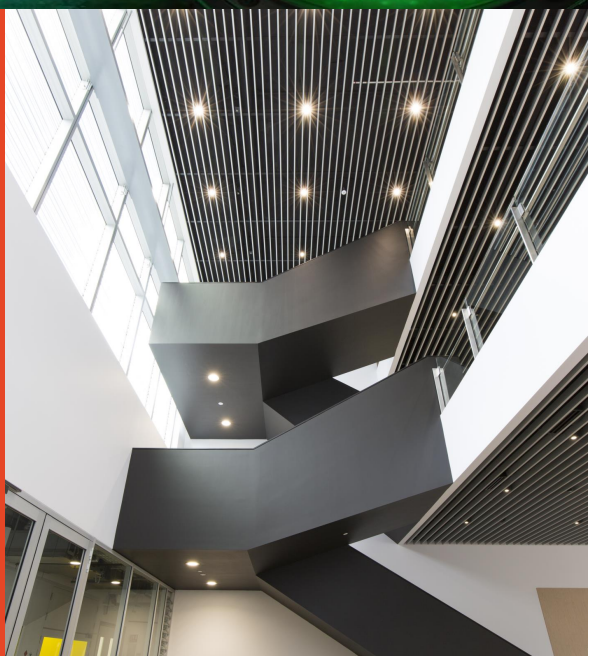
CMP Lecture 5

School of Physics
The University of Sydney

THE UNIVERSITY OF SYDNEY



Crystal structure
Lattices and unit cells

- Bravais lattice, unit cell
- Primitive cell, conventional cell, basis
- Wigner-Seitz (primitive) cell
- Common crystal structures

The crystal lattice: “lattice” or “Bravais lattice”

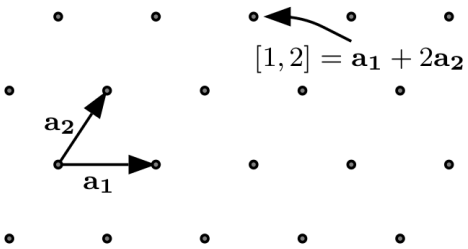
A **lattice** is an infinite set of points, defined by integer sums of a set of linearly independent **primitive lattice vectors**

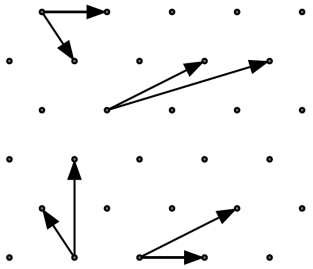
A **lattice** is an infinite set of vectors where addition of any two vectors in the set give a third vector in the set

A **lattice** is a set of points where the environment of any given point is equivalent to the environment of any other given point.

In two dimensions

$\mathbf{R}_{mn} = m\mathbf{a}_1 + n\mathbf{a}_2$ (m,n integers)





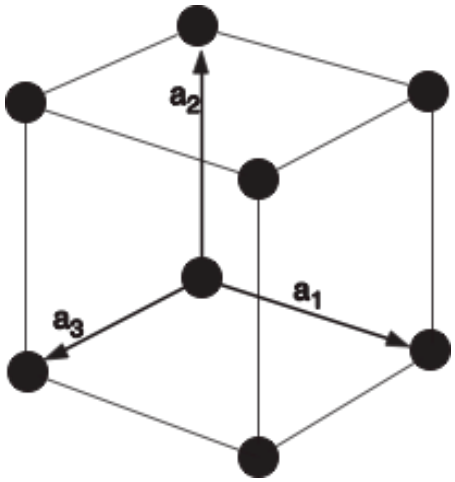
Choice of primitive lattice vectors for a lattice is not unique.

The lattice looks exactly the same from every point

The crystal lattice: Bravais lattice (3D)

$\mathbf{R} = m\mathbf{a}_1 + n\mathbf{a}_2 + o\mathbf{a}_3$

called “simple cubic”



This reflects the translational symmetry of the lattice

Unit cell, primitive cell

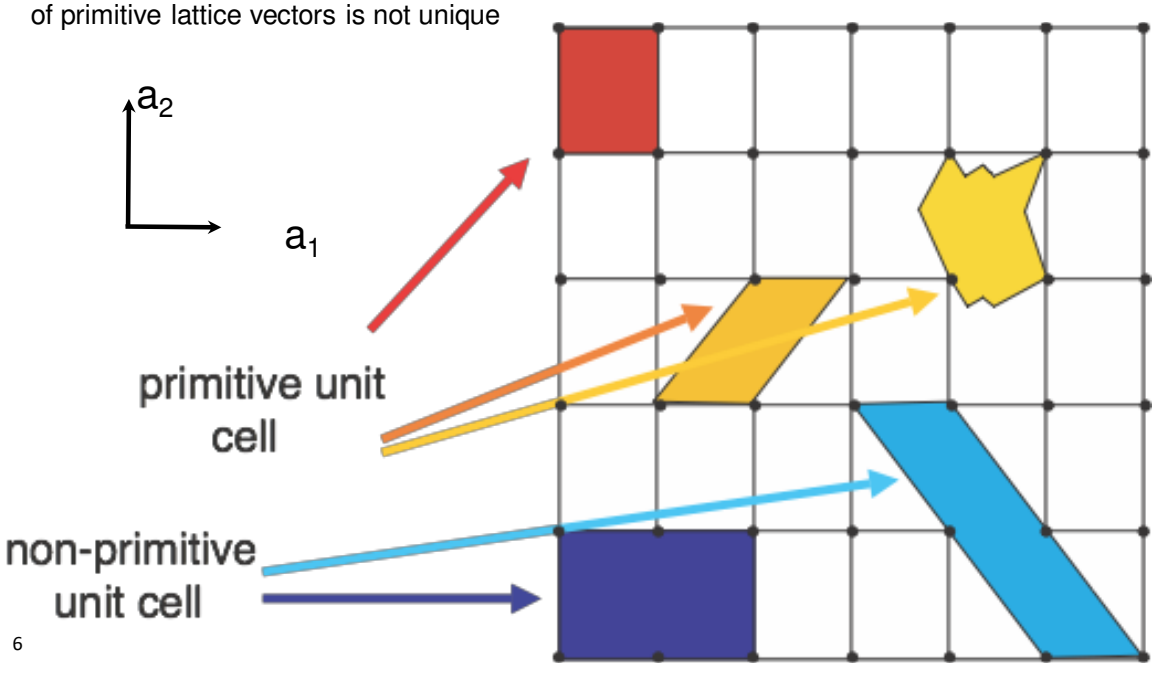
A **unit cell** is a region of space such that when many identical units are stacked together it tiles (completely fills) all of space and reconstructs the full structure.

A **unit cell** is a repeated motif which is the elementary building block of the periodic structure.

A **primitive unit cell** for a periodic crystal is a unit cell containing only a single lattice point.

The crystal lattice: primitive unit cell

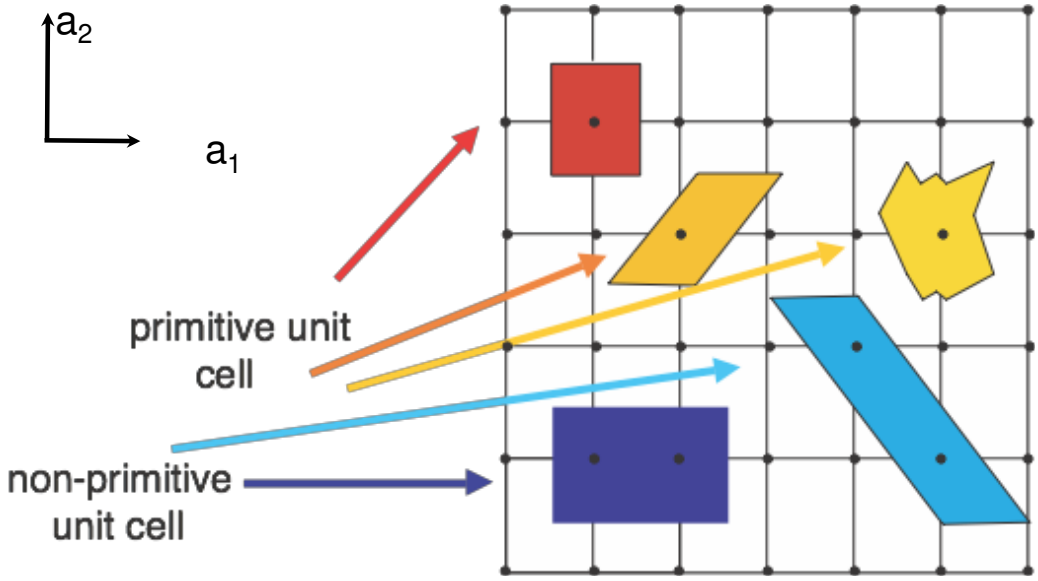
In two- and three-dimensions the choice of primitive lattice vectors is not unique



The crystal lattice: primitive unit cell

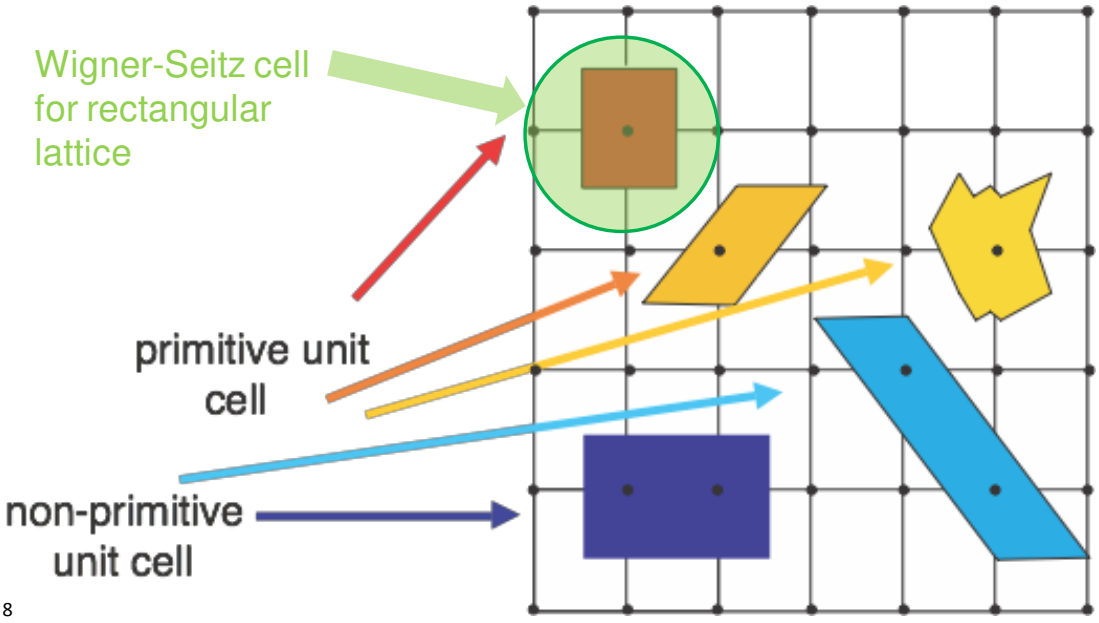
Primitive unit cell: any volume of space which containing one lattice point, when translated through all the vectors of the Bravais lattice, fills space without overlap and without leaving voids.

We can put these unit cells wherever we want - the primitive unit cell contains only one lattice point - the non-primitive unit cells contain more than one.



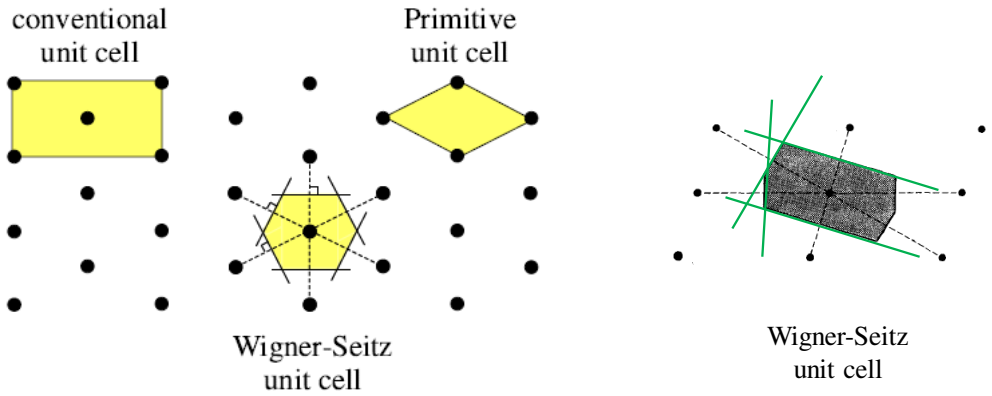
The crystal lattice: Wigner-Seitz cell

Wigner-Seitz cell: special choice of primitive unit cell: region of points closer to a given lattice point than to any other.

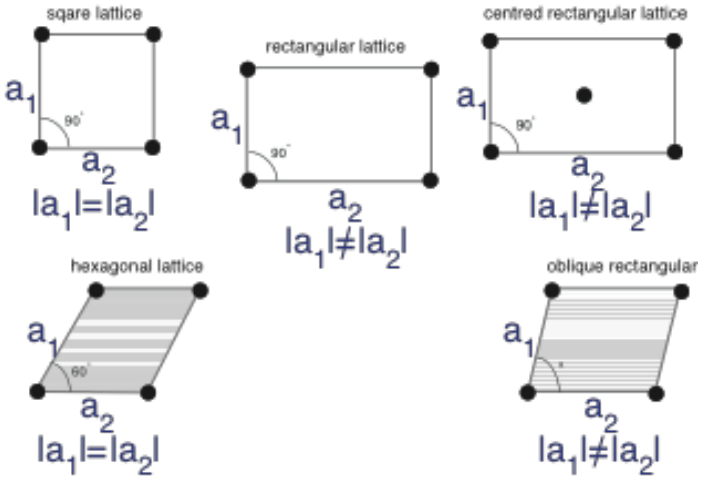


Unit cells: conventional, primitive, Wigner-Seitz

Sometimes useful to define a unit cell that is not primitive so that it is simpler to work with usually with orthogonal axes – called a **conventional unit cell**.



Bravais lattice (2D)

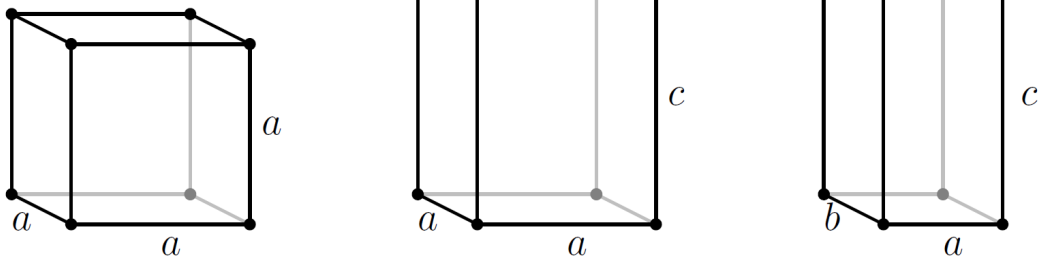


- The number of possible Bravais lattices (of fundamentally different symmetry) is limited to 5 (2D) and 14 (3D).

Ashcroft & Mermin, Ch. 7

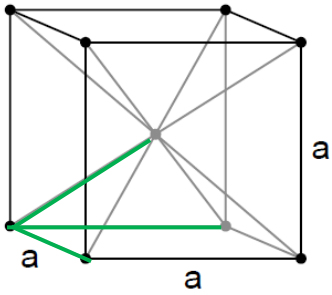
Structure of solids

Orthogonal unit cells



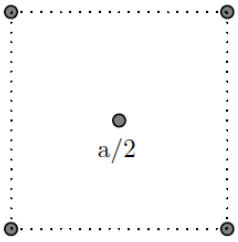
Structure of solids

Body-centered cubic (bcc)



perspective view

There are 8 lattice points on the corners of the cell (1/8 inside) and 1 point in the centre. Thus, the cell contains 2 lattice Points (2=8x1/8 +1)



plan view – 2D projection from the top where heights are labelled to show the third dimension.

$\hat{x},\hat{y},\hat{z}$

Primitive lattice vectors

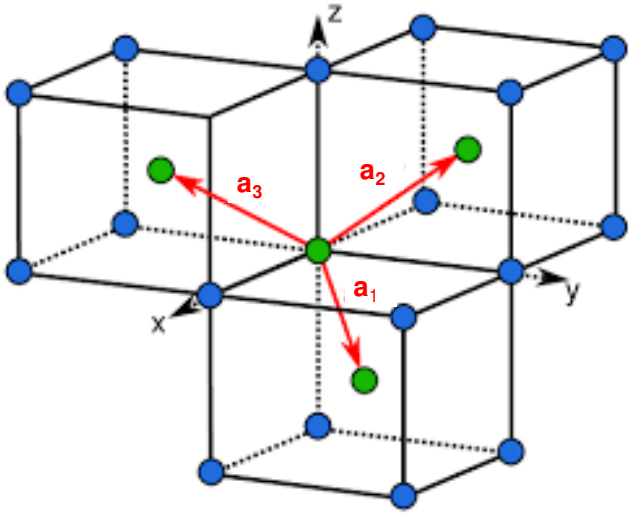
$$\mathbf{a_1} = [a, 0, 0]$$
$$\mathbf{a_2} = [0, a, 0]$$
$$\mathbf{a_3} = [\frac{a}{2}, \frac{a}{2}, \frac{a}{2}]$$

(n_1,n_2,n_3 integers)

$$\mathbf{R} = n_1\mathbf{a_1} + n_2\mathbf{a_2} + n_3\mathbf{a_3}$$

defines lattice

Another common set of primitive vectors for bcc

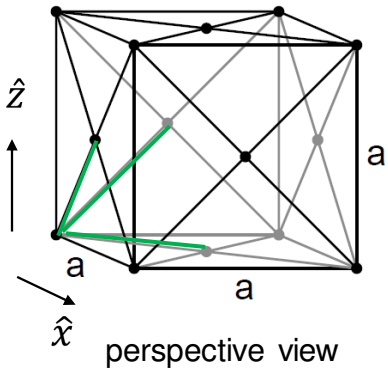


$$\boldsymbol{a}_1 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z})$$

$$\boldsymbol{a}_2 = \frac{a}{2}(-\hat{x} + \hat{y} + \hat{z})$$

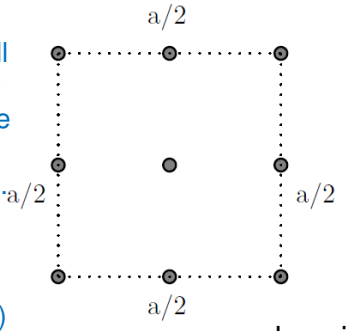
$$\boldsymbol{a}_3 = \frac{a}{2}(\hat{x} - \hat{y} + \hat{z})$$

Face-centered cubic (fcc)



perspective view

There are 8 lattice points on the corners of the cell (1/8 inside) and 1 point in the centre of each of the 6 faces (1/2 inside). Thus, the cell contains 4 lattice points (4=8x1/8 + 6x1/2)



plan view

Primitive lattice vectors

$$\mathbf{a_1} = [\frac{a}{2}, \frac{a}{2}, 0] = \frac{a}{2}(\hat{x} + \hat{y})$$

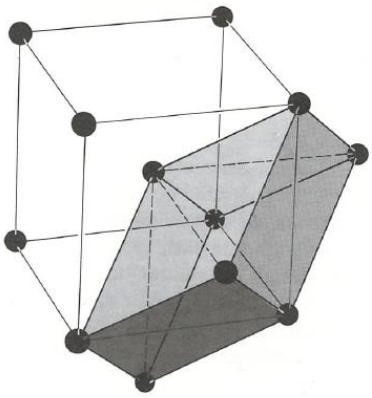
$$\mathbf{a_2} = [\frac{a}{2}, 0, \frac{a}{2}] = \frac{a}{2}(\hat{x} + \hat{z})$$

$$\mathbf{a_3} = [0, \frac{a}{2}, \frac{a}{2}] = \frac{a}{2}(\hat{y} + \hat{z})$$

$$\mathbf{R} = n_1\mathbf{a_1} + n_2\mathbf{a_2} + n_3\mathbf{a_3}$$ defines lattice

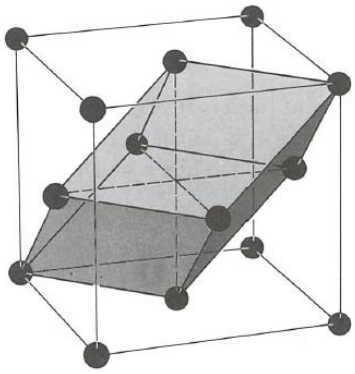
Primitive and conventional cells

BCC



Primitive and conventional cell of the body centred cubic Bravais lattice. The volume of conventional cell is **two times larger** than that of the primitive cell.

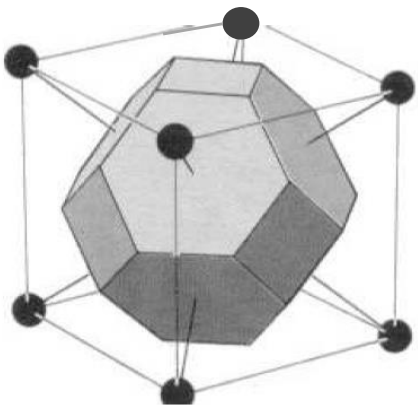
FCC



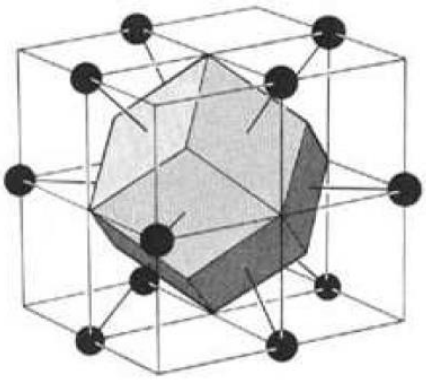
Primitive and conventional cell of the face centred cubic Bravais Lattice. The volume of conventional cell is **four times larger** than that of the primitive cell.

Wigner-Seitz cell: bcc fcc

BCC



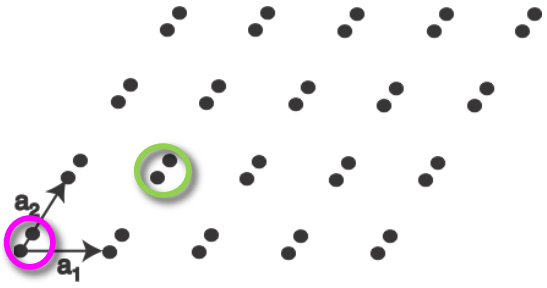
FCC



It is constructed around each lattice point and encloses all space that is closer to that lattice point than to any other point in the lattice.

The crystal lattice: basis

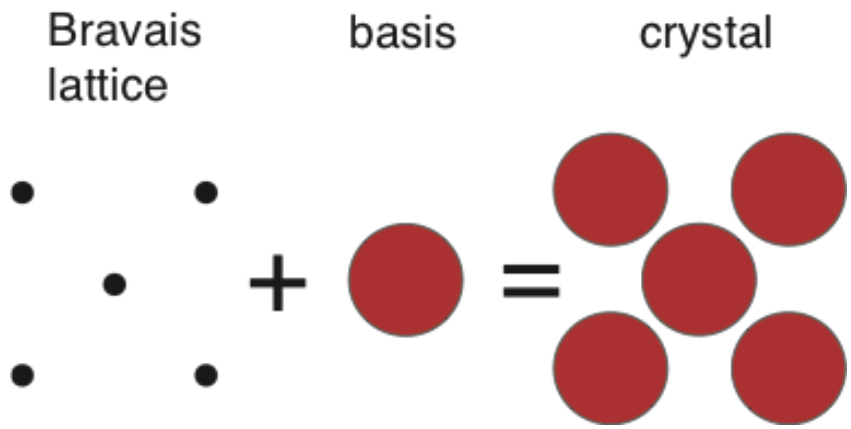
- We could think: all that remains to do is to put atoms on the lattice points of the Bravais lattice.
- But: not all crystals can be described by just a Bravais lattice.
- BUT: all crystals can be described by the combination of a Bravais lattice and a basis.
- The **basis** is what one "puts on the lattice points".



The description of objects in the unit cell with respect to the reference lattice point in the unit cell is known as a **basis**.

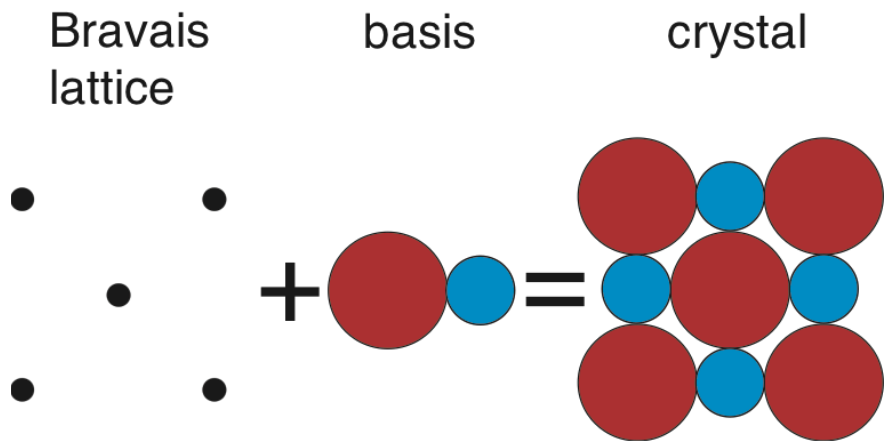
The crystal lattice: one atomic basis

- The basis can also just consist of one atom.



The crystal lattice: basis

- Or it can be several atoms.

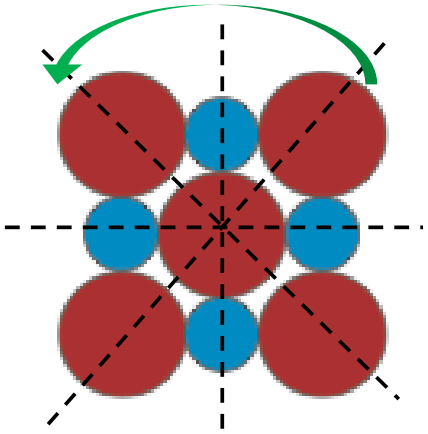


The crystal lattice: basis

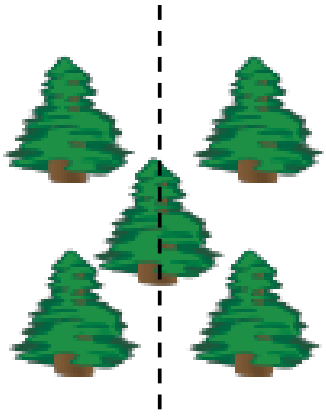
- Or it can be molecules, proteins and pretty much anything else.

The crystal lattice: one more word about symmetry

- The other symmetry to consider is point symmetry. The Bravais lattice for these two crystals is identical; basis different:



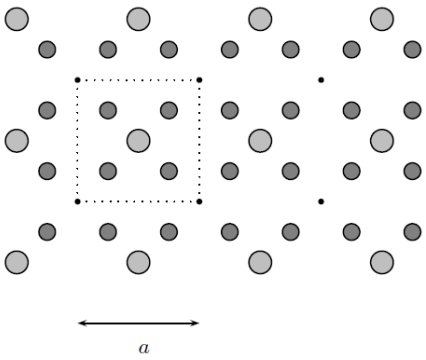
four mirror lines
4-fold rotational axis
inversion

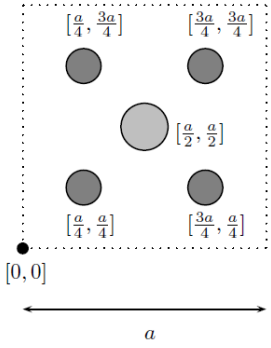


one mirror line

So the basis can change the point symmetry of a given Bravais lattice

Example of a lattice with a basis

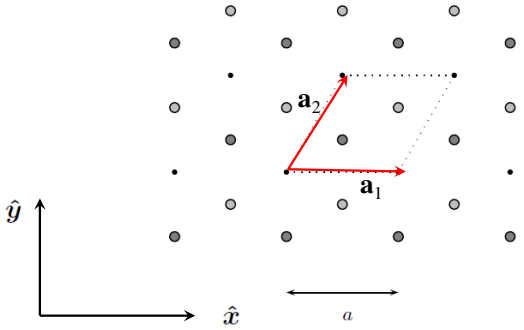


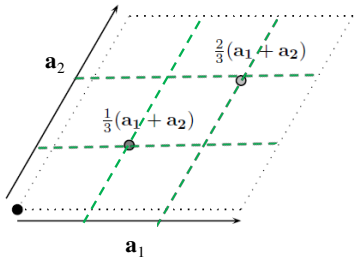


The basis:

Large Light Gray Atom	Position=	$[a/2, a/2]$
Small Dark Gray Atoms	Position=	$[a/4, a/4]$ $[a/4, 3a/4]$ $[3a/4, a/4]$ $[3a/4, 3a/4]$

Another example: triangular lattice with basis





Primitive lattice vectors:

$$\mathbf{a}_1 = a\,\hat{x}$$
$$\mathbf{a}_2 = (a/2)\,\hat{x} + (a\sqrt{3}/2)\,\hat{y}$$

Coordinates of grey circles (atoms) with respect to reference point (black point, which forms a triangular lattice):

$$\frac{1}{3}(\mathbf{a}_1+\mathbf{a}_2) \qquad \frac{2}{3}(\mathbf{a}_1+\mathbf{a}_2)$$

- What structure do the solids have? Can we predict it?
- Could just put the spheres together in order to fill all space.
- A simple cubic structure? fcc? bcc?

Consider atomic packing factor

- Atomic Packing Factor (APF) is defined as the volume of atoms within the unit cell divided by the volume of the unit cell.

Assumes the atom is spherical

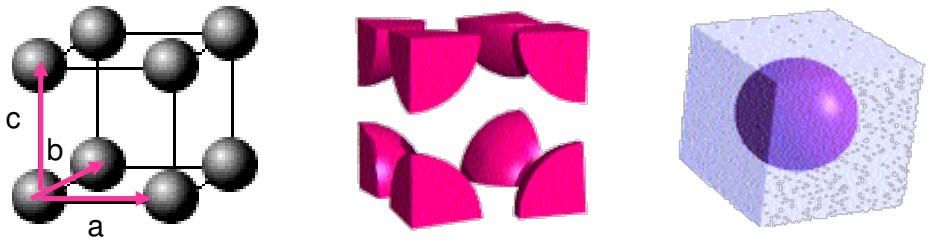
$$\text{APF} = \frac{\text{Volume of Atoms in Unit Cell}}{\text{Volume of Unit Cell}}$$

Simple cubic (SC)

- Simple cubic has one lattice point.
- In the unit cell on the left/centre, the atoms at the corners are cut because only a portion (in this case 1/8) belongs to that cell. The rest belongs to neighboring cells.

So the number of atoms in the unit cell is 8 x 1/8 = 1

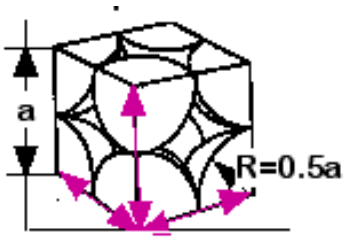
Crystal structure of simple cubic



"Coordination number" of simple cubic is 6.

Atomic packing factor of SC

R = radius of atomic spheres – taken to be the maximum value such that the atoms (spheres) do not overlap.



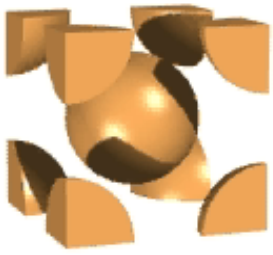
contains 8 x 1/8 = 1atom/unit cell

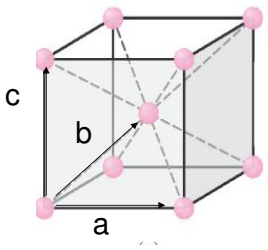
APF = 0.52 for simple cubic

$$APF = \frac{\text{atom}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3}$$

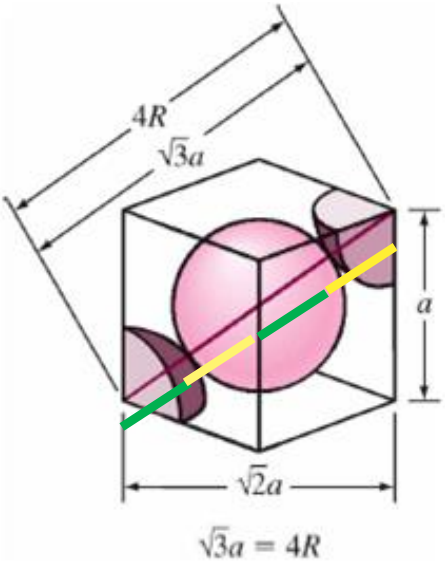
Body centered cubic (BCC)

- BCC has two lattice points (in the conventional cell) – can see one at the centre and 8 x 1/8 at the corners.
- BCC has eight nearest neighbors, so coordination number is 8.
- Each atom is in contact with its neighbors only along the body-diagonal directions.
- Many metals (Fe, Li, Na.. etc), including the alkalis (Li, Na, K, Rb) and several transition metal elements adopt the BCC structure.





Atomic packing factor of BCC



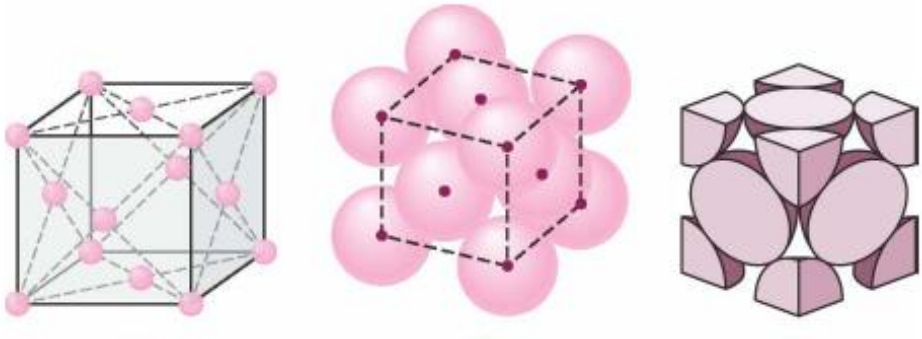
$$APF_{BCC} = \frac{V_{atoms}}{V_{unit\,cell}} = 0.68$$

$$APF = \frac{\text{atom}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{2 \cdot \frac{4\pi}{3}(0.433a)^3}{a^3}$$

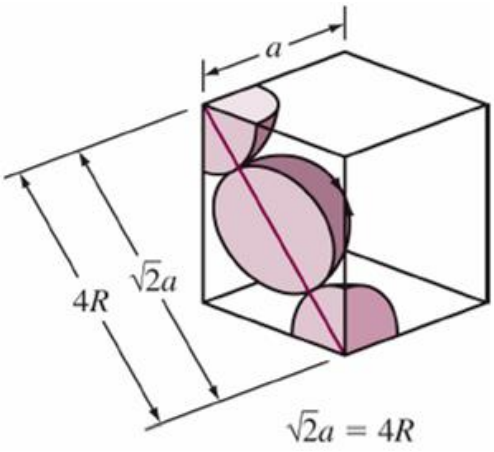
$$R = \sqrt{3}a/4 = 0.433\,a$$

Face centered cubic (FCC)

- There are atoms at the corners of the unit cell and at the center of each face.
- Face centered cubic has 4 atoms in its conventional cell (8 corners with 1/8 atom = 1 atom, 6 faces with ½ atom = 3 atoms).
- Many of common metals (Cu, Ni, Pb.. etc) crystallize in FCC structure.



Atomic packing factor of FCC

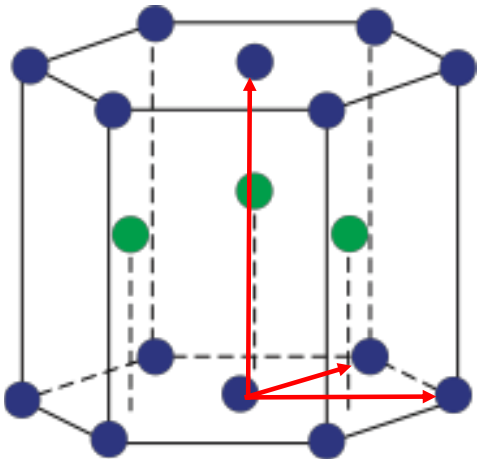


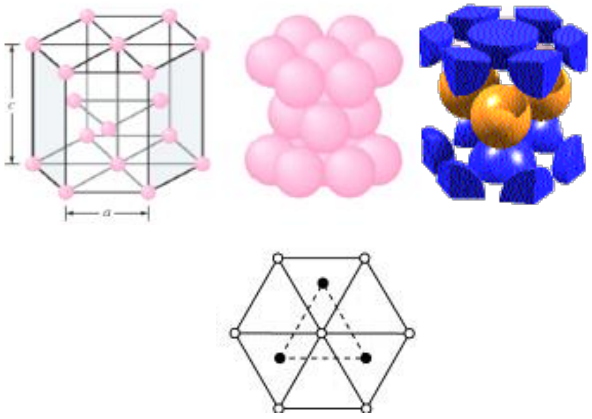
$$APF_{FCC} = \frac{V_{atoms}}{V_{unit\,cell}} = 0.74$$

$$APF = \frac{\text{atom}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \cdot \frac{\text{volume}}{\text{unit cell}} = \frac{4 \cdot \frac{4}{3}\pi (0.353a)^3}{a^3}$$

$$R = \sqrt{2}a/4 = 0.353\,a$$

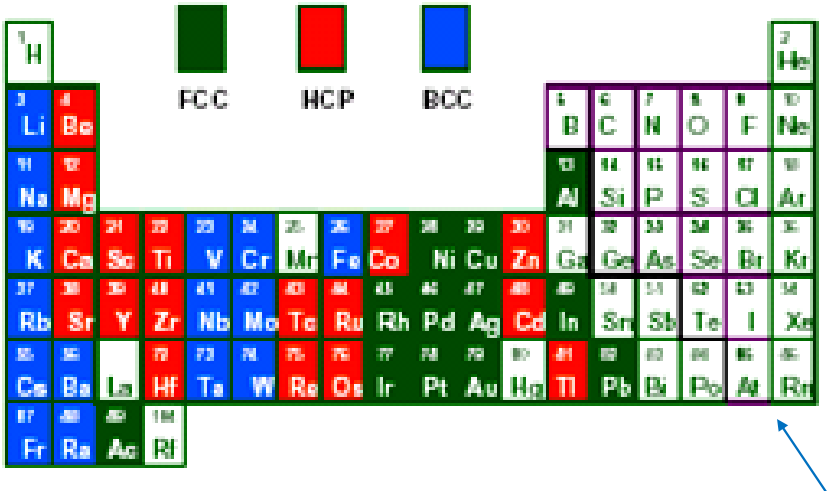
Hexagonal close-packed: hcp





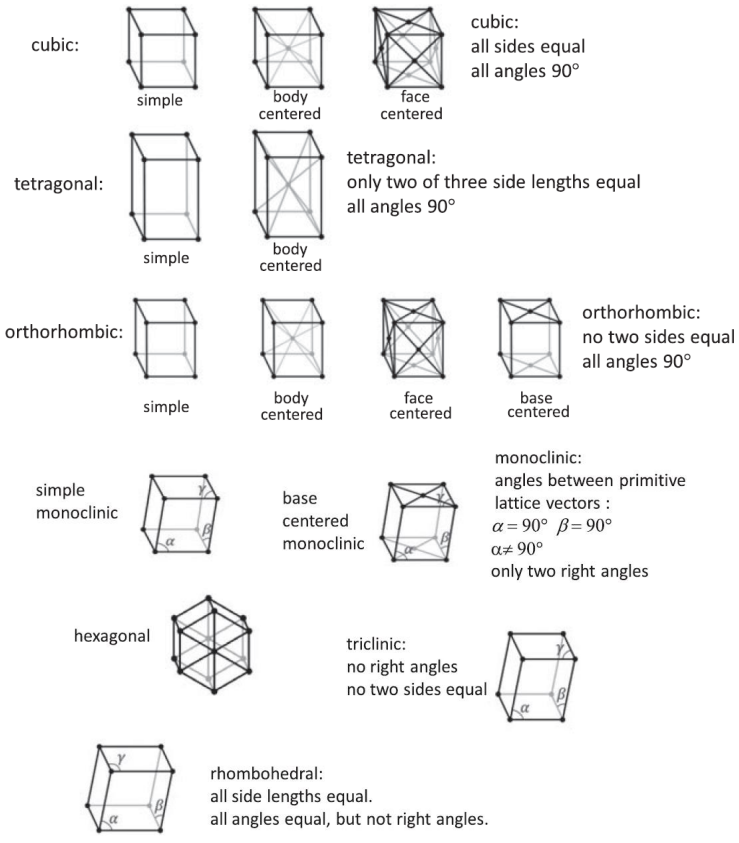
- The hcp lattice is NOT a Bravais lattice. It can be constructed from a hexagonal Bravais lattice with a basis containing two atoms.
- The packing efficiency is exactly the same as for the fcc structure (74% of space occupied).

Face-centred-cubic FCC
Hexagonal-close-packed HCP
Body-centred-cubic BCC



All the 14
three-dimensional
Bravais lattice types
(conventional unit cells)

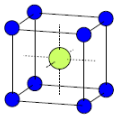
There are only 14 lattice types in 3D (proof beyond the scope of lectures). The key result is that any crystal, no matter how complicated, has a lattice which is one of these 14 types.



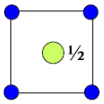
Some examples of real crystals with simple structures

cesium chloride (CsCl)

lattice: cubic P
basis :
Cs 000
Cl ½½½

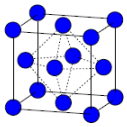


Plan view

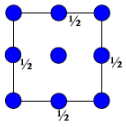


copper (Cu)

lattice: cubic F
basis :
Cu 000

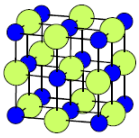


Plan view

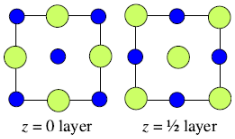


sodium chloride (NaCl)

lattice: cubic F
basis :
Na 000
Cl ½½½

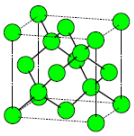


Plan view

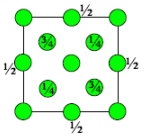


diamond (C) — also Si, Ge

lattice: cubic F
basis :
C 000
C ¼¼¼



Plan view



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Close-packed structures

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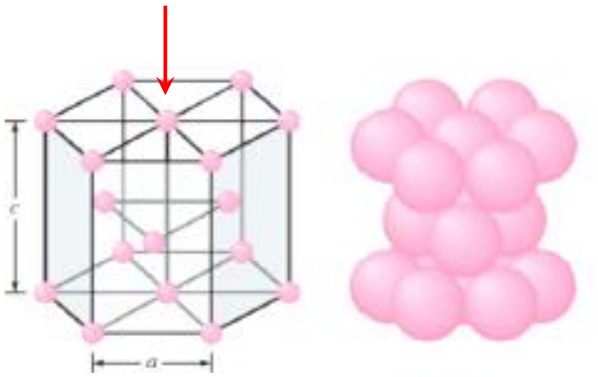
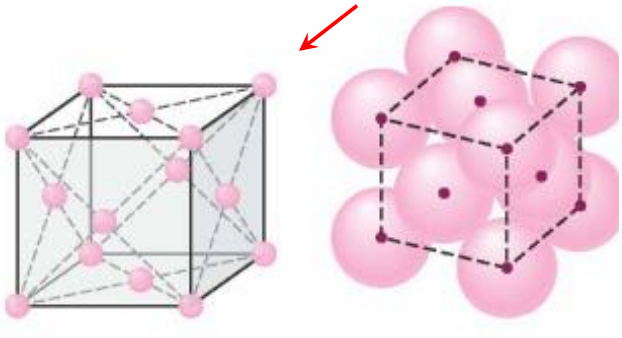
Close-packed structures: HCP and FCC

Hexagonal close-packed

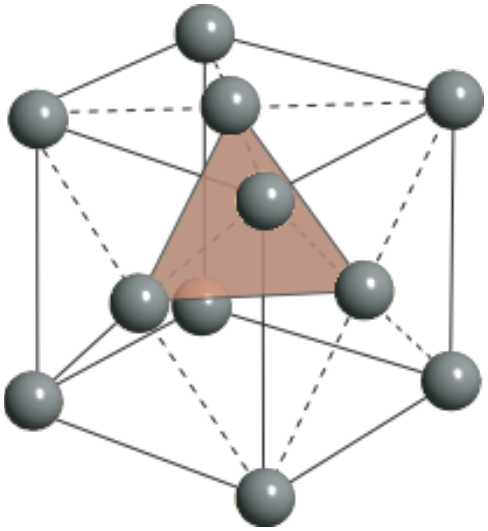


Face-centred-cubic:

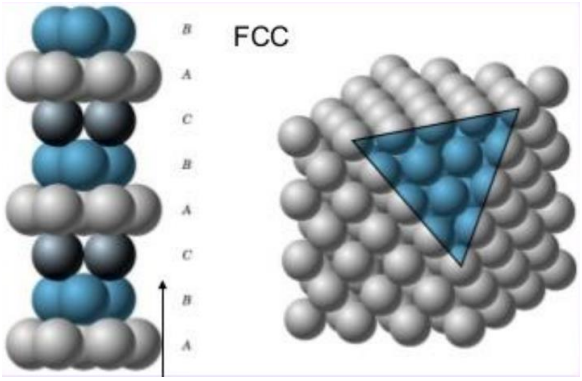
Both structures have hexagonal planes for views along certain crystallographic directions



The FCC structure

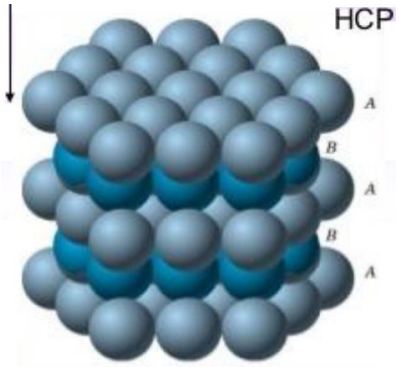


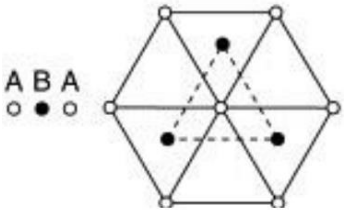
Comparing the FCC and HCP planes stacking



Looking down (111) plane

Looking down (0001) plane





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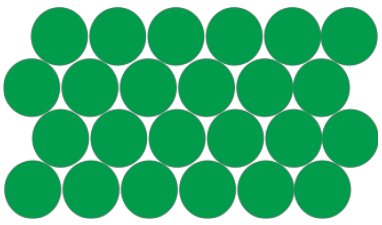
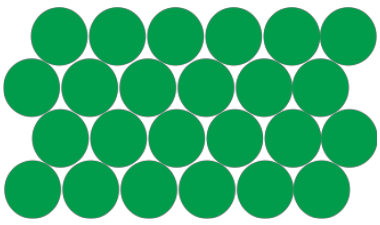
Close-packed structures: fcc and hcp

hcp
ABABAB...



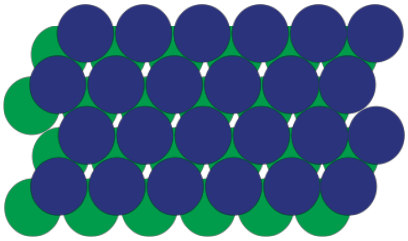
fcc
ABCABCABC...



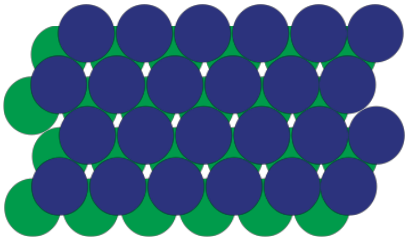
40

Close-packed structures: fcc and hcp

hcp
ABABAB...

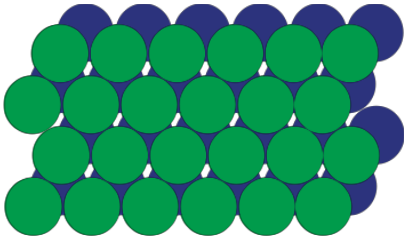


fcc
ABCABCABC...

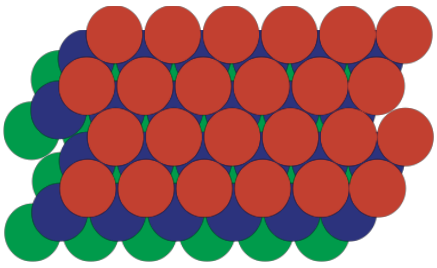


Close-packed structures: fcc and hcp

hcp
ABABAB...

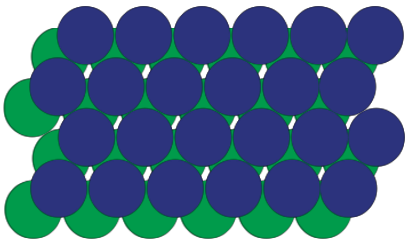


fcc
ABCABCABC...

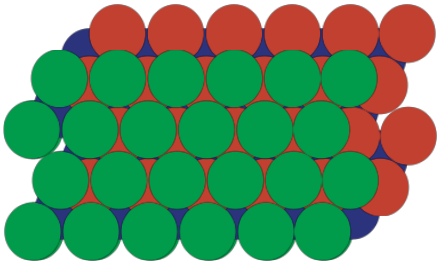


Close-packed structures: fcc and hcp

hcp
ABABAB...

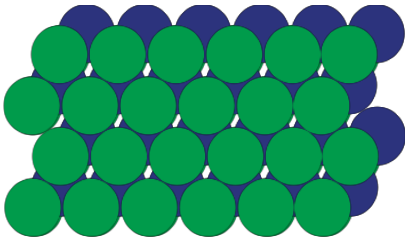


fcc
ABCABCABC...

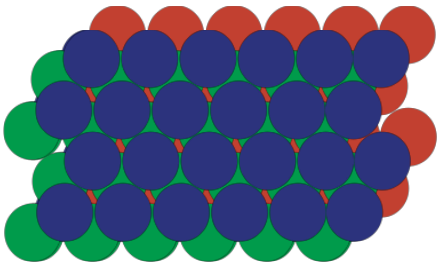


Close-packed structures: fcc and hcp

hcp
ABABAB...



fcc
ABCABCABC...



- The hexagonal close-packed (hcp) and face-centred cubic (fcc) and structure have the same packing fraction

Close-packed structures

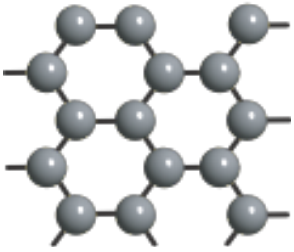
- Close-packed structures are found for inert solids and for metals.
- For metals, the conduction electrons are smeared out and directional bonding is not important. Close-packed structures have a big overlap of the wave functions.
- Most elements crystallize as hcp (36) or fcc (24).

Non-close packed structures

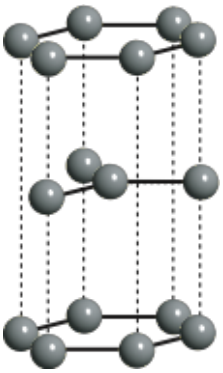
- Covalent materials (bond direction more important than packing)

Verify this

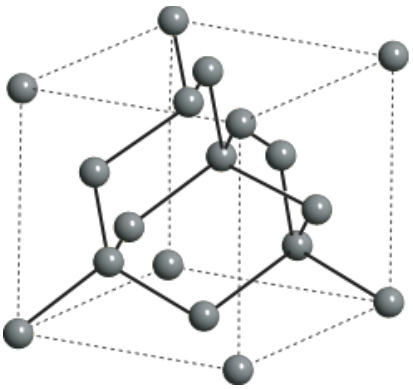
graphene



graphite



diamond (only 34% packing)



Crystal structures online

http://lampx.tugraz.at/~hadley/ss1/crystalstructure/crystalstructure.php

End