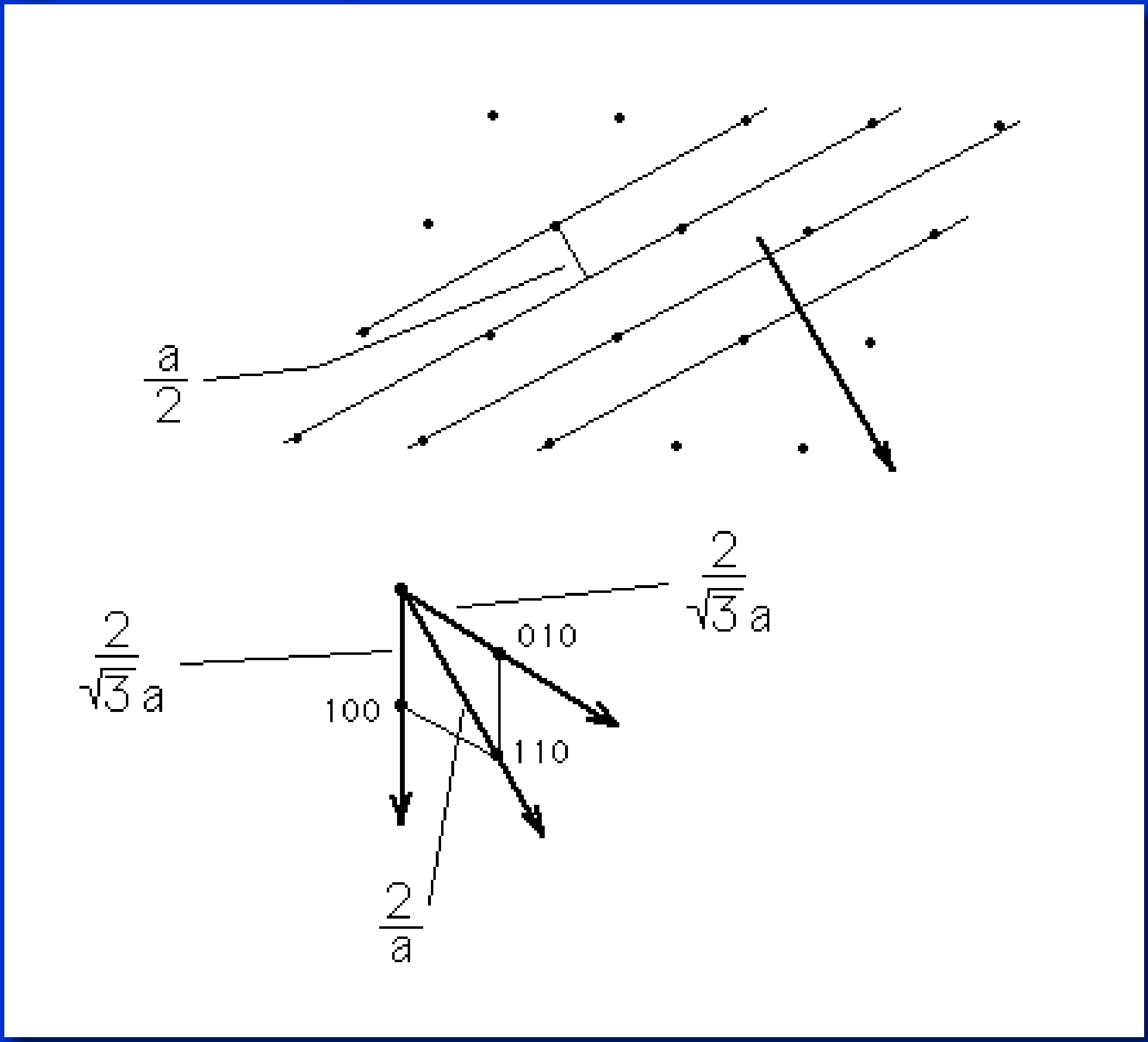
Reciprocal lattice

Hexagonal real space lattice



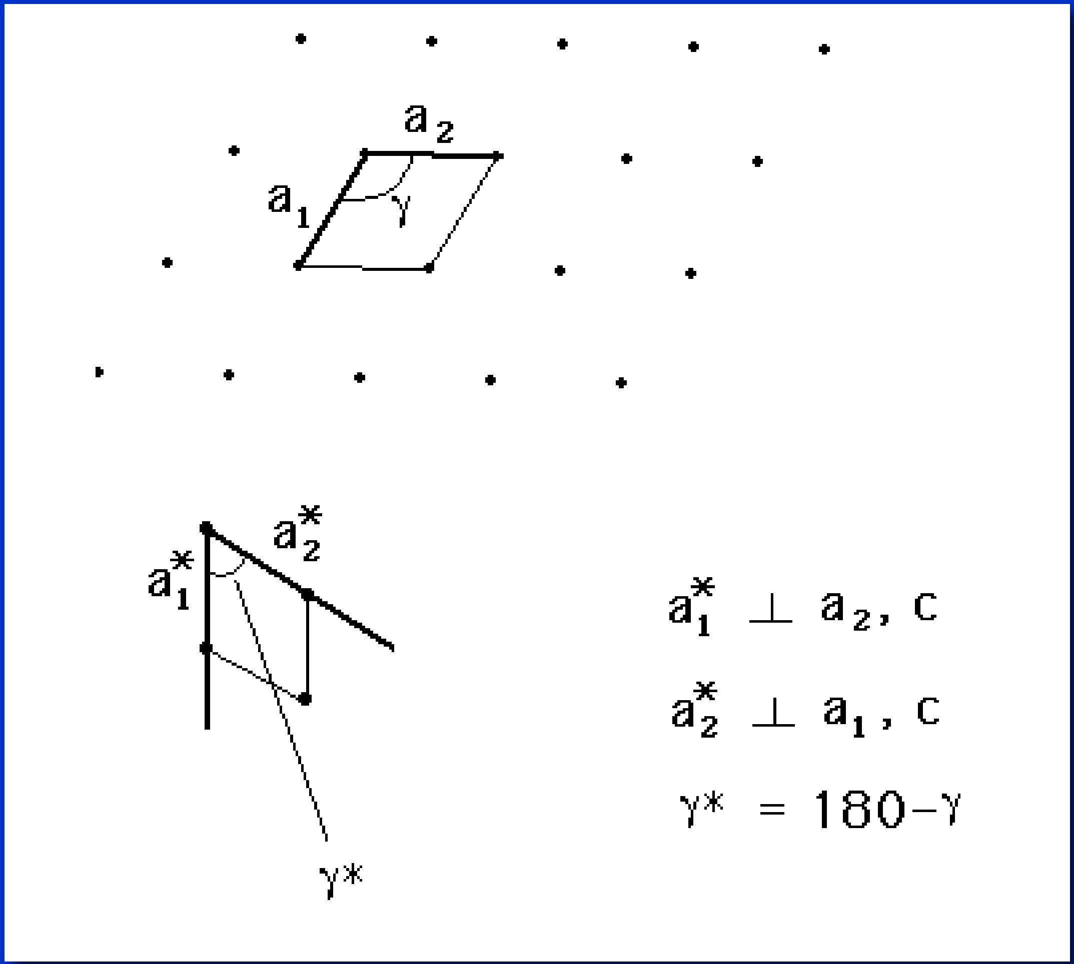
Reciprocal lattice

Hexagonal real space lattice



Reciprocal lattice

Hexagonal real space lattice



Reciprocal lattice

Reciprocal lattice vectors:

In general:

$$a^* = \frac{b \times c}{a \cdot b \times c}$$

$$b^* = \frac{c \times a}{a \cdot b \times c}$$

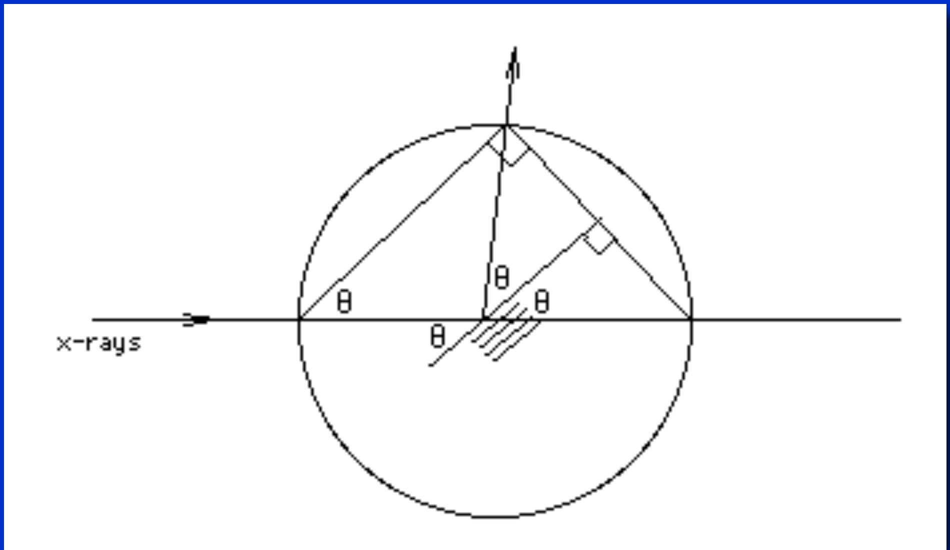
$$c^* = \frac{a \times b}{a \cdot b \times c}$$

Ewald construction

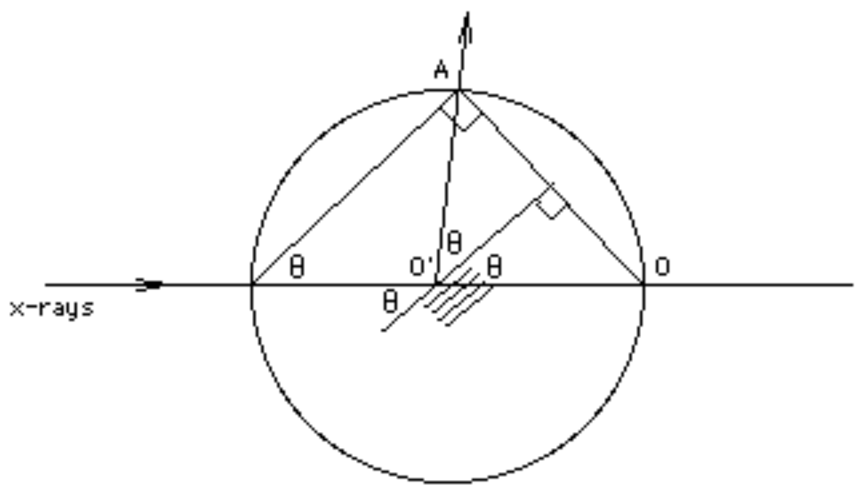
Think of set of planes reflecting in x-ray beam

Center sphere on specimen origin
x-ray beam is a sphere diameter

Construct lines as below



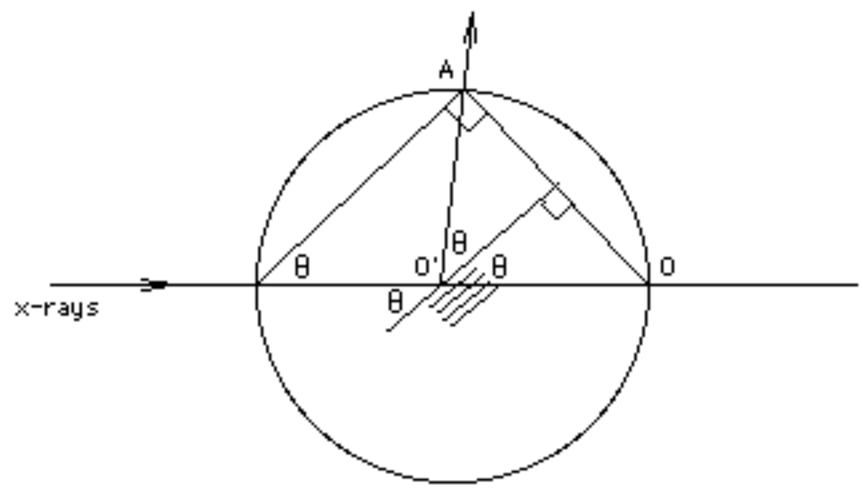
Ewald construction



sphere radius = $1/\lambda$

$$\sin\theta = \frac{AO}{2/\lambda} \qquad 2\sin\theta = AO \cdot \lambda$$

Ewald construction

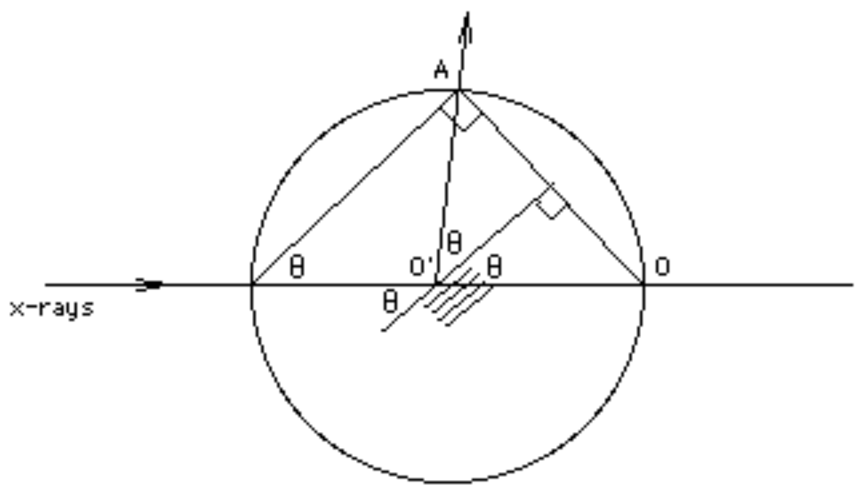


sphere radius = $1/\lambda$

$2 \sin \theta \;=\; AO \cdot \lambda$

Braggs' law if AO = 1/d
AO is normal to planes

Ewald construction



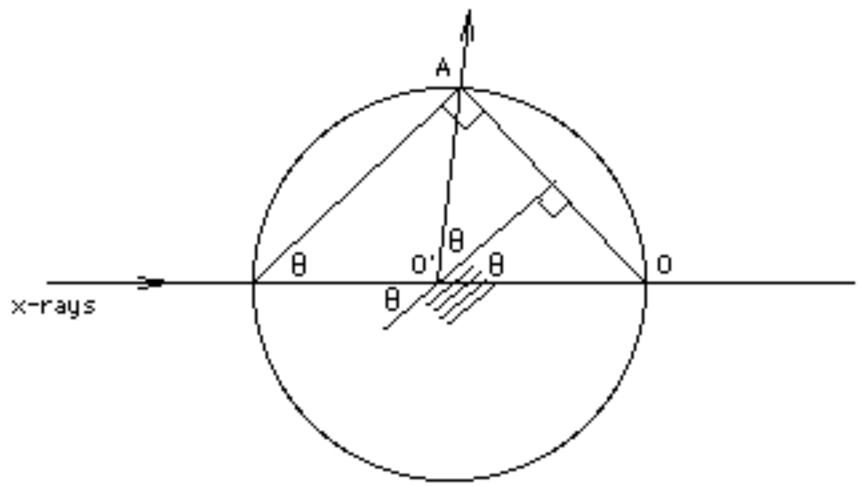
sphere radius = $1/\lambda$

$2 \sin \theta = AO \cdot \lambda$

Braggs' law if AO = 1/d
AO is normal to planes

If O is origin then A is a reciprocal lattice point

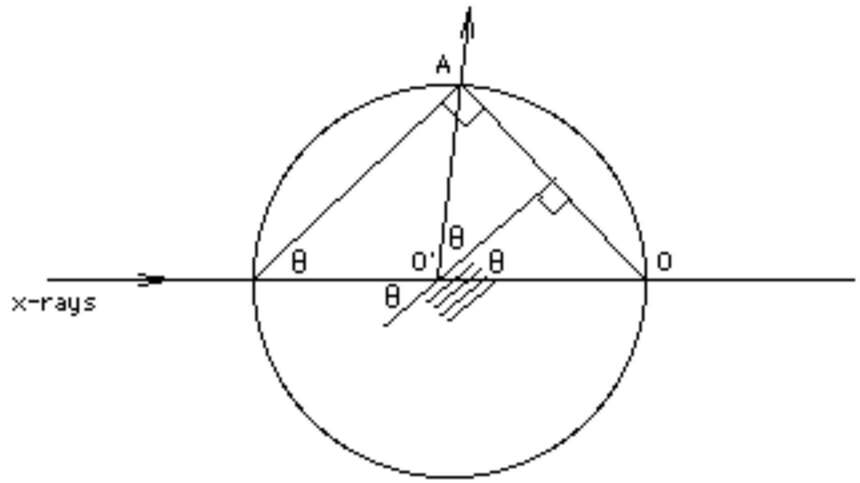
Ewald construction



Criterion: if the origin of the reciprocal lattice is placed at O, then, for any reciprocal lattice point on the Ewald sphere, there be reflection along the direction from the center of the sphere to the point on the sphere.

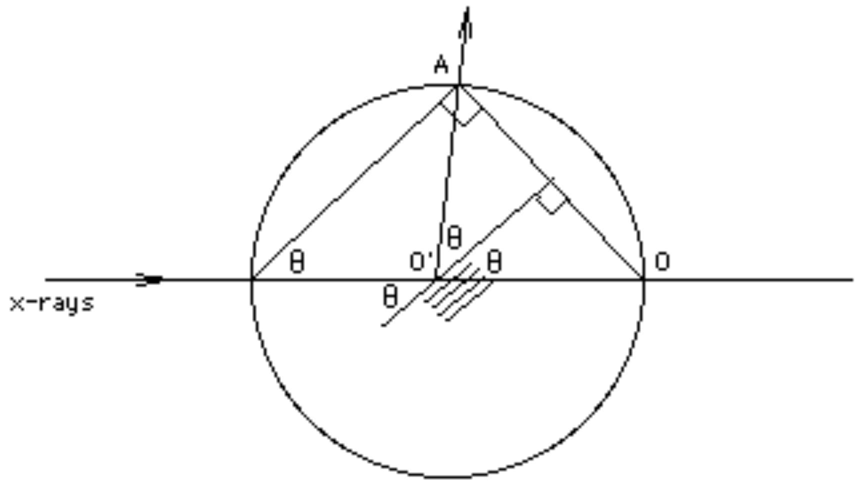
Any point in the reciprocal lattice which does not lie on the sphere corresponds to sets of planes which are not in a position to reflect.

Ewald construction



In general, reciprocal lattice points do not lie on the sphere.

Ewald construction



In general, reciprocal lattice points do not lie on the sphere.

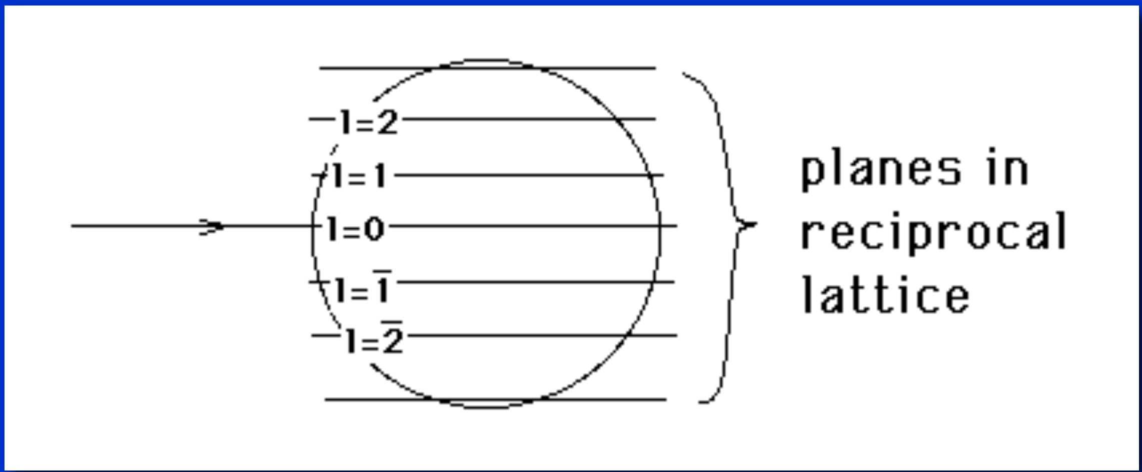
To observe the reflections, then, we must:

1. move the sphere
2. move the crystal (rotate)
3. change the size of the sphere

Ewald construction

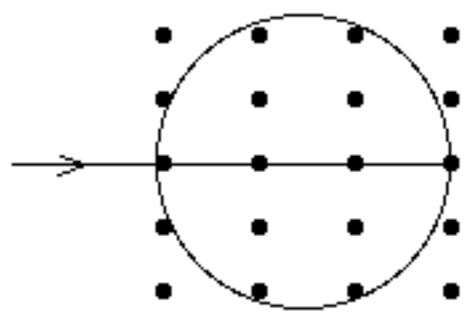
Most common in single crystal studies is to move (usually rotate) crystal

Consider crystal placed at sphere center oriented w/ planes of points in reciprocal lattice as below



Ewald construction

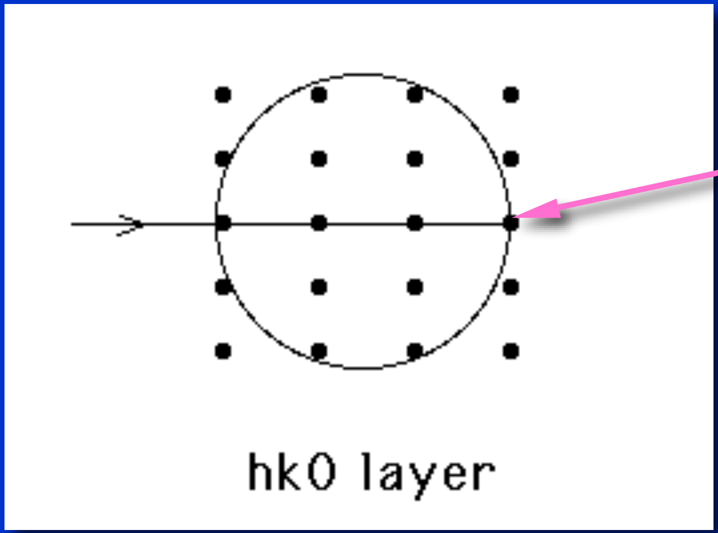
Looking down on one plane of points....
the equatorial plane:


hk0 layer

Ewald construction

Looking down on one plane of points....
the equatorial plane

No points on sphere (here, in 2-D, a circle);
must rotate reciprocal lattice to
observe reflections.

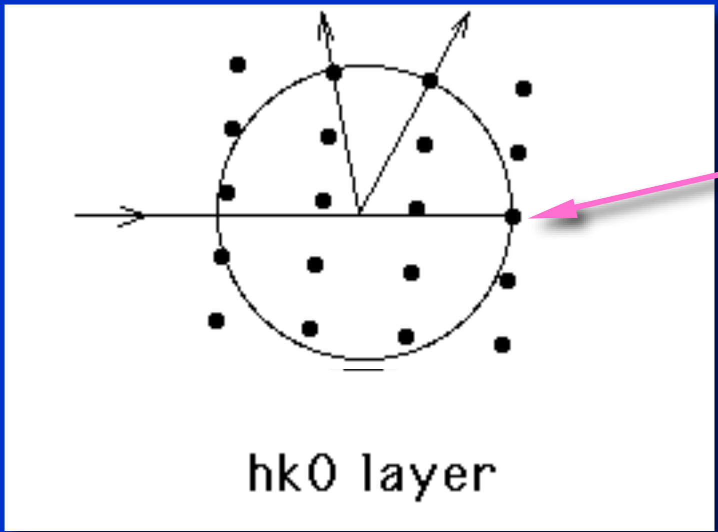


rotate around axis here,
perpendicular to screen

Ewald construction

Looking down on one plane of points....
the equatorial plane

Must rotate reciprocal lattice to
observe reflections.

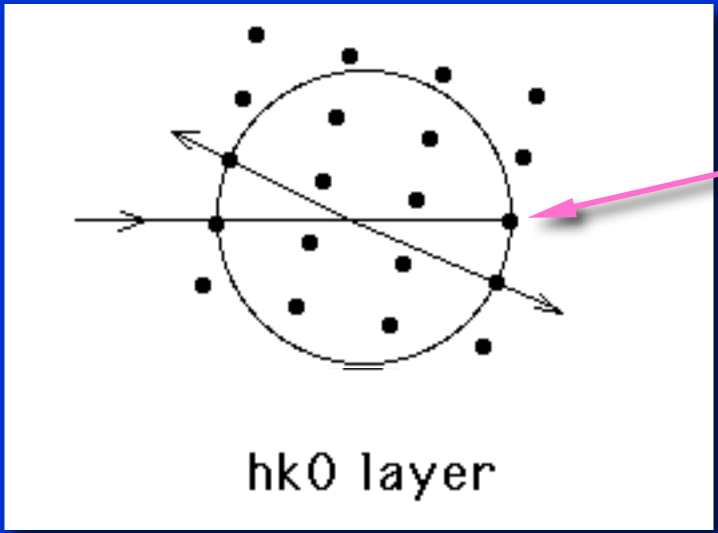


rotate around axis here,
perpendicular to screen

Ewald construction

Looking down on one plane of points....
the equatorial plane

Must rotate reciprocal lattice to
observe reflections.

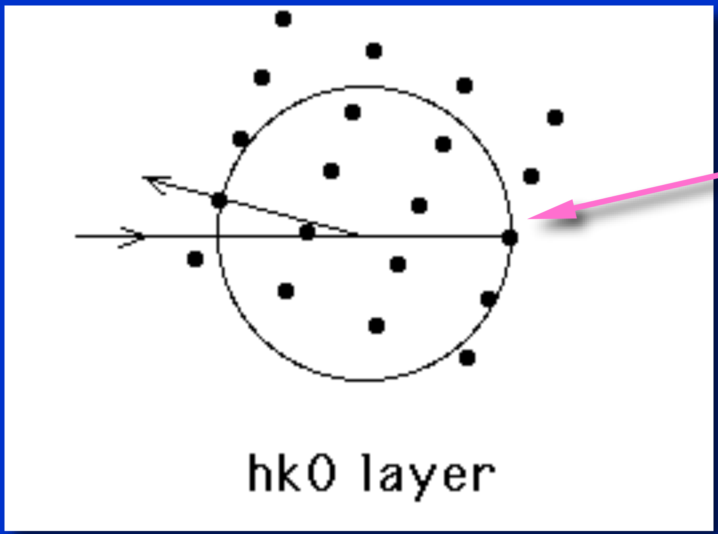


rotate around axis here,
perpendicular to screen

Ewald construction

Looking down on one plane of points....
the equatorial plane

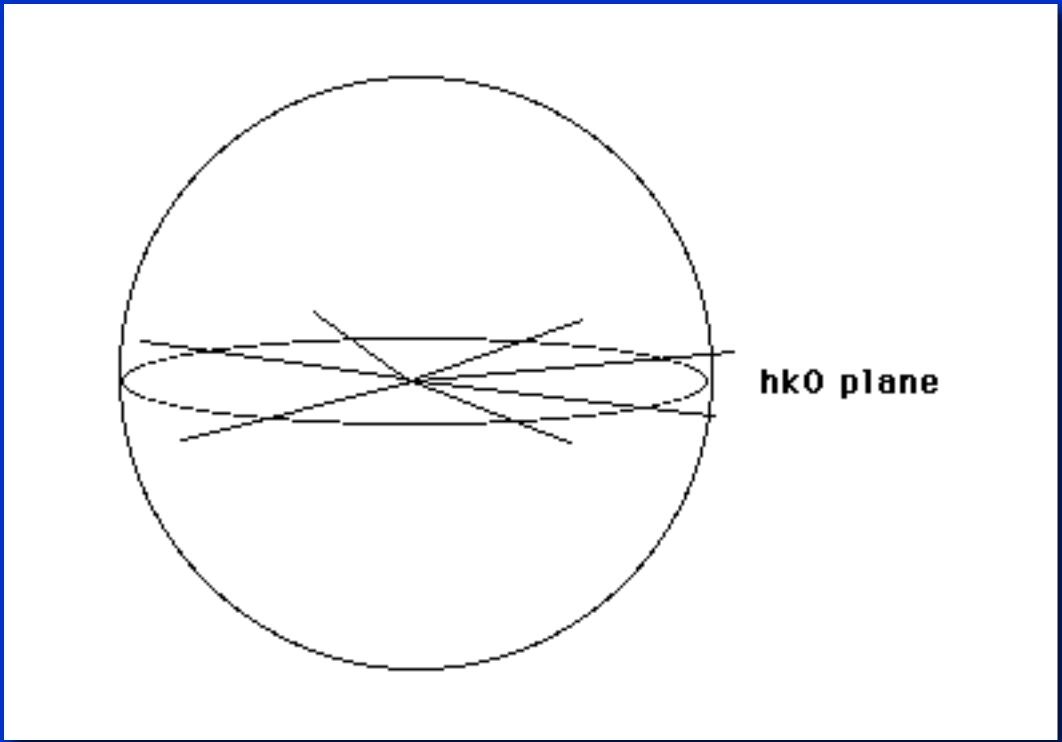
Must rotate reciprocal lattice to
observe reflections.



rotate around axis here,
perpendicular to screen

Ewald construction

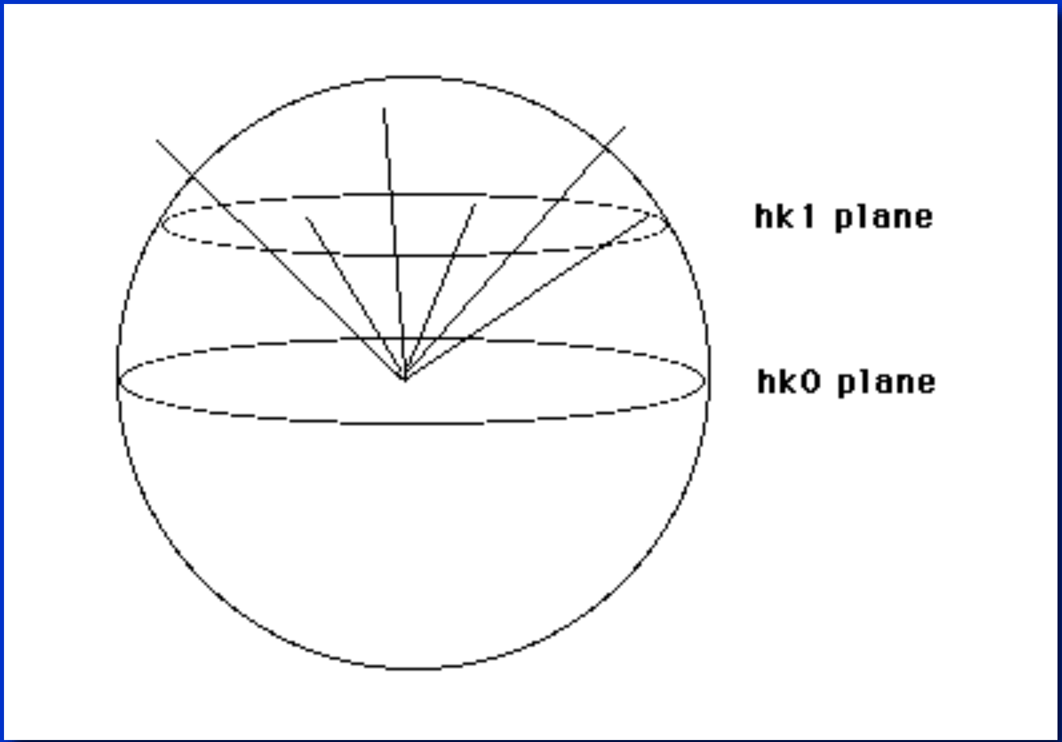
hk0 reflected rays all lie in the equatorial plane.



Ewald construction

hk0 reflected rays all lie in the equatorial plane.

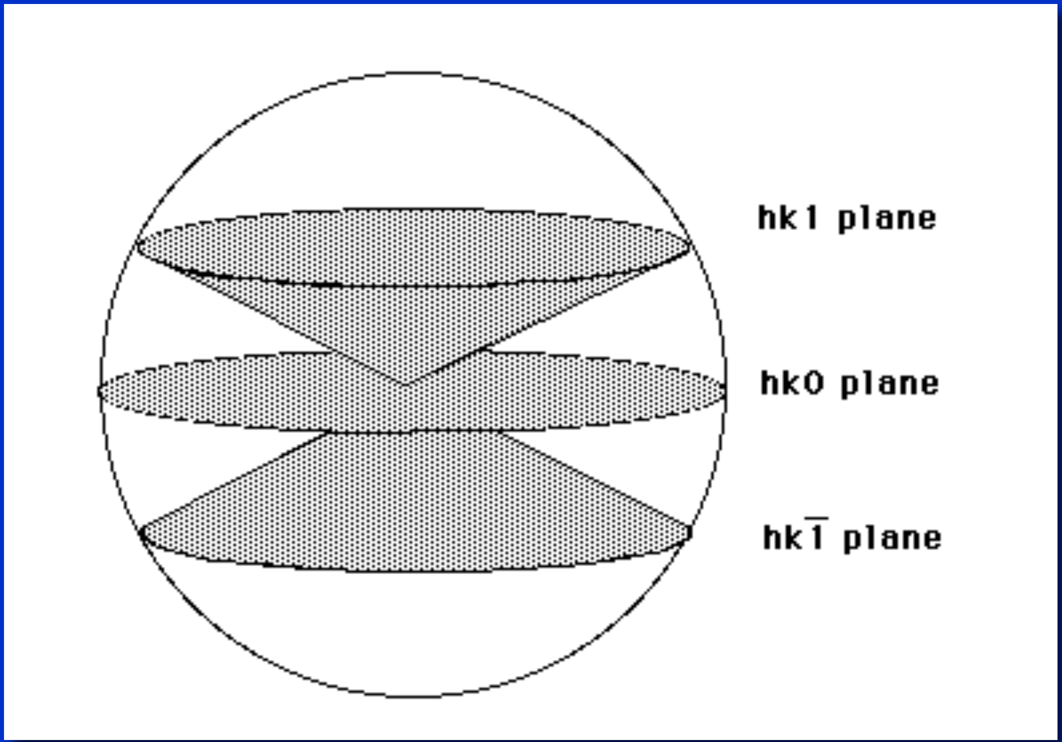
hk1 reflected rays lie on a cone.



Ewald construction

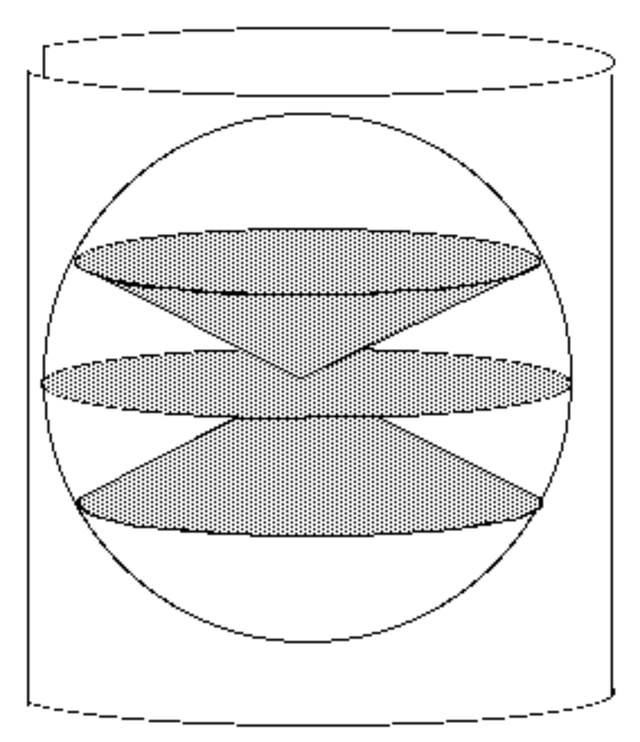
hk0 reflected rays all lie in the equatorial plane.

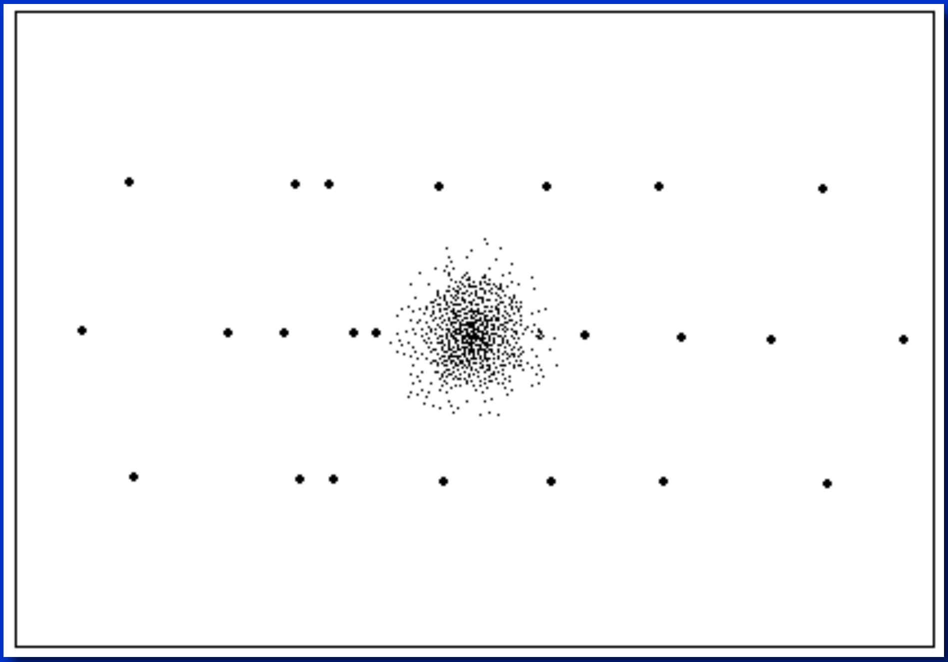
hk1 reflected rays lie on a cone.



Ewald construction

Sheet of film or image paper wrapped cylindrically around crystal…. looks like this after x-ray exposure of oscillating crystal …..when flattened:



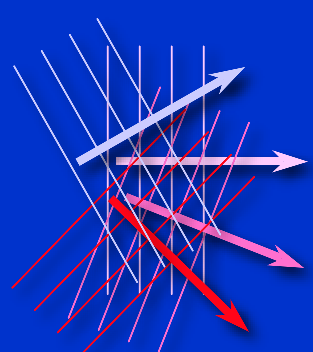


Ewald construction

To see reflections:

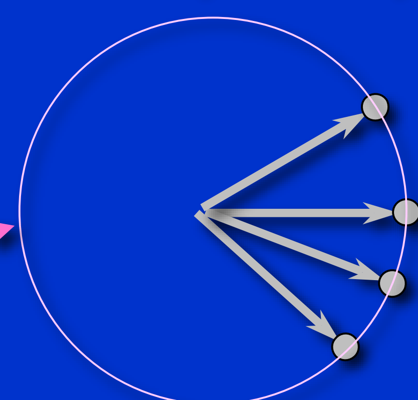
move sphere
move crystal
change sphere size
use polycrystalline sample

real space

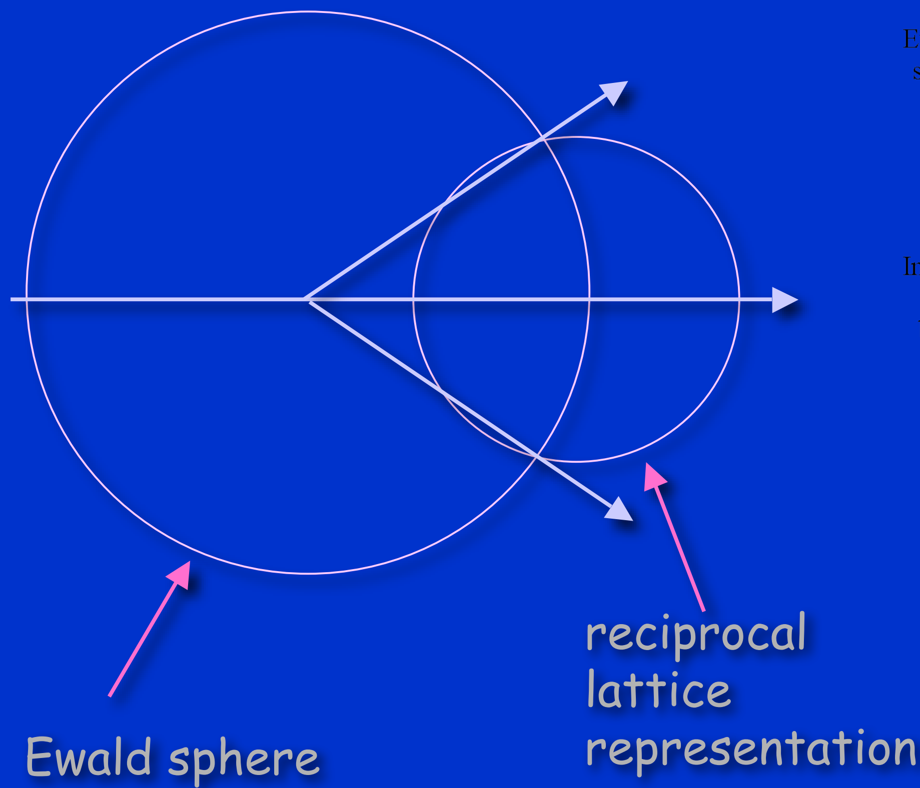


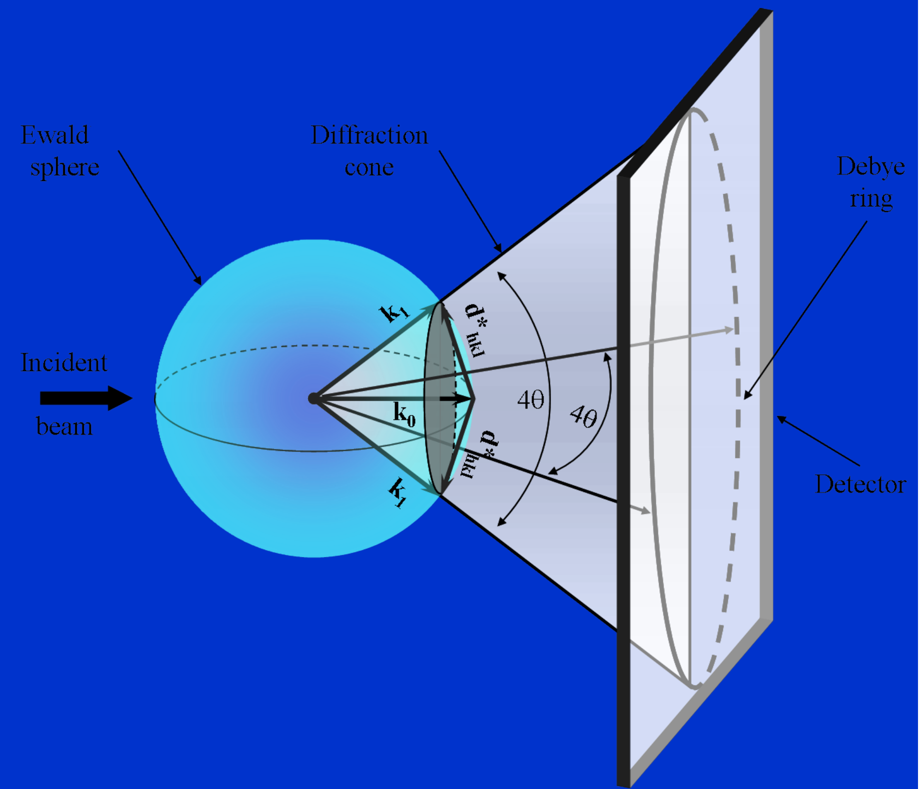
only one set of planes - one (hkl)

reciprocal space

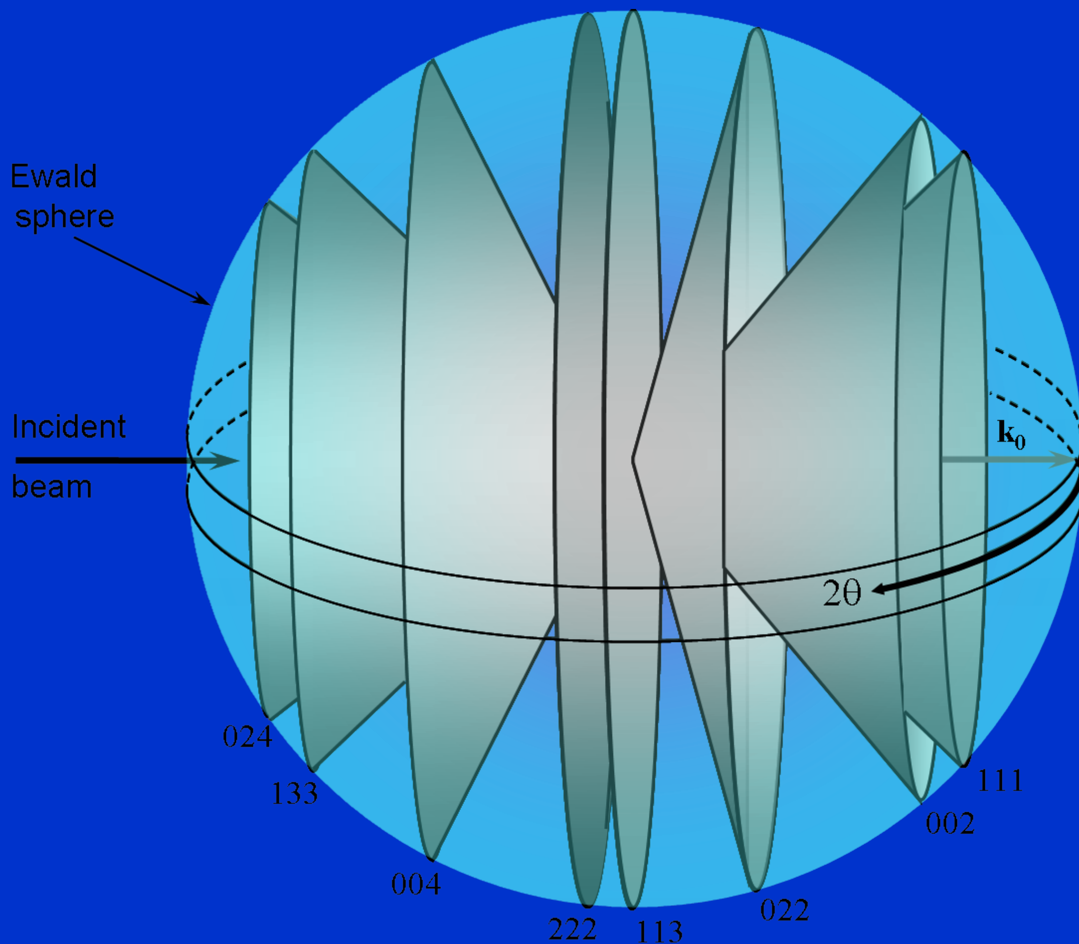


Ewald construction

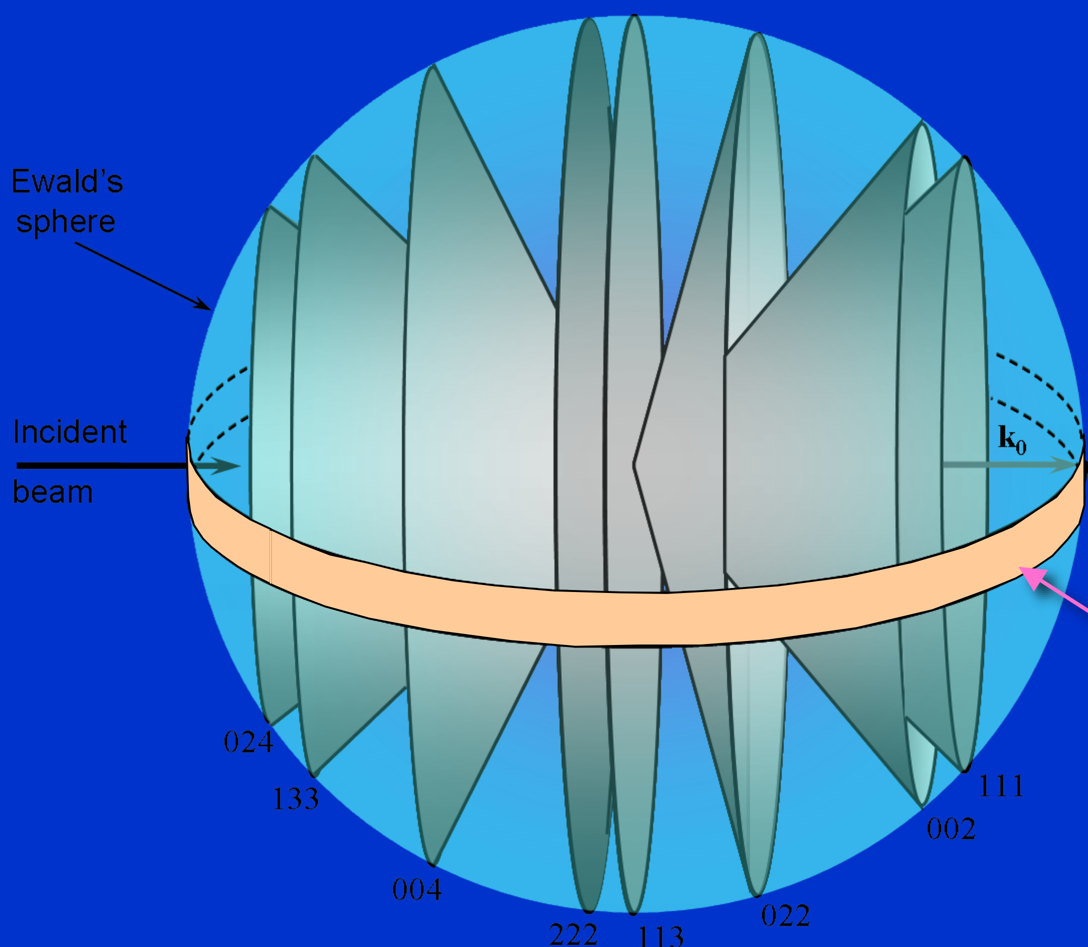




Ewald construction



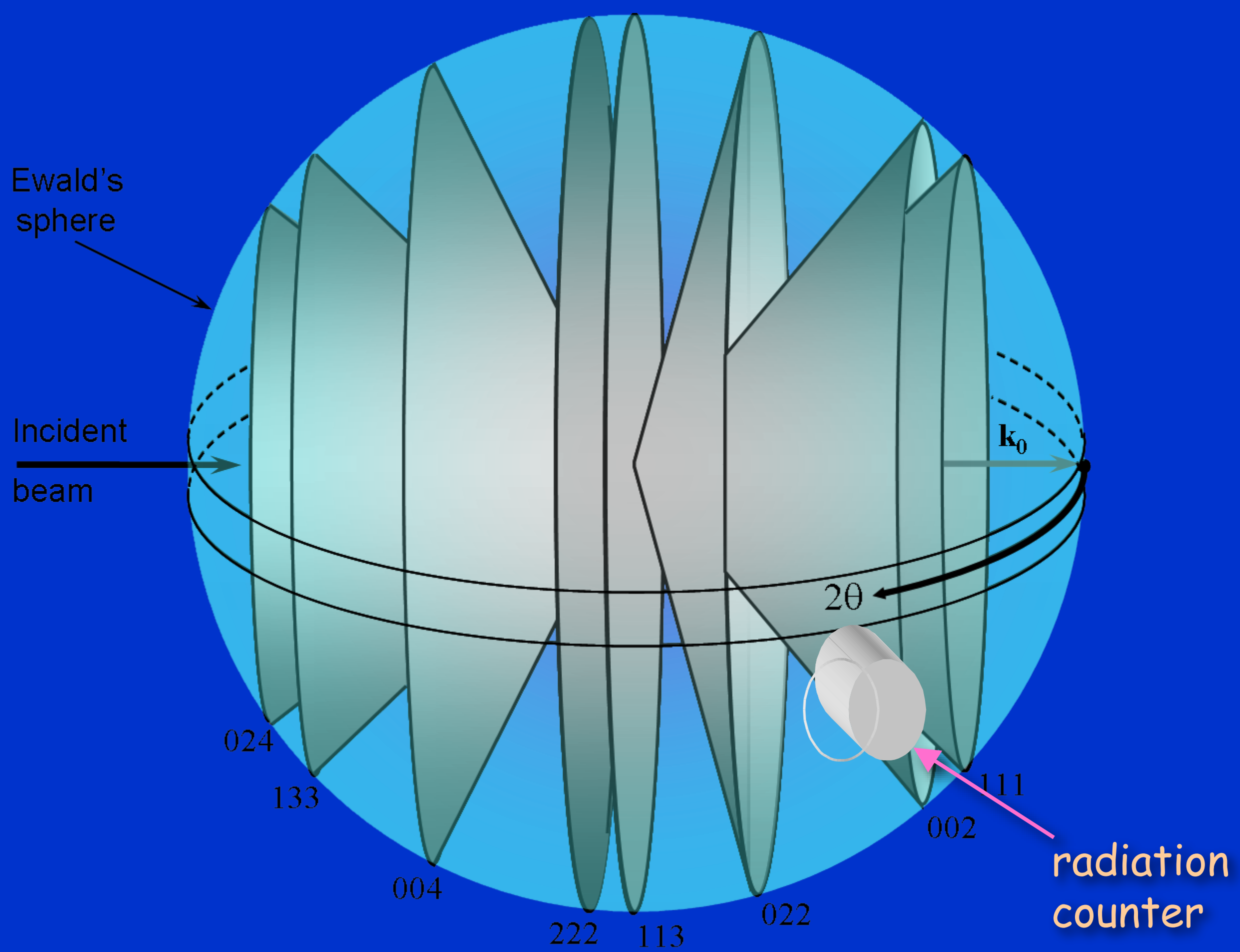
X-ray powder diffractometer



rarely used now

film or image paper

X-ray powder diffractometer

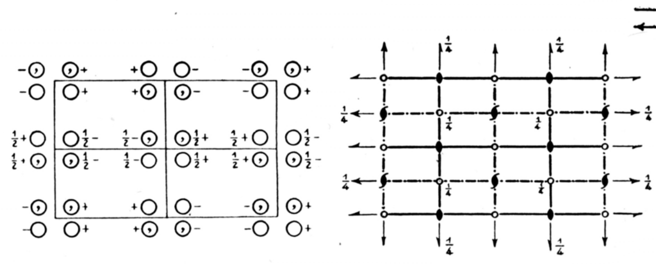


Crystal structures

Ex:

YCu_2 is Imma, with a = 4.308, b = 6.891, c = 7.303 Å, Y in 4e, z = 0.5377, B = 0.82 Å^2 and Cu in 8h, y = 0.0510, z = 0.1648, B = 1.13 Å^2

Imma D_{2h}^{28} No. 74 $I\,2/m\,2/m\,2/a$ $m\,m\,m$ Orthorhombic



Origin at centre ($2/m2_11$)

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions $(0,0,0;\ \tfrac12,\tfrac12,\tfrac12)+$	Conditions limiting possible reflections
				General:
16	*j*	1	$x,y,z;\ x,\bar y,\bar z;\ x,\tfrac12+y,\bar z;\ x,\tfrac12-y,z;$ $\bar x,\bar y,\bar z;\ \bar x,y,z;\ \bar x,\tfrac12-y,z;\ \bar x,\tfrac12+y,\bar z.$	hkl: $h+k+l=2n$; $0kl$: $(k+l=2n)$; $h0l$: $(l+h=2n)$; $hk0$: $h=2n$; $(k=2n)$; $h00$: $(h=2n)$; $0k0$: $(k=2n)$; $00l$: $(l=2n)$
				Special: as above, plus
8	*i*	*m*	$x,\tfrac14,z;\ \bar x,\tfrac34,\bar z;\ \bar x,\tfrac14,z;\ x,\tfrac34,\bar z.$	no extra conditions
8	*h*	*m*	$0,y,z;\ 0,\bar y,\bar z;\ 0,\tfrac12+y,\bar z;\ 0,\tfrac12-y,z.$	
8	*g*	2	$\tfrac14,y,\tfrac14;\ \tfrac34,\bar y,\tfrac34;\ \tfrac34,y,\tfrac14;\ \tfrac14,\bar y,\tfrac34.$	hkl: $h=2n$; $(k+l=2n)$
8	*f*	2	$x,0,0;\ \bar x,0,0;\ x,\tfrac12,0;\ \bar x,\tfrac12,0.$	hkl: $k=2n$; $(l+h=2n)$
4	*e*	*mm*	$0,\tfrac14,z;\ 0,\tfrac34,\bar z.$	no extra conditions
4	*d*	$2/m$	$\tfrac14,\tfrac14,\tfrac34;\ \tfrac34,\tfrac14,\tfrac34.$	hkl: $h=2n$; $(k+l=2n)$
4	*c*	$2/m$	$\tfrac14,\tfrac14,\tfrac14;\ \tfrac34,\tfrac14,\tfrac14.$	
4	*b*	$2/m$	$0,0,\tfrac12;\ 0,\tfrac12,\tfrac12.$	hkl: $k=2n$; $(l+h=2n)$
4	*a*	$2/m$	$0,0,0;\ 0,\tfrac12,0.$	

Intensities

$$F_{hkl} = \sum_{j=1}^{N} f_j \, e^{2\pi i (hx_j + ky_j + lz_j)}$$

Now

$$I_{hkl} = \text{scale factor} \cdot p \cdot LP \cdot A \cdot |F_{hkl}|^2 \cdot e^{-2M(T)}$$

$e^{-2M(T)}$ = temperature factor (also called Debye-Waller factor)

$$2M(T) = 16\pi^2 (\mu(T))^2 (\sin\theta)^2/\lambda^2$$

μ^2 = mean square amplitude of thermal vibration of atoms direction normal to planes (hkl)

$$\frac{I(\text{high } T)}{I(\text{low } T)} = \frac{e^{-2M(\text{high } T)}}{e^{-2M(\text{low } T)}} = \frac{1}{e^{2M(\text{high } T) - 2M(\text{low } T)}}$$

Intensities —> crystal structure

So, OK, how do we do it?

Outline of procedure:

Measure reflection positions in x-ray diffraction pattern -
index, get unit cell type and size, possible space groups

Measure density, if possible, to get
number formula units/unit cell (N)
density = N x formula wt/(cell volume x Avogadro's no.)

Measure reflection intensities, get F-values, calculate electron density distribution from

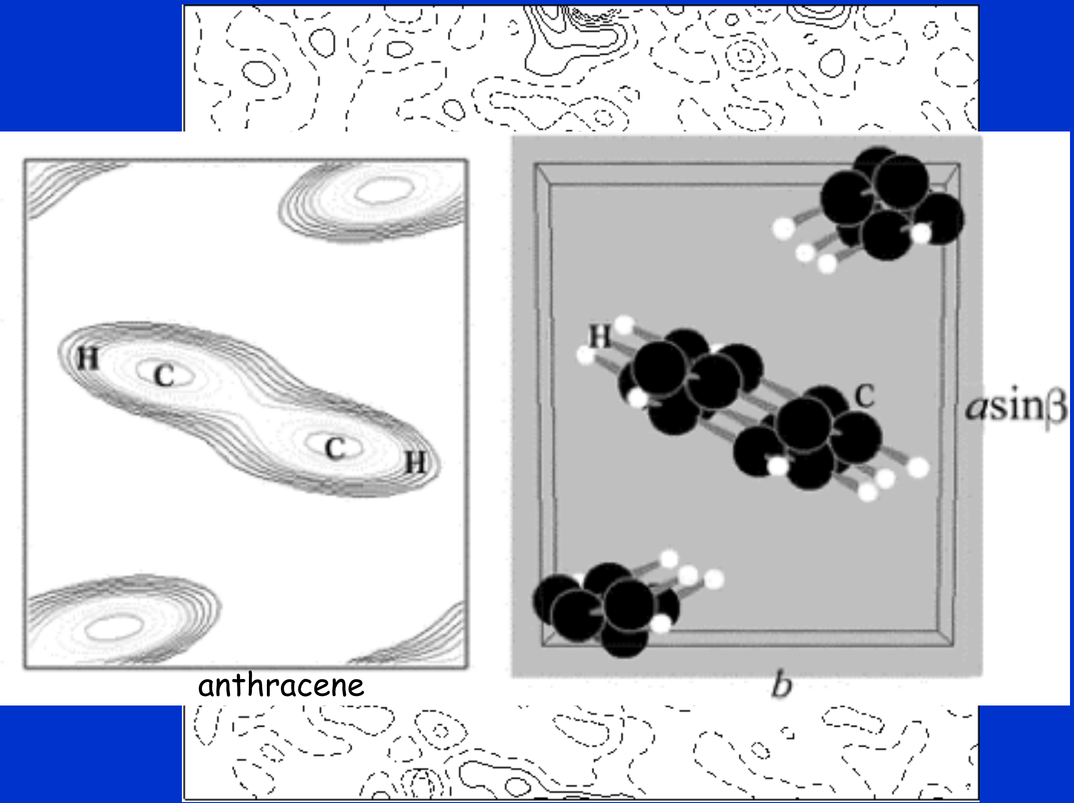
$$\rho(xyz) = \left(\frac{1}{V}\right)\sum_h \sum_k \sum_l \mathbf{F}(hkl)e^{-2\pi i(hx+ky+lz)}$$

Intensities —> crystal structure

$$\rho(xyz) = \left(\frac{1}{V}\right)\sum_h \sum_k \sum_l \mathbf{F}(hkl)e^{-2\pi i(hx+ky+lz)}$$

Electron density distribution tells where the atoms are

ρ(XYZ) is plotted and contoured to show regions of high electron density (atom positions)



Intensities —> crystal structure

But WAIT!!!

$I_{hkl} = K\,|F_{hkl}|^2 = K\,F_{hkl}^* \times F_{hkl}$

$= K\,(A_{hkl} - iB_{hkl})\,(A_{hkl} + iB_{hkl}) = K\,(A_{hkl}^2 + B_{hkl}^2)$

$\sqrt{I_{hkl}/K} = \sqrt{(A_{hkl}^2 + B_{hkl}^2)}$

So, can't use I_{hkl}s directly to calculate F_{hkl}s and $\rho(XYZ)$!!

$$\rho(xyz) = \left(\frac{1}{V}\right)\sum_h \sum_k \sum_l \mathbf{F}(hkl)e^{-2\pi i(hx+ky+lz)}$$

Many techniques for using I_{hkl}s to determine atom positions have been developed, most of which, at some stage, involve formulating a model for the crystal structure, and then adjusting it to fit the intensity data