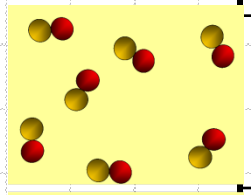
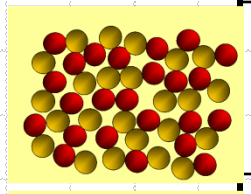
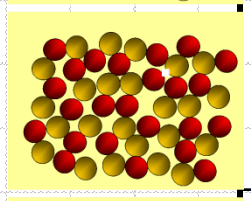
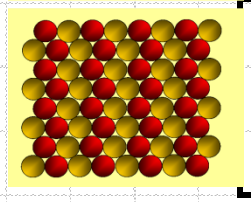
Geometry of Crystals

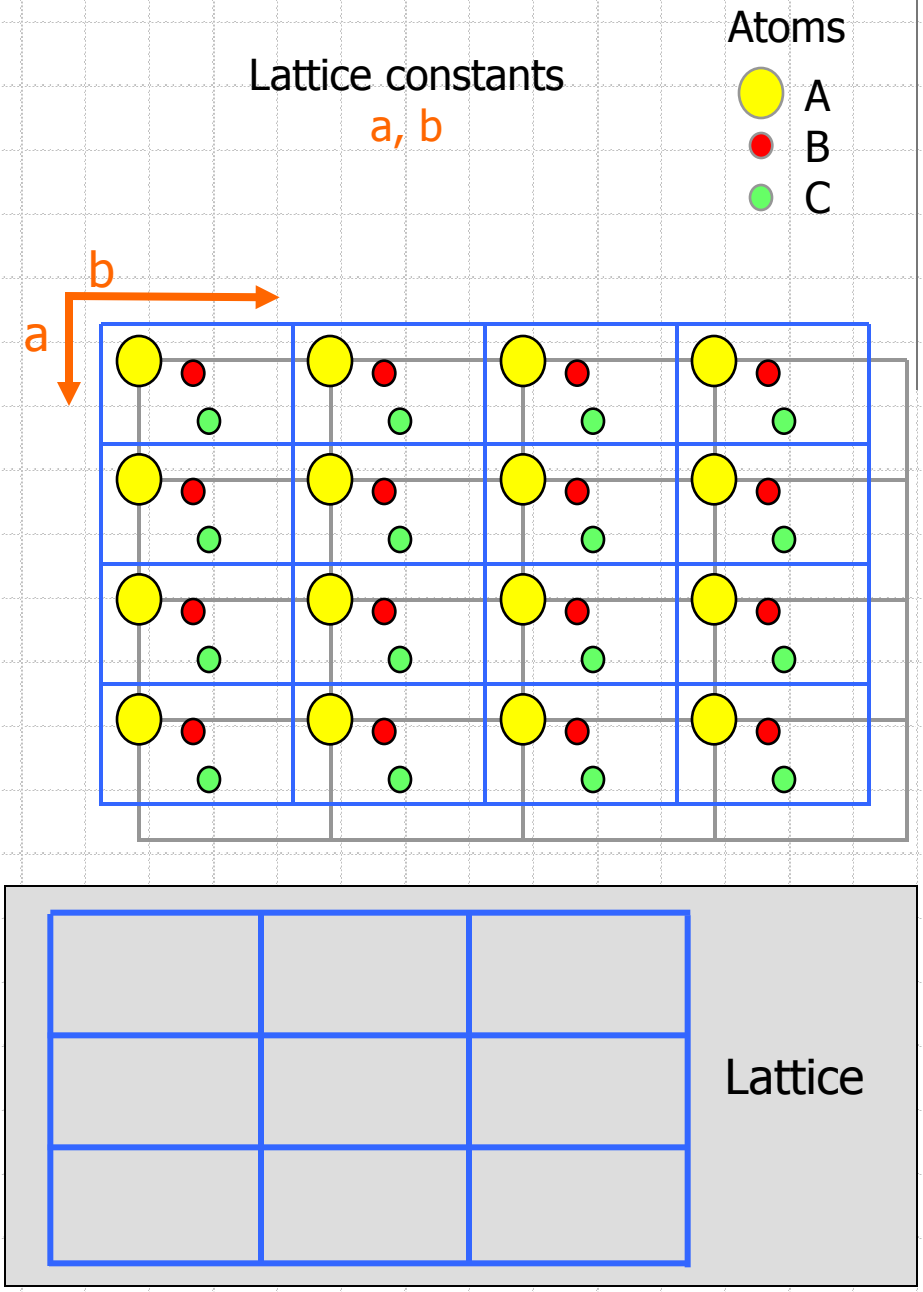
Crystal is a solid composed of atoms, ions or molecules that demonstrate long range periodic order in three dimensions

The Crystalline State

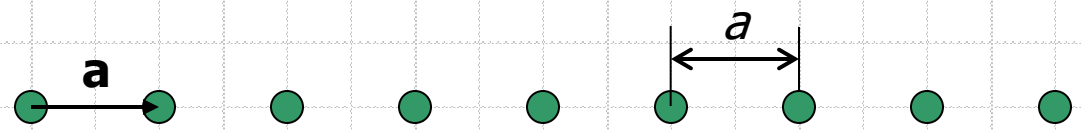
	State of Matter	Fixed Volume	Fixed Shape	Order	Properties
	Gas	No	No	No	Isotropic
	Liquid	Yes	No	Short-range	Isotropic
	Solid (amorphous)	Yes	Yes	Short-range	Isotropic
	Solid (crystalline)	Yes	Yes	Long-range	Anisotropic

Crystal Lattice

- Not only atom, ion or molecule positions are repetitious – there are certain symmetry relationships in their arrangement.

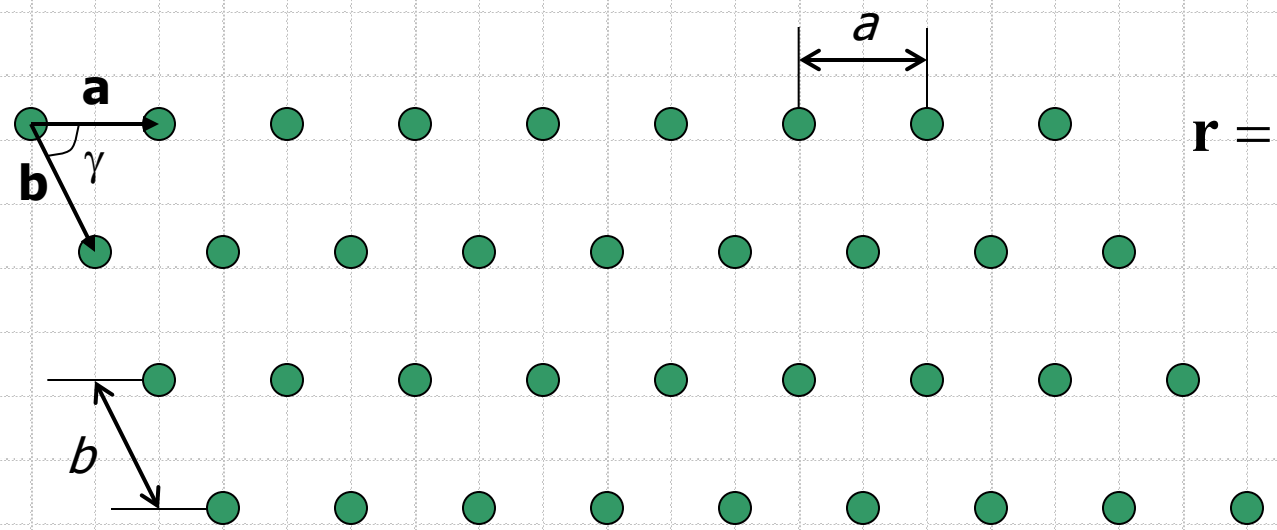


Crystal Lattice



$$\mathbf{r} = u\mathbf{a}$$

One-dimensional lattice with lattice parameter *a*

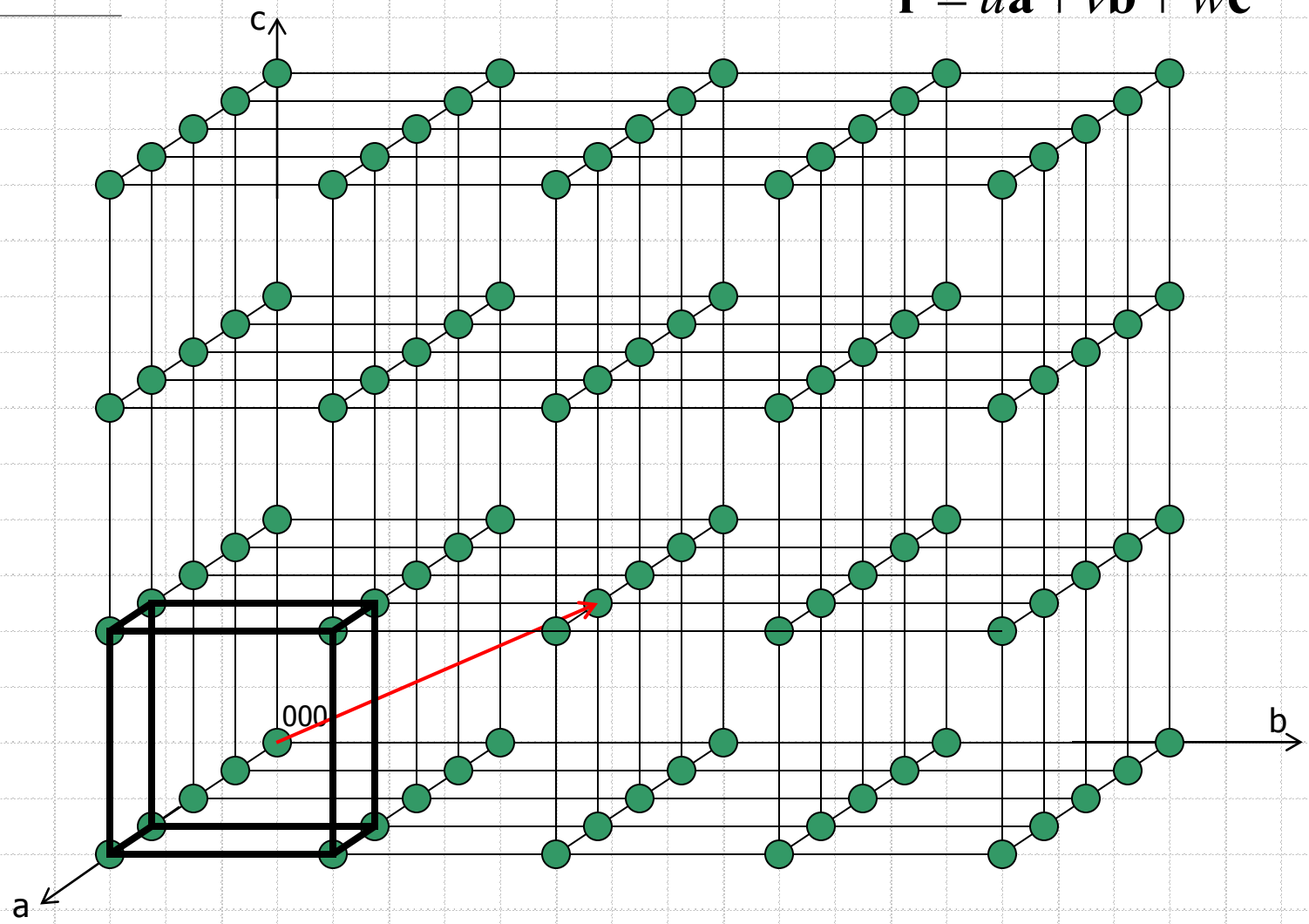


$$\mathbf{r} = u\mathbf{a} + v\mathbf{b}$$

Two-dimensional lattice with lattice parameters *a*, *b* and γ

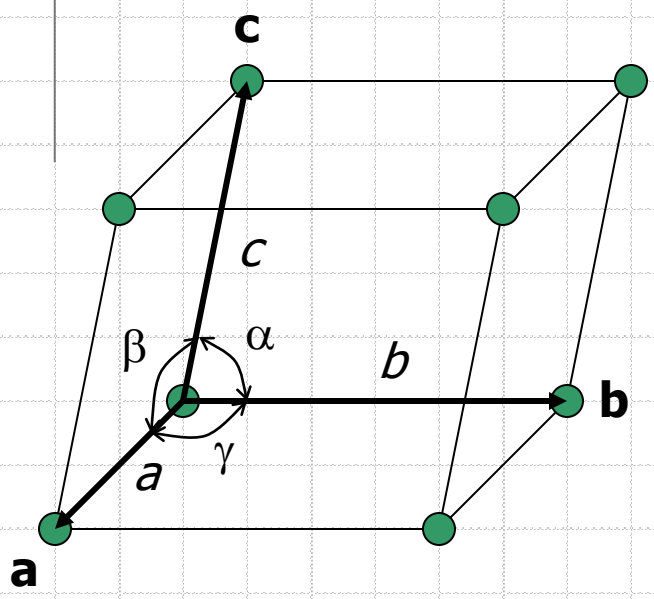
Crystal Lattice

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$



Crystal Lattice

- Lattice vectors, lattice parameters and interaxial angles

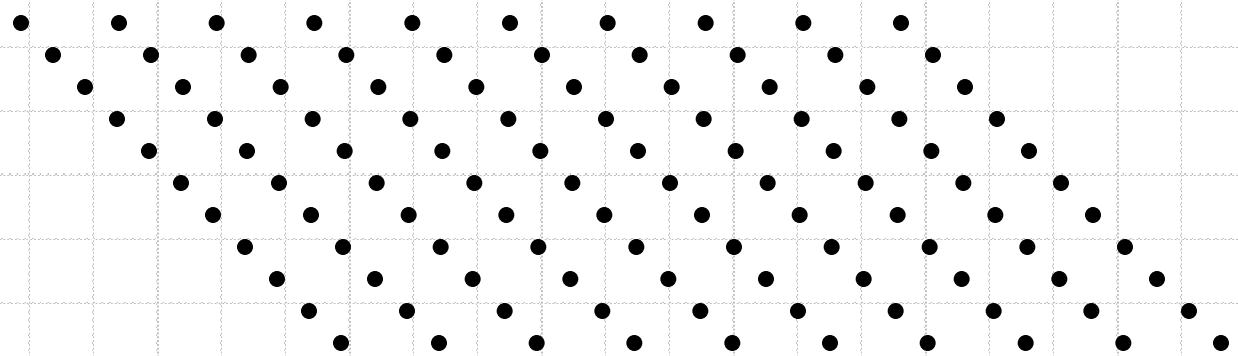


Lattice vector	**a**	**b**	**c**
Lattice parameter	*a*	*b*	*c*
Interaxial angle	α	β	γ

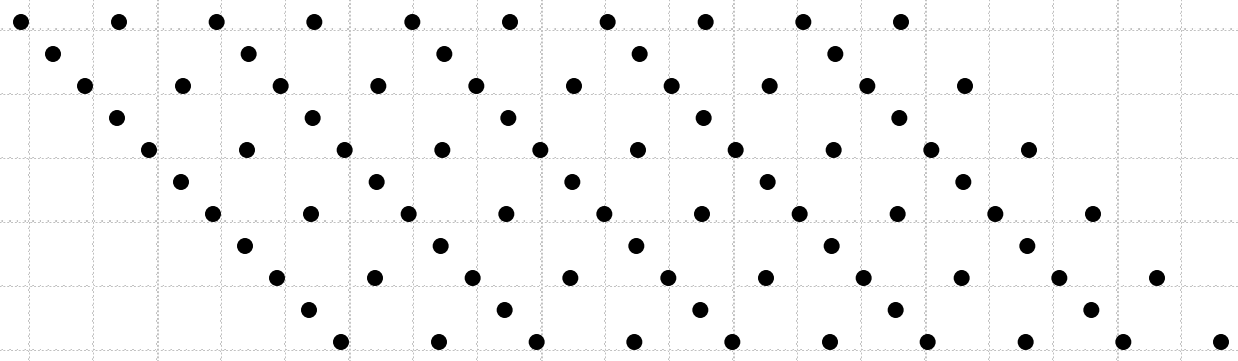
$$\vec{a} \wedge \vec{b} = \gamma$$
$$\vec{a} \wedge \vec{c} = \beta$$
$$\vec{b} \wedge \vec{c} = \alpha$$

A lattice is an array of points in space in which the environment of each point is identical

Crystal Lattice

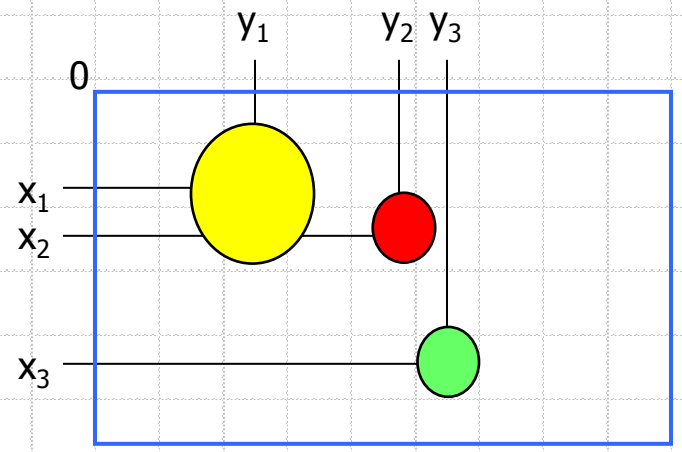


Lattice

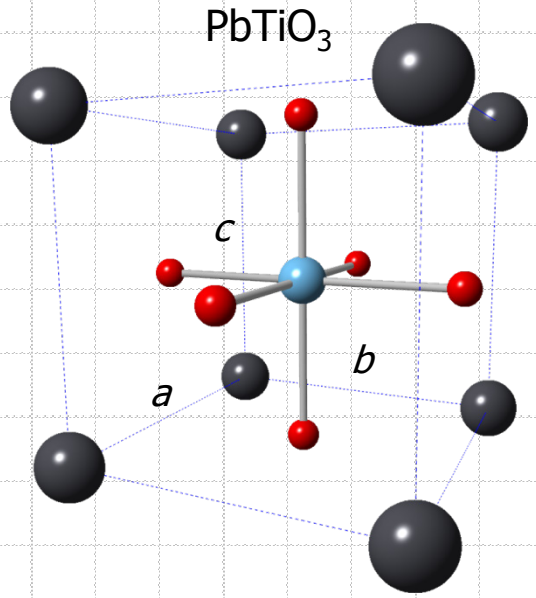


Not a lattice

Crystal Lattice



- Unit cell content
  - Coordinates of all atoms
  - Types of atoms
  - Site occupancy
  - Individual displacement parameters



$a = b = 3.902$ Å, $c = 4.156$ Å

Density: $\varrho = \frac{m}{V}$ (g cm^{-3})

Mass of atoms in a unit cell: $m = Z \times \frac{M}{N_A}$

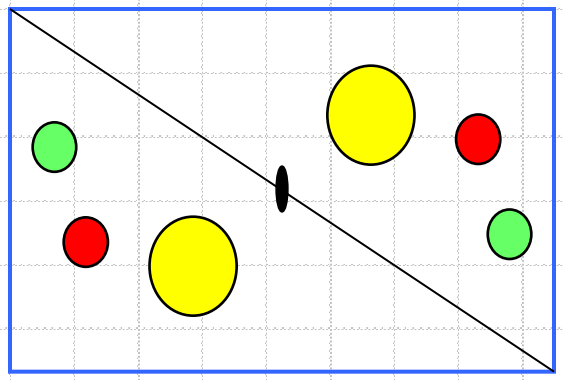
where:
Z – number of chemical formula units per unit cell
M – molar mass
$N_A = 6.023 \times 10^{23}$ mol^{-1} – Avogadro number

Then: $\varrho = \frac{Z \times M}{N_A \times V}$ (g cm^{-3})

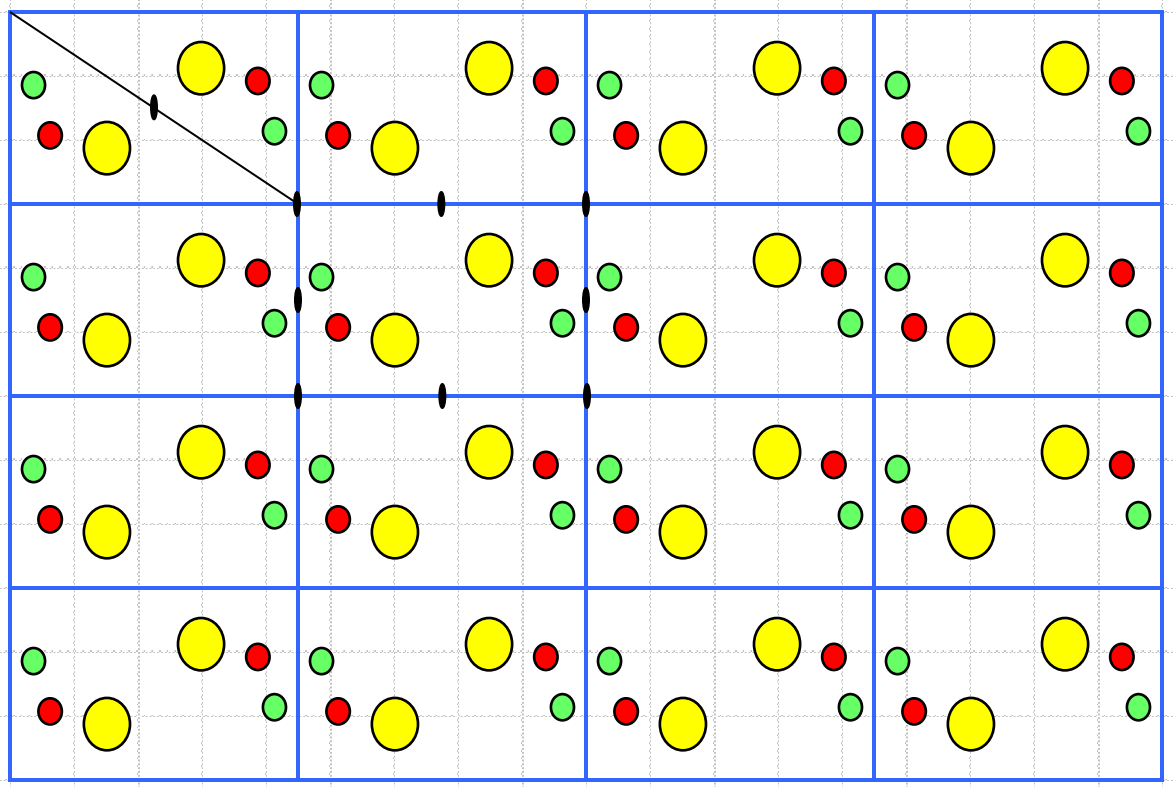
For $PbTiO_3$: $\varrho = \frac{1 \times 303.067}{6.023 \cdot 10^{23} \times 63.278 \cdot 10^{-24}} = 7.952$ (g cm^{-3})

Crystal Lattice

- Usually unit cell has more than one molecule or group of atoms
- They can be represented by symmetry operators



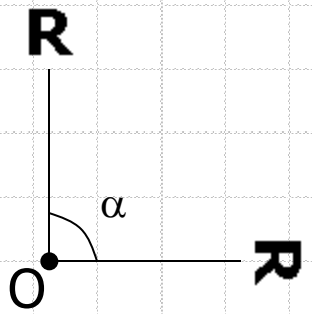
180° rotation



Symmetry

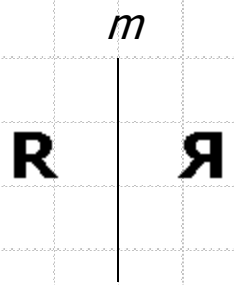
- Symmetry is a property of a crystal which is used to describe repetitions of a pattern within that crystal.
- Description is done using symmetry operators

Translation

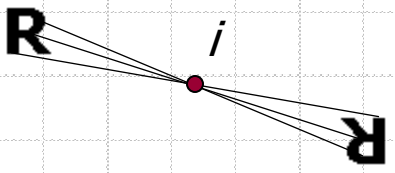


Rotation (about axis O)

$\alpha = 360°/n$
where n is the *fold* of the axis
n = 1, 2, 3, 4 or 6)



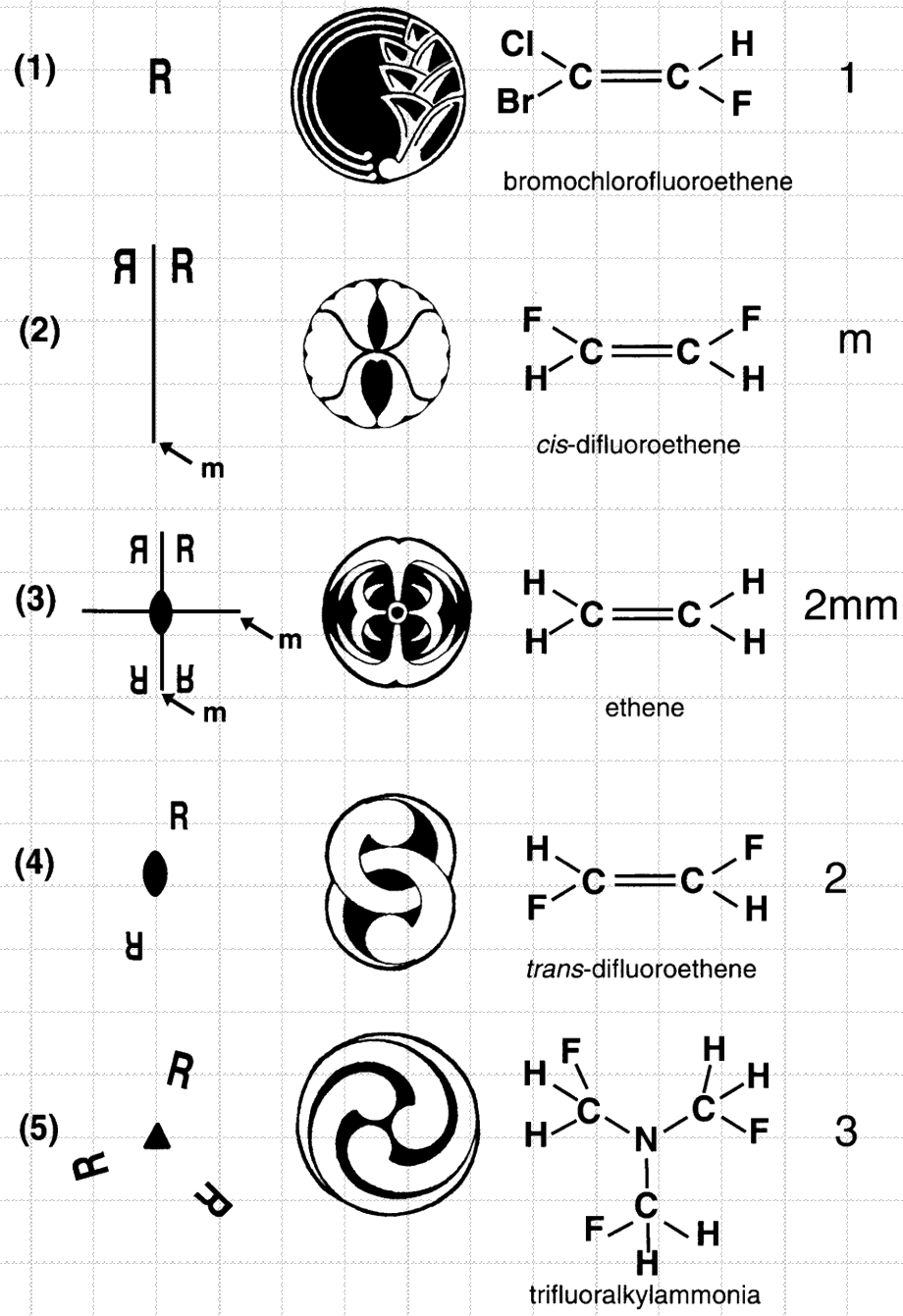
Mirror reflection



Inversion

Two-dimensional Symmetry Elements

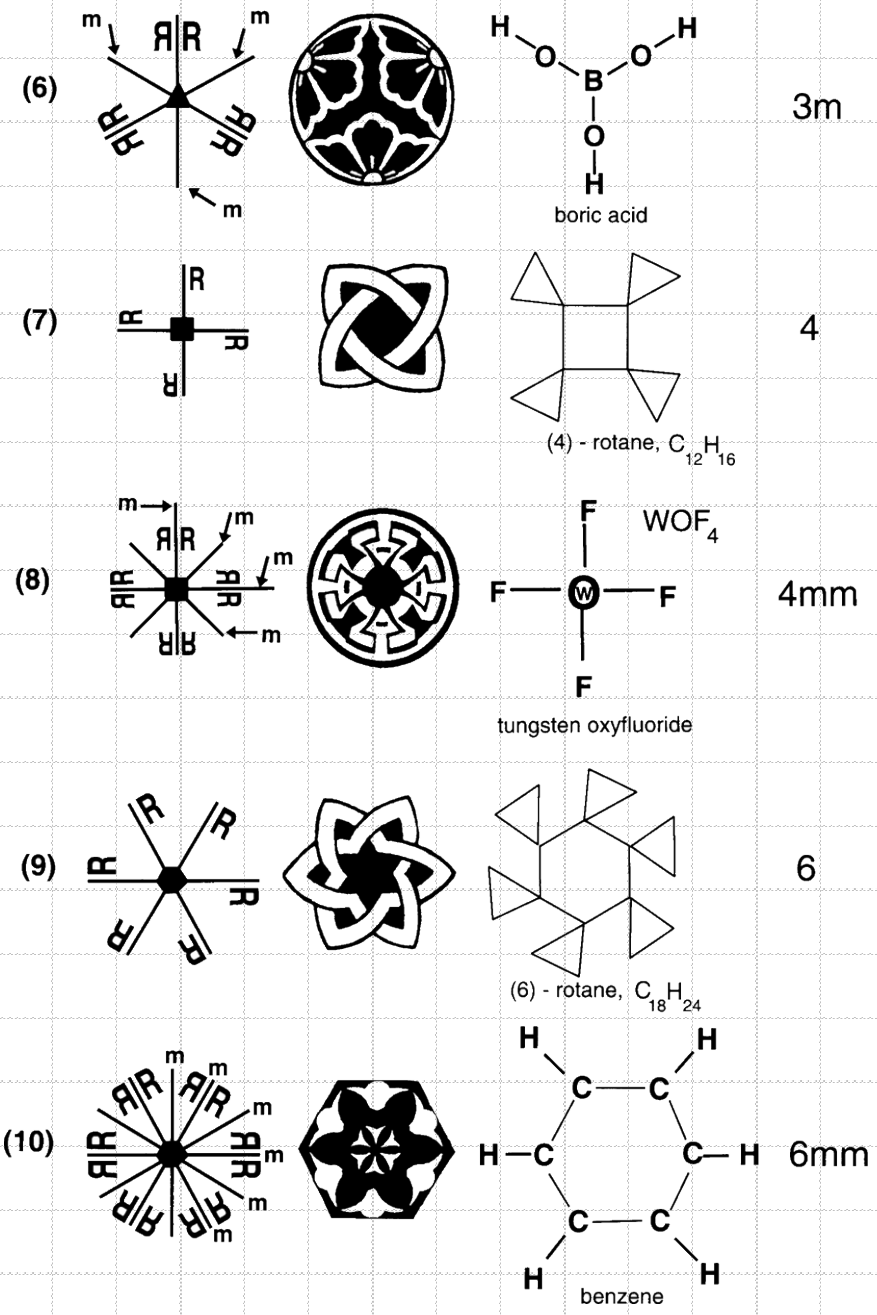
1. One-fold axis (no symmetry)
2. Vertical mirror line
3. Vertical and horizontal mirror lines
4. Two-fold rotation axis
5. Three-fold rotation axis



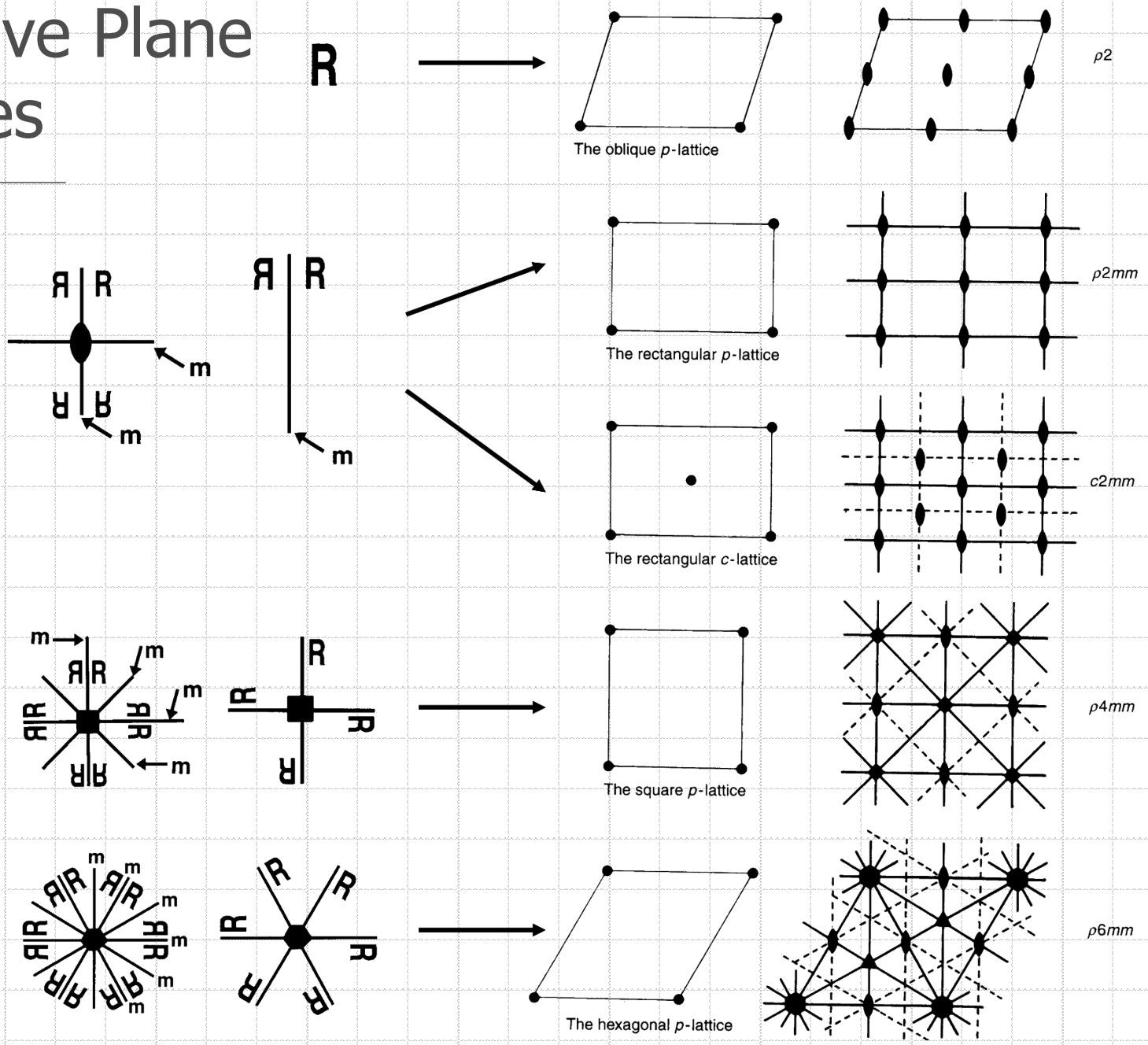
Two-dimensional Symmetry Elements

6. Tree-fold axis + vertical mirror line
7. Four-fold axis
8. Four-fold axis + mirror lines
9. Six-fold axis
10. Six-fold axis + mirror lines

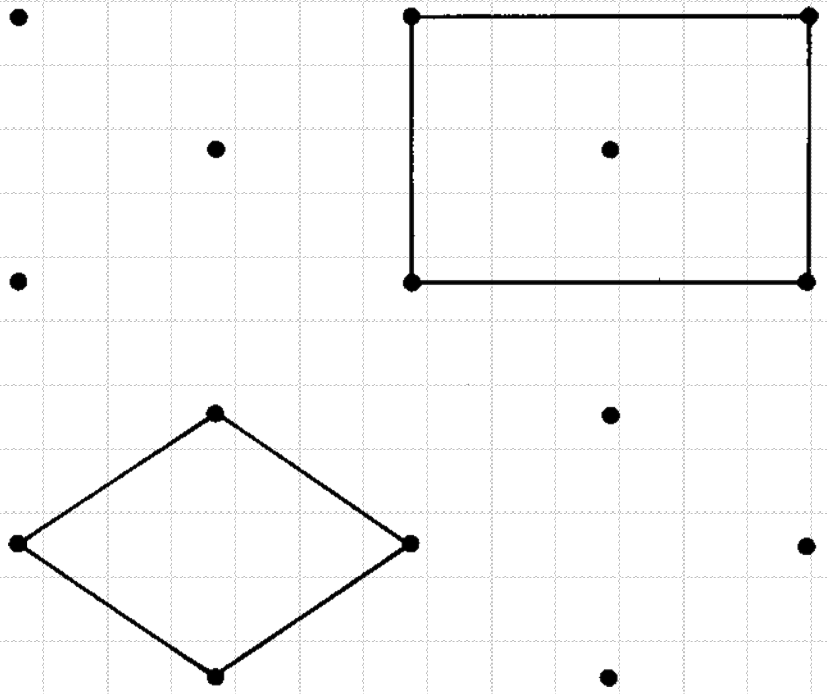
10 two-dimensional crystallographic or plane point groups



The Five Plane Lattices



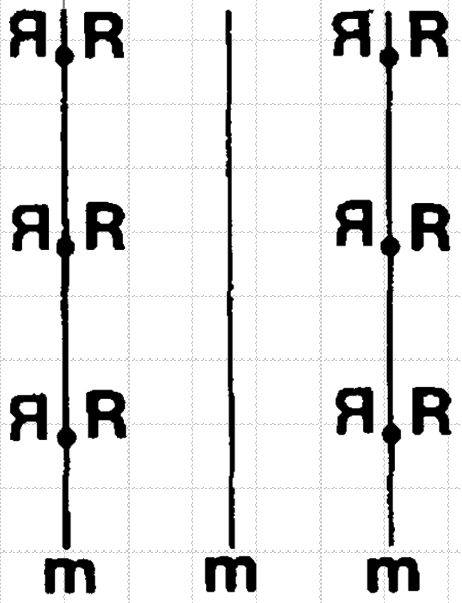
Rectangular *c* lattice and primitive rhombic *p* lattice



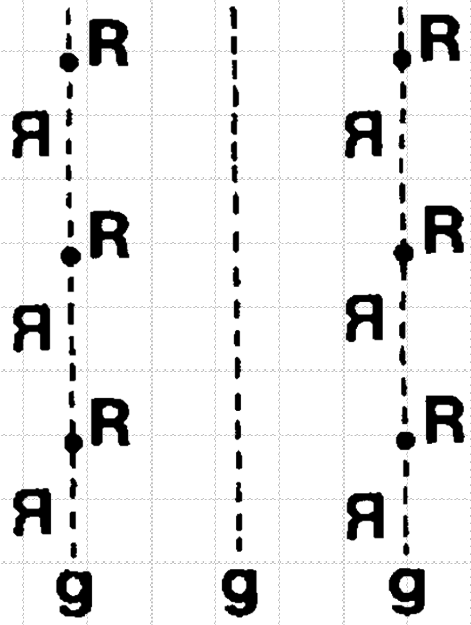
Choice of a unit cell is arbitrary.
Any four lattice points which outline parallelogram can be joined up to form a unit cell.

Two-dimensional Symmetry Elements

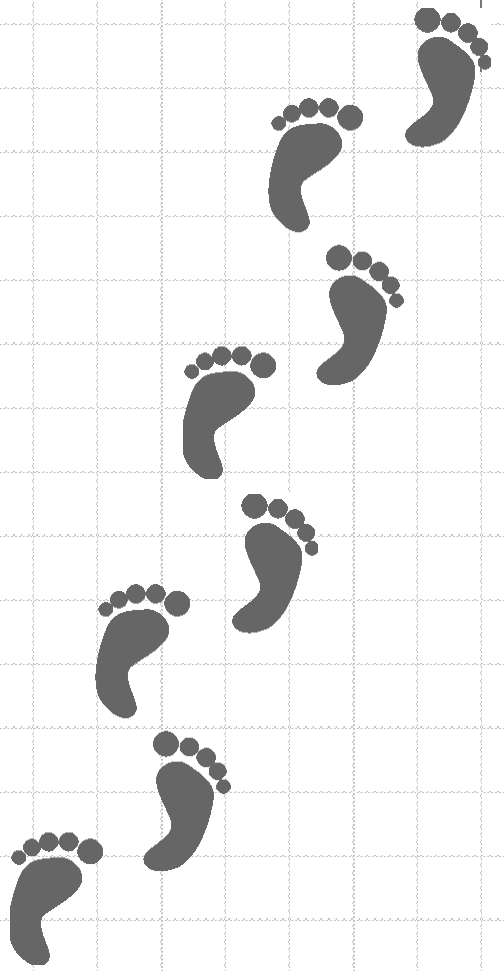
Combination of a point group symmetries with the lattice gives rise to an additional symmetry element: a **glide line**



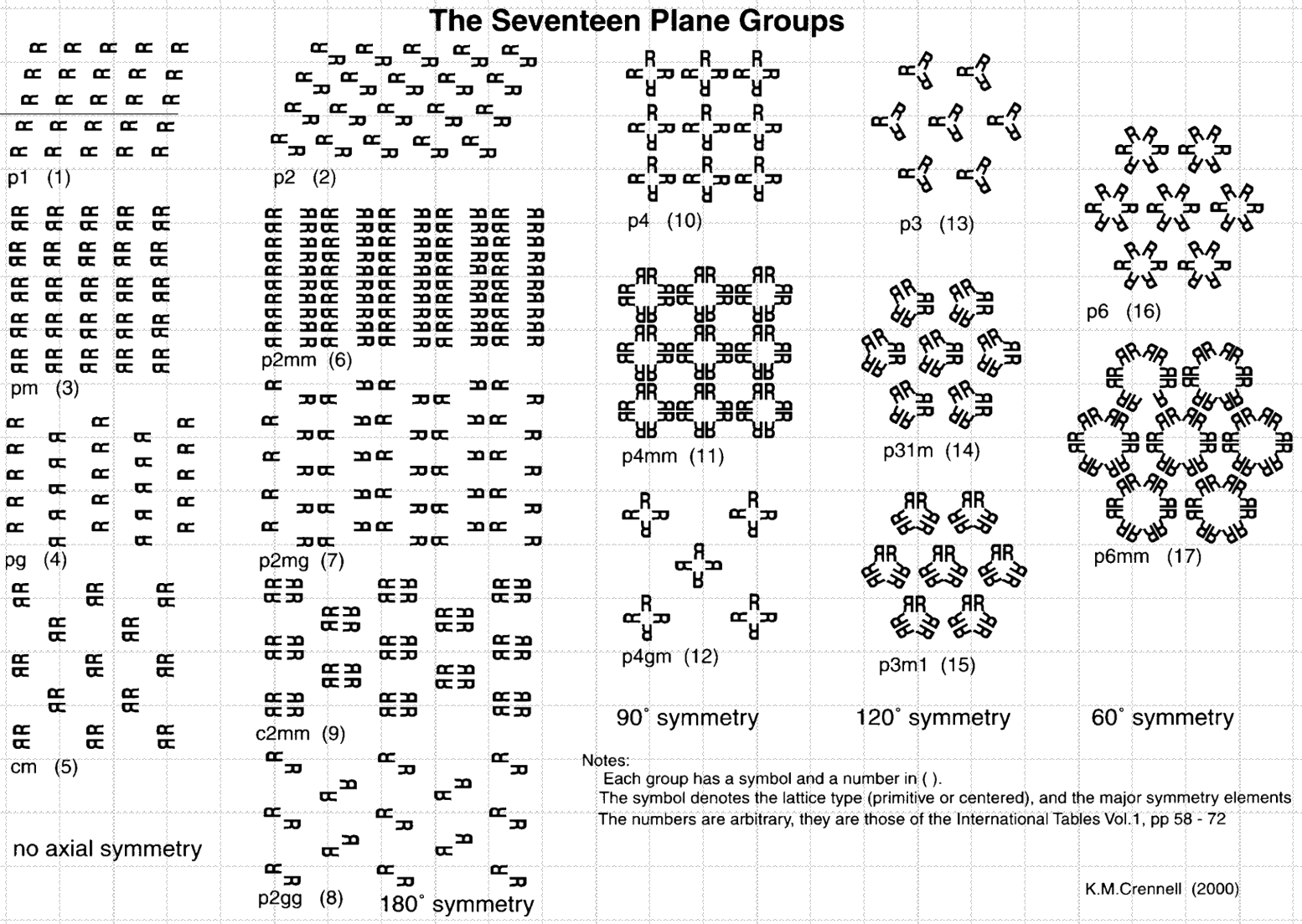
Reflection symmetry



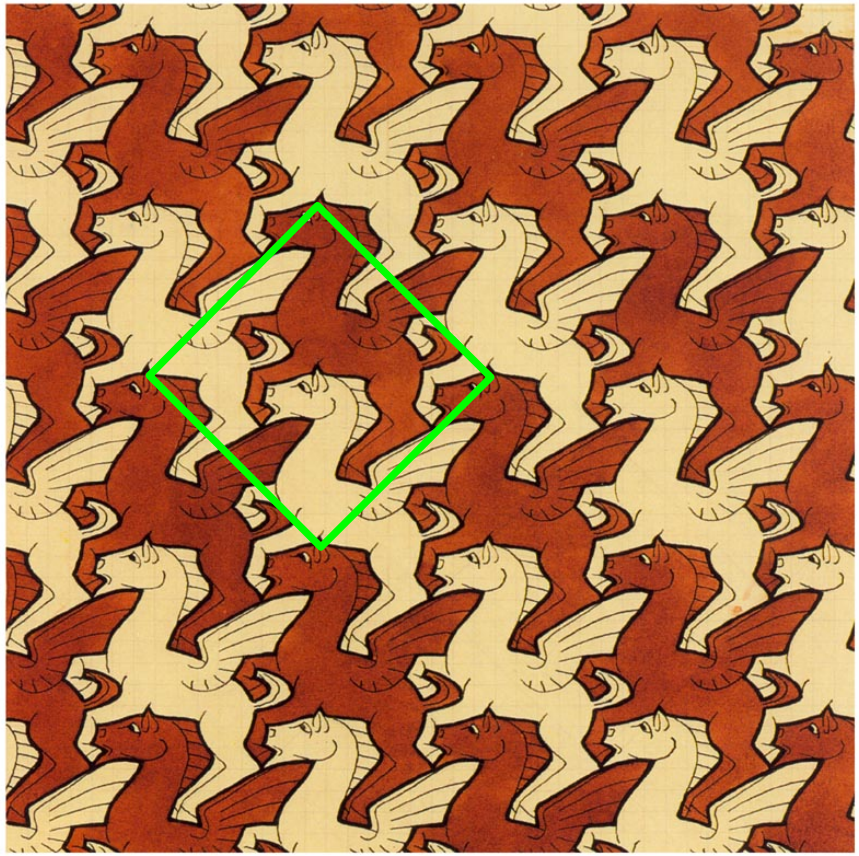
Reflection-glide symmetry

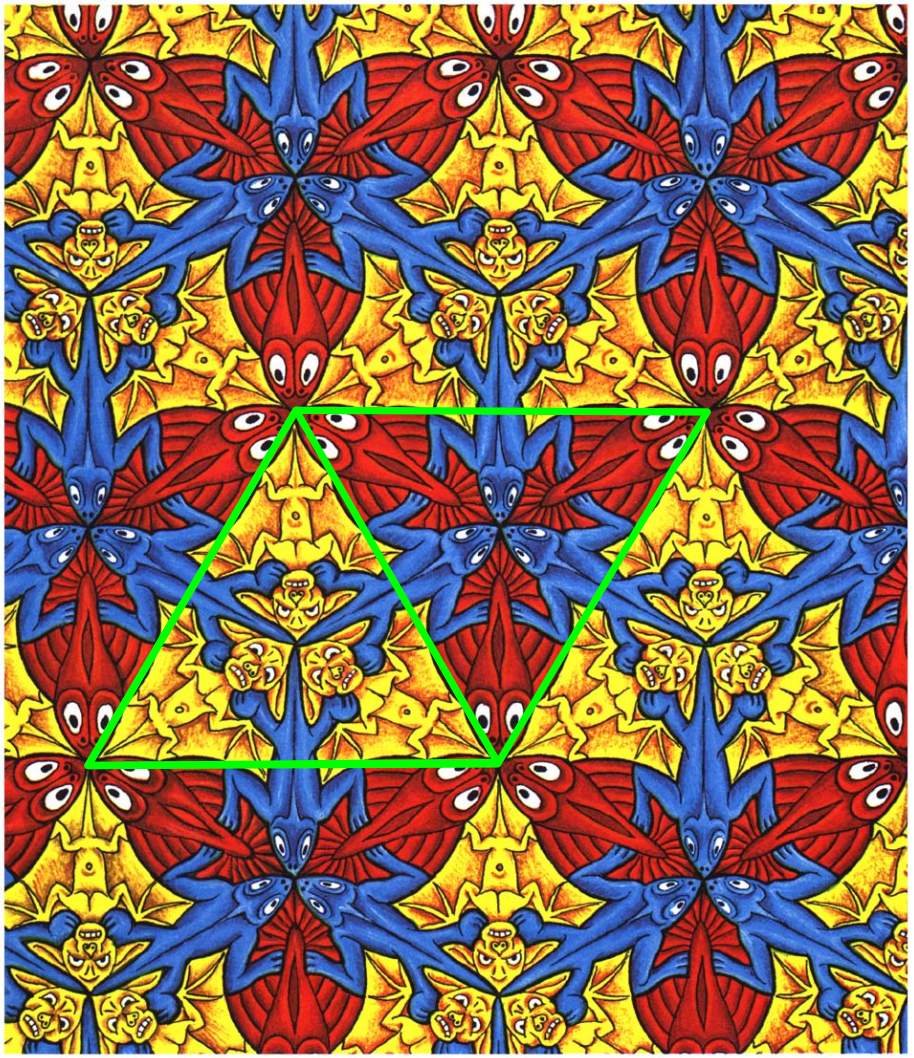


Two-dimensional Symmetry Elements



Lattice type: *p* for primitive, *c* for centred.
Symmetry elements: *m* for mirror lines, *g* for glide lines, 4 for 4-fold axis etc.





Design by M.C. Escher

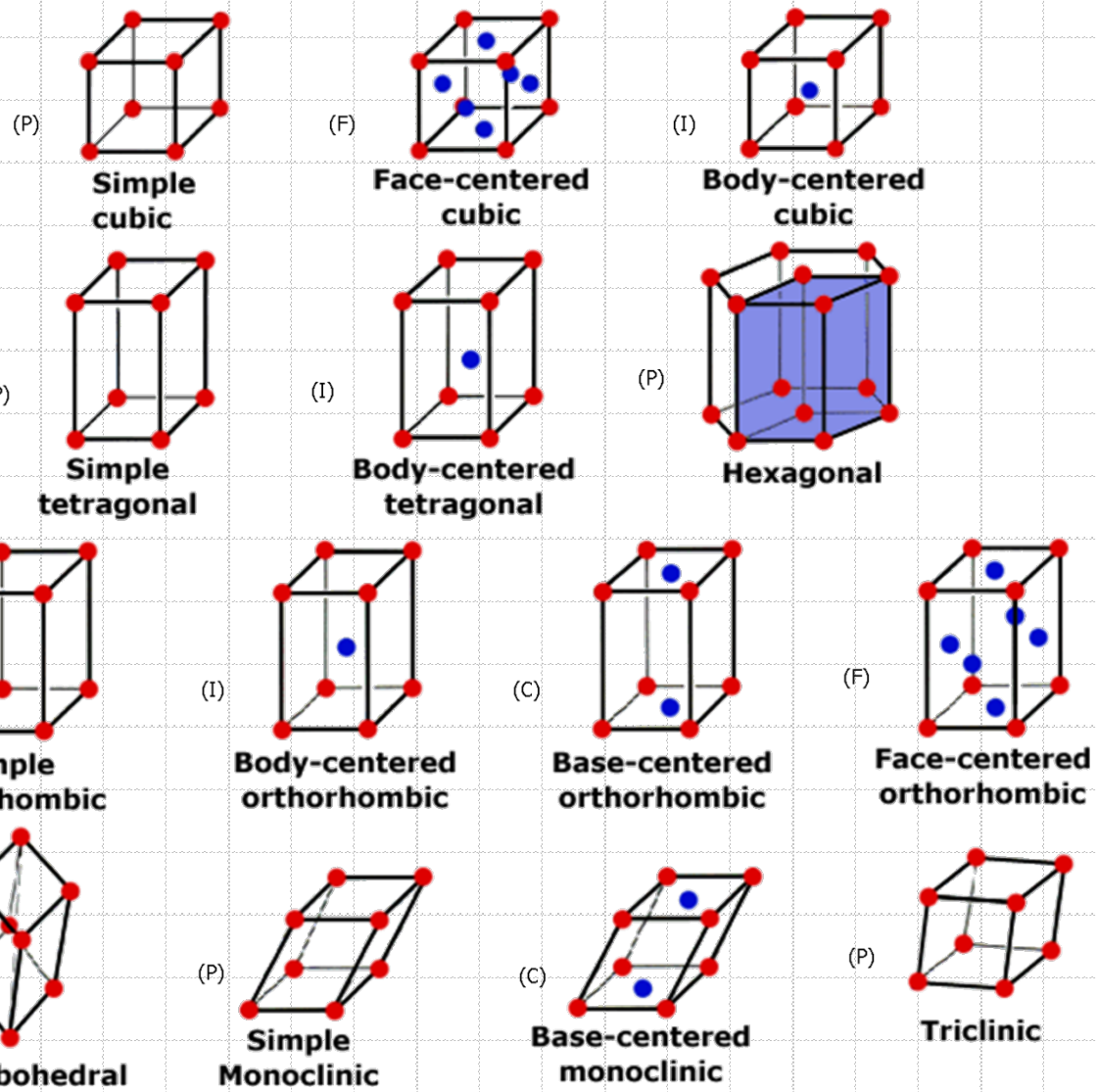
Bravais Lattices and Crystal Systems

- In three dimensions: point symmetry elements and translational symmetry elements.
- For point symmetry elements:
  - centers of symmetry
  - mirror planes
  - inversion axes
- For translational symmetry elements:
  - glide planes
  - screw axes

We end up with 230 space groups (was 17 plane groups) **distributed among 14 space lattices** (was 5 plane lattices) **and 32 point group symmetries** (instead of 10 plane point symmetries)

The 14 Space (Bravais) Lattices

- The systematic work was done by Frankenheim in 1835. Proposed 15 space lattices.
- In 1848 Bravais pointed that two of his lattices were identical (unfortunate for Frankenheim).
- Today we have 14 Bravais lattices.



a, *b*, *c* – unit cell lengths; α, β, γ - angles between them

Crystal Symmetry

- 7 axial systems + 32 point groups $\rightarrow$ 230 unique space groups
- A 3-D crystal must have one of these 230 arrangements, but the atomic coordinates (i.e. occupied equipoints) may be very different between different crystals

Crystal Class	Non-centrosymmetric Point Group	Centrosymmetric Point Group	Minimum Rotational Symmetry
Triclinic	1	$\bar{1}$	One 1-fold
Monoclinic	$2,\ m$	$2/m$	One 2-fold
Orthorombic	$222,\ mm2$	mmm	Three 2-folds
Tetragonal	$4,\ 422,\ \bar{4},\ 4mm,\ \bar{4}2m$	$4/m,\ 4/mmm$	One 4-fold
Rhombohedral	$3,\ 32,\ 3m$	$\bar{3},\ \bar{3}m$	One 3-fold
Hexagonal	$6,\ 622,\ \bar{6},\ 6mm,\ \bar{6}m2$	$6/m,\ 6/mmm$	One 6-fold
Cubic	$23,\ 432,\ \bar{4}3m$	$m\bar{3},\ m\bar{3}m$	Four 3-folds

Centrosymmetric Lattices

Space group symbols for the 14 centrosymmetric Bravais lattices

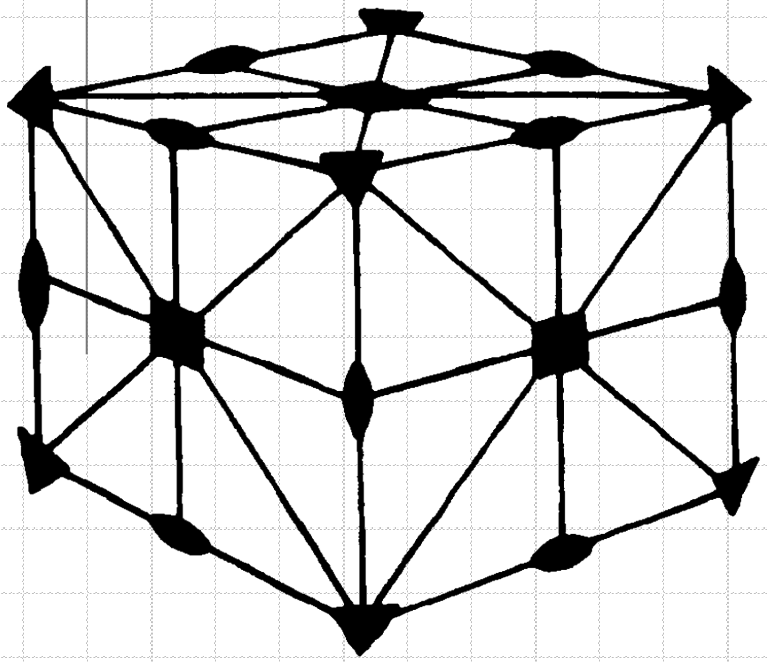
	P	C	I	F
Triclinic	P $\bar{1}$			
Monoclinic	P 2/m	C 2/m		
Orthorhombic	P 2/m 2/m 2/m	C 2/m 2/m 2/m	I 2/m 2/m 2/m	F 2/m 2/m 2/m
Tetragonal	P 4/m 2/m 2/m		I 4/m 2/m 2/m	
Trigonal	P 6/m 2/m 2/m		R $\bar{3}$ 2/m	
Hexagonal				
Cubic	P 4/m$\bar{3}$ 2/m		I 4/m$\bar{3}$2/m	F 4/m$\bar{3}$2/m

Number and coordinates of the lattice points in the unit cells of the Bravais lattices

Lattice	No. of lattice points in unit cell	Coordinates of lattice points in unit cell
P	1	0,0,0
A	2	$0,0,0;\ 0,\frac{1}{2},\frac{1}{2}$
B	2	$0,0,0;\ \frac{1}{2},0,\frac{1}{2}$
C	2	$0,0,0;\ \frac{1}{2},\frac{1}{2},0$
I	2	$0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}$
R	3	$0,0,0;\ \frac{2}{3},\frac{1}{3},\frac{1}{3};\ \frac{1}{3},\frac{2}{3},\frac{2}{3}$
F	4	$0,0,0;\ \frac{1}{2},\frac{1}{2},0;\ \frac{1}{2},0,\frac{1}{2};\ 0,\frac{1}{2},\frac{1}{2}$

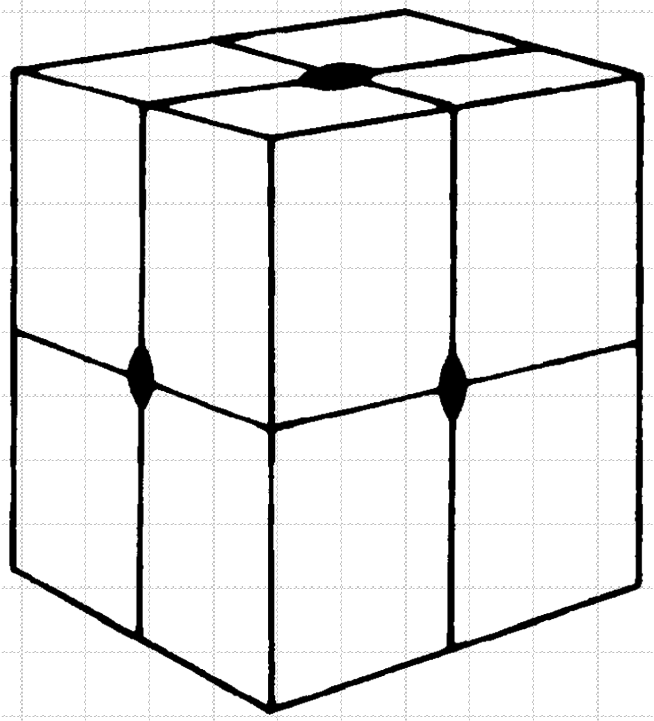
The Symmetry of Bravais Lattices

Point group symmetry of the cube



- Nine mirror planes
- Three four-fold axes
- Four three-fold axes
- Six two-fold axes

Point group symmetry of the orthorhombic cell



- Three mirror planes
- Three two-fold axes

The 14 Space (Bravais) Lattices

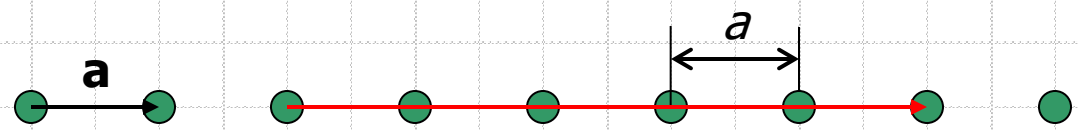
System	Axial lengths and angles	Bravais lattice	Lattice symbol
Cubic	Three equal axes at right angles $a = b = c, \quad \alpha = \beta = \gamma = 90°$	Simple Body-centered Face-centered	P I F
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \quad \alpha = \beta = \gamma = 90°$	Simple Body-centered	P I
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \quad \alpha = \beta = \gamma = 90°$	Simple Body-centered Base-centered Face-centered	P I C F
Rhombohedral*	Three equal axes, equally inclined $a = b = c, \quad \alpha = \beta = \gamma \neq 90°$	Simple	R
Hexagonal	Two equal coplanar axes at 120°, third axis at right angles $a = b \neq c, \quad \alpha = \beta = 90° \quad (\gamma = 120°)$	Simple	P
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \quad \alpha = \gamma = 90° \neq \beta$	Simple Base-centered	P C
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \quad (\alpha \neq \beta \neq \gamma \neq 90°)$	Simple	P

* Also called trigonal.

7 crystal systems

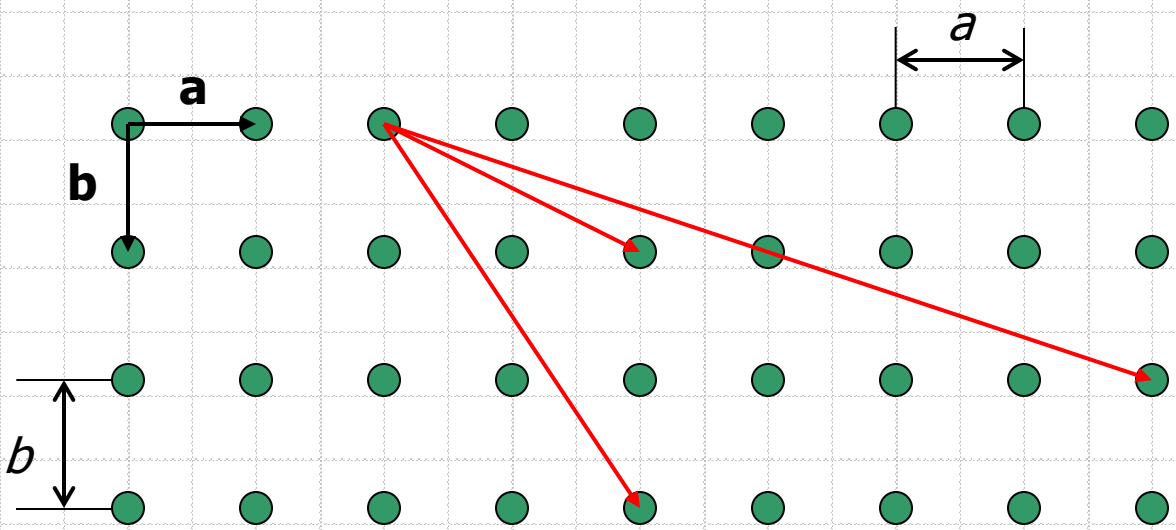
Crystal Axes and the Reciprocal Lattice

Crystal Lattice & Directions



$$\mathbf{r} = u\mathbf{a}$$

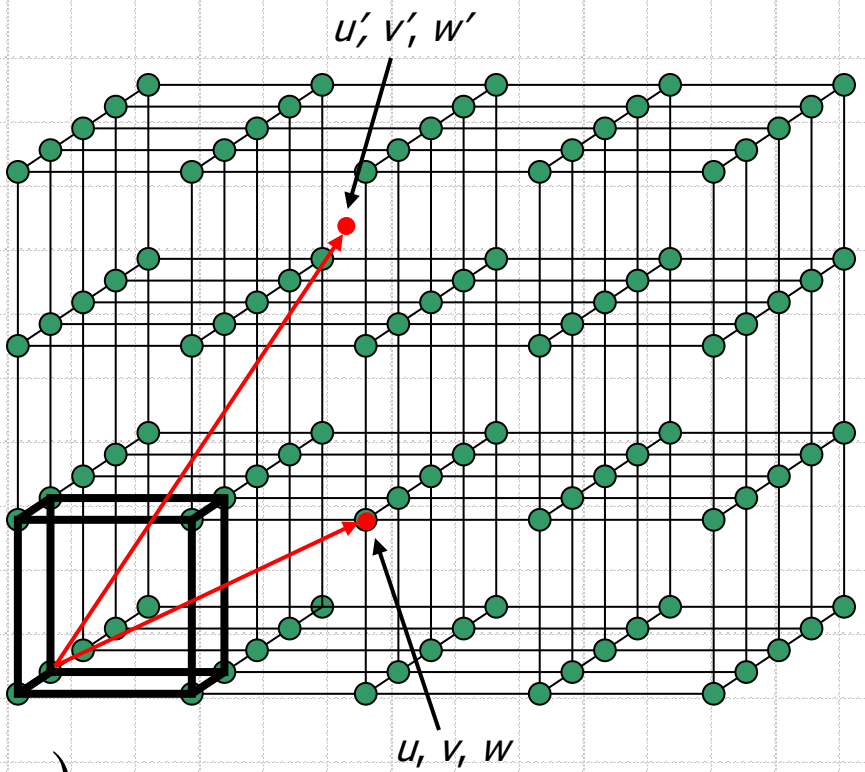
One-dimensional lattice with parameter *a*



$$\mathbf{r} = u\mathbf{a} + v\mathbf{b}$$

Two-dimensional lattice with parameters *a* and *b*

Lattice Directions



For the lattice points u, v, w:

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

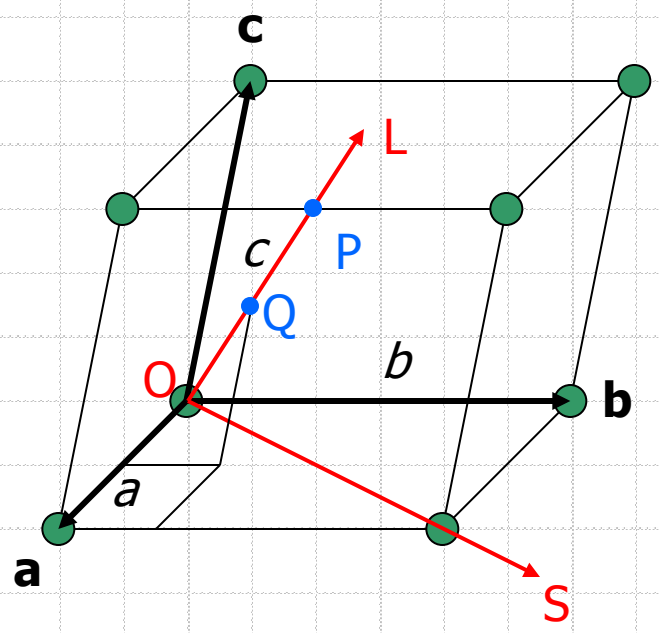
For the points in space u', v', w' that are not lattice points:

$$\mathbf{r} = u'\mathbf{a} + v'\mathbf{b} + w'\mathbf{c}$$
$$= (n + u_1)\mathbf{a} + (p + v_1)\mathbf{b} + (q + w_1)\mathbf{c}$$
$$= (n\mathbf{a} + p\mathbf{b} + q\mathbf{c}) + (u_1\mathbf{a} + v_1\mathbf{b} + w_1\mathbf{c})$$

n, p, q – integers
u_1, v_1, w_1 – fractions

Indexing Lattice Directions

- Direction must pass through the origin
- Coordinates of point P (in fractions of *a*, *b* and *c*) are 1, ½, 1 ⇒ [212]
- For point Q coordinates are ½, ¼, ½ ⇒ [212]



[212] – defines direction for OL

For OS – the direction is [110]

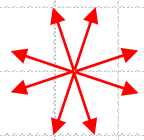
$$\mathbf{r}_{102} = 2\mathbf{a} + 1\mathbf{b} + 2\mathbf{c}$$

$$\mathbf{r}_{110} = 1\mathbf{a} + 1\mathbf{b} + 0\mathbf{c}$$

Indexing Lattice Directions

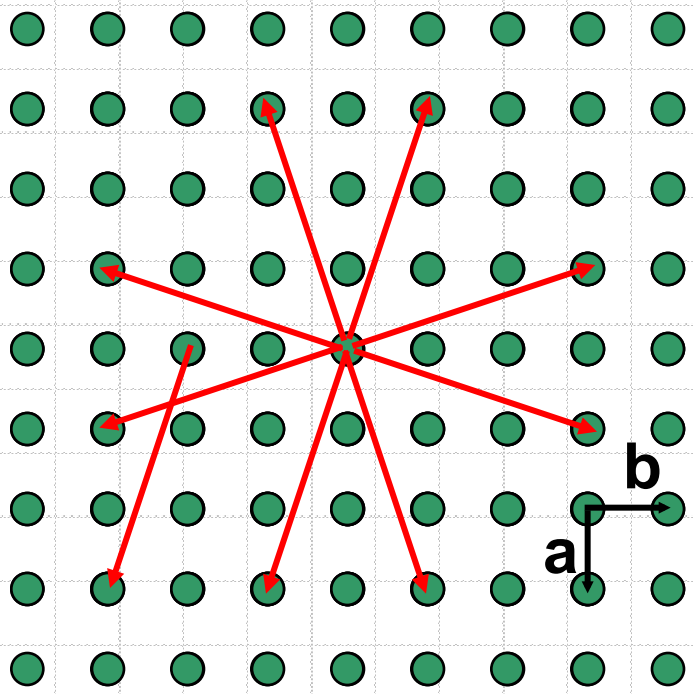
- Specific direction ⇒ [*uvw*] Family of directions ⇒ <*uvw*>

Example:



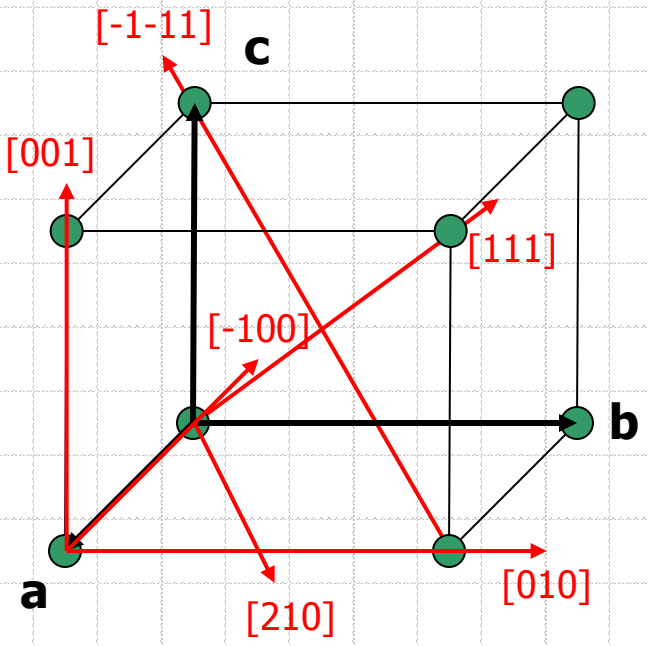
<310>

[3-10]



Indexing Lattice Directions

- Directions related by symmetry are called *directions of a form*.



We have: [111], [-111], [-1-1-1], [11-1], …

⇩

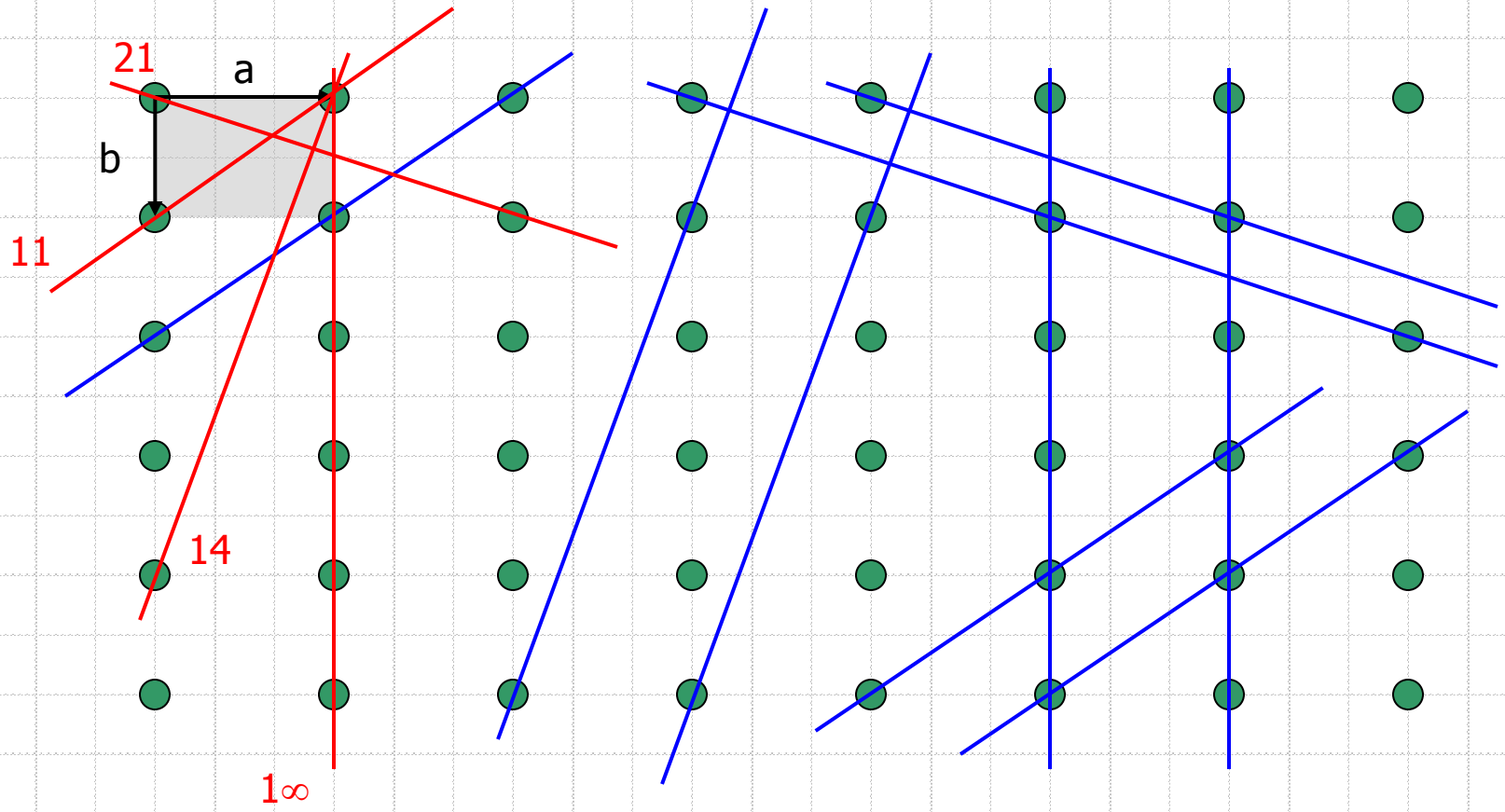
<111>

Specific direction ⇒ [*uvw*]

Family of directions ⇒ <*uvw*>

The Crystallographic Planes

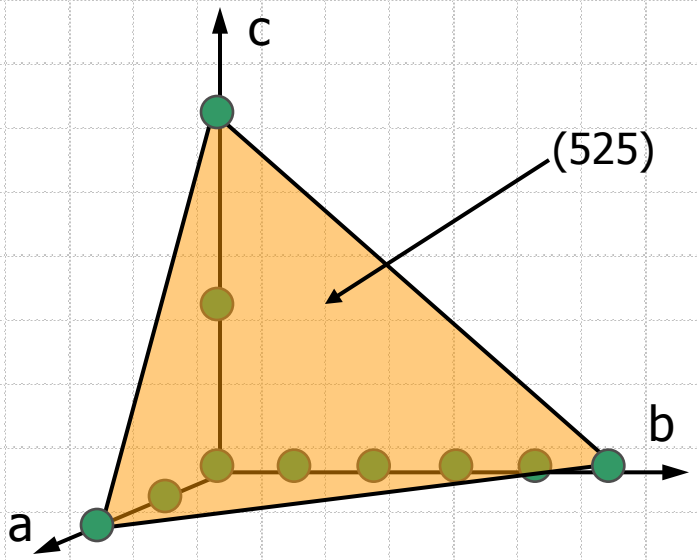
1 1		1 1		(11)
2 1	⇒	1/2 1	=	(12)
1 4		1 1/4		(41)
1 ∞		1 1/∞		(10)



Definition of the Miller Indices

- Let's draw a plane at $2\times a$, $5\times b$, $2\times c$.

	a	**b**	**c**
The intercepts	2	5	2
The reciprocals	1/2	1/5	1/2
Multiply by 10	5	2	5
The Miller indices	(525)		

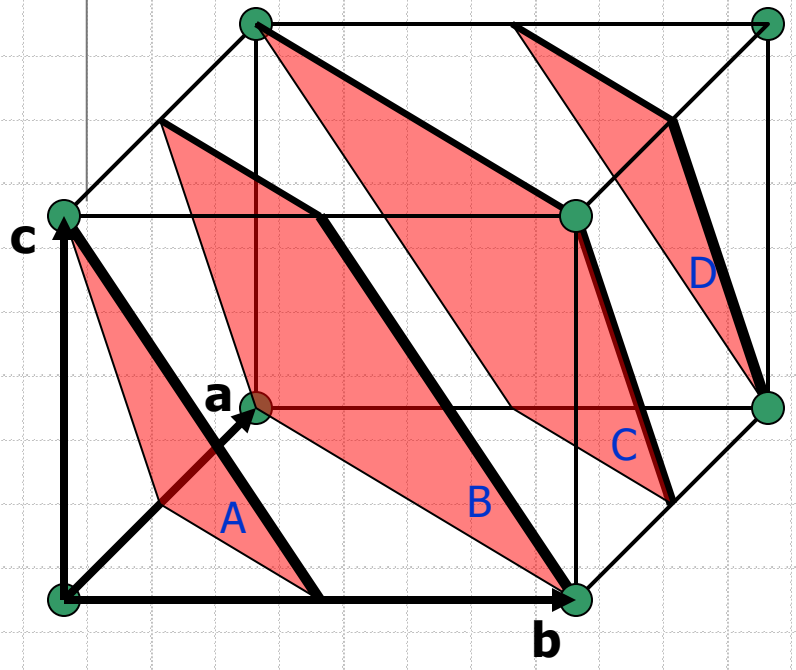


Specific plane $\Rightarrow$ (*hkl*)

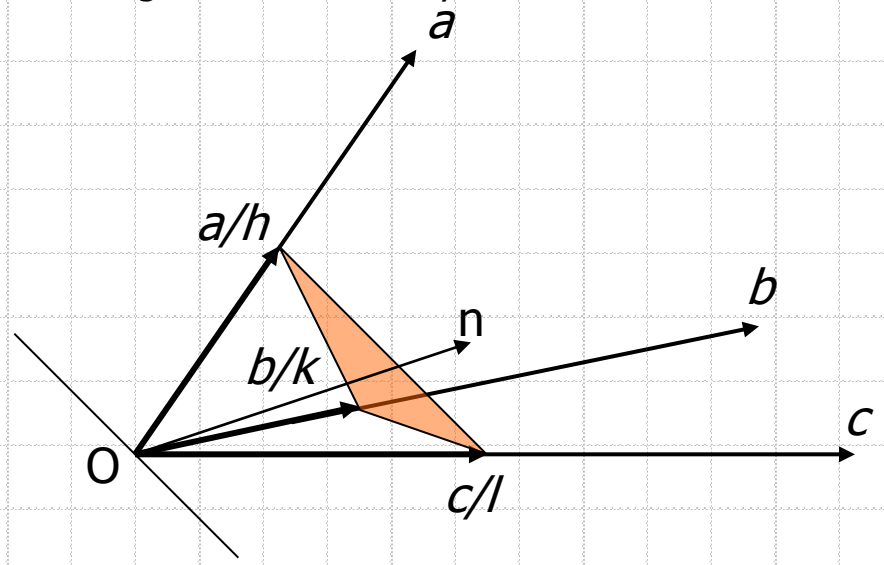
Family of planes $\Rightarrow$ {*hkl*}

Definition of the Miller Indices

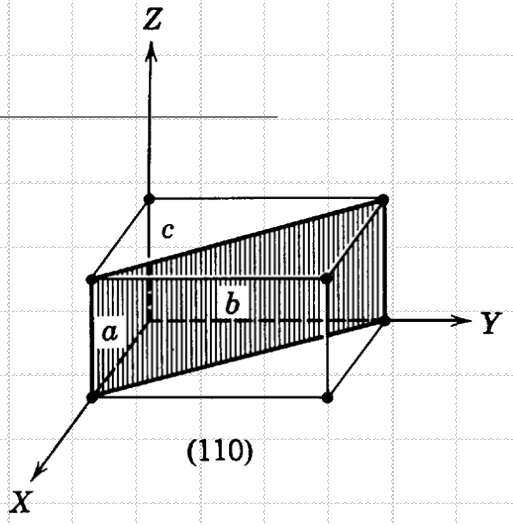
- For plane A $a/2$, $b/2$, and $1c \Rightarrow$ 2, 2, 1 $\Rightarrow$ plane is (221)
- For plane B $1a$, $1b$, and $2c \Rightarrow$ 1, 1, 1/2 $\Rightarrow$ 2, 2, 1 $\Rightarrow$ plane is (221)
- For plane C $3a/2$, $3b/2$, and $3c \Rightarrow$ 2/3, 2/3, 1/3 $\Rightarrow$ 2, 2, 1 $\Rightarrow$ plane is (221)
- For plane D $2a$, $2b$, and $4c \Rightarrow$ 1/2, 1/2, 1/4 $\Rightarrow$ 2, 2, 1 $\Rightarrow$ plane is (221)



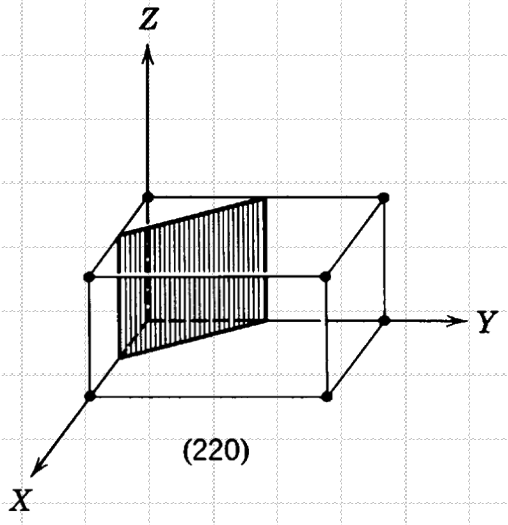
- By the set of crystallographic planes *hkl*, we mean a set of parallel equidistant planes, one of which passes through the origin, and the next nearest makes intercepts *a/h*, *b/k*, and *c/l* on the three crystallographic axes.
- The integers *hkl* are usually called the Miller indices.



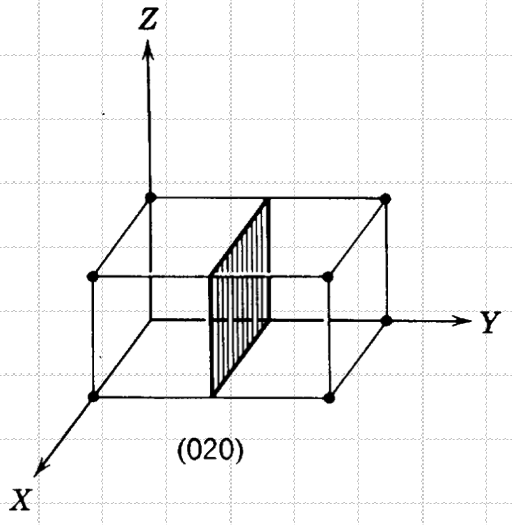
Miller Indices



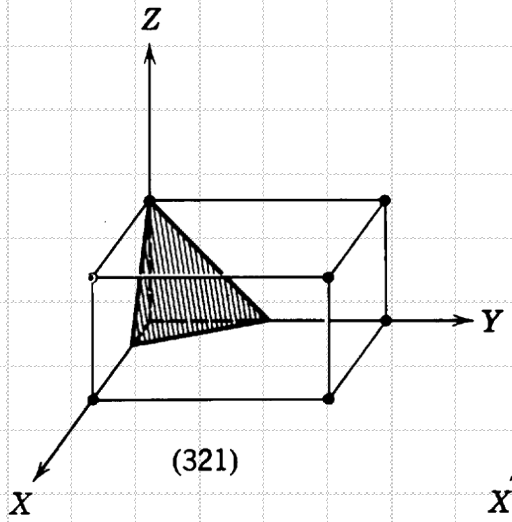
(110)



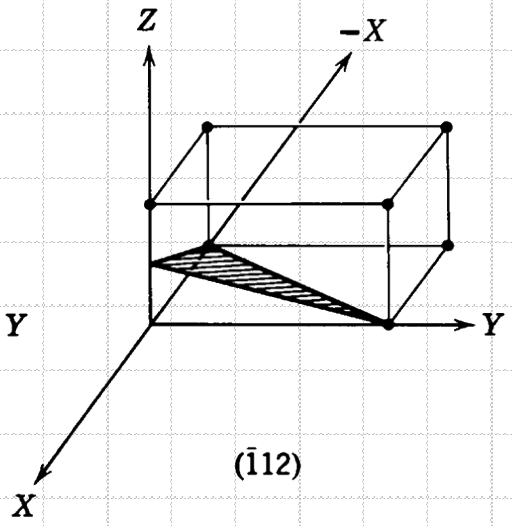
(220)



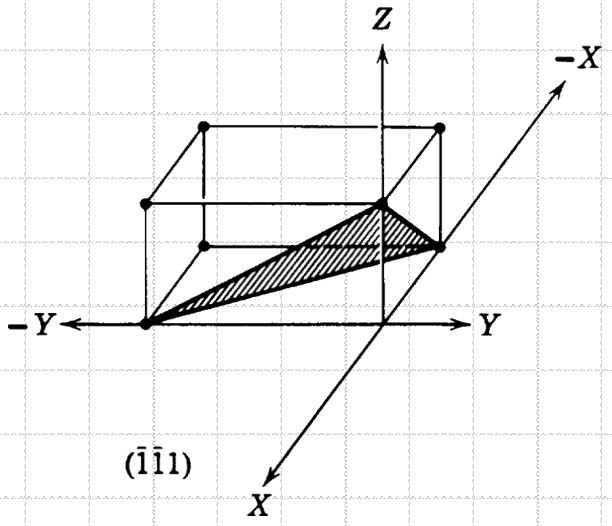
(020)



(321)



($\bar{1}12$)



($\bar{1}\bar{1}1$)

Miller Indices and Zone Axis Symbols

Closures for crystallographic indices

[*uvw*] = square brackets designate a direction in the lattice from the origin to a point. Used to collectively include all the faces of a crystals whose intersects (i.e., edges) parallel each other. These are referred to as crystallographic **zones** and they represent a direction in the crystal lattice.

<*uvw*> – designate family of directions.

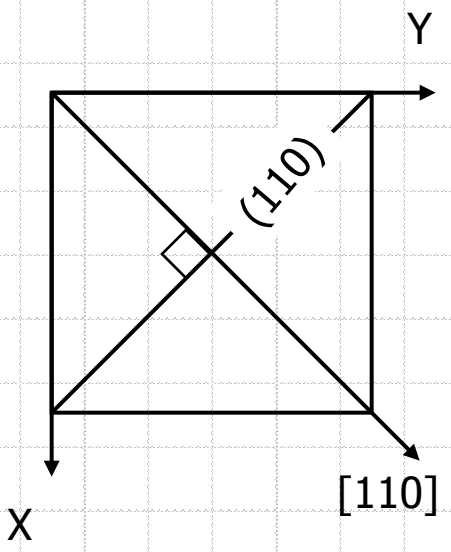
(*hkl*) = parenthesis designate a *crystal face* or a *family of planes* throughout a crystal lattice.

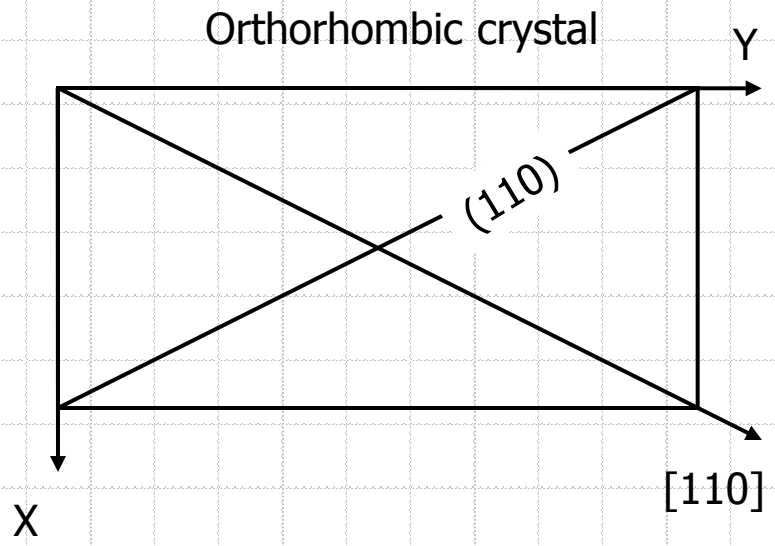
{*hkl*} = "squiggly" brackets or braces designate a set of faces that are equivalent by the symmetry of the crystal. The set of face planes results in the **crystal form**. {100} in the isometric class includes (100), (010), (001), (-100), (0-10) and (00-1), while for the triclinic {100} only the (100) is included.

d-spacing is defined as the distance between adjacent planes. When X-rays diffract due to interference amongst a family of similar atomic planes, then each diffraction plane may be reference by it's indices d_{hkl}

Miller Indices and Zone Axis Symbols

- For cubic crystal:
  - Direction symbols
    - <100> ⇒ [100], [-100], [010], 0 -10], [001], [00 -1]
    - <111> ⇒ [11 -1], [-1 -11], [1 -11], [-11 -1], [-111], [1 -1 -1], [111], [-1 -1 -1]
    - <110> ⇒ 12 combinations
  - Miller indices
    - {100} ⇒ (100), (-100), (010), (0 -10), (001), (00 -1)





Lattice Plane Spacings

- For crystal with orthogonal axes:

$$OA\cos\alpha = ON \rightarrow (a/h)\cos\alpha = d_{hkl} \rightarrow \cos\alpha = \left(\frac{h}{a}\right)d_{hkl}$$

- For angles β and γ:

$$\cos\beta = \left(\frac{k}{b}\right)d_{hkl}$$

$$\cos\gamma = \left(\frac{l}{c}\right)d_{hkl}$$

- Since for orthogonal axes:

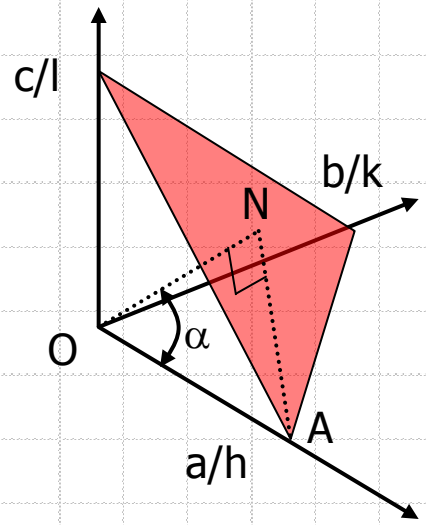
$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$$

- We write:

$$\left(\frac{h}{a}\right)^2 d_{hkl}^2 + \left(\frac{k}{b}\right)^2 d_{hkl}^2 + \left(\frac{l}{c}\right)^2 d_{hkl}^2 = 1$$

- For a cubic crystal $a = b = c$, hence

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



Lattice plane – (*hkl*)
ON – interplanar spacing

Lattice Plane Spacings

Cubic:
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

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

Hexagonal:
$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Rhombohedral:
$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

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

Monoclinic:
$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

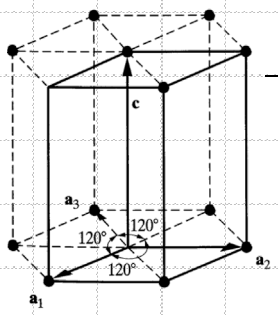
Triclinic:
$$\frac{1}{d^2} = \frac{1}{V^2}(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

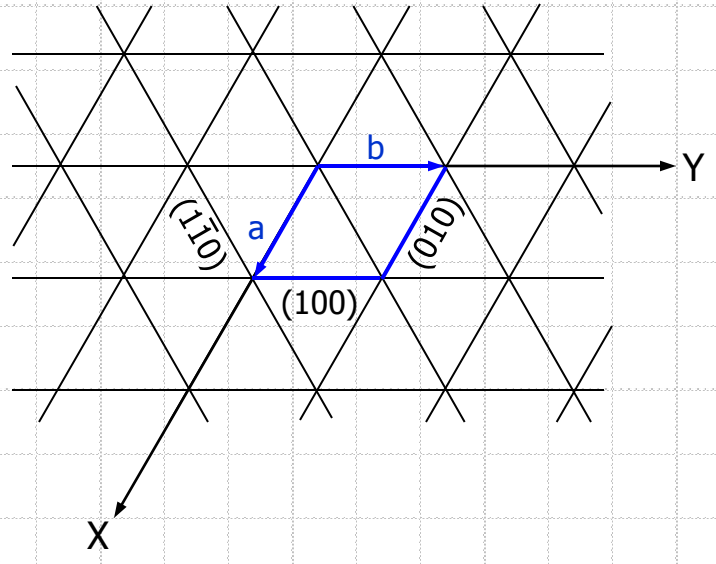
$$V = \text{volume of unit cell}$$
$$S_{11} = b^2c^2\sin^2\alpha,$$
$$S_{22} = a^2c^2\sin^2\beta,$$
$$S_{33} = a^2b^2\sin^2\gamma,$$
$$S_{12} = abc^2(\cos\alpha\cos\beta - \cos\gamma),$$
$$S_{23} = a^2bc(\cos\beta\cos\gamma - \cos\alpha),$$
$$S_{13} = ab^2c(\cos\gamma\cos\alpha - \cos\beta).$$

Special Case: Trigonal & Hexagonal Lattices

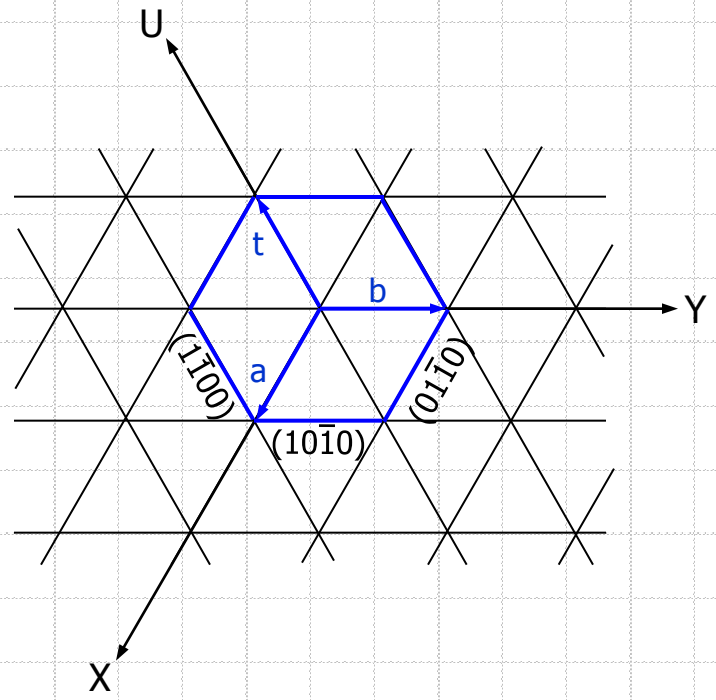
- (1 -10), (100), and (010) are indices different in type but describe crystallographically equivalent lattice planes.
- Introducing the fourth axis – U. We have Miller-Bravais indices (*hkil*).
- All indices of the planes are of the same form – {10 -10}.

$h + k + i = 0 \Rightarrow i = -(h + k) \Rightarrow \{hk.l\}$





(a)



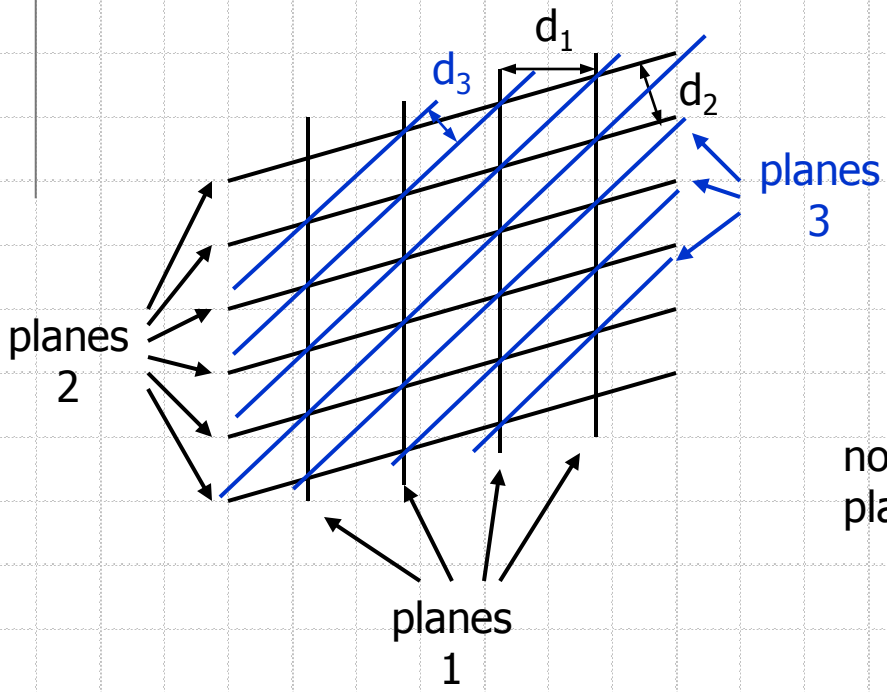
(b)

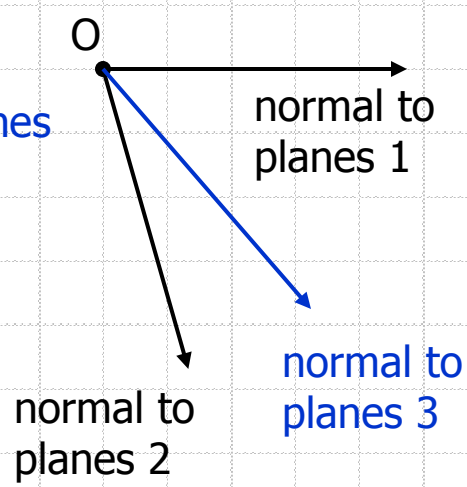
The Reciprocal Lattice

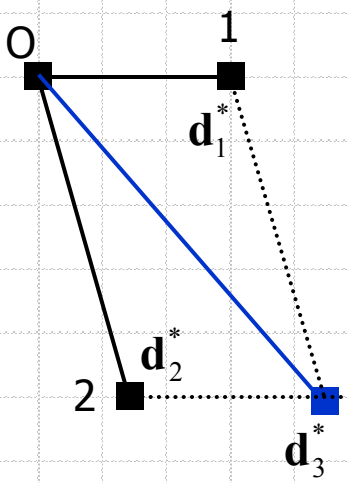
- Reciprocal lattice vectors

$$\mathbf{d}_1^* = K / d_1,$$
$$\mathbf{d}_2^* = K / d_2,$$
$$\mathbf{d}_3^* = K / d_3$$

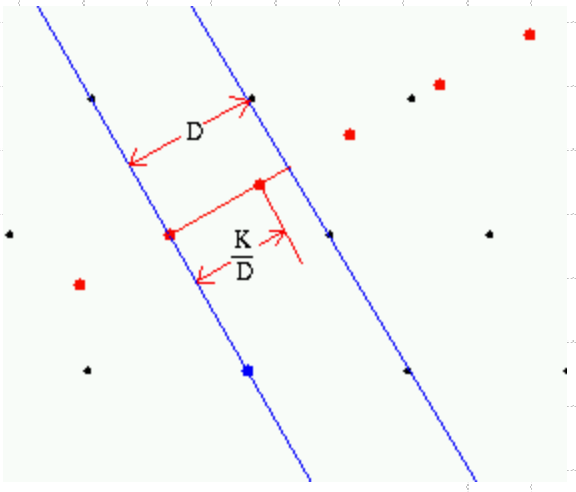
K – is a constant

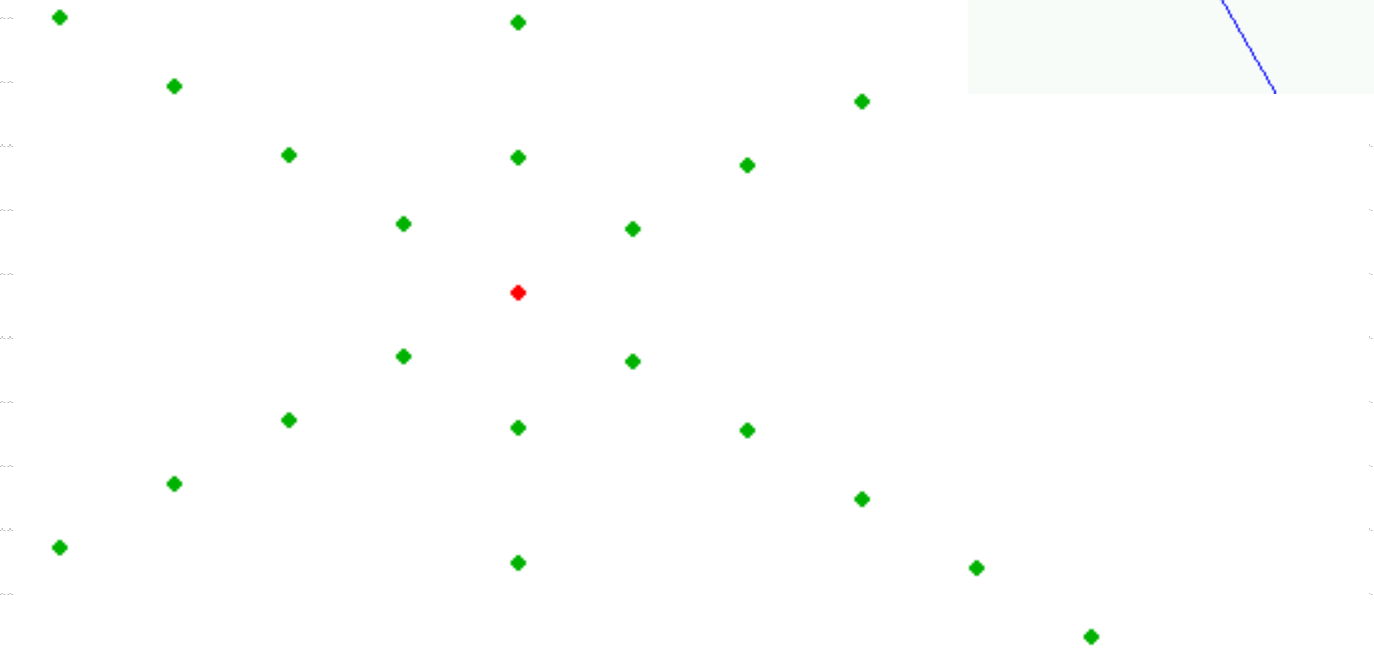




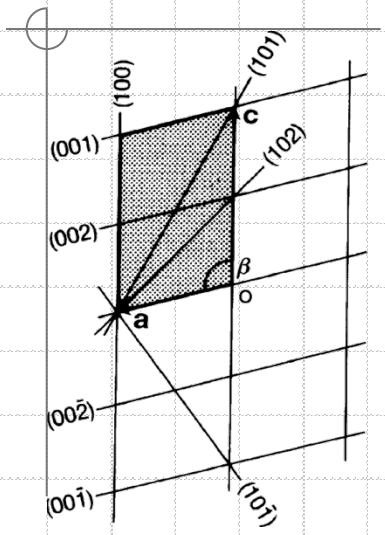


The Reciprocal Lattice

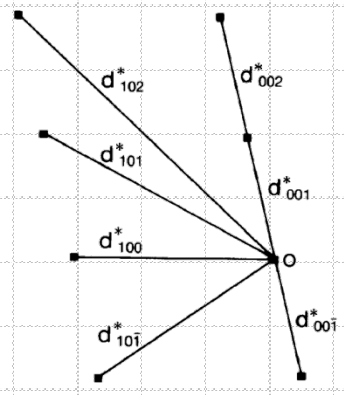




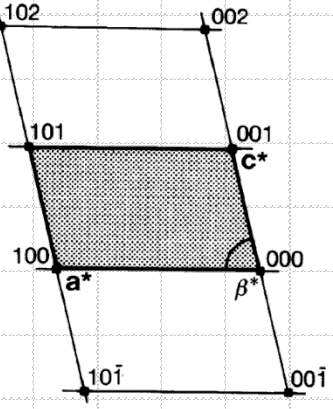
The Reciprocal Lattice



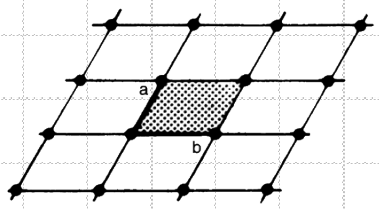
Monoclinic unit cell planes $\{h\,0\,l\}$

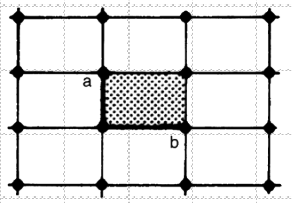


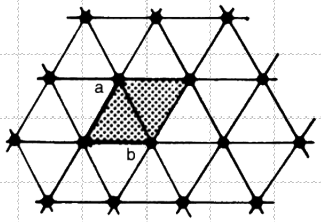
Reciprocal lattice vectors

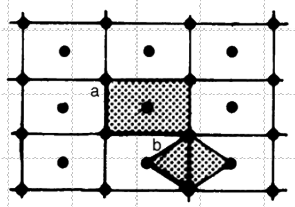


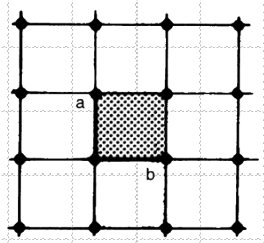
Reciprocal lattice unit cell

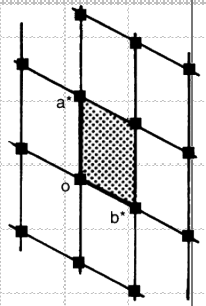


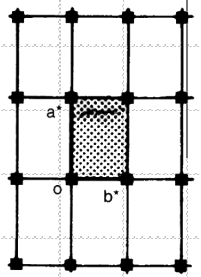


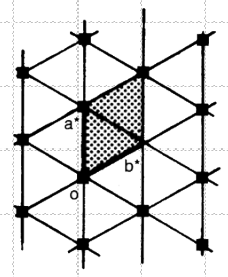


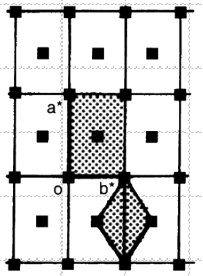


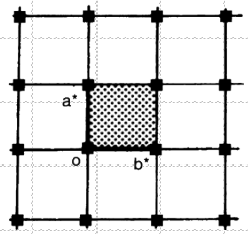








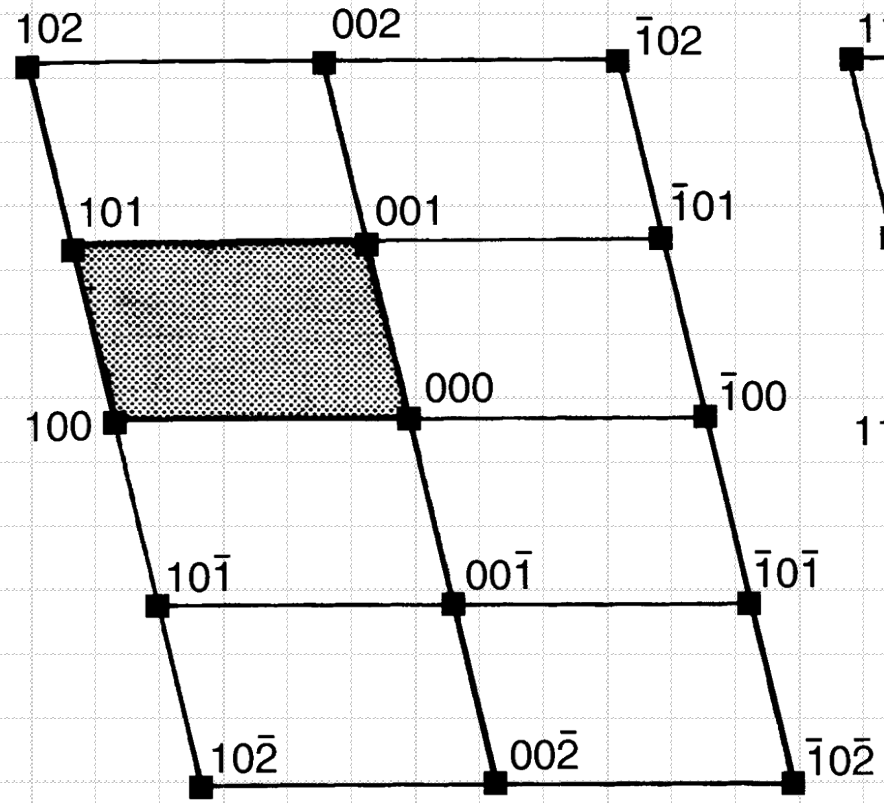




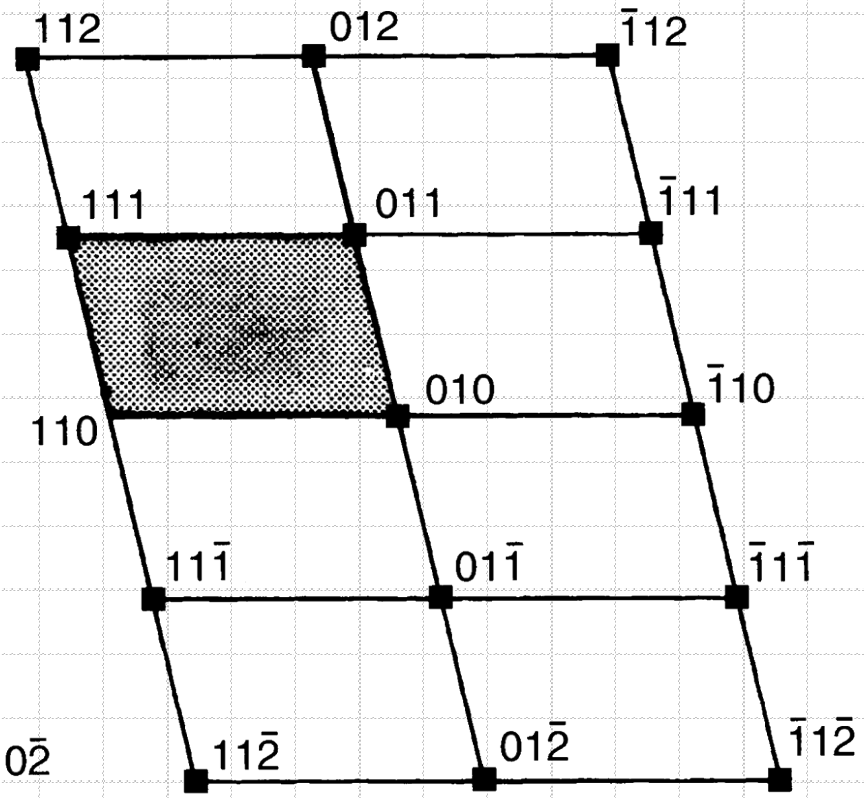
$$\mathbf{a}^* = \mathbf{d}^*_{100} \text{ and } \left|\mathbf{a}^*\right| = 1/d_{100};$$

$$\mathbf{c}^* = \mathbf{d}^*_{001} \text{ and } \left|\mathbf{c}^*\right| = 1/d_{001}$$

The Reciprocal Lattice



h0l section



h1l section

The Reciprocal Lattice

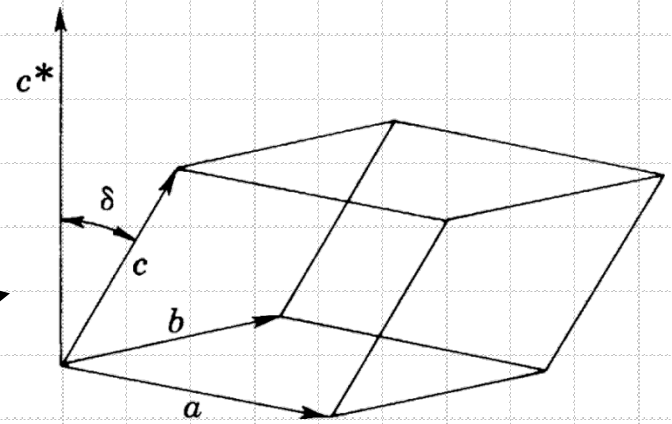
- Consider a real space unit cell with real lattice basis vectors **a**, **b** and **c**
- We define a set of reciprocal lattice basis vectors by:

$$\mathbf{a}^* = \frac{1}{V}(\mathbf{b}\times\mathbf{c}) = \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$$

volume of real space unit cell

$$\mathbf{b}^* = \frac{1}{V}(\mathbf{c}\times\mathbf{a})$$

$$\mathbf{c}^* = \frac{1}{V}(\mathbf{a}\times\mathbf{b})$$



$c^* \perp$ a-b plane

The Reciprocal Lattice

- Just like we can define a real space lattice in terms of our real space lattice vectors, we can define a reciprocal space lattice in terms of our reciprocal space lattice vectors:

$$\mathbf{r}^* = \mathbf{d}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

The real and reciprocal space lattice vectors form an orthonormal set:

$$\left.\begin{aligned} \mathbf{a}^* \cdot \mathbf{b} = \mathbf{a}^* \cdot \mathbf{c} = 0 \\ \mathbf{a}^* \cdot \mathbf{a} = 1 \end{aligned}\right\}$$ similar for ***b**** and ***c****

We can define a reciprocal unit cell with volume ***V****:

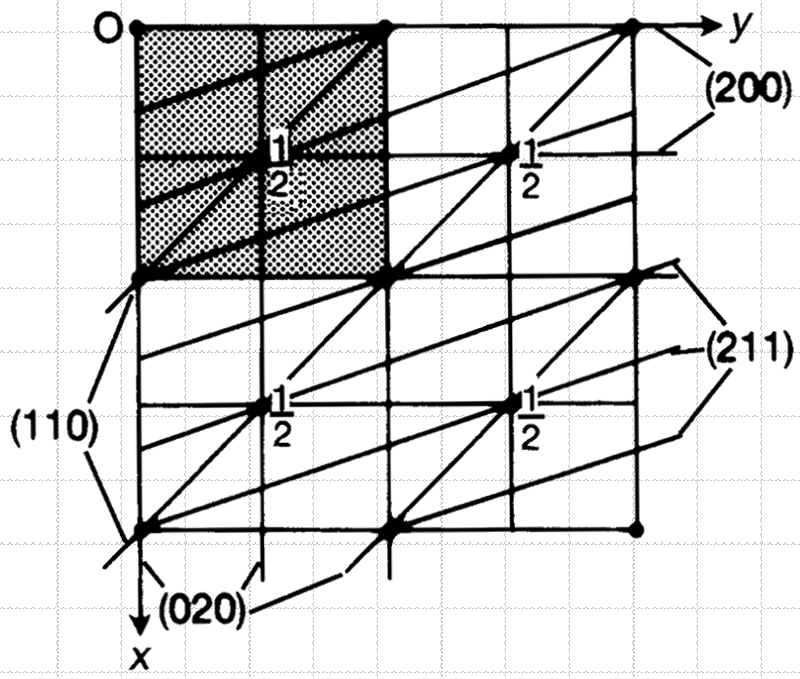
$$V^* = \mathbf{a}^* \cdot \left(\mathbf{b}^* \times \mathbf{c}^*\right) \qquad V^* \cdot V = 1$$

- Now we can write:

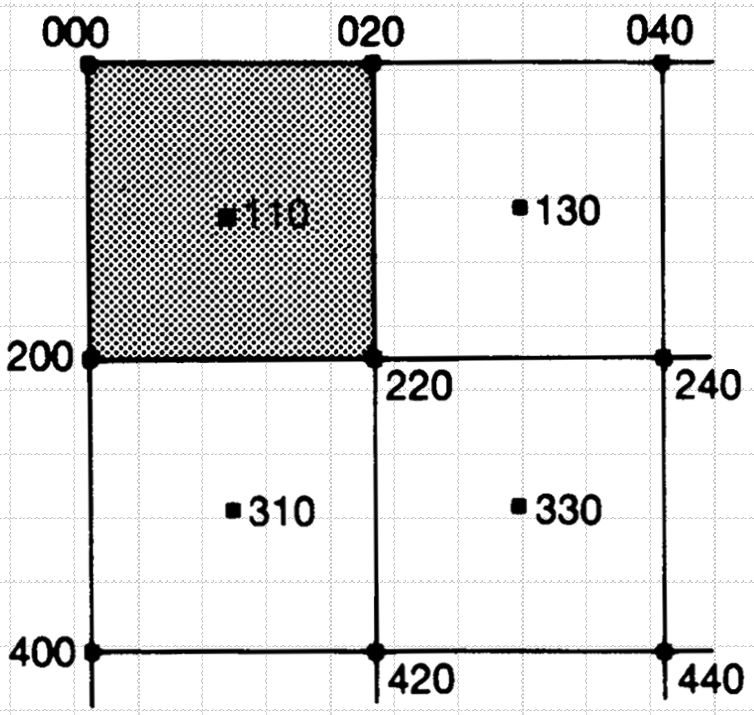
$$\mathbf{r}_{uvw} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

$$\mathbf{d}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

The Reciprocal Lattice

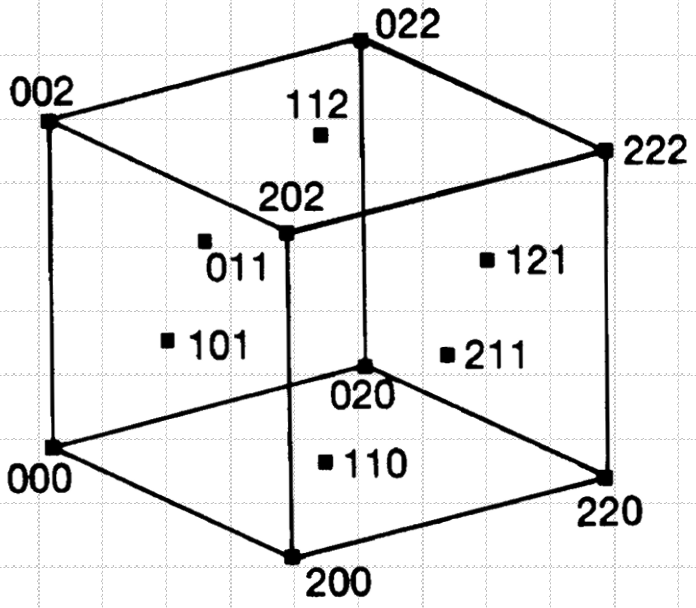


Plane of a cubic I crystal $\perp$ z-axis

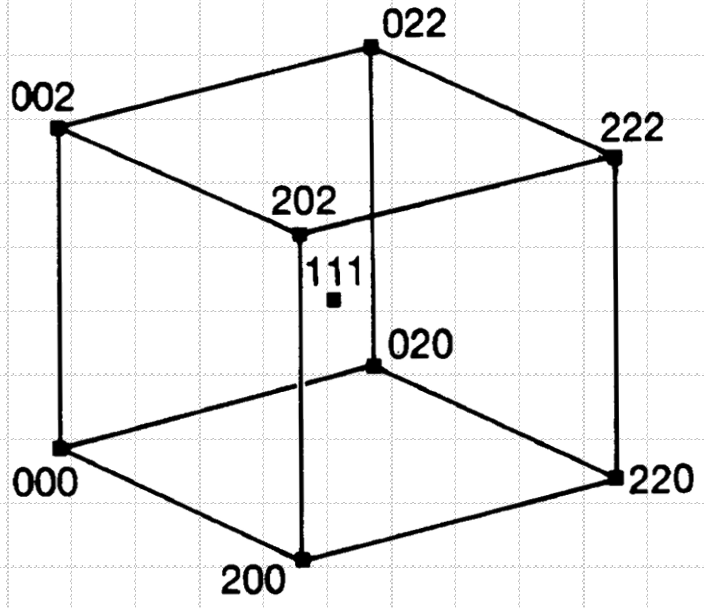


Reciprocal lattice points

The Reciprocal Lattice



Cubic *F* reciprocal lattice unit cell of a cubic *I* direct lattice



Cubic *I* reciprocal lattice unit cell of a cubic *F* direct lattice

The Reciprocal Lattice

- d-spacing of lattice planes

$$\mathbf{d}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

$$\mathbf{d}^*_{hkl} \cdot \mathbf{d}^*_{hkl} = \frac{1}{d^2_{hkl}} = (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$$

for orthorombic, tetragonal, cubic: $\mathbf{a}^* \cdot \mathbf{b}^* = 0$

therefore:

$$\frac{1}{d^2_{hkl}} = h\mathbf{a}^* \cdot h\mathbf{a}^* + k\mathbf{b}^* \cdot k\mathbf{b}^* + l\mathbf{c}^* \cdot l\mathbf{c}^* = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

$$\left(\mathbf{a}^* \cdot \mathbf{a}^* = \frac{1}{a^2} \right)$$

- Angle ρ between plane normals $(h_1 k_1 l_1)$ and $(h_2 k_2 l_2)$

the angle between two vectors is $\cos\rho = \dfrac{\mathbf{a} \cdot \mathbf{b}}{ab}$

therefore: $\cos\rho = \dfrac{\mathbf{d}^*_{h_1 k_1 l_1} \cdot \mathbf{d}^*_{h_2 k_2 l_2}}{\left|\mathbf{d}^*_{h_1 k_1 l_1}\right| \left|\mathbf{d}^*_{h_2 k_2 l_2}\right|}$