

Lecture 9: Close-Packed Structures and Examples of Crystal Structures

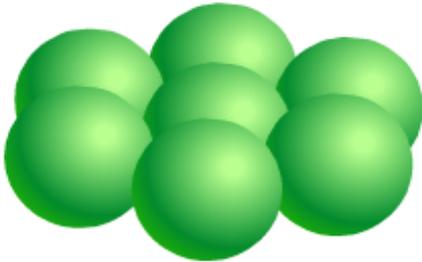
1. Close Packing of Atoms

Let us consider identical atoms (or hard spheres) centered on lattice points. We aim to **stack these atoms in layers such that the empty space between them is minimized.**

The stacking of these layers can be described as follows:

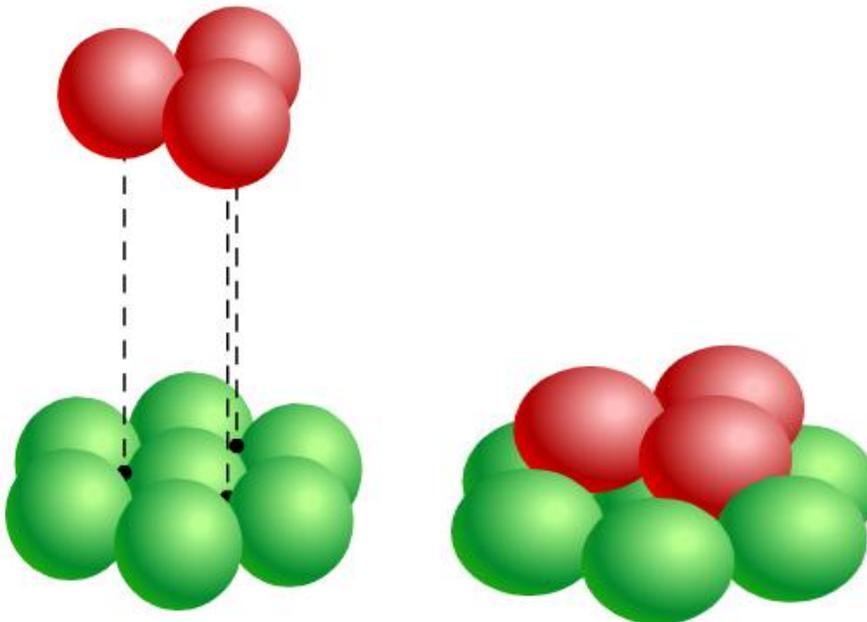
First layer (A):

Atoms in the first layer are arranged so that each atom touches six surrounding atoms.



Second layer (B):

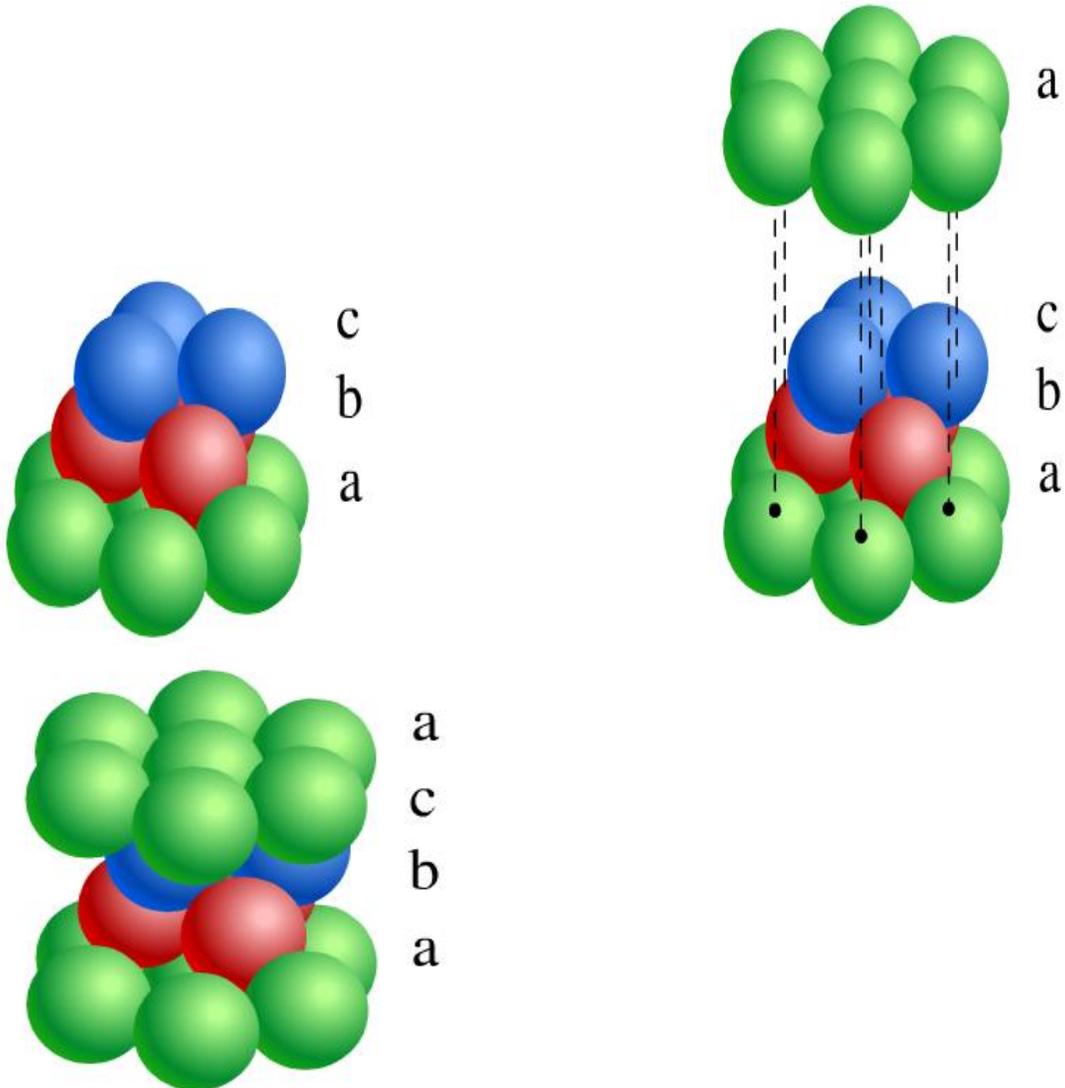
The second layer is placed on top of the first layer such that each atom in layer B touches three atoms in layer A. In other words, atoms in layer B sit above the **triangular voids of layer A.**

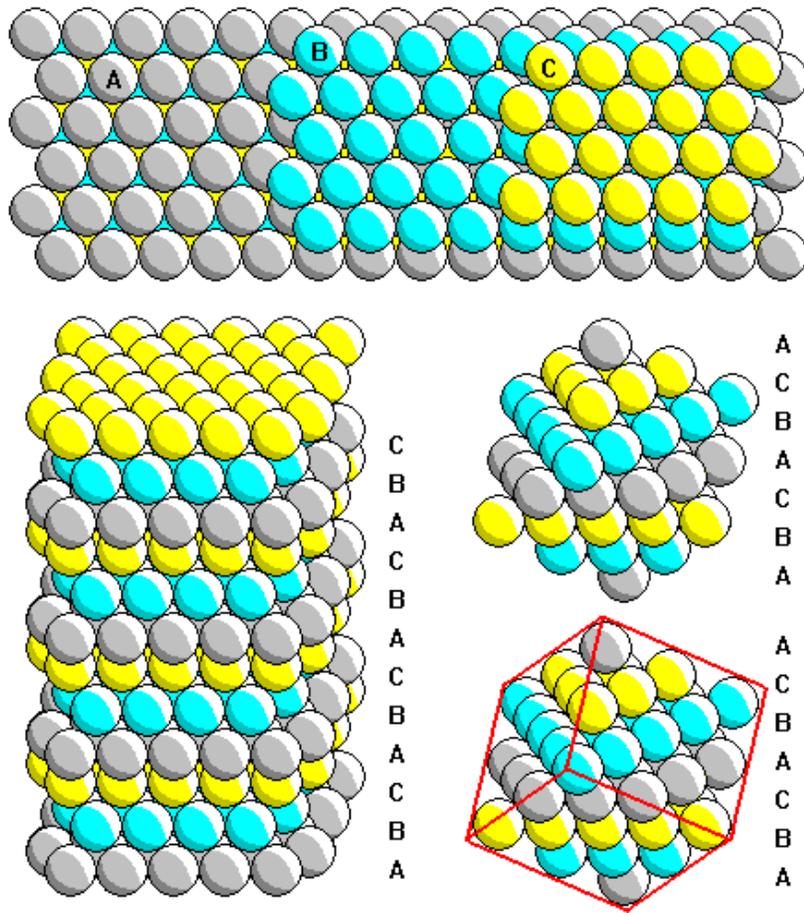


Third layer (C):

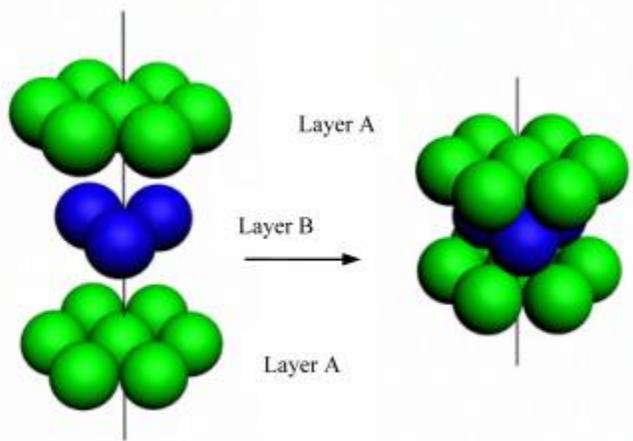
There are two possible stacking arrangements:

1. The atoms in layer C are placed above the voids of both layers A and B. In this case, the fourth layer becomes identical to layer A. This stacking sequence produces the face-centered cubic (FCC) structure, with stacking order ABCABC...



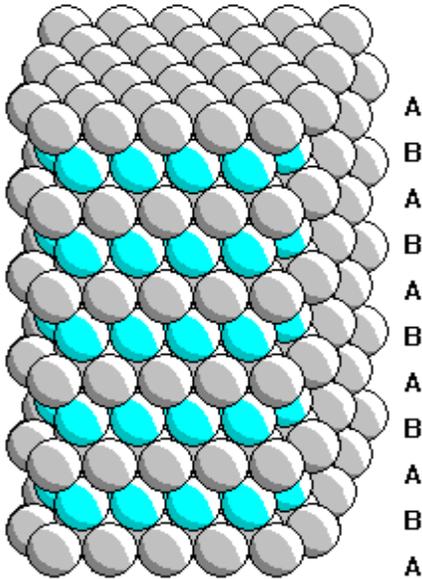


2. The atoms in layer C are placed directly above the atoms of layer A. This results in the stacking sequence ABABAB..., which corresponds to the hexagonal close-packed (HCP) structure.



Materials with the HCP structure include Zinc (Zn), cadmium (Cd), and magnesium (Mg). This structure is characterized by a fixed ratio between the lattice constants c (along the z-axis) and a (along the x-axis).

$$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$$



Exercise:

Show that the ideal ratio c/a for the hexagonal close-packed structure is constant.

$$\left(\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633\right).$$

2. Packing Factor

The packing factor (also called **packing efficiency**) is defined as the ratio between the volume occupied by the atoms in the unit cell and the total volume of the unit cell.

Packing factor F is given by:

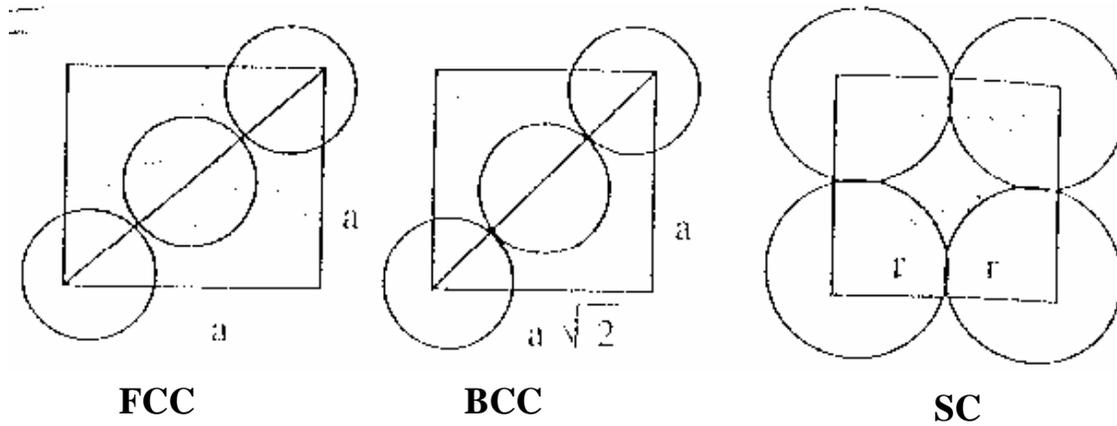
$$F = (n V) / a^3$$

where:

- V is the volume of one atom,
- n is the number of atoms per unit cell,
- a is the lattice constant,
- r is the atomic radius.

The packing factors for common cubic structures are:

- Simple cubic (SC)
- Body-centered cubic (BCC)
- Face-centered cubic (FCC)



$$F_{SC} = \frac{nV}{a^3} = \frac{1 \times 4\pi r^3}{3 \times 8r^3} = \frac{\pi}{6} = 0.52$$

$$F_{BCC} = \frac{2 \times 4\pi r^3}{3 \times \left(\frac{4}{\sqrt{3}}r\right)^3} = \frac{\pi\sqrt{3}}{8} = 0.68$$

$$F_{FCC} = \frac{4 \times 4\pi r^3}{3 \times (2\sqrt{2}r)^3} = \frac{\pi\sqrt{2}}{6} = 0.74$$

For FCC, the detailed solution is given as follows:

Step 1: Number of atoms per FCC unit cell

In an FCC lattice:

- 8 corner atoms contribute $8 \times (1/8) = 1$ atom
- 6 face-centered atoms contribute $6 \times (1/2) = 3$ atoms

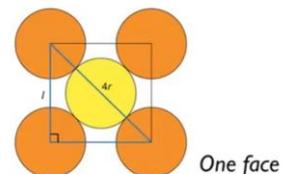
Total number of atoms per unit cell:

$$1 + 3 = 4 \text{ atoms}$$

Step 2: Relationship between lattice parameter and atomic radius

In FCC, atoms touch along the face diagonal.

The face diagonal equals $4r$.



Using geometry:

$$a^2 + a^2 = (4r)^2$$

$$2a^2 = 16r^2$$

$$a^2 = 8r^2$$

$$a = \sqrt{8} r$$

Step 3: Volume of atoms in unit cell

Each atom is approximated as a sphere with volume $(4/3)\pi r^3$.

Since there are 4 atoms per unit cell:

$$\text{Volume of atoms} = 4 \times (4/3)\pi r^3 = (16/3)\pi r^3$$

Step 4: Volume of the unit cell

Volume of the cubic unit cell:

$$V_{\text{cell}} = a^3 = (\sqrt{8} r)^3$$

Step 5: Packing Fraction Calculation

$$\text{Packing Fraction} = [(16/3)\pi r^3] / [(\sqrt{8} r)^3]$$

Simplifying:

$$= (16\pi r^3/3) / (8\sqrt{8} r^3)$$

$$= 2\pi / (3\sqrt{8})$$

$$= \pi / (3\sqrt{2})$$

$$\approx 0.74 \text{ (74\%)}$$

Therefore, the packing fraction of the FCC structure is 0.74 (74%).

Discussion

- **74% space filled**
- Highest packing efficiency for cubic structures.
- Coordination number = 12.
- This is a **close-packed structure**.
- Same packing efficiency as HCP.

◇ Comparative Discussion

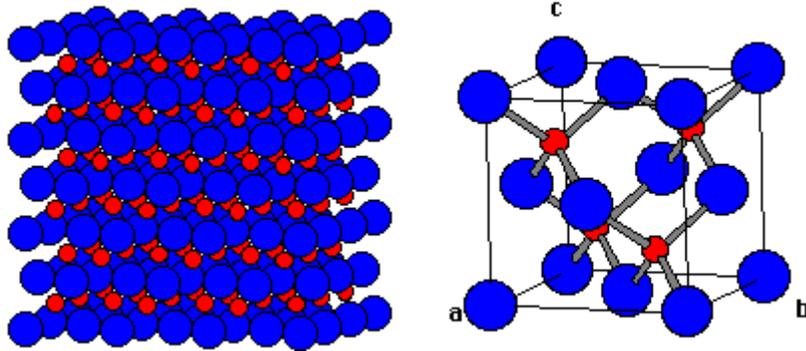
Structure	Atoms/Cell	CN	F	Packing Efficiency
SC	1	6	0.52	Poor
BCC	2	8	0.68	Moderate
FCC	4	12	0.74	Close-packed

As the packing factor increases:

- Density increases (for the same atomic mass)
- Mechanical stability improves
- Coordination number increases

3. Examples of Crystal Structures

3.1 Zinc-Blende Structure (ZnS)



The zinc-blende structure consists of two types of atoms: Zn and S. Materials with this structure include GaAs, GaP, and InAs.

See the visualization of the structure :

https://ssd.phys.strath.ac.uk/resources/crystallography/crystal_models/zincblende_structure/

Bravais lattice: Face-centered cubic (FCC).

Basis: Two atoms per lattice point, as shown in the figure.

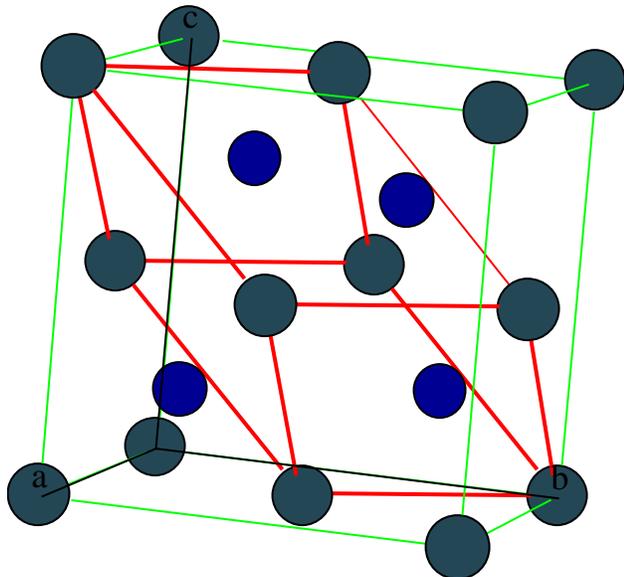
Note that the conventional unit cell contains four atoms.

Coordination number:

Each atom has four nearest neighbors.

The primitive cell:

The primitive cell of the Zinc-Blende (ZnS) structure is a Rhombohedral.

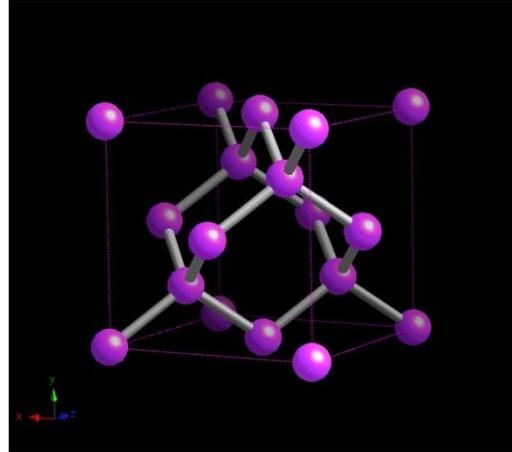


3.2 Diamond Structure

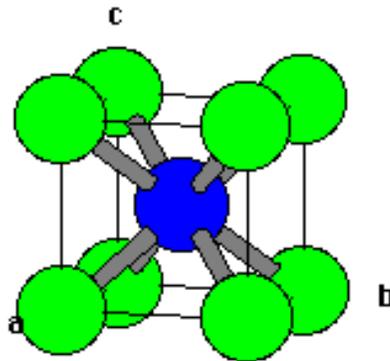
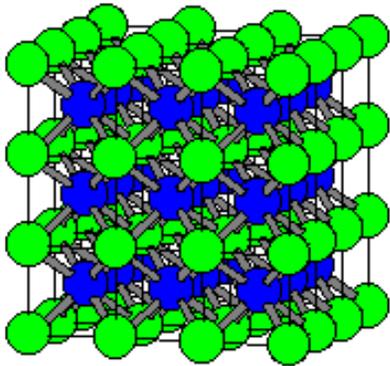
The diamond structure is similar to the zinc-blende structure, but with both Zn and S replaced by carbon atoms.

Unlike ZnS, it is not possible to choose a primitive cell with a one-atom basis for the diamond structure.

Materials with the diamond structure include carbon (C), silicon (Si), and germanium (Ge).



3.3 Cesium Chloride Structure (CsCl)



In the cesium chloride structure, the primitive unit cell is identical to the conventional unit cell and has a simple cubic geometry.

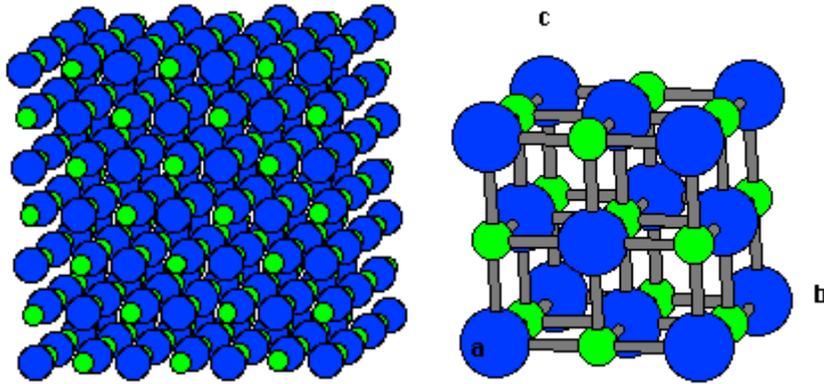
Basis:

Two atoms per unit cell.

Coordination number:

Each atom has eight nearest neighbors.

3.4 Sodium Chloride Structure (NaCl)



The sodium chloride structure has a conventional cubic unit cell.

Sodium (Na) atoms occupy the corners and face centers of the cube, while chlorine (Cl) atoms are located at the centers of the cube edges.

Since each type of atom in the NaCl structure forms a **face-centered cubic lattice**, there are four Na and four Cl atoms per NaCl unit cell.

Na⁺:

$$1 (\text{center}) + 12 (\text{edges}) \times 1/4 = 4 \text{ sodium ions per unit cell}$$

Cl⁻:

$$4 (\text{faces}) \times 1/2 + 8 (\text{corners}) \times 1/8 = 4 \text{ chloride ions per unit cell}$$

Therefore, the unit cell contains 4 Na⁺ and 4 Cl⁻ ions.

See the video about the structure of NaCl:

<http://www.youtube.com/watch?v=csfOBynrF8E>

Primitive cell of the NaCl structure:

<https://www.youtube.com/watch?v=lmQlxbU9CEI>