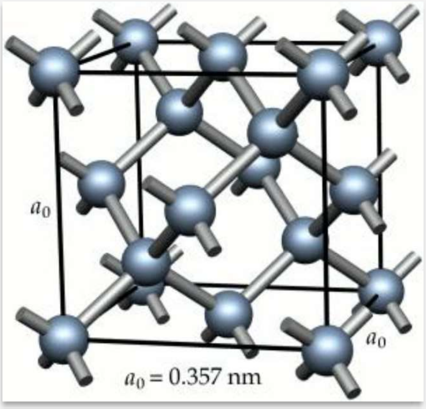
Crystal Structure

Lecture 2

Learning outcomes of the lecture

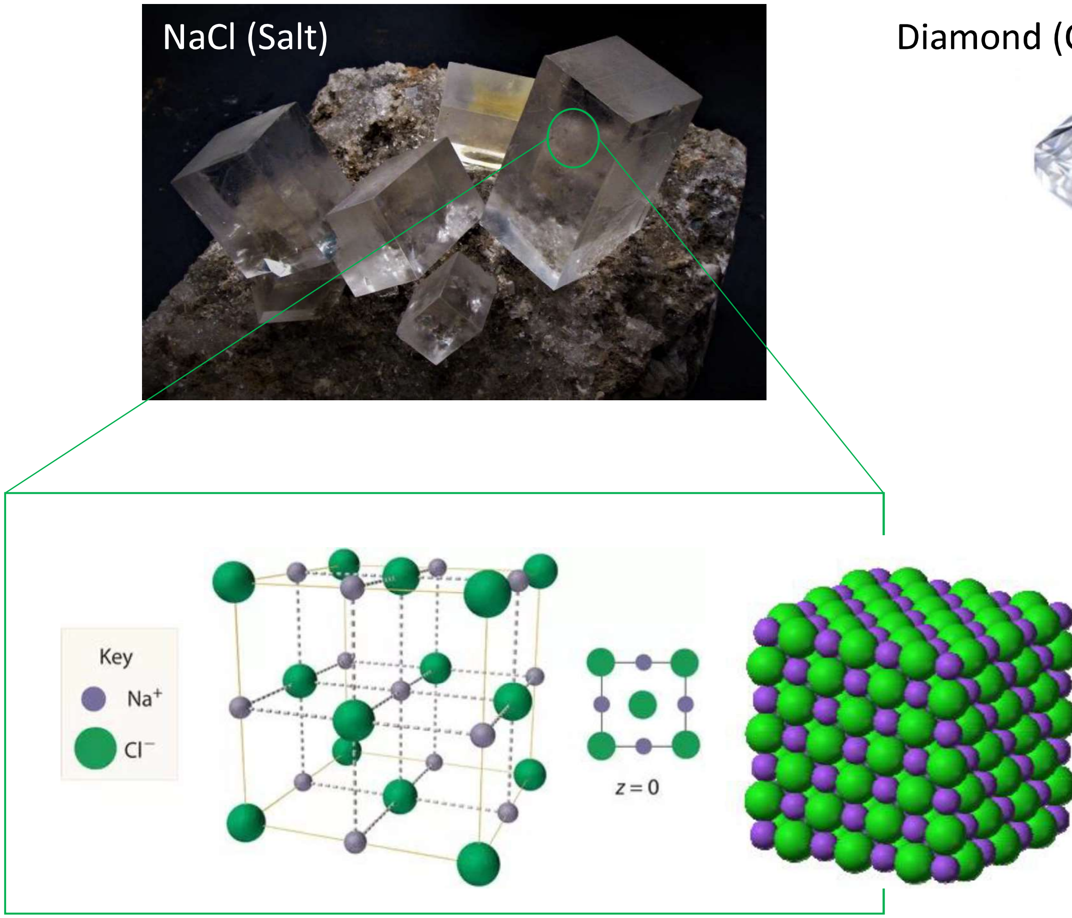
- ➢ **Describe a crystal structure**



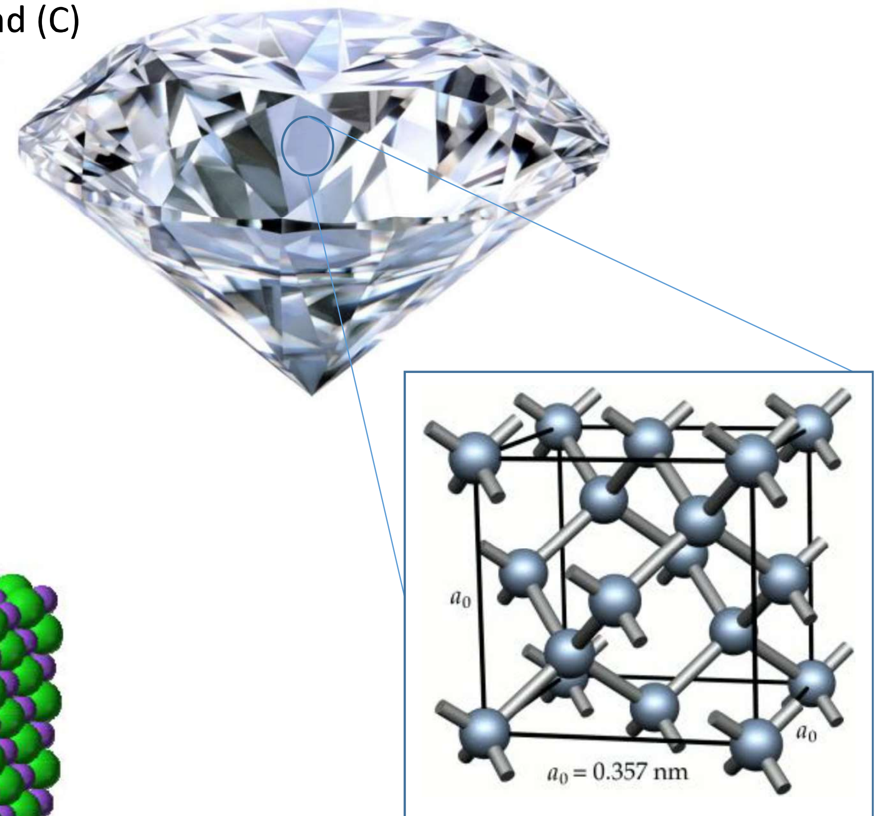
see, for instance,
Kittel - Chapter 1

Recap

A **crystal** is a periodic array of atoms or group of atoms



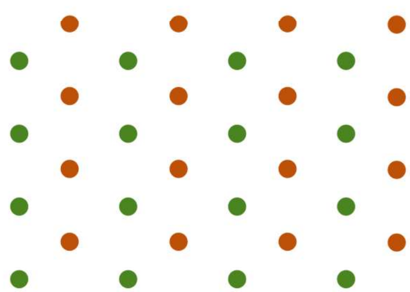
Diamond (C)



Recap

A **crystal** consists of a repeating pattern of objects (i.e. atoms or molecules) in an effectively infinite 3D array

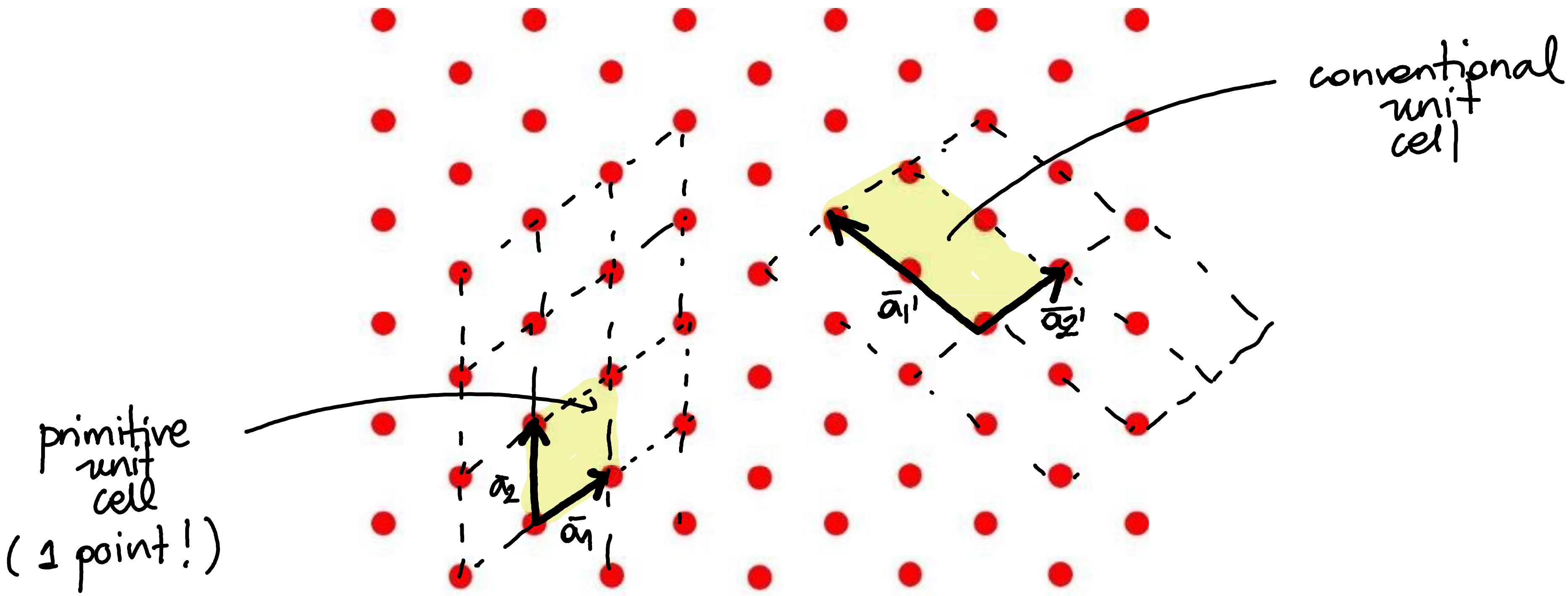
Crystal	**=**	**Lattice**	**+**	**Basis**



Lattice of points
(Bravais Lattice)

Basis of atoms

Recap



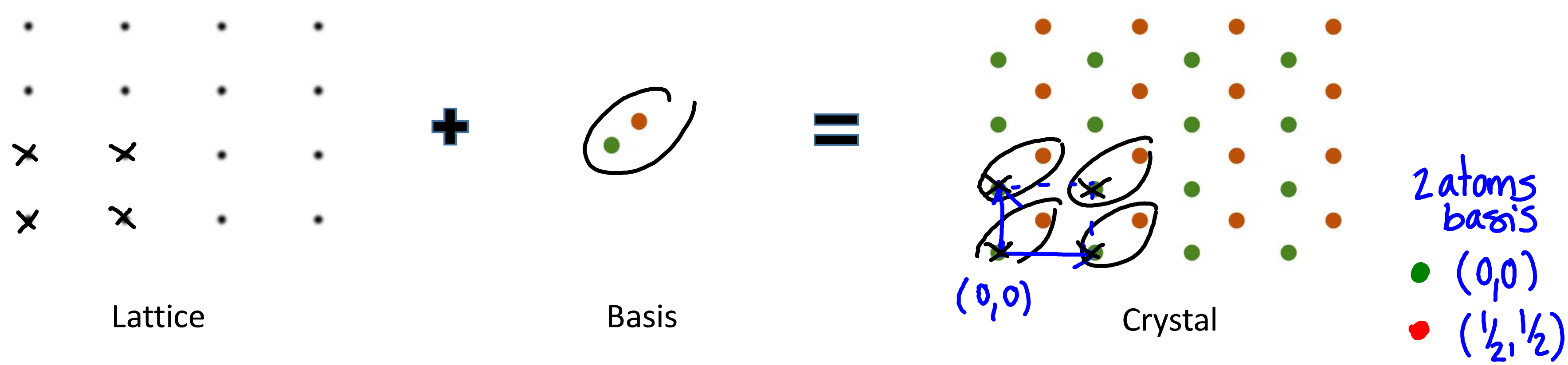
$$\vec{r}\,' = \vec{r} + \vec{T} = \vec{r} + \underbrace{u_1\bar{a}_1 + u_2\bar{a}_2 + u_3\bar{a}_3}_{\vec{T}}$$

$\bar{a}_i$: primitive Lattice vectors if all Lattice points can be reached with u_i integers

Basis

- Physical element (atom, ion, molecule, group of atoms...) attached to every lattice point, with every basis identical

* The crystal is made by adding a basis to each lattice point



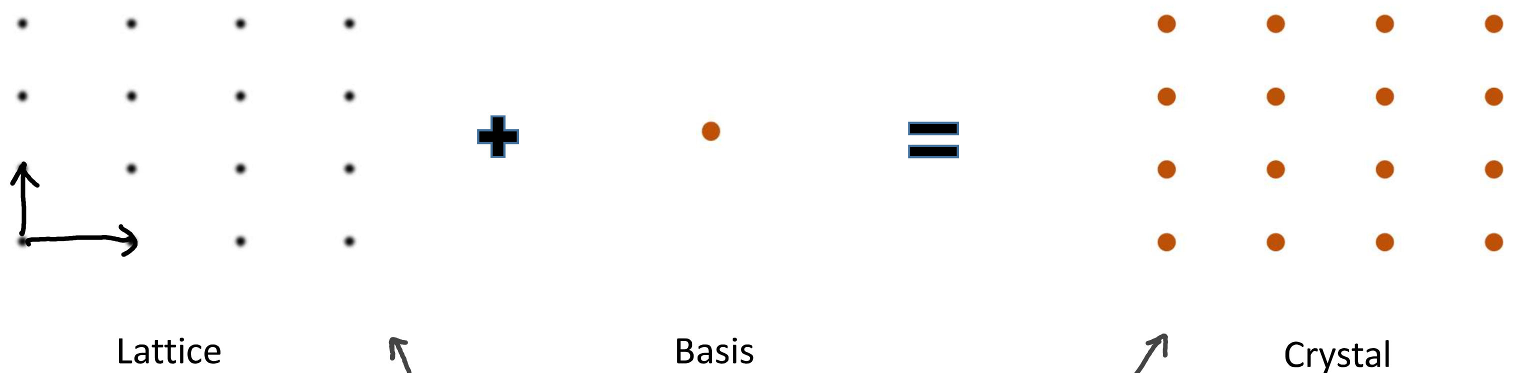
- the basis can be identified once the crystal axis are chosen

- Position of the r_j atom of the basis relative to the associate Lattice

$$\vec{r}_j = x_j \bar{a}_1 + y_j \bar{a}_2 + z_j \bar{a}_3$$

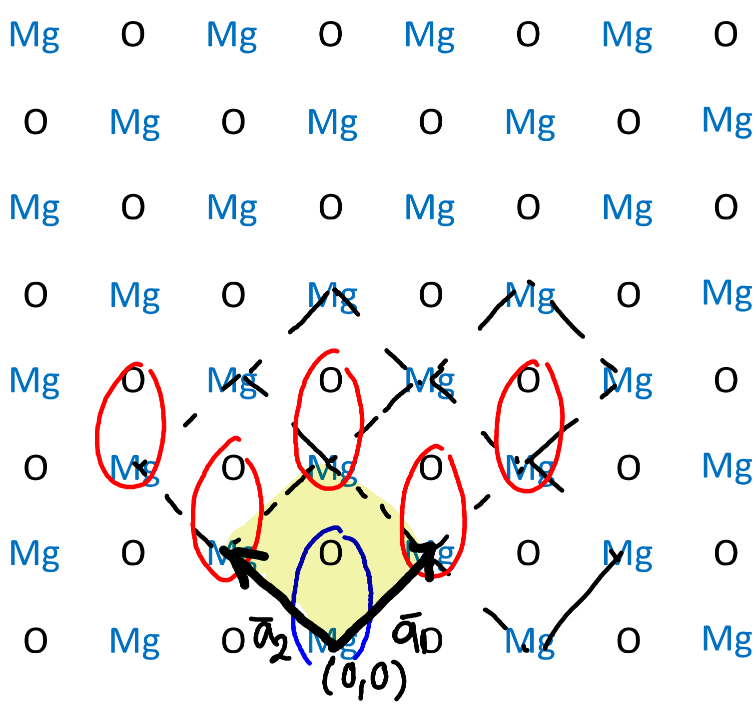
$$0 \leq x_j, y_j, z_j \leq 1$$

the number of atoms in a basis can be one or more
(but each basis in a crystal is identical to any other in composition, arrangement and orientation)



simplest case: 1 atom per basis
@ • (0,0)

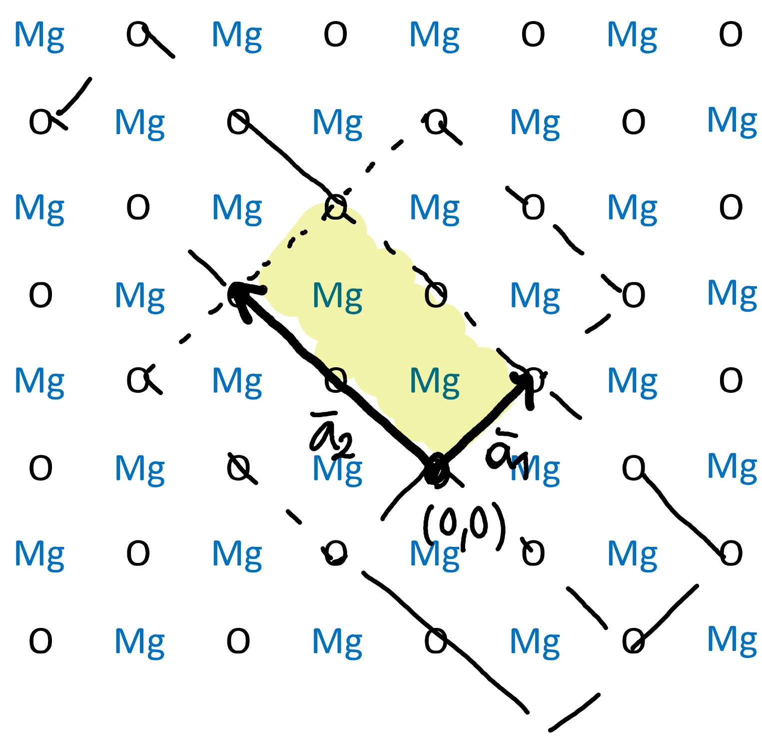
they are not "the same": the lattice consists of points, not atoms



Square lattice

Basis : Mg (0,0) – O $(\frac{1}{2}, \frac{1}{2})$

2 atoms



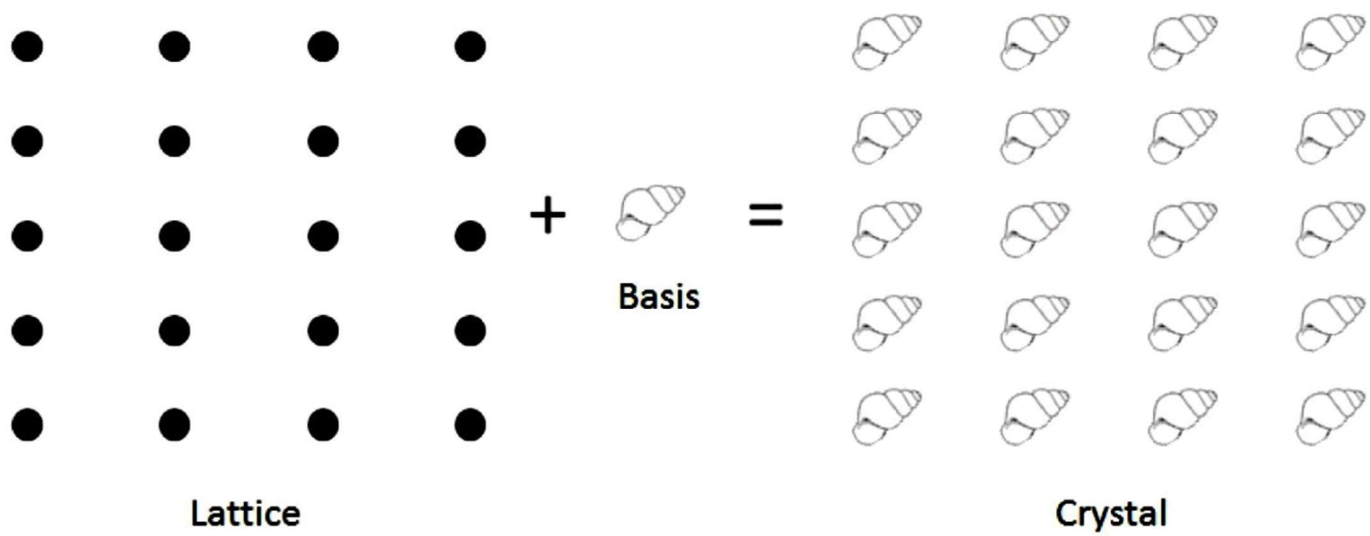
Like the lattice vectors,
the basis is not unique
[different choices]

Here, now: 4 atoms basis

O $(0,0)$, $(0,\frac{1}{2})$

Mg $(\frac{1}{2},\frac{1}{4})$, $(\frac{1}{2},\frac{3}{4})$

Any periodic structure can be expressed as a lattice of repeating motives!



Bar Floor

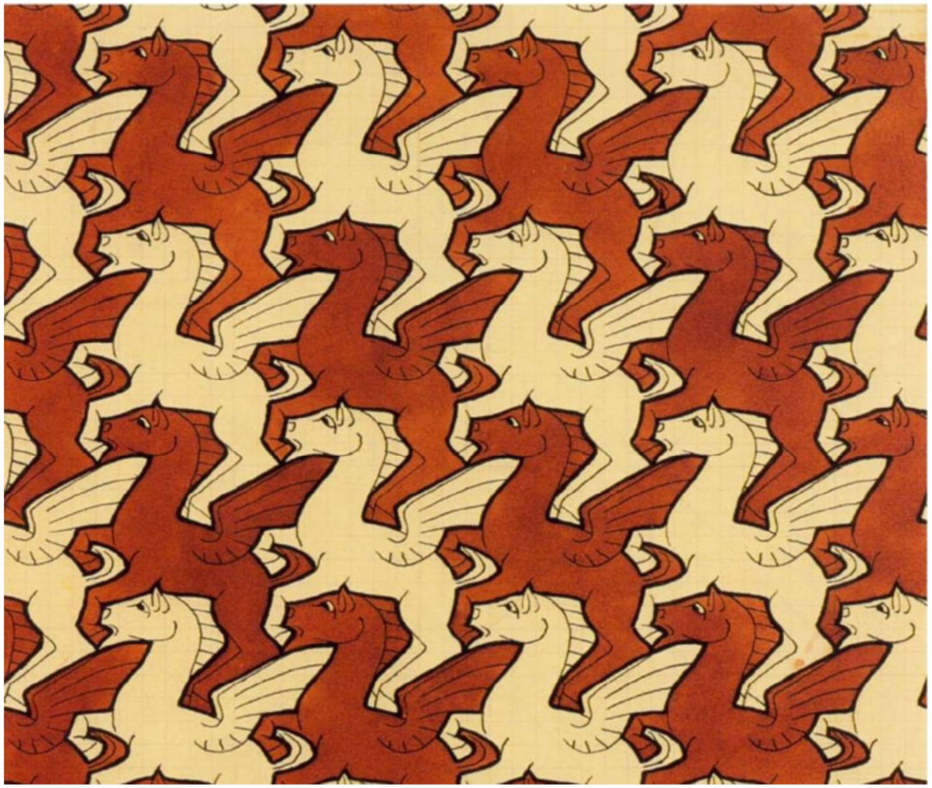
$$\vec{T} = u_1\bar{a}_1 + u_2\bar{a}_2$$

Basis

◆ @ (0,0)

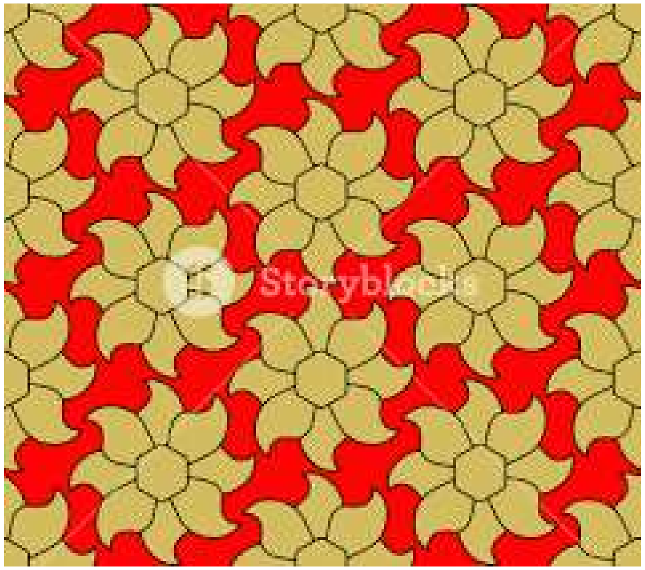
◇ @ ($\frac{1}{2}$,$\frac{1}{2}$)

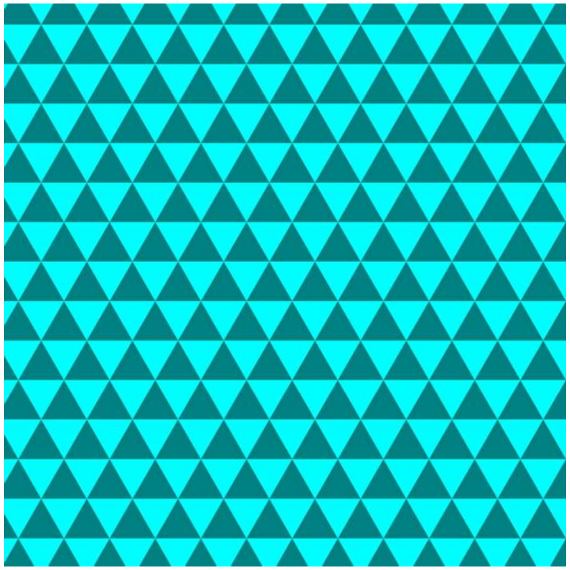
Escher Tessellations

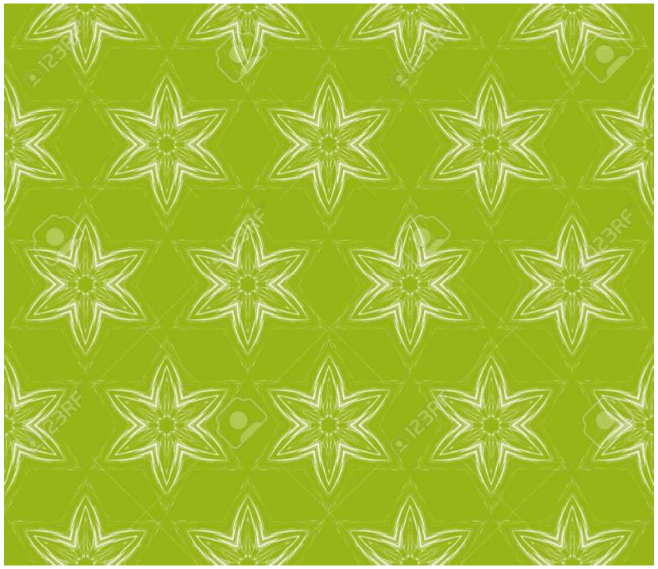


- *Lattice?*
- *Basis?*

Wallpapers patterns



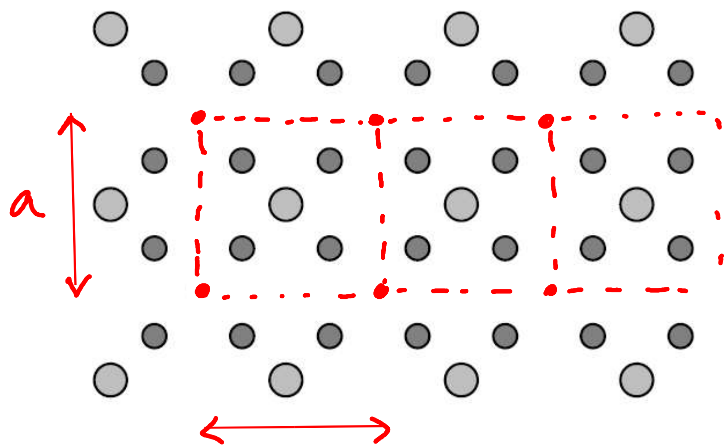




- *Lattice?*
- *Basis?*

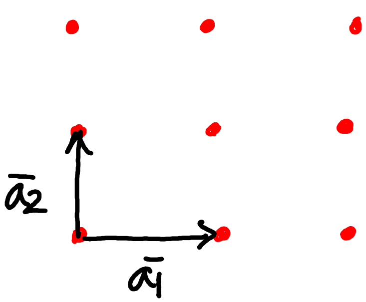
Description of a crystal:

1. What is the lattice?
2. What choice of $\mathbf{a_1}$, $\mathbf{a_2}$, $\mathbf{a_3}$ do we wish to make?
3. What is the basis?

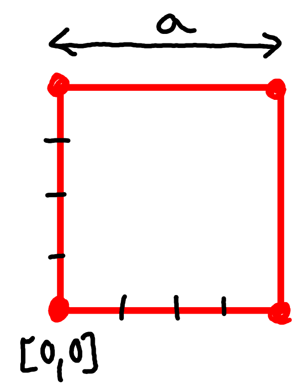


a = lattice constant

Lattice.



zoom of the unit cell



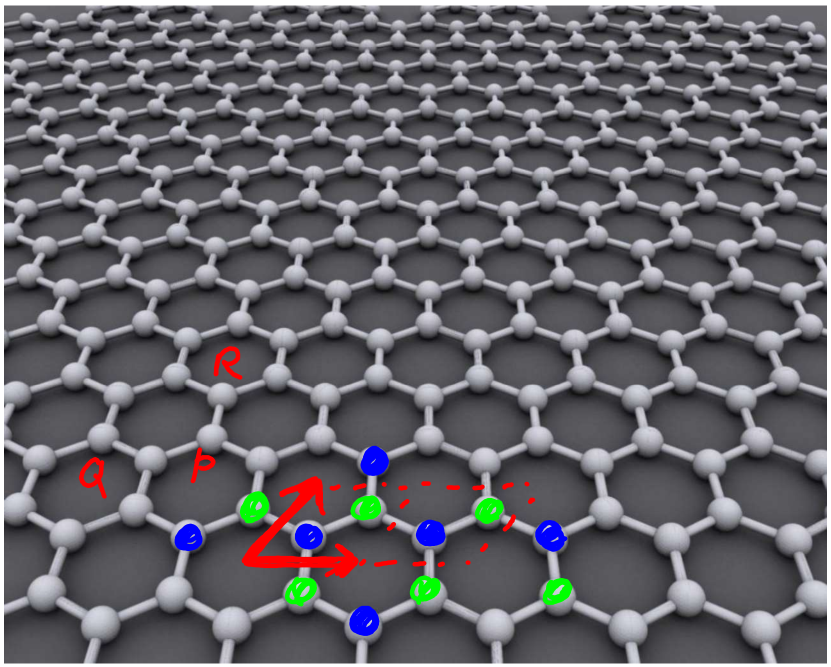
Basis

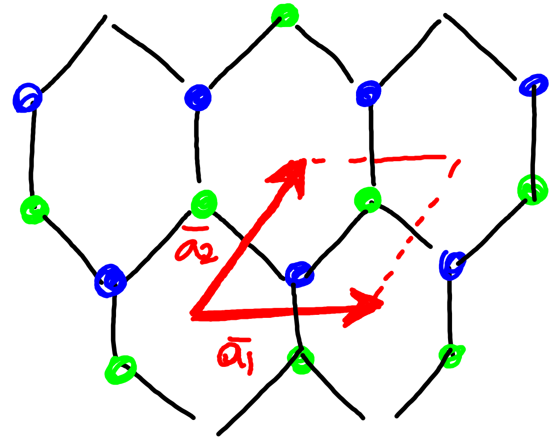
○ $\left[\frac{a}{2}, \frac{a}{2}\right]$

● $\left[\frac{a}{4}, \frac{a}{4}\right]$; $\left[\frac{a}{4}, \frac{3a}{4}\right]$

$\left[\frac{3a}{4}, \frac{a}{4}\right]$; $\left[\frac{3a}{4}, \frac{3a}{4}\right]$

Quiz: Is the honeycomb a lattice?





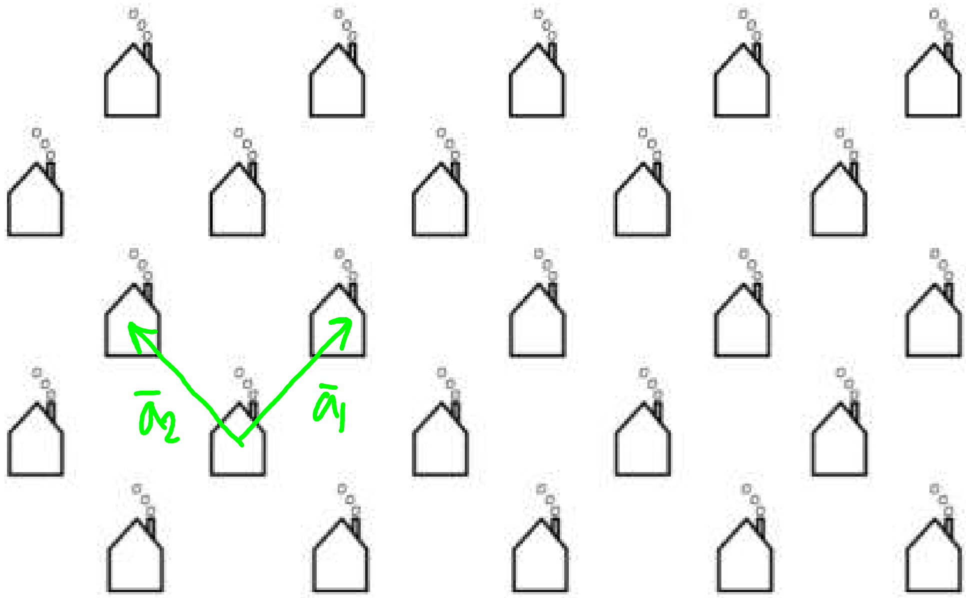
Basis $\left[\frac{a_1}{3}, \frac{a_2}{3}\right]$

$\left[\frac{2a_1}{3}, \frac{2a_2}{3}\right]$

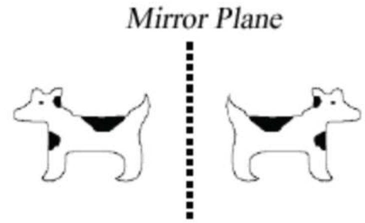
the honeycomb is not a lattice
(points P & R are not equivalent)
(Q & R yes)

All crystal lattices can be carried into themselves by the lattice translation $\vec{T}$

$\vec{r}\,' = \vec{r} + \vec{T}$



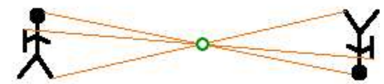
Point Symmetry



Reflection in a plane (m) - expressed by a coordinate transformation

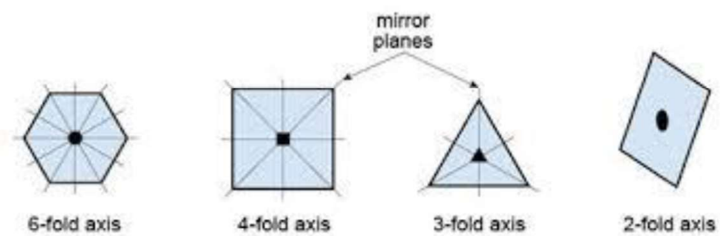
i.e. $x' = -x,\ y' = y,\ z' = z$

Inversion symmetry ($\bar{1}$) – described by the coordinate transformation $x' = -x,\ y' = -y,\ z' = -z$



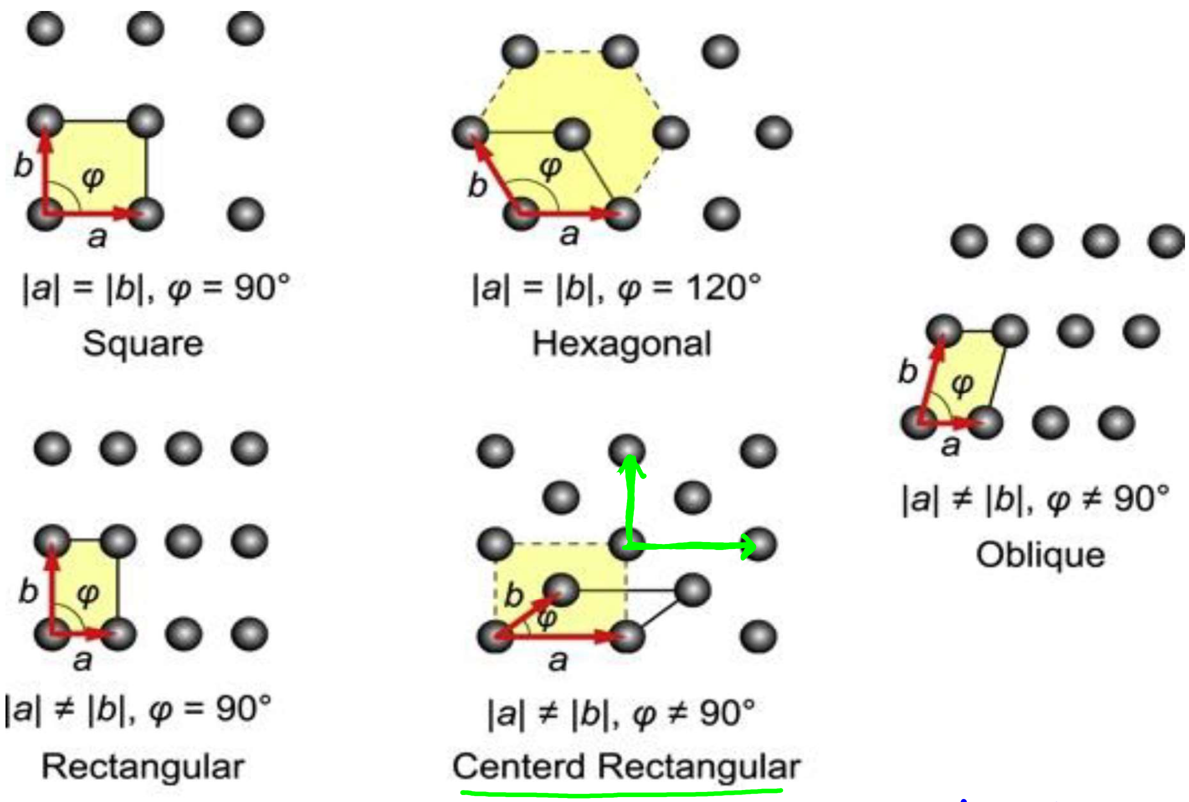
Rotational symmetry (1, 2, 3, 4, 6) – when rotation through a particular angle about a certain axis leads to an identical structure

$\frac{2\pi}{n}$ $n = 1, 2, 3, 4, 6$



Rotation-Inversion Axes ($\bar{2}, \bar{3}, \bar{4}, \bar{6}$) – when rotation with simulateneous inversion are combined leading to an identical structure identical structure

5 Bravais Lattice in two dimensions

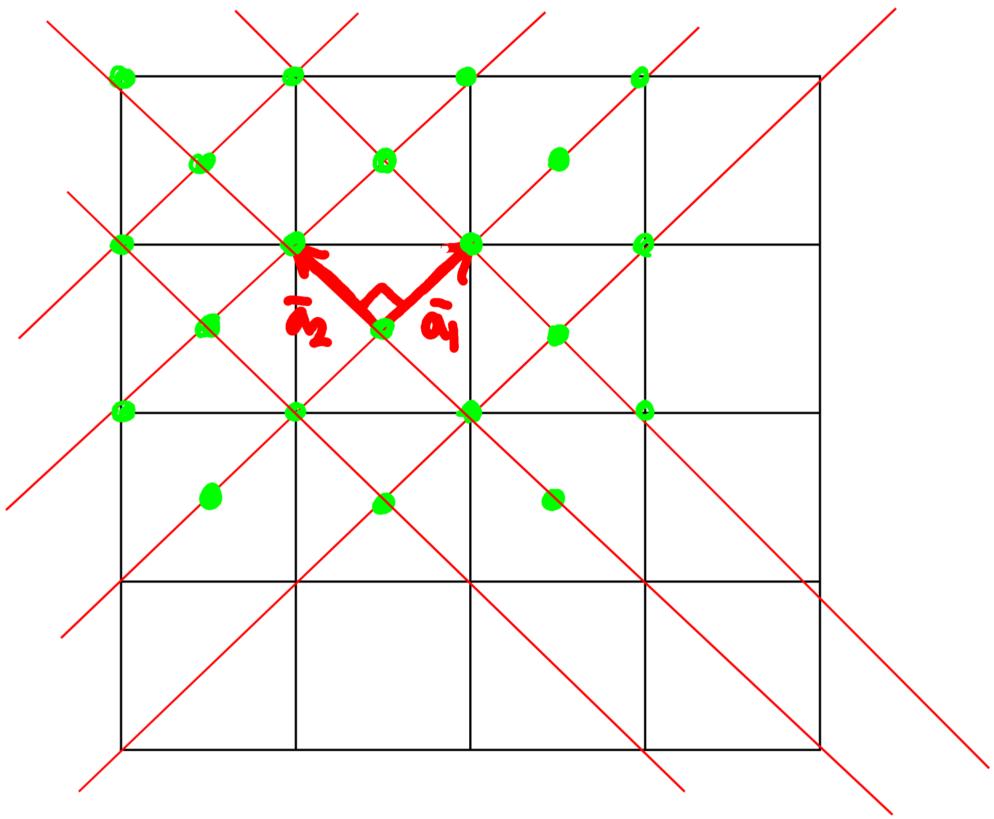


not primitive unit cell
(but this choice reflects better the symmetry of the Lattice)

These are the only possible special crystal types (Bravais lattices) in two dimensions

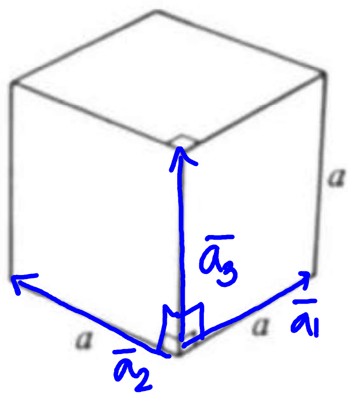
Why does not exist in 2D the centered-square lattice?

Smaller Square Lattice can be defined



Some 3D lattices

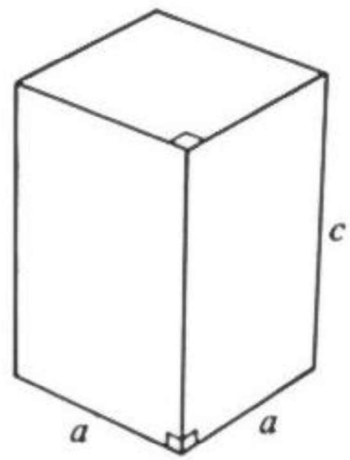
Cubic
unit cell



$a_1 = a_2 = a_3$

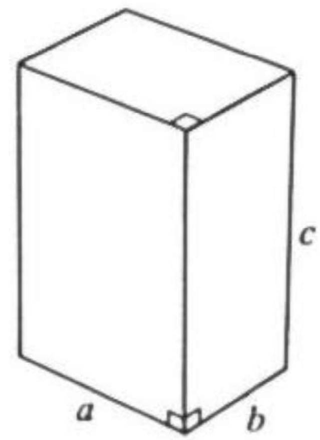
$\varphi = 90$

Tetragonal
unit cell



$a_1 = a_2 \neq a_3$

Orthorhombic
unit cell



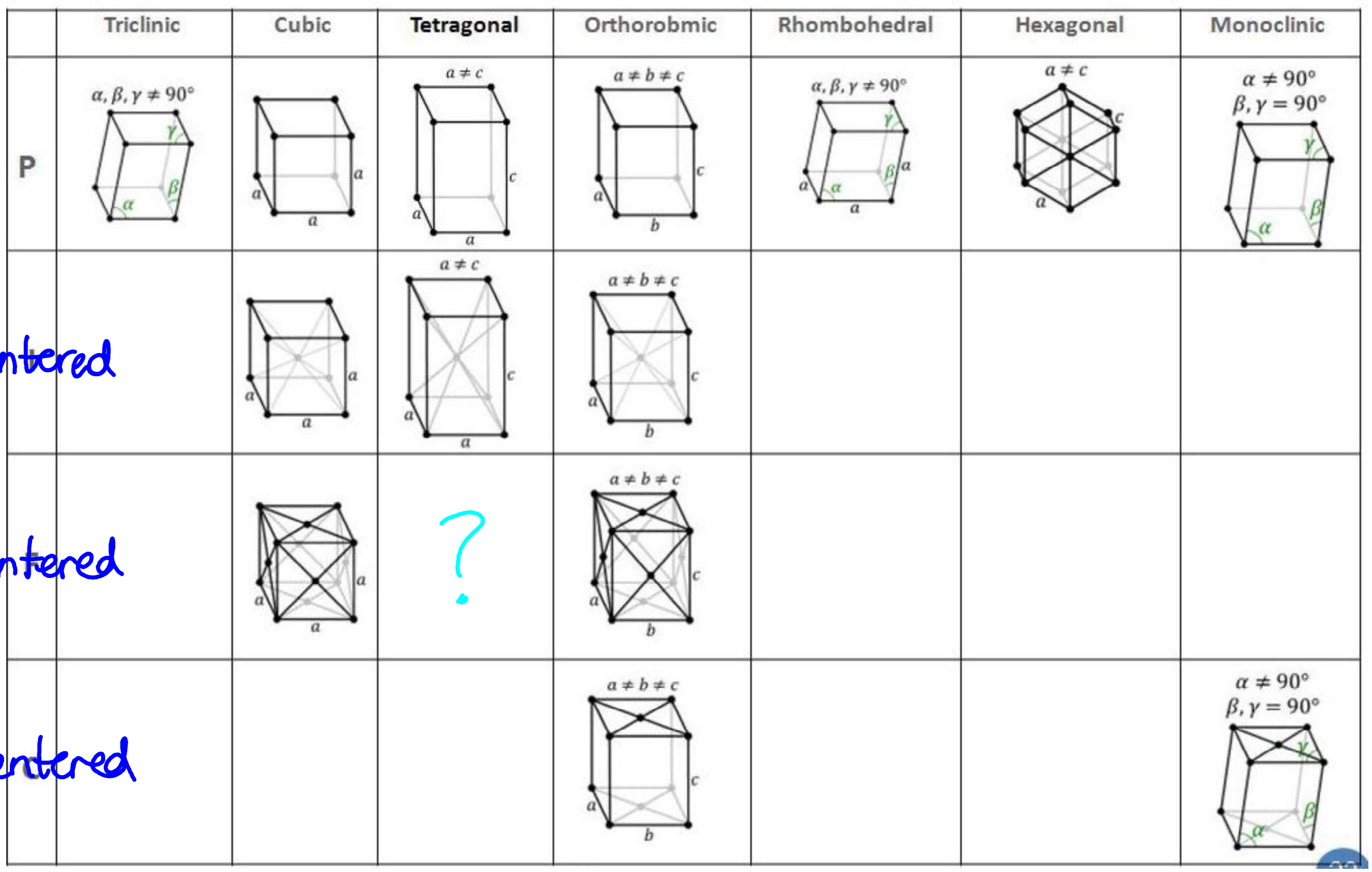
$a_1 \neq a_2 \neq a_3$

but still with orthogonal axis

14 Bravais Lattice in three dimensions

Name	Number of Bravais lattices	Conditions
Triclinic	1	$a_1 \neq a_2 \neq a_3$, $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$, $\alpha = \beta = 90° \neq \gamma$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$, $\alpha = \beta = \gamma = 90°$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$
Cubic	3	$a_1 = a_2 = a_3$, $\alpha = \beta = \gamma = 90°$
Trigonal	1	$a_1 = a_2 = a_3$, $\alpha = \beta = \gamma < 120° \neq 90°$
Hexagonal	1	$a_1 = a_2 \neq a_3$, $\alpha = \beta = 90°$, $\gamma = 120°$

14 Bravais Lattice in three dimensions



Simple

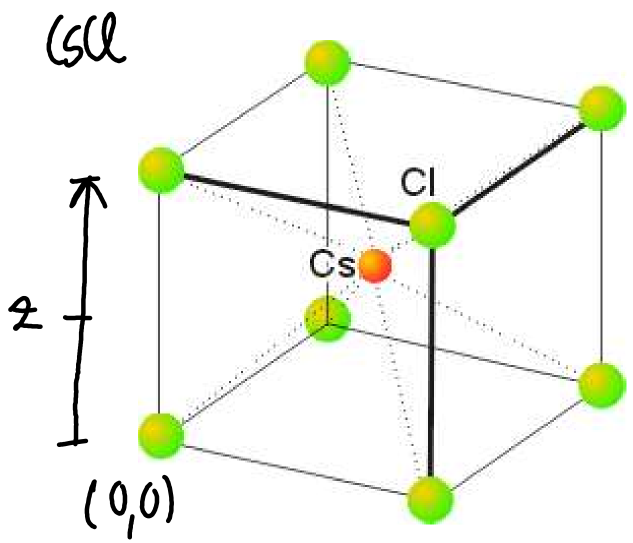
Body - centered

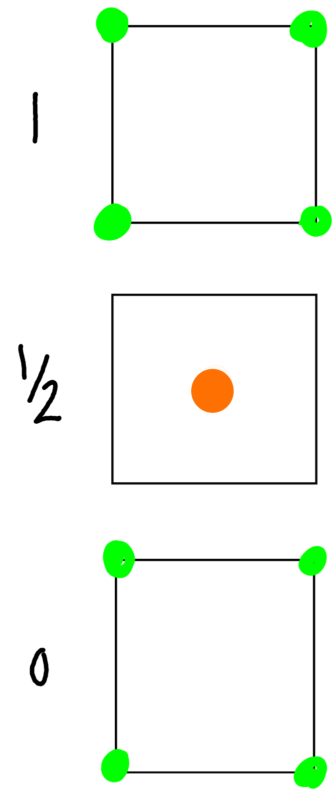
Face - centered

?

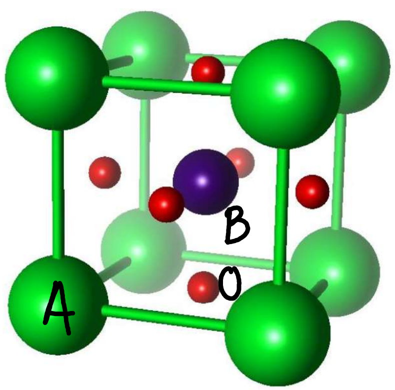
Base - centered

Planar View

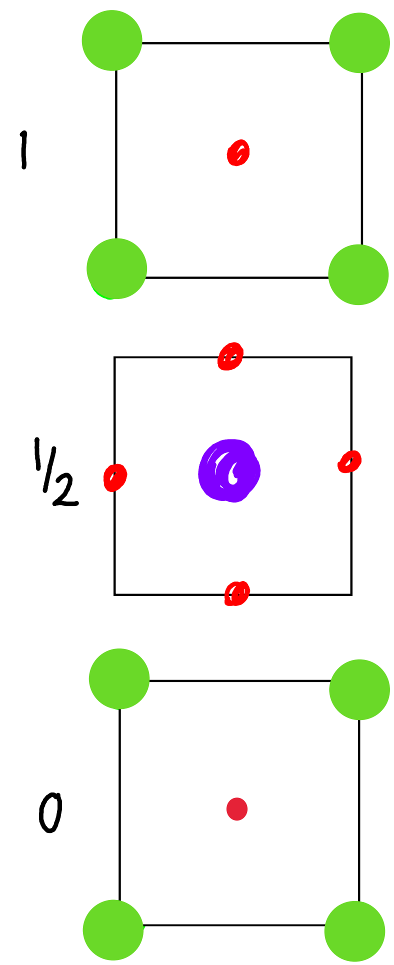


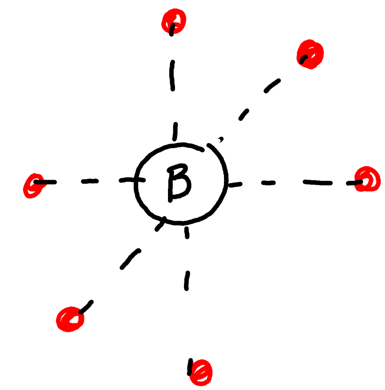


Planar View



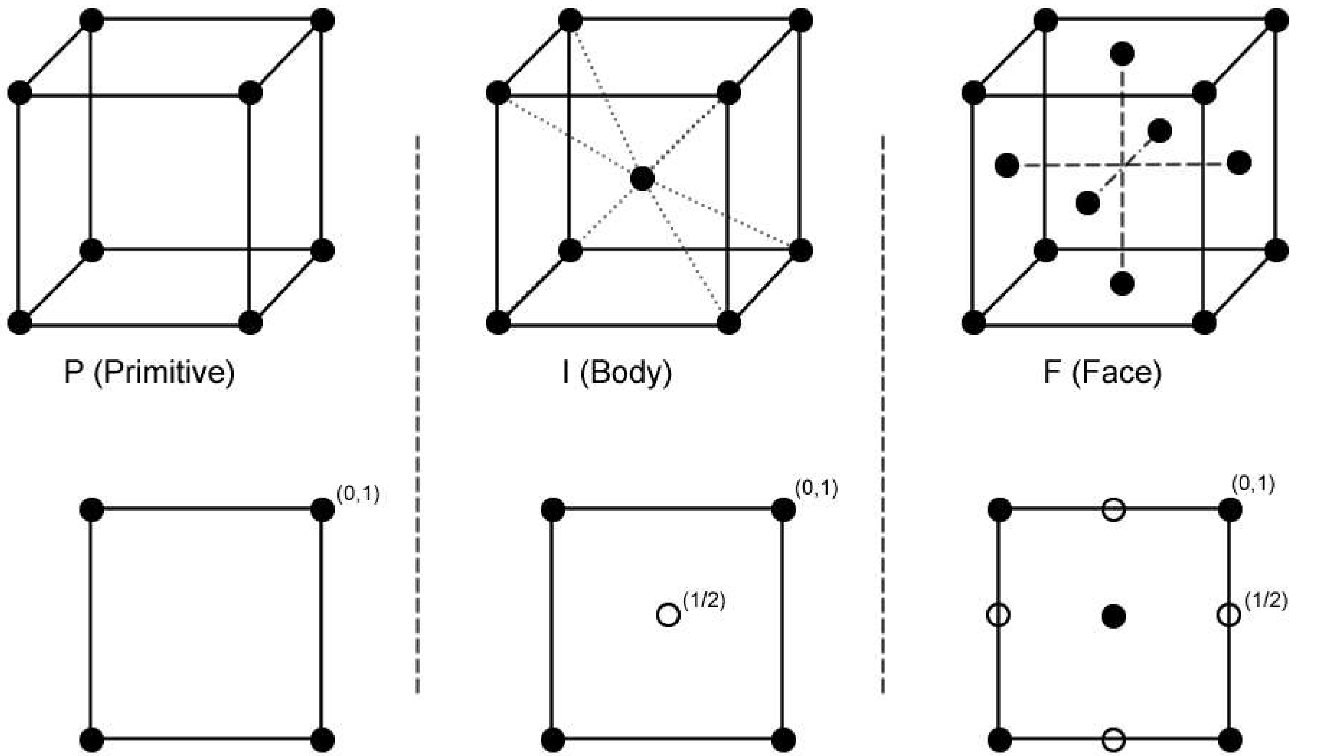
Perovskite ABO_3





Cubic Lattices

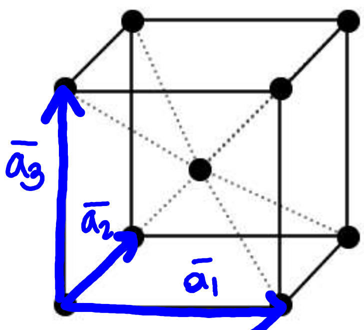
Simple cubic | Body-centered cubic (bcc) | Face-centered cubic (fcc)



Body-centered cubic (bcc)

Li, Na, K, Fe, Mo, Cs...

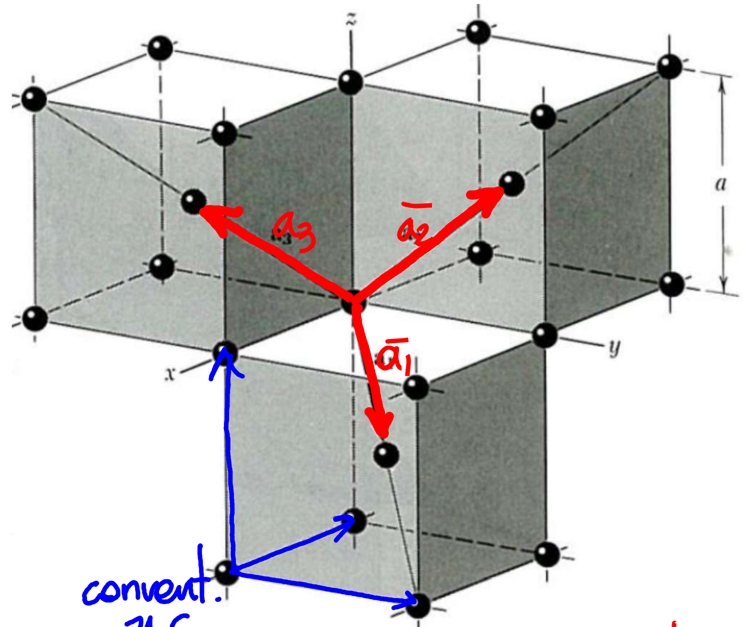
Coordination number
nearest neighbour = 8



(0,0,0) I (Body)

Lattice points: $\frac{1}{8} \times 8 + 1 = 2$

Useful thinking:
simple cubic lattice
with a basis of 2 atoms
per conventional u.c.
@ $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$



convent.
u.c.

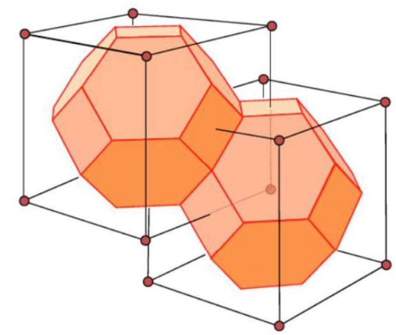
Primitive translation
vectors

$\bar{a}_1 = a\left(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\right)$

$\bar{a}_2 = a\left(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$

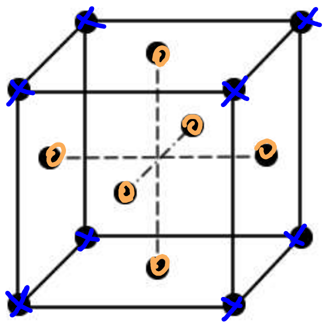
$\bar{a}_3 = a\left(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}\right)$

Wigner-seitz



Face-centered cubic (fcc)

Al, Ca, Au, Pb, Ni, Cu, Ag...



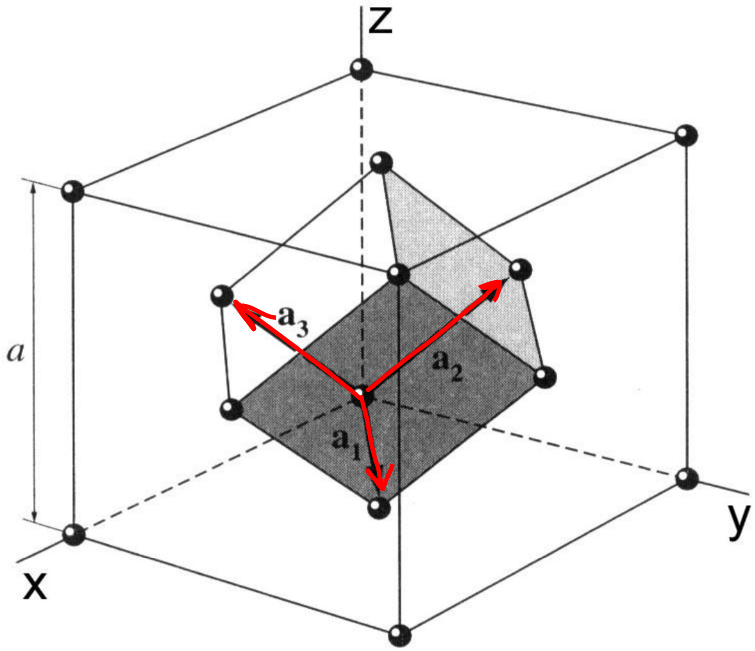
F (Face)

Lattice points.

$$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

Useful thinking:
simple cubic with 4 atoms basis

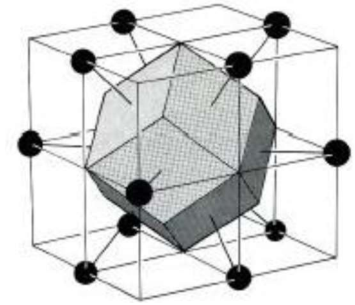
$(0,0,0)$, $(\frac{1}{2},\frac{1}{2},0)$, $(0,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},0,\frac{1}{2})$



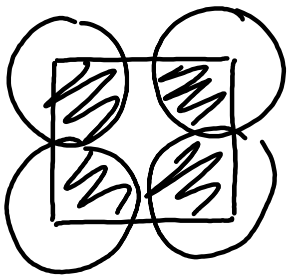
Primitive lattice vectors

$$\bar{a}_1 = a\left(\tfrac{1}{2}, \tfrac{1}{2}, 0\right]$$
$$\bar{a}_2 = a\left[0, \tfrac{1}{2}, \tfrac{1}{2}\right]$$
$$\bar{a}_3 = a\left[\tfrac{1}{2}, 0, \tfrac{1}{2}\right]$$

Wigner-seitz



Sphere Packing

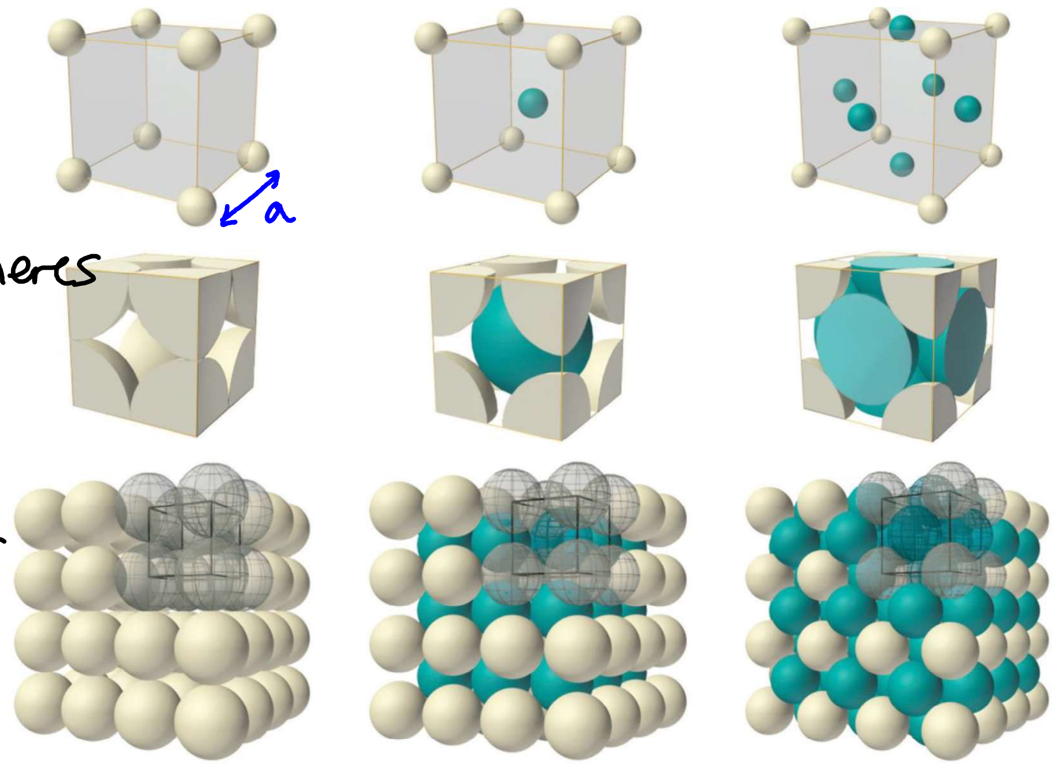


Assume N hard spheres of volume $\frac{4}{3}\pi R^3$

Packing Fraction =

$$= \frac{\text{total volume spheres}}{\text{volume unit cell}}$$

$$= \frac{N \, \frac{4}{3}\pi R^3}{\text{vol. unit cell}}$$

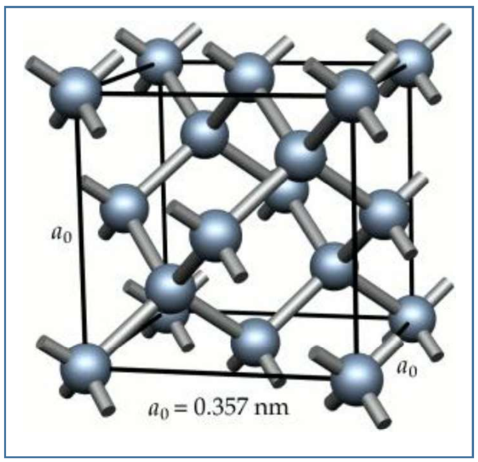


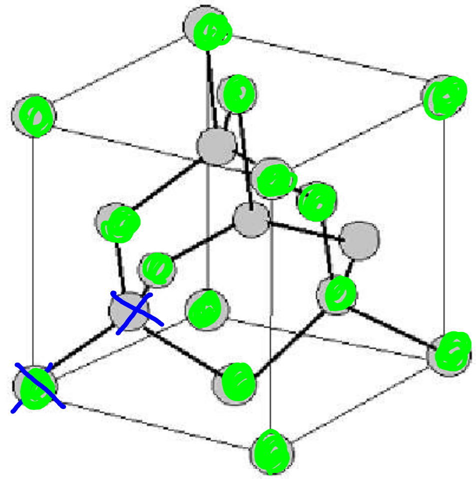
(a) Simple cubic (b) Body-centered cubic (c) Face-centered cubic

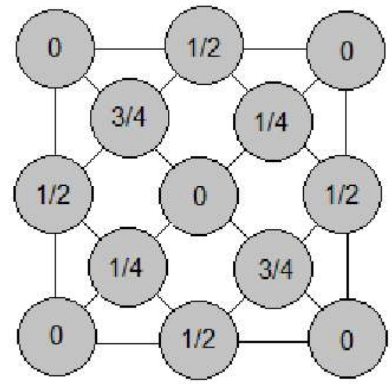
simple cubic: $PF = \frac{\frac{4}{3}\pi R^3}{a^3} = \frac{\frac{4}{3}\pi \left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6} \simeq 0.52$

Diamond structure

(also Si and Ge)



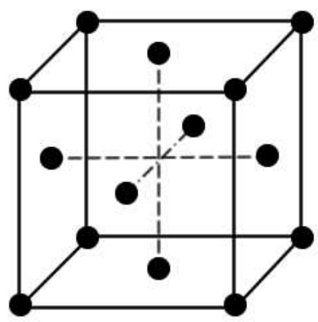




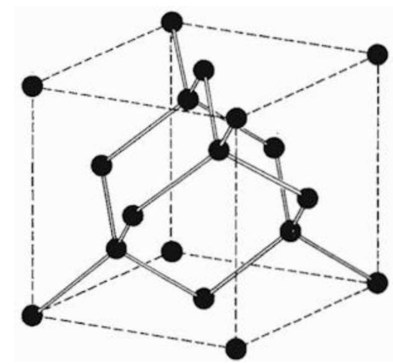
FCC

Basis: 2 identical atoms (C)
@ (0,0,0), (1/4,1/4,1/4)

Use "Plane view" approach to compare the FCC and the Diamond structure



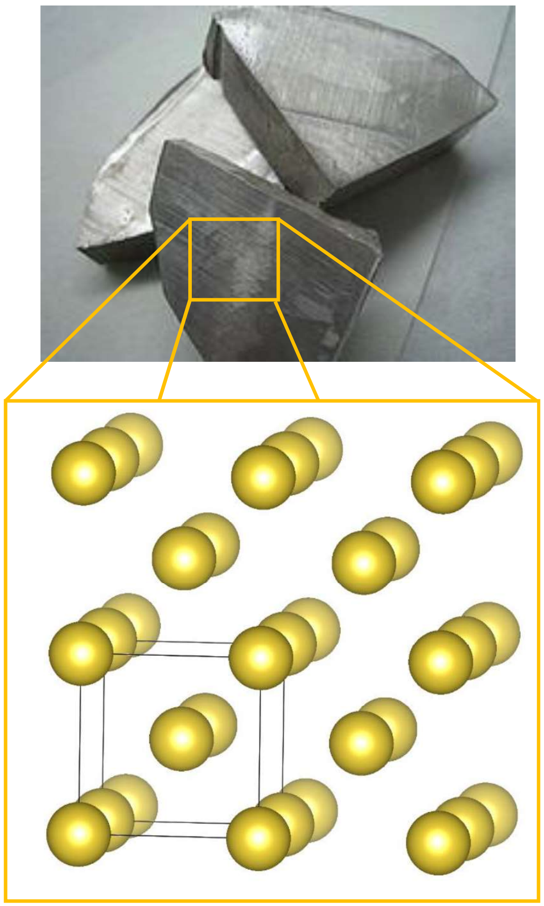
FCC

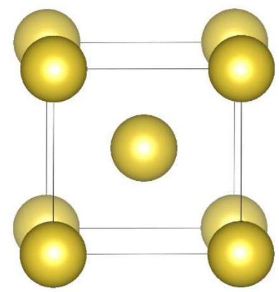


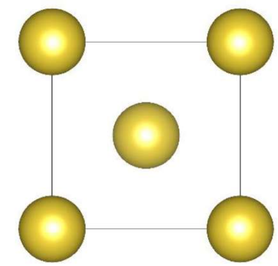
Diamond

Some real crystals

Sodium (Na)

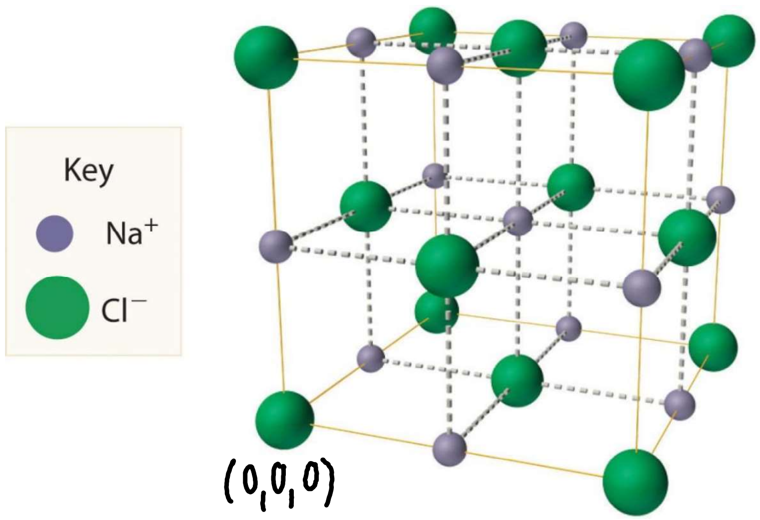


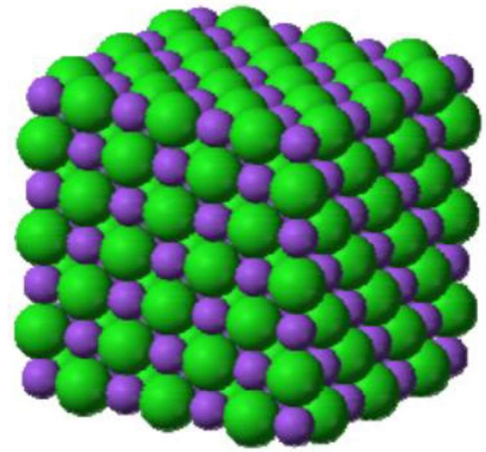




BCC

NaCl structure



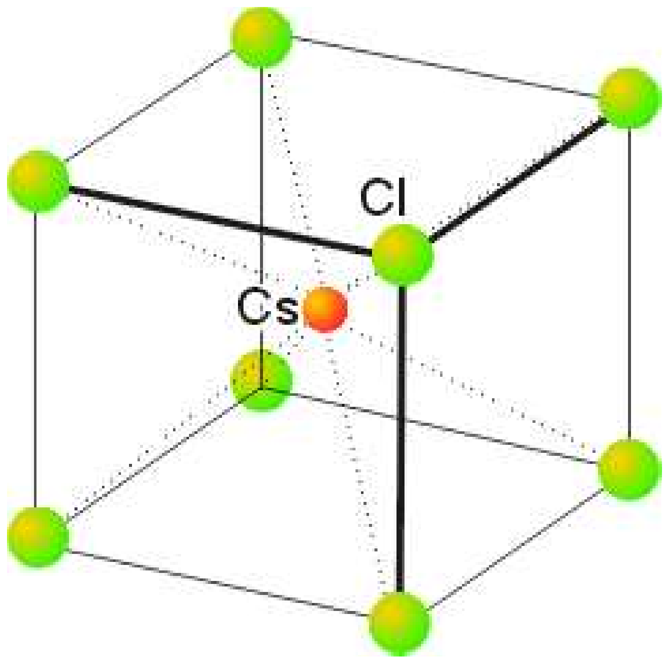


FCC

Basis Na $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$

Cl $(0,0,0)$

CsCl Structure



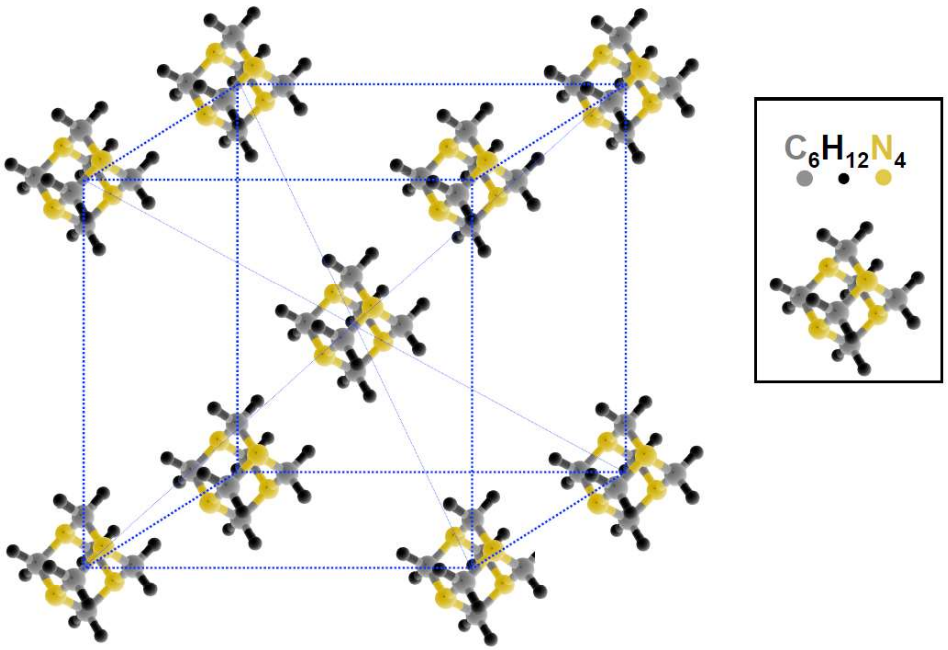
simple cubic

Basis 2 atoms

Cl (0, 0, 0)

Cs (½, ½, ½)

it is not a bcc!



- simple cubic?
- bcc?
- fcc?

Zinc blende structure