EE113FZ
Solid State Electronics
Lecture 8: Bonding & Structures

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What is to be Discussed Today?

- Review of bonding;
- Energy diagrams of ionic & covalent bonds;
- Crystal structure:
  - Terms to describe crystal structure;
  - Bravais lattice in 3D;
  - Cubic lattice;
  - Calculating the number of atoms in a unit cell;
  - Packing ratio and close-packed structure;
  - Coordination number;
  - Crystal planes and Miller indices.
- Crystal structure of silicon.

Reminder on Solids

- Remind yourself about the characteristics of solids that were discussed in Lecture 1: Matter;
- Solids can be classified in 3 broad types:
  - Crystals which include metals, non-metallic insulators and dielectrics, and semiconductors;
  - Amorphous which include glasses and polymers;
  - Composites which include rock, cement, wood, etc.
- We are particularly interested in crystals.

Return to Solids

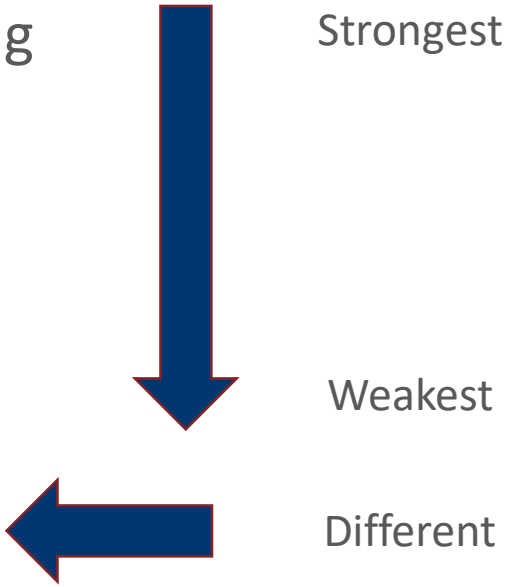
- What makes a solid ‘solid’?
- What holds a solid together?
- The answer is bonding!
- Bonding occurs between electrons of various atoms.
- We will look at examples of bonding types for pure crystals.

How Does Bonding Occur?

- Atoms can attach to each other electrostatically, a positive atom to a negative one (ionic bonds);
- Other more complicated methods that include quantum effects that we don't need to worry about.

Bonding

- There are 3 different types of bonding mechanisms found in materials:
  - Primary – Ionic and covalent bonding
  - Secondary – Intermolecular forces
    - Hydrogen bonding;
    - Dipole-dipole;
    - Dipole-induced dipole;
    - London dispersion forces;
    - van der Waals forces.
  - —Metallic bonding



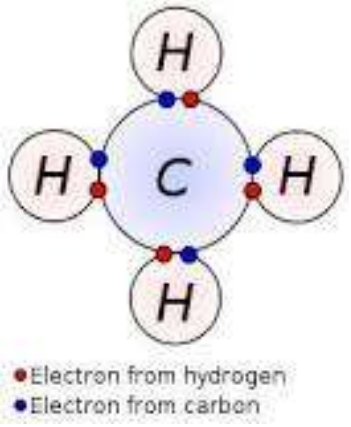
Ionic Bonds

- Occurs between oppositely charged ions;
- Bond is an electrostatic force;
- Forms crystalline solids;
- High melting and boiling points;
- Conduct electricity when in liquid form;
- Typically formed with elements at the opposite sides of the periodic table (contrast in electronegativity);
- One atom loses an electron while the other gains an electron;
- Typical example is table salt (NaCl).

Covalent Bonds

- Electrons are shared!
- Can be either gas, liquid or solid at RT;
- Can have either high melting and boiling points (covalently bonded network) or low melting and boiling points (discrete covalent molecules);
- Poor at conducting electricity in any state (with very few exceptions, e.g., graphite);
- Electrons are shared!
- Typical examples: methane (CH_4).

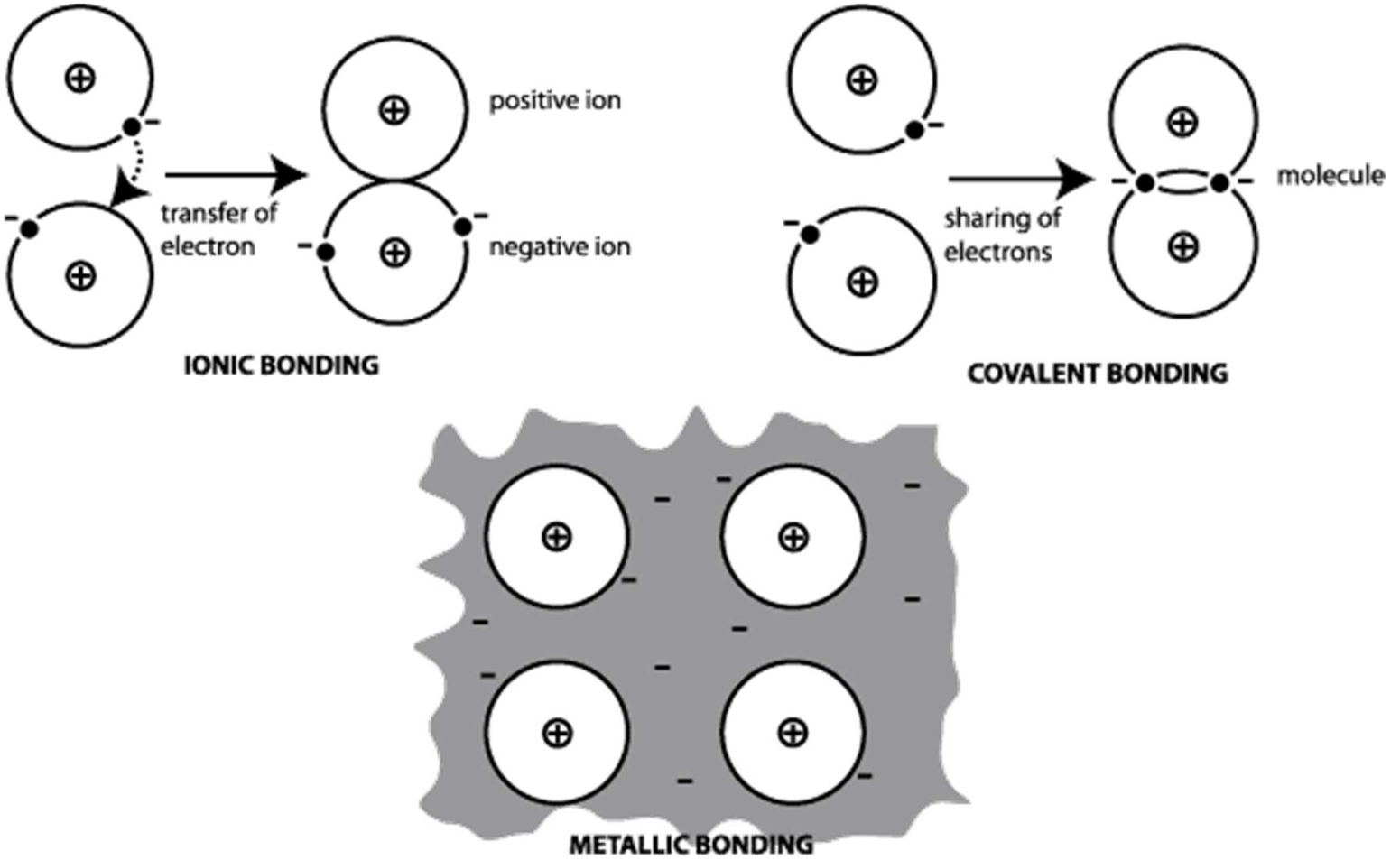
For interested folks, here is a great video:
https://youtu.be/LkAykOv1foc



Metallic Bonds

- Bonding within metals;
- Forces between delocalised electrons (conduction electrons) and positively charged metal ions;
- Strength due to electrostatic attraction of electrons and protons;
- Responsible for the physical properties of metals (thermal and electrical resistivity, strength, ductility, and opacity, etc).
- Better at electrical and heat conduction than ionic materials.
- Typical examples: Cu, Au, Al, etc.

Graphical Representation of Bonding Types

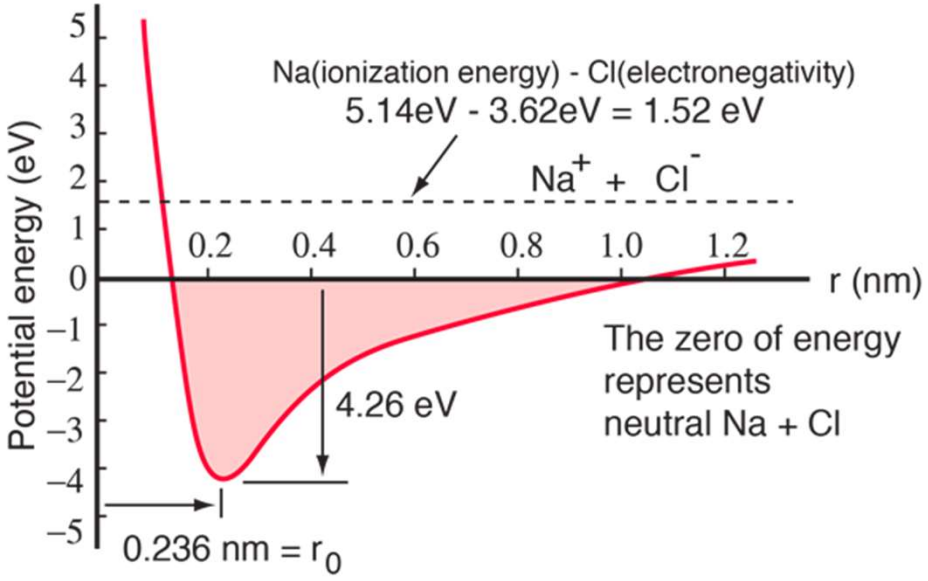


https://depts.washington.edu/matseed/ces_guide/bonding.htm

Why Do We Want to Know About Bonding?

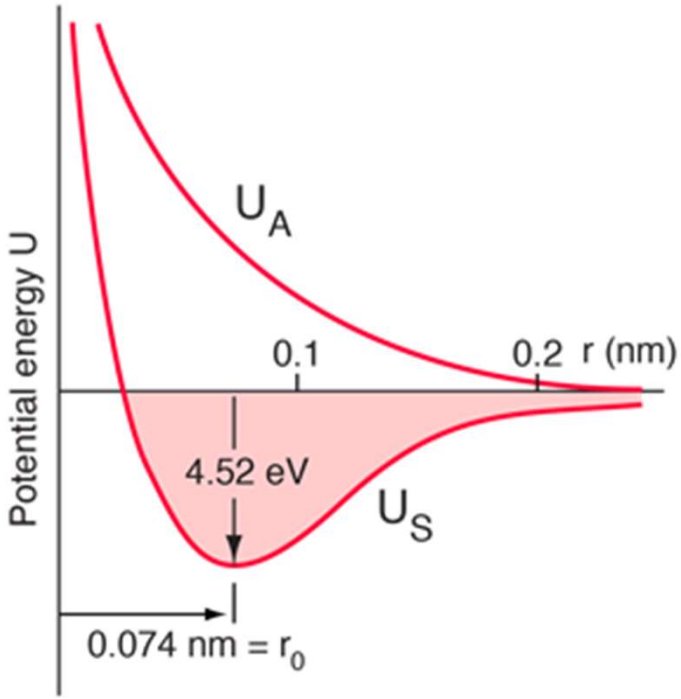
- In a word, ENERGY!
- All bonding processes need energy:
  - Making;
  - Breaking;
  - Relocating.
- This has significant implications for what materials we can design, build and use.

Energy Diagrams of Chemical Bonds



Na-Cl Ionic Bond

It takes a long distance to reach a 0 eV level.



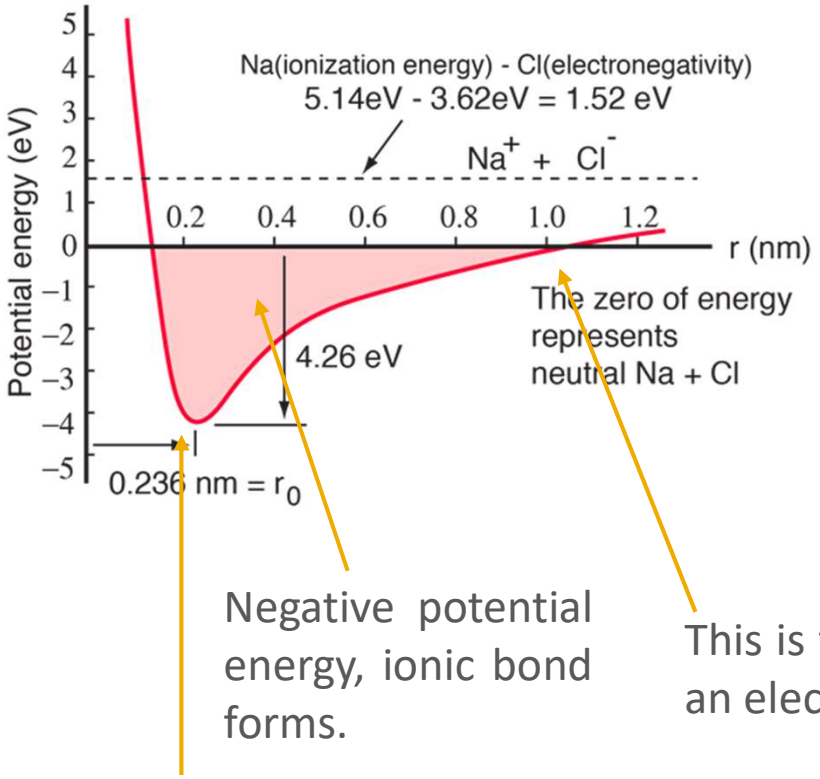
Hydrogen Covalent bond

It takes a short distance to reach a 0 eV level.

Energy Diagrams: Explanation

- Let's look at the details in the energy diagram of NaCl;
- Na (sodium) has 1 electron in its outer shell;
- Cl (chlorine) needs 1 electron to fill its outer shell;
- As we bring the Na atom and the Cl atom closer to each other a point is reached where it becomes easy to transfer an electron from Na to Cl.

Ionic Bond in NaCl



r (nm) is the distance that the ions are apart.

We move from the right (Na^+ and Cl^- ions are far away from each other) to the left (Na^+ and Cl^- atoms are closer together).

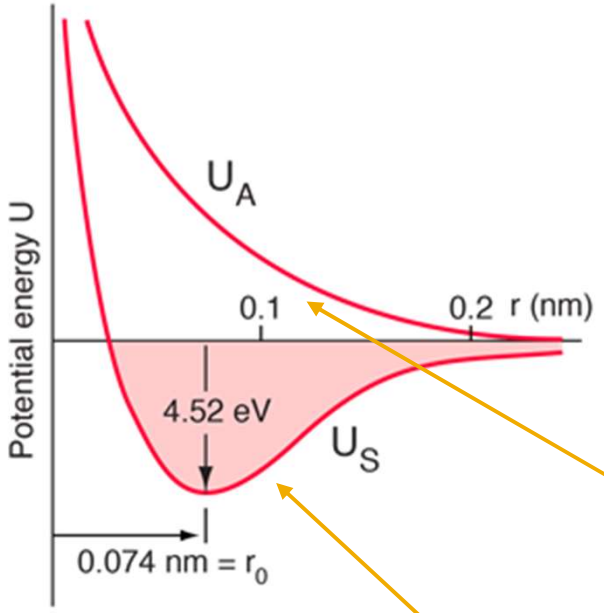
The potential energy for $r \to +\infty$ is not zero since there is an energy cost to transfer an electron from the Na atom to the Cl atom.

Negative potential energy, ionic bond forms.

This is the point where it costs no energy to transfer an electron from Na to Cl ($r \approx 0.94$ nm).

For $r < r_0$, steep rise of the potential energy due to both an electrostatic repulsion force between electron clouds and the Pauli exclusion principle.

Covalent Bond in H_2



r (nm) is the distance that the H atoms are apart.

There are 2 curves here, indicating different arrangements of how electrons are shared.

The total energy of a hydrogen molecule when the spins of two electrons are parallel. This is called an antibonding configuration.

The total energy of a hydrogen molecule when the spins of two electrons are antiparallel. This is the bonding configuration.

Structure due to Bonding

- As a result of the atoms sharing or donating electrons, the atoms will arrange themselves into different patterns;
- The structure of these patterns give rise to physical and chemical characteristics that we have already studied;
- The patterns are also a result of the radius of the orbiting electrons of atoms;
- The fraction of volume in a crystal that is occupied by constituent atoms is called the packing ratio or the atomic packing factor (APF). To be discussed later.

Forming of Crystallographic Patterns

- We may assume that atoms are regular spheres;
- In lattice arrangements, these spheres form symmetric patterns;
- We will only deal with regular lattice as it makes calculations easier.

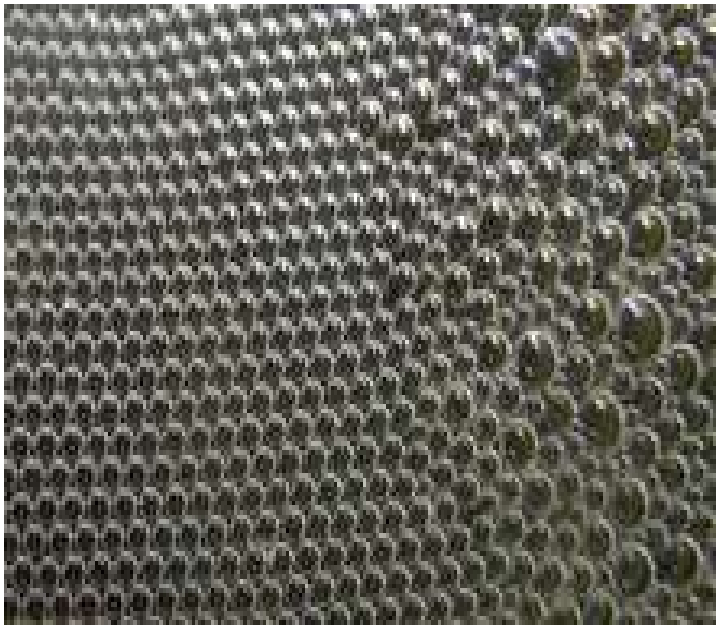
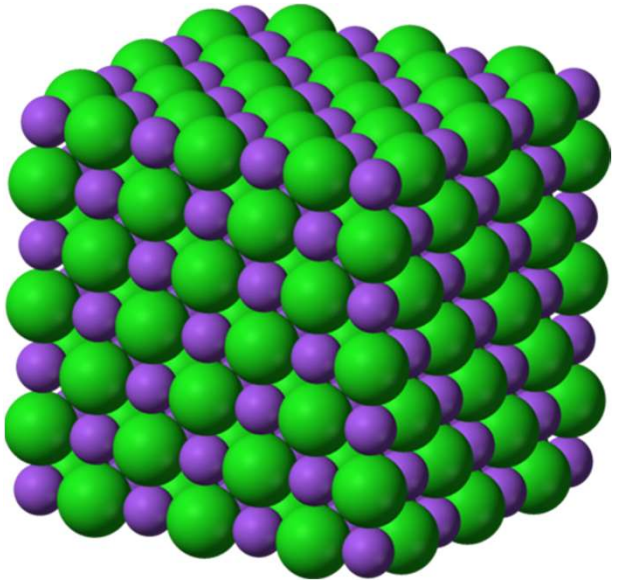


Image showing both regular and irregular lattice structures.

How do We Describe the Crystal Structure?

- Crystal structure depicts the ordered arrangement of atoms, ions or molecules in a crystalline material;
- Crystal structure occurs due to the intrinsic nature of constituent particles to form symmetric patterns that repeat along principal directions.



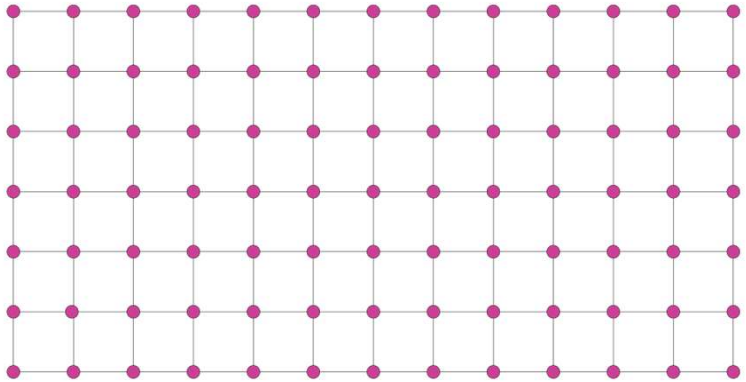
Crystal structure of NaCl (table salt)

https://en.wikipedia.org/wiki/Crystal_structure

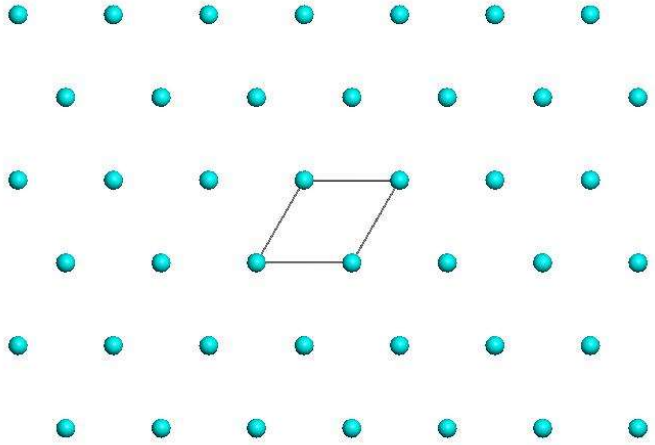
Lattice & Basis

- A (Bravais) lattice is an ordered indefinitely extended array of points describing the arrangement of particles that form a crystal. Each point in a lattice (called a lattice point) is surrounded in an identical way by its neighbours;
- A basis is a particular collection of atoms in space. It can be made up of either a single atom or multiple atoms. It identifies the group of atoms that are associated with each lattice point.

Examples of 2D Lattice



https://commons.wikimedia.org/wiki/File:2d_lattice.svg



https://www.geo.arizona.edu/xtal/geos306/fall11-10.htm

Lattice + Basis = Crystal Structure

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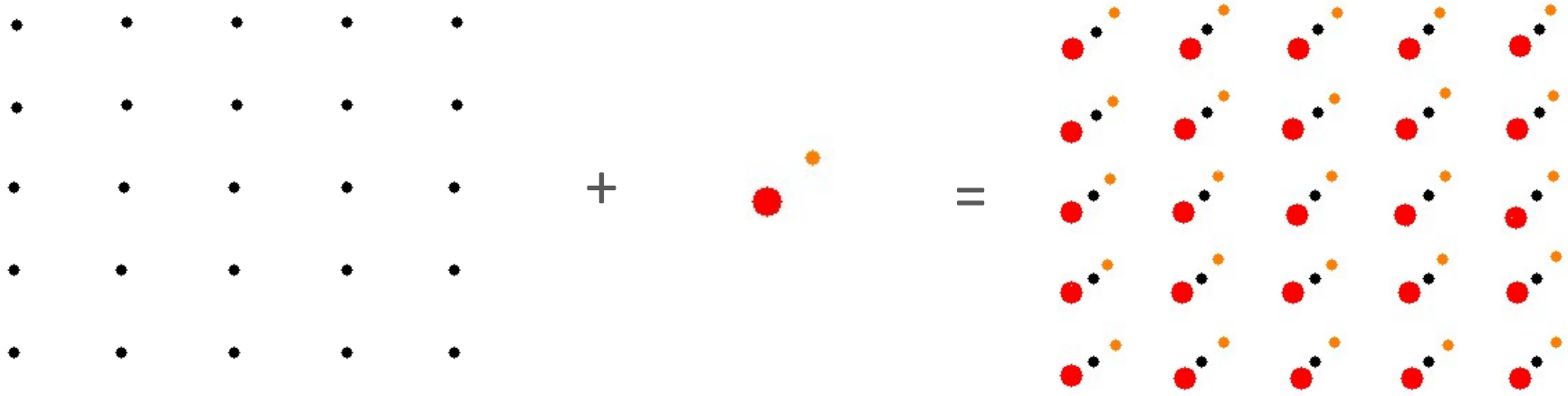

http://www.abhipod.com/researchpage/UGCMRP_05_06_ForWeb/elearningnode4.html

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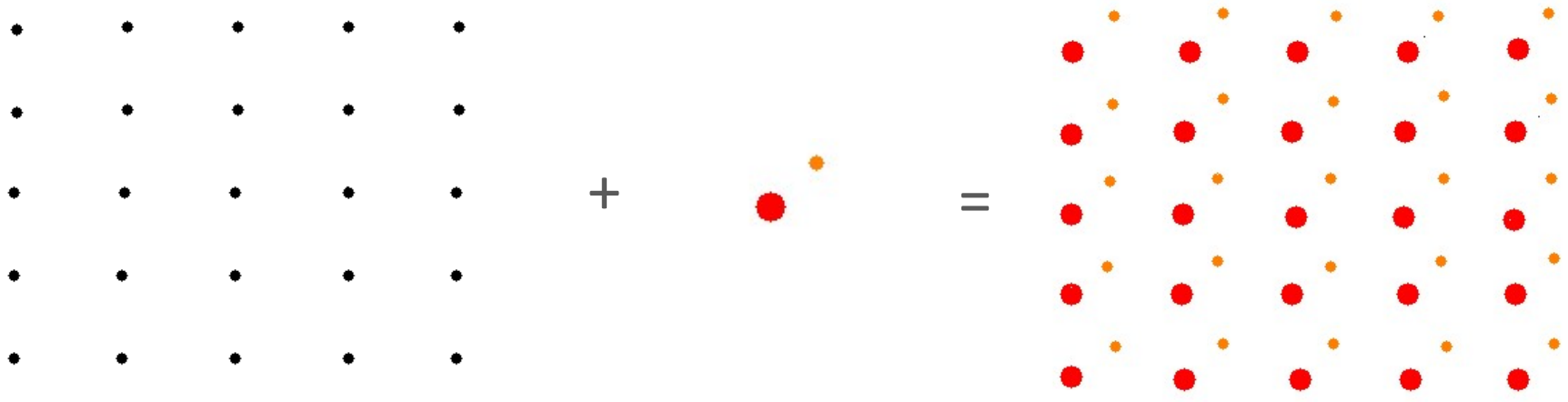


http://www.abhipod.com/researchpage/UGCMRP_05_06_ForWeb/elearningnode4.html

Primitive Vectors

- In 2D, (Bravais) lattice points can be described as

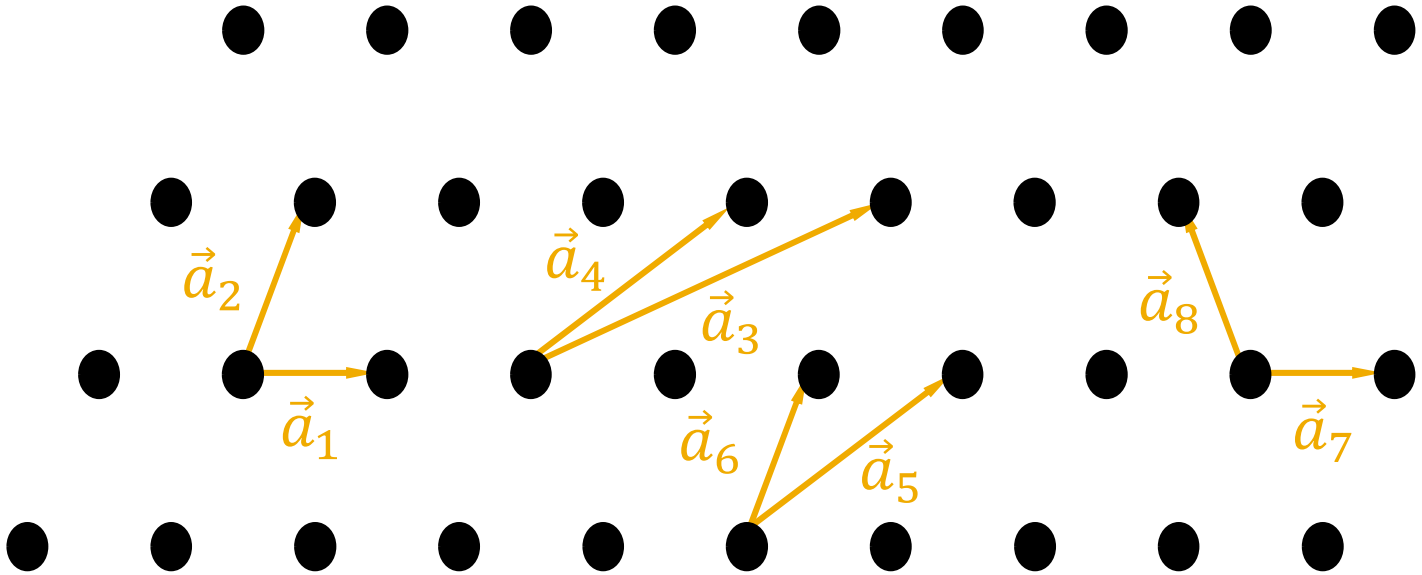
$$\vec{R}_{2\mathrm{D}} = a\vec{i} + b\vec{j}$$

- In 3D, (Bravais) lattice points can be described as

$$\vec{R}_{3\mathrm{D}} = a\vec{i} + b\vec{j} + c\vec{k}$$

- Vectors $\vec{i}$, $\vec{j}$, and $\vec{k}$ in the above equations are called primitive vectors.

Primitive Vectors are NOT Unique

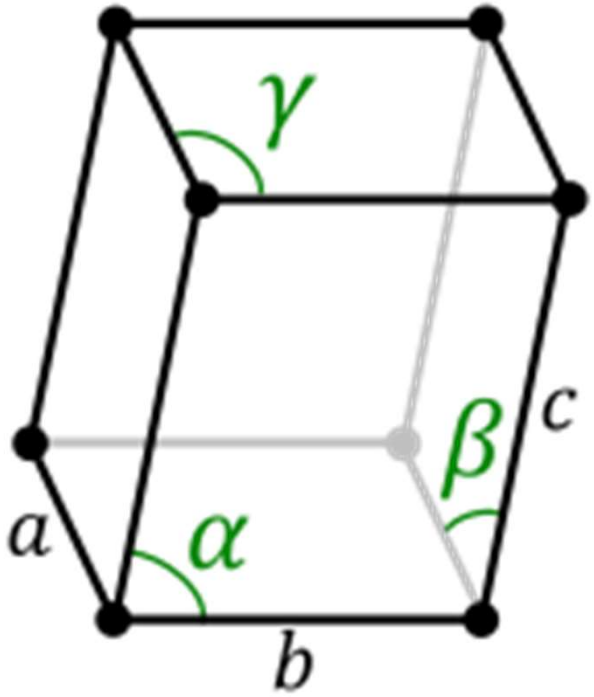


Primitive Cells & (Conventional) Unit Cells

- Primitive cell: The smallest unit cell that corresponds to only a single lattice point. It can be repeated to form the lattice. The symmetry of the crystal structure may not be obvious from the primitive cell;
- (Conventional) unit cell is the smallest repeating unit having the full symmetry of the crystal structure;
- A crystal structure can be built up by repetitively translating the primitive cell or the unit cell along its principal axes;
- In a 3D crystal, the geometry of the unit cell is defined by 6 lattice parameters, namely, the lengths of the cell edges (a, b, c) and the angles between them (α, β, γ).

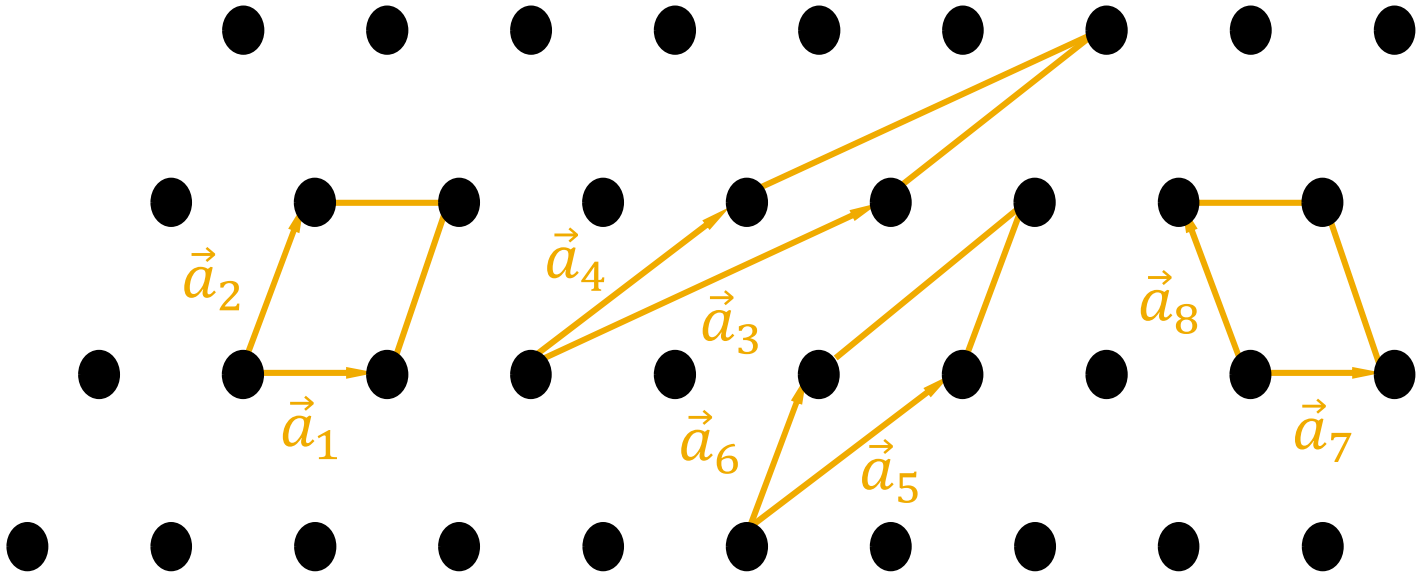
Lattice Parameters

- See the following diagram for the six lattice parameters.



https://en.wikipedia.org/wiki/Bravais_lattice

Primitive Cells are NOT Unique



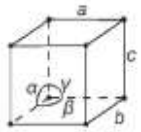
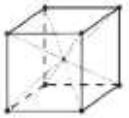
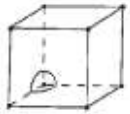
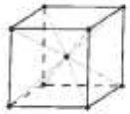
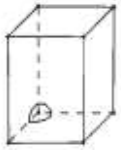
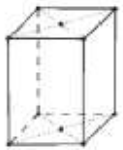
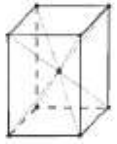
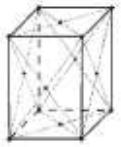
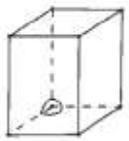
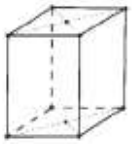
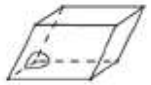
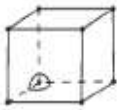
The area of the different choices of primitive cells is the same.

Bravais Lattices in 3D

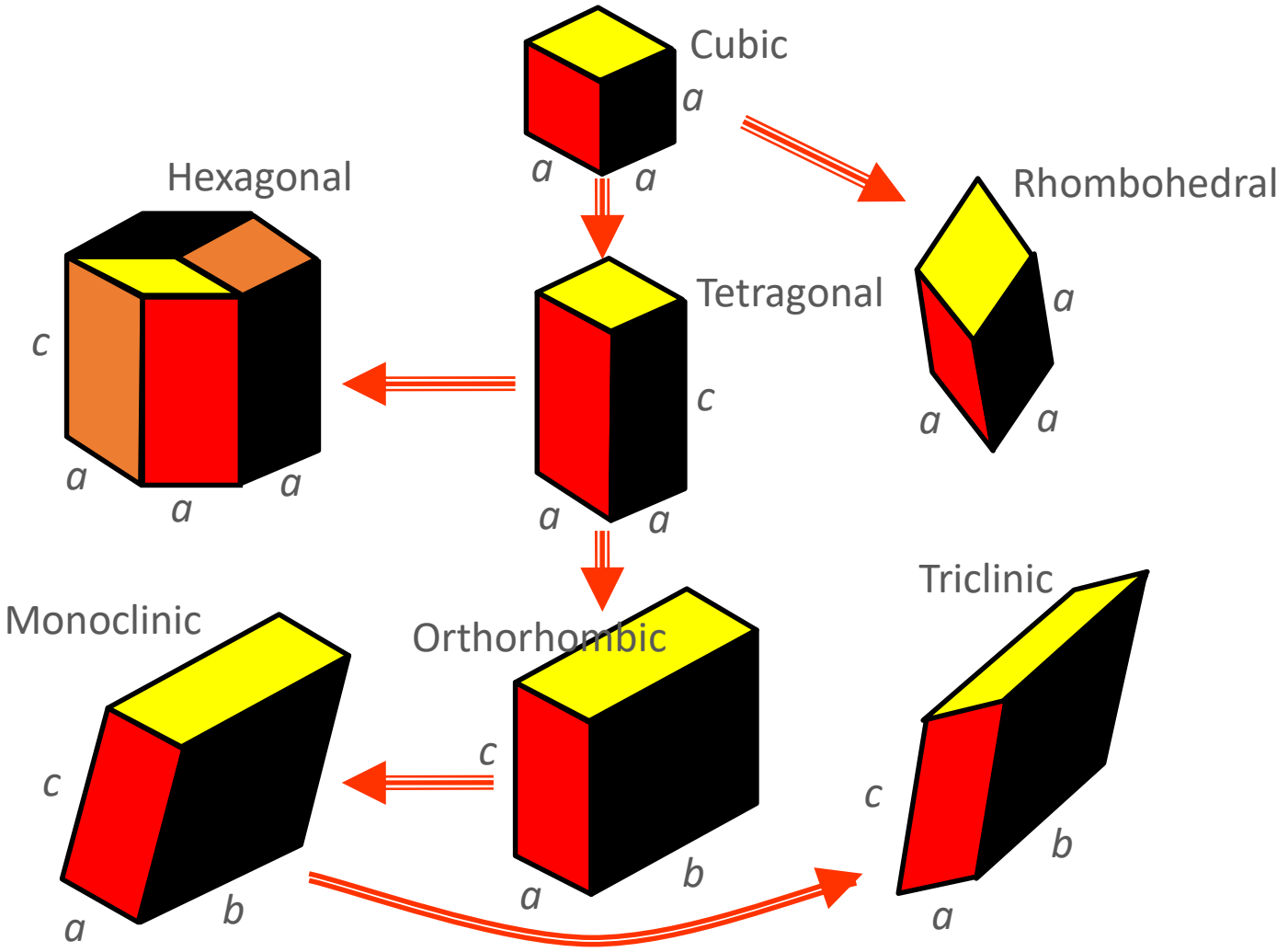
- There are 7 types of lattice systems with 14 different Bravais lattices in 3D;
- We will just look at 1 type of lattice system, namely, cubic, with 3 Bravais lattices;
- You need to be able to draw the unit cells of and describe the differences between these 3 different Bravais lattices;
- You are also required to know the number of atoms in each unit cell.

7 Lattice Systems & 14 Bravais Lattices

Table 3.1. The seven crystal systems and 14 Bravais lattices in three dimensions

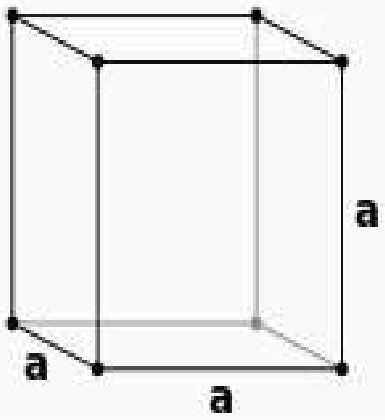
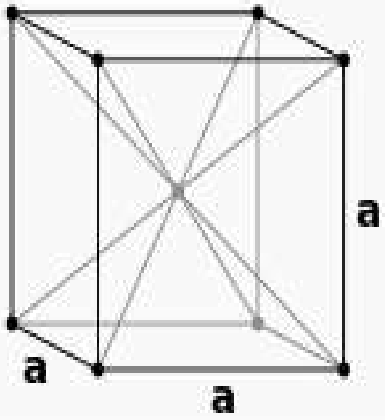
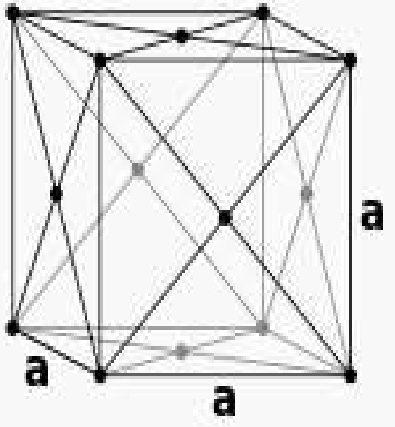
	Simple	Base Centered	Body Centered	Face Centered
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90°$				
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90°$				
Orthorhombic $a \neq b \neq c \neq a$ $\alpha = \beta = \gamma = 90°$				
Monoclinic $a \neq b \neq c \neq a$ $\alpha = \gamma = 90°$ $\beta \neq 90°$				
Triclinic $a \neq b \neq c \neq a$ $\alpha, \beta, \gamma \neq 90°$ $\alpha \neq \beta \neq \gamma \neq \alpha$				
Hexagonal $a = b \neq c$ $\alpha = \gamma = 90°$ $\beta = 120°$				
Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90°$				

7 Crystal Systems & 14 Bravais Lattices

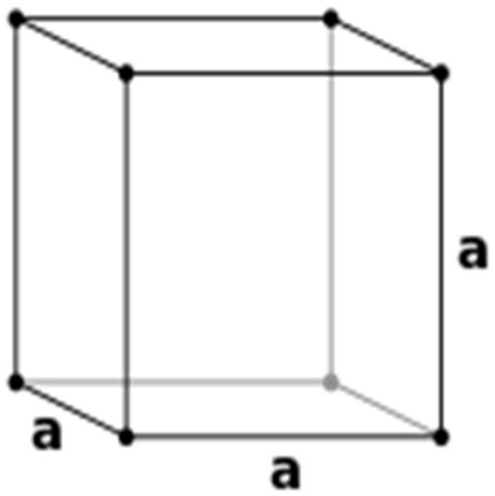


Cubic Lattice System

- $a = b = c$ and $\alpha = \beta = \gamma = 90°$.

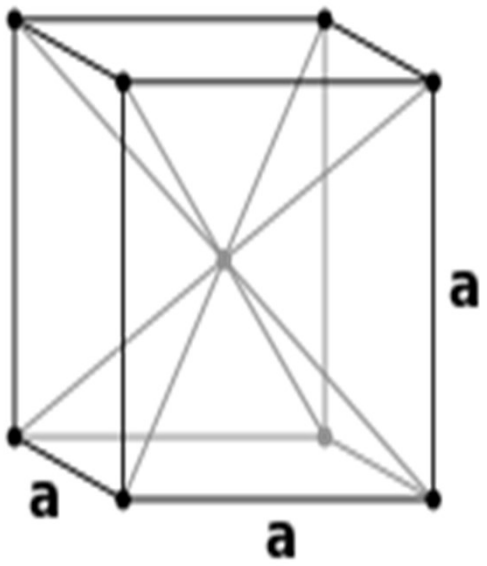
Cubic lattices			
Name	Primitive cubic	Body-centered cubic	Face-centered cubic
Unit cell			

Primitive Cubic (cP)



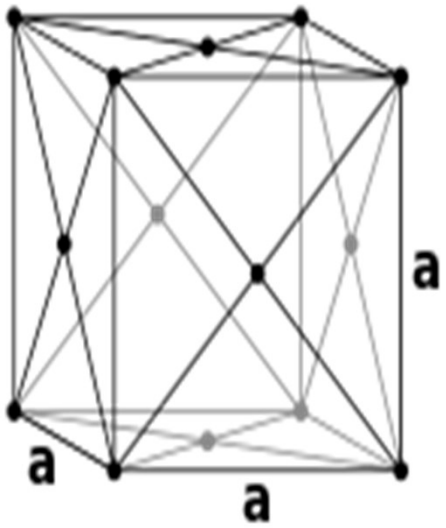
- A lattice point on each corner;
- An atom on each corner;
- Each atom at the lattice point is shared equally between 8 other cubes;
- 1 unit cell has 1 atom in total, 1/8 of an atom at each corner times 8;
- $1/8 \times 8 = 1$.

Body Centred Cubic (BCC)



- Starts just like the primitive cubic but has an additional point at the intersection of the internal diagonals;
- 1 unit cell has 2 atoms. One atom from the primitive cubic structure on the corners and another whole atom on its own in the middle;
- $1/8 \times 8 + 1 = 2$.

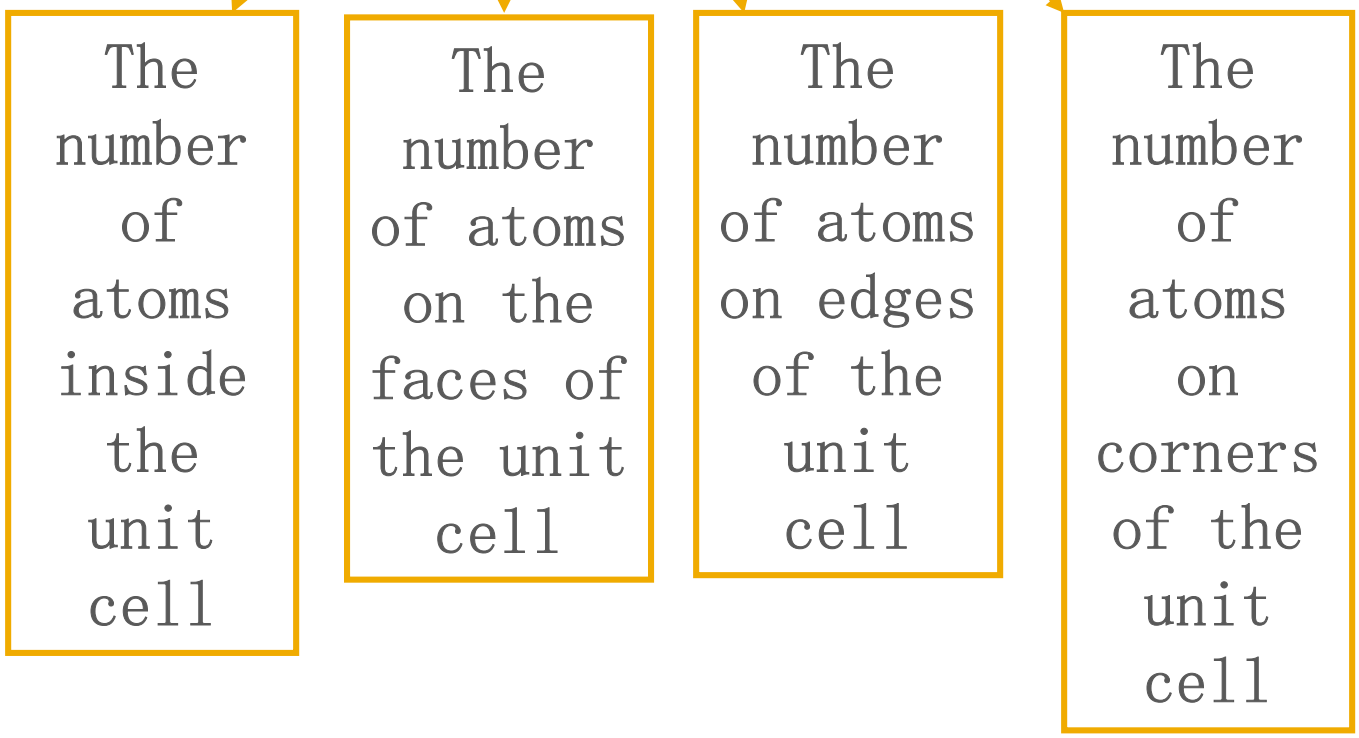
Face Centred Cubic (FCC)



- As the primitive cubic but with an atom at the intersection of the diagonal on each face;
- 1 unit cell has 4 atoms, 1/8 from each corner and 1/2 from each face;
- $1/8 \times 8 + 1/2 \times 6 = 1 + 3 = 4$.

Total Number of Atoms in a Unit Cell

$$N = n_i + \frac{1}{2}n_f + \frac{1}{4}n_e + \frac{1}{8}n_c$$



Packing Ratio (Atomic Packing Factor)

- A measure of how closely packed together a set of spheres are;
- For equal spheres in regular order (one-component structures) the maximum packing ratio is ~74%.
- Different arrangements of atoms usually lead to different packing ratios.

Just like stacking oranges!

How to Calculate the Packing Ratio

- Step 1: Find the volume of the unit cell.

$$V_{\text{cell}} = a^3 \text{ (length of the cell edge)}$$

- Step 2: Find the volume of each particle in the unit cell.

$$V_{\text{particle}} = \frac{4}{3}\pi r^3 \text{ (}r\text{: radius of a particle)}$$

- Step 3: Find the total volume of all particles in the unit cell.

$V_{\text{p total}} = N \cdot V_{\text{particle}}$ (N: number of particles in unit cell)

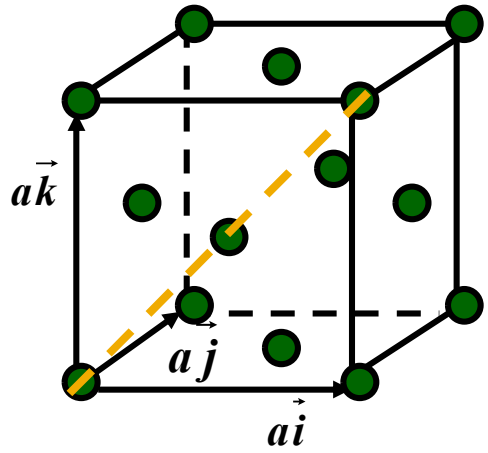
- Step 4: Find the packing ratio.

$$\text{Packing Ratio} = \frac{V_{\text{p total}}}{V_{\text{cell}}} = \frac{N \cdot V_{\text{particle}}}{V_{\text{cell}}}$$

Example: Packing Ratio of FCC Structure

$$N = n_i + \frac{1}{2}n_f + \frac{1}{4}n_e + \frac{1}{8}n_c$$

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

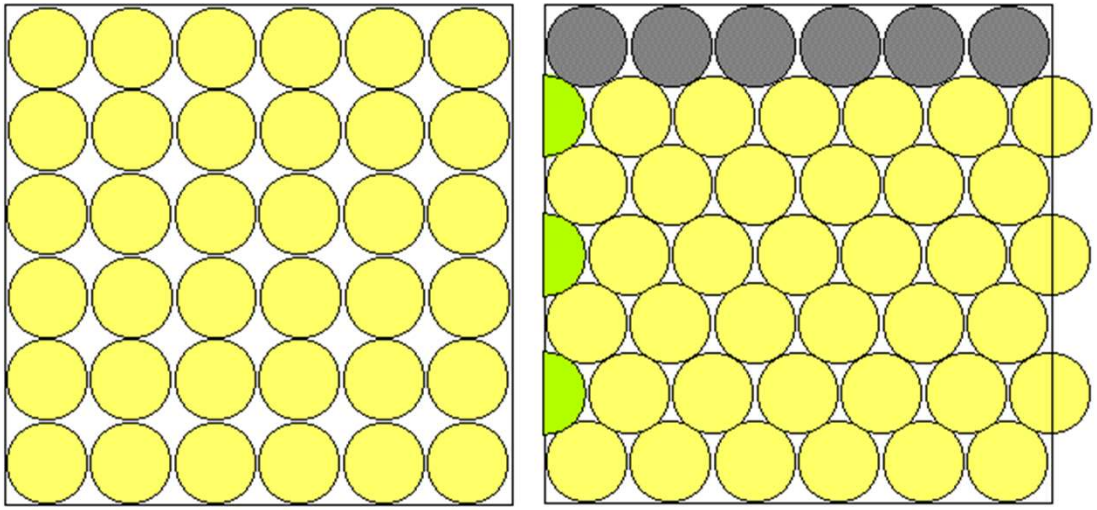


Using a face diagonal, we can find that $4r = \sqrt{2}a$.

$$\text{Packing Ratio} = 4 \times \frac{4}{3}\pi\left(\frac{\sqrt{2}}{4}\right)^3 = \frac{\sqrt{2}\pi}{6} \approx 0.74 = 74\%$$

Close Packing

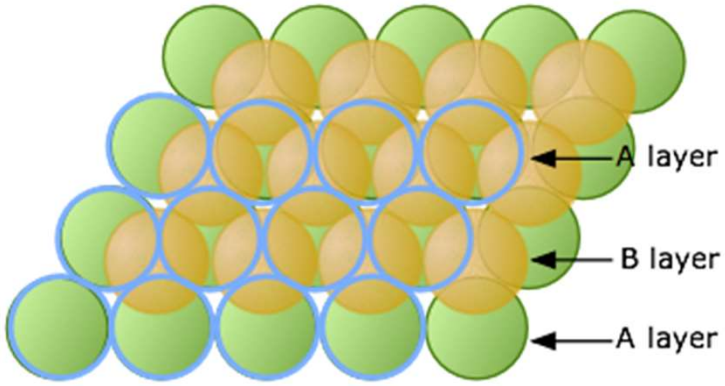
- The FCC is an example of close packing;
- This is where the atoms are moved slightly to allow for more atoms in the same space;
- Another example is hexagonal close-packed structure.

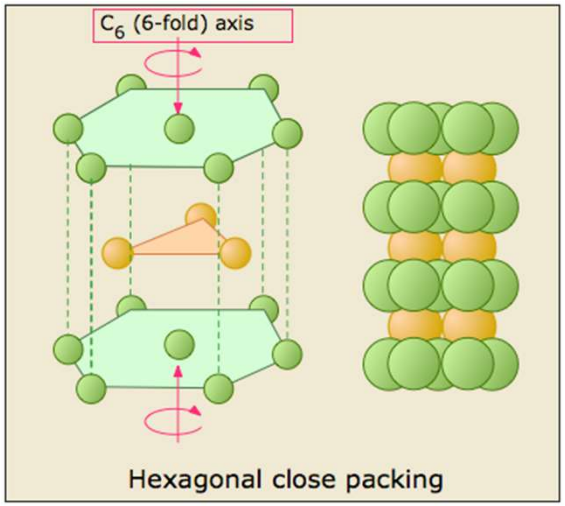


Standard Packing Close Packing

Hexagonal Close-Packed Structure

- The hexagonal close-packed structure has a six-fold symmetry axis;
- The sequence of the close-packed layers is ABABAB…



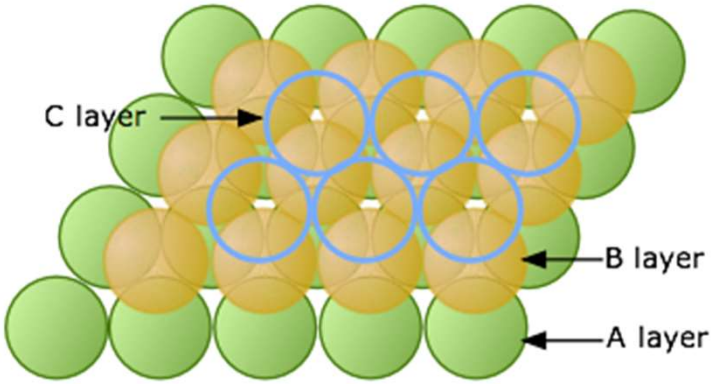


https://chem.libretexts.org/Bookshelves/General_Chemistry/

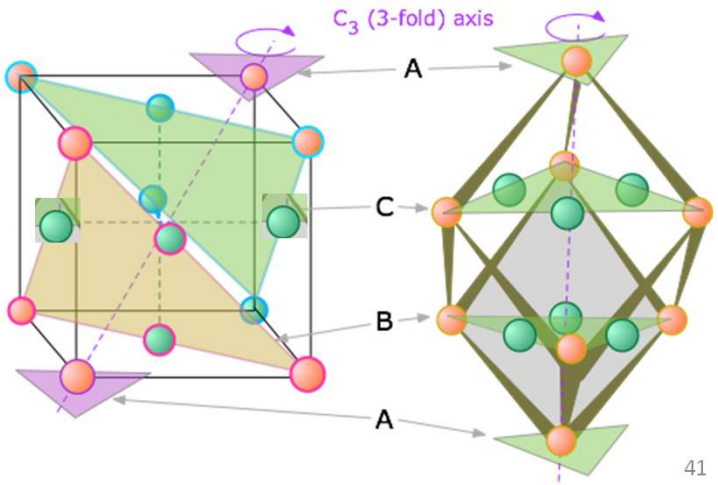
Cubic Close-Packed Structure: FCC

- The FCC close-packed stack is inclined with respect to the faces of the cube;
- It is perpendicular to one of the three-fold axes passing through opposite corners;
- The sequence of the close-packed layers is ABCABC…

https://chem.libretexts.org/Bookshelves/General_Chemistry/



ABC face-centered cubic



Characteristics of Close-Packed Structure

- The total energy is very low, so the structure is very stable;
- The coordination number is 12;
- Most of the noble gas crystals and metal crystals belong to close-packed structure.

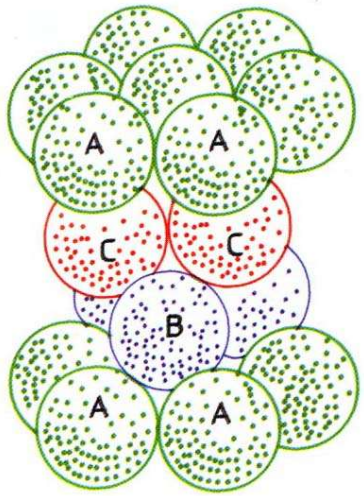
Coordination Number

- Coordination number: The total number of neighbors of a central atom in a molecule or crystal (the number of atoms, molecules, or ions that are bonded to a central atom);
- It describes how closely the atoms are arranged in a crystal, and the closer the particles are arranged, the greater the coordination number is.

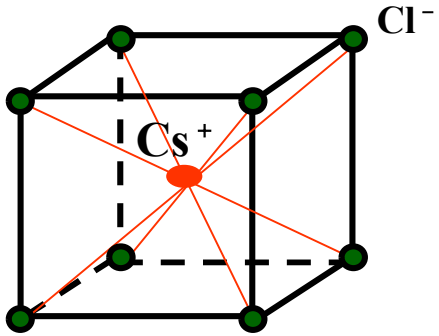
Possible Values of Coordination Numbers

- 12 (close-packed structure);
- 8 (CsCl);
- 6 (NaCl);
- 4 (Diamond);
- 3 (Graphite layered structure);
- 2 (Chain structure).

Possible Values of Coordination Numbers

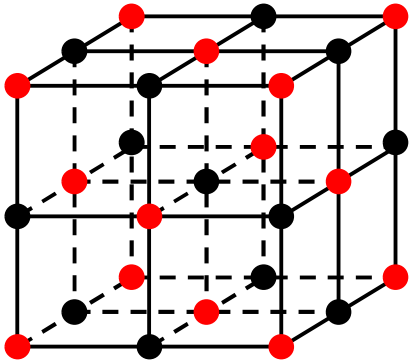


12 (close-packed structure)

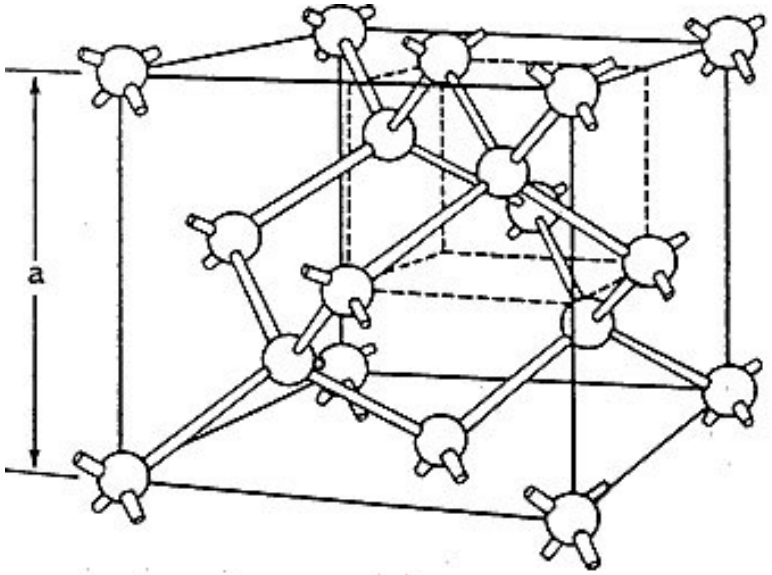


8 (CsCl)

Possible Values of Coordination Numbers

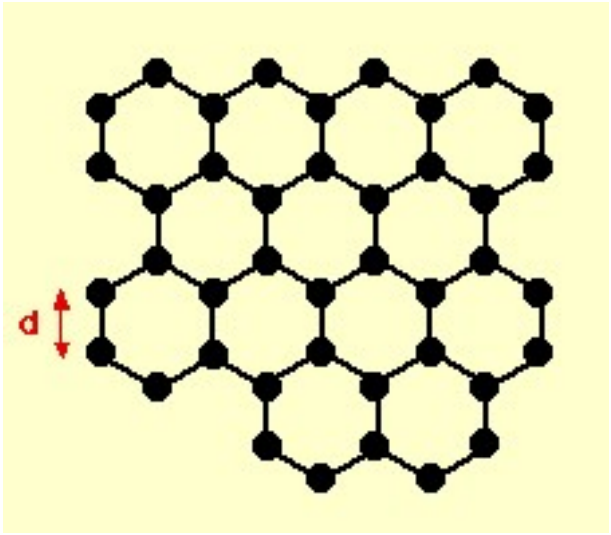


6 (NaCl)

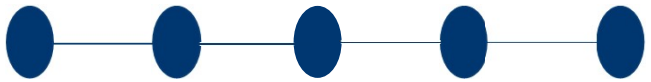


4 (Diamond)

Possible Values of Coordination Numbers



3 (Graphite layered structure)



2 (Chain structure)

Characteristics of Cubic Lattice Structures

	Number of Atoms in a Unit Cell	Positions of Atoms	The Nearest Distance	Coordinate Number
cP	1	(000)	a	6
BCC	2	(000), $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	$\frac{\sqrt{3}a}{2}$	8
FCC	4	(000), $(\frac{1}{2}\frac{1}{2}0)$, $(\frac{1}{2}0\frac{1}{2})$, $(0\frac{1}{2}\frac{1}{2})$	$\frac{\sqrt{2}a}{2}$	12

Crystal Planes & Miller Indices

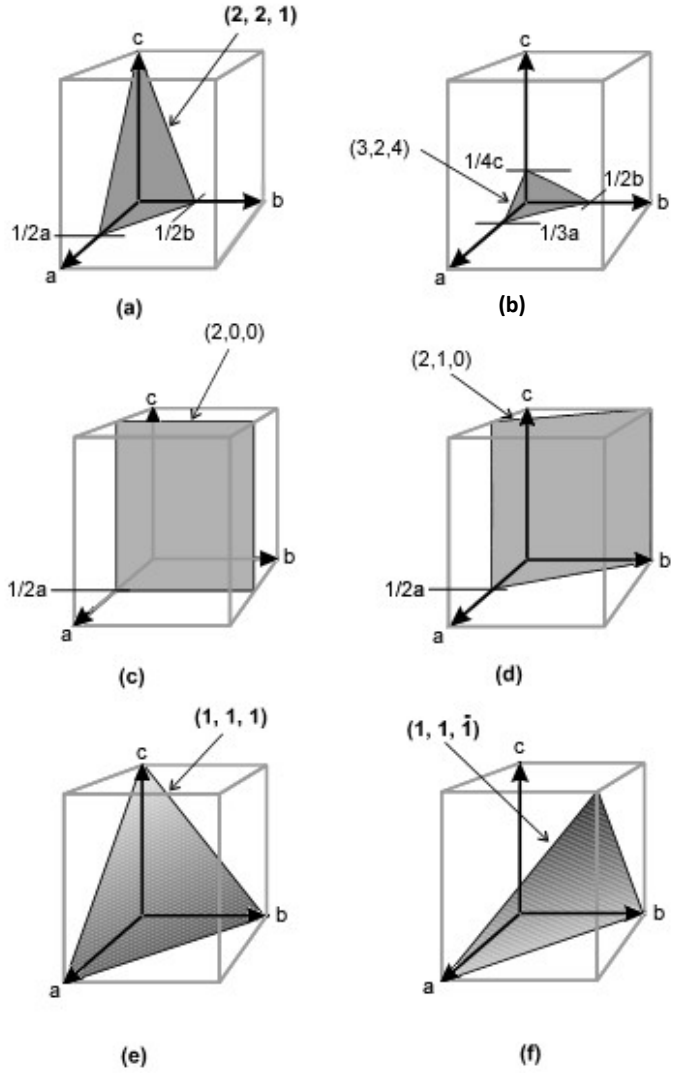
- A plane is just a flat surface that joins a series of points within a unit cell;
- A certain crystal plane includes a set of parallel and evenly spaced planes which are extended to fill the entire crystal. Each plane is at the same distance, *d*, from its neighbouring planes (we will come back to this point later);
- Crystal planes are defined by the intercepts they make on the crystal axes of the unit cell, and it is called Miller indices.

How to Determine the Miller Indices

- Determine the intercepts on the axis in units of the primitive vectors *a*, *b* and *c*;
- Take the reciprocal of each number;
- Reduce these numbers to the three smallest integers *h*, *k* and *l*, having the same ratio;
- The values *h*, *k* and *l* are called the Miller indices and are enclosed in parentheses (*hkl*) to denote a crystal plane .

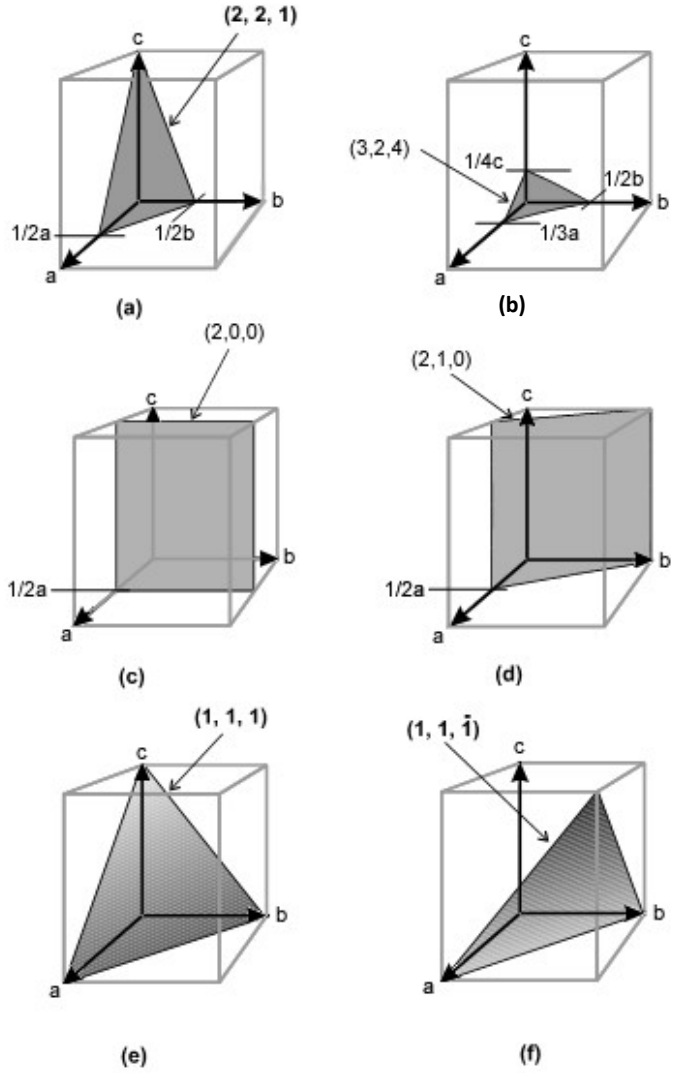
Examples: Miller Indices Determination

- Determine the Miller indices for the planes shown in the figure.



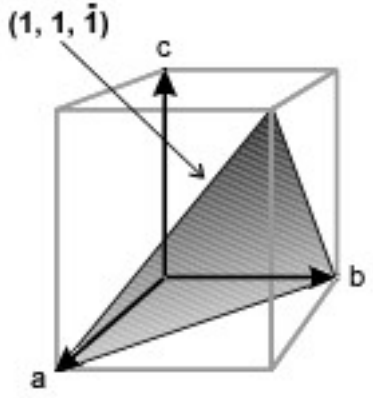
Examples: Miller Indices Determination

- In (a), the intercepts are ½, ½, 1 and the Miller indices are (221);
- In (c) the intercepts on *b* and *c* are at infinity, the inverse of which is 0 and the Miller indices are (20 0);
- In (f) the plane cuts the negative *c* axis at -1 and thus the Miller indices are $(11\bar{1})$.

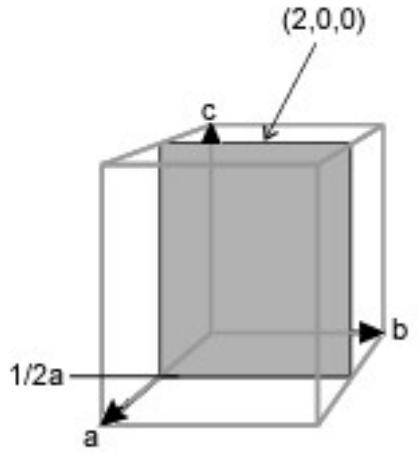


Miller Indices Determination: Special Cases

- If a plane intercepts an axis at a negative value, this is denoted by placing a bar over the corresponding Miller index;

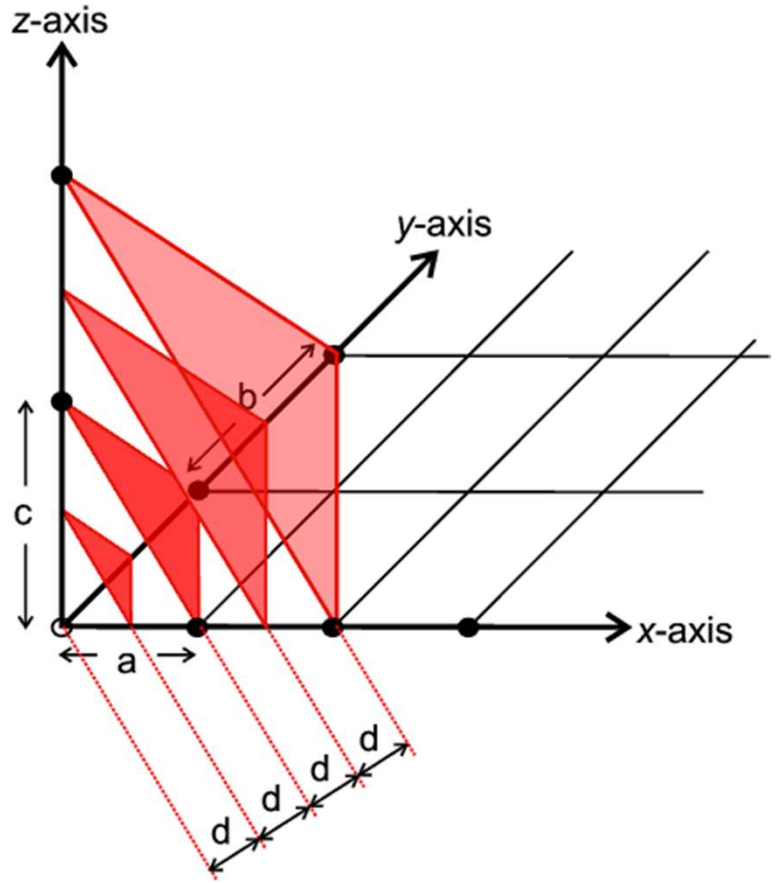


- If a plane is parallel to a particular axis, the corresponding Miller index is zero (In effect, we are saying that the intercept with the axis occurs at infinity and the reciprocal of infinity is zero).



Miller Indices are for a Set of Parallel Planes

- The Miller indices (*hkl*) represent the crystal planes. They do not actually denote a single plane but a set of parallel planes.



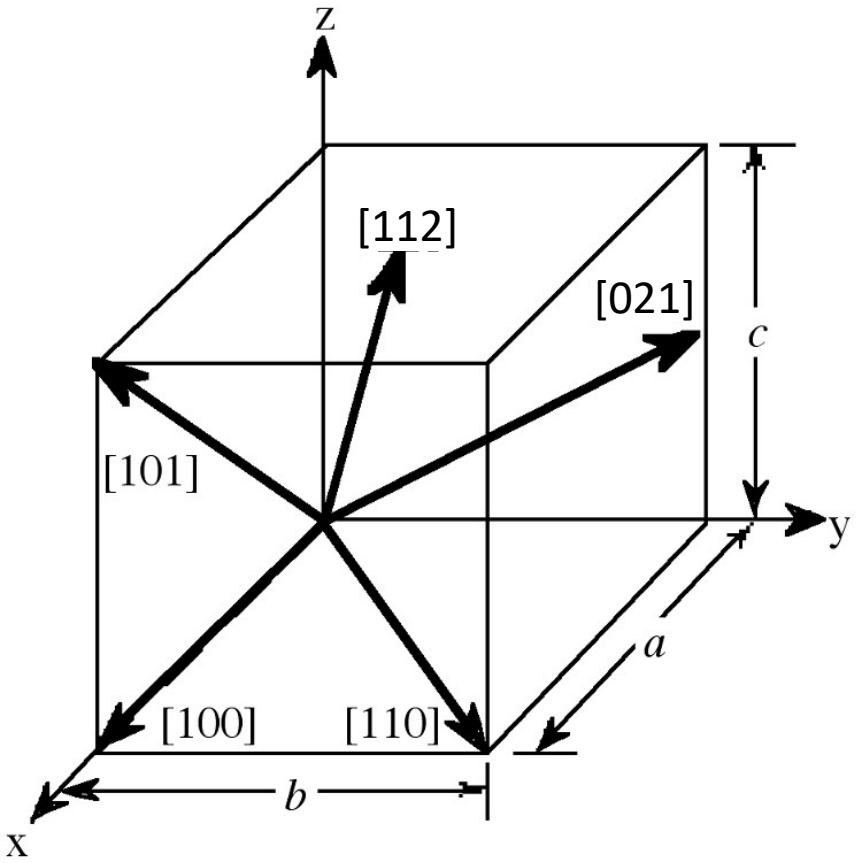
Family of Equivalent Planes

- The set of equivalent crystal planes (i.e., those which have the same symmetry) is denoted by using braces {*hkl*}, e.g., in a cubic lattice {100} refers to the (100), ($\bar{1}$00), (010), (0$\bar{1}$0), (001), and (00$\bar{1}$) planes.

Crystal Directions

- A direction in a lattice is specified using square brackets [*hkl*];
- This is defined as the direction perpendicular to the plane (*hkl*);
- [*hkl*] is called orientation indices;
- If a direction can be denoted as $\vec{R} = l_1'\vec{i} + l_2'\vec{j} + l_3'\vec{k}$ in which l_1', l_2', and l_3' are integers, its Miller indices can be denoted as $[l_1 l_2 l_3]$ and l_1, l_2, and l_3 are co-prime numbers reduced from l_1', l_2', and l_3'.

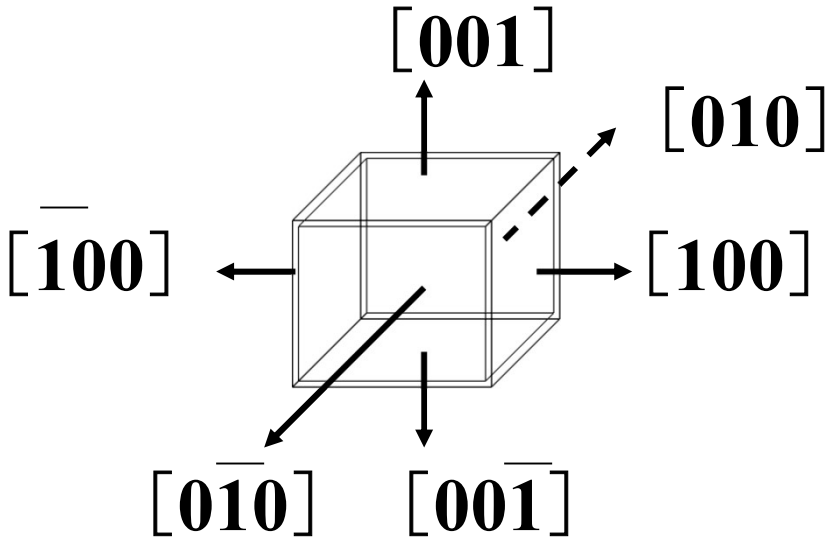
Crystal Directions in a Cubic Unit Cell



https://www.jobilize.com/physics4/test/crystal-directions-crystal-structure-by-openstax

Family of Crystal Directions

- The set of equivalent directions (i.e., those which have the same symmetry) is denoted by using angle brackets <*hkl*>, e.g., in a cubic lattice <100> refers to the [100], $[\bar{1}00]$, [010], $[0\bar{1}0]$, [001], and $[00\bar{1}]$ directions.

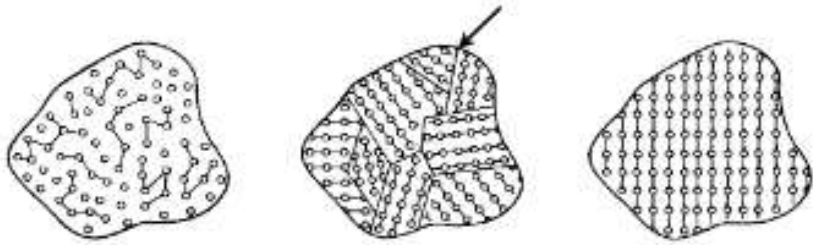


Examination of Silicon

- As most of the semiconductors and devices that we will be looking at in the second part of this course will be silicon (Si) based, the next number of slides will examine the effects of different forms of silicon.

Forms of Silicon

- Amorphous: randomly orientated atoms, e.g., glass;
- Polycrystalline: sections are ordered, but on a random fashion;
- Crystal: ordered arrays of atoms.



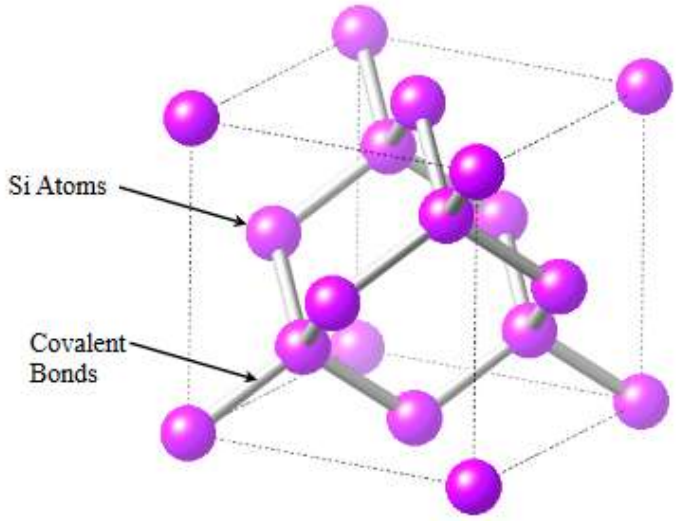
Amorphous
Randomly oriented atoms, e.g. Glass

Polycrystalline
Crystal grains/ domains oriented in random directions, which meet at grain boundaries

Crystal
Entire solid is made of an ordered array of atoms

Rendering of Si Bonding

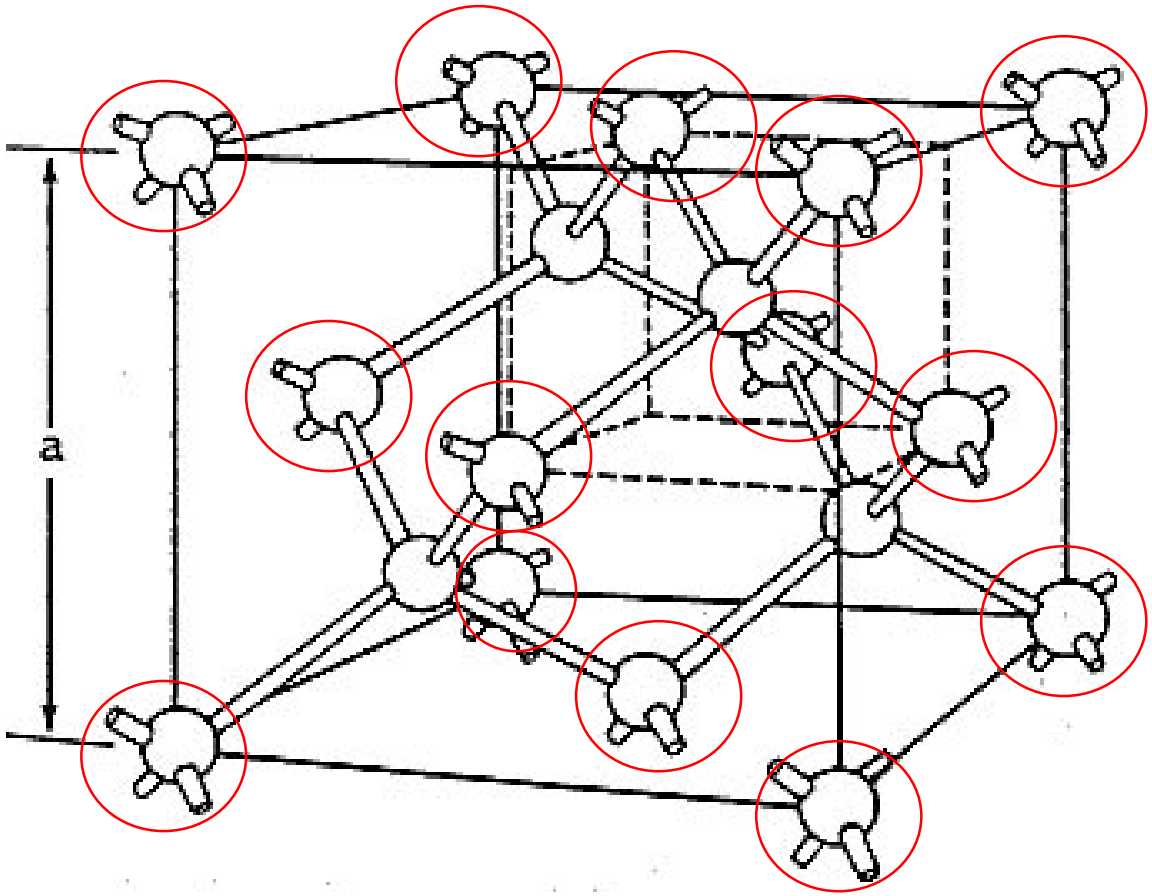
- Silicon has a cubic lattice, covalent bonds with 4 others in a diamond lattice structure.



Note: Bonds outside of Cubic Lattice are not shown

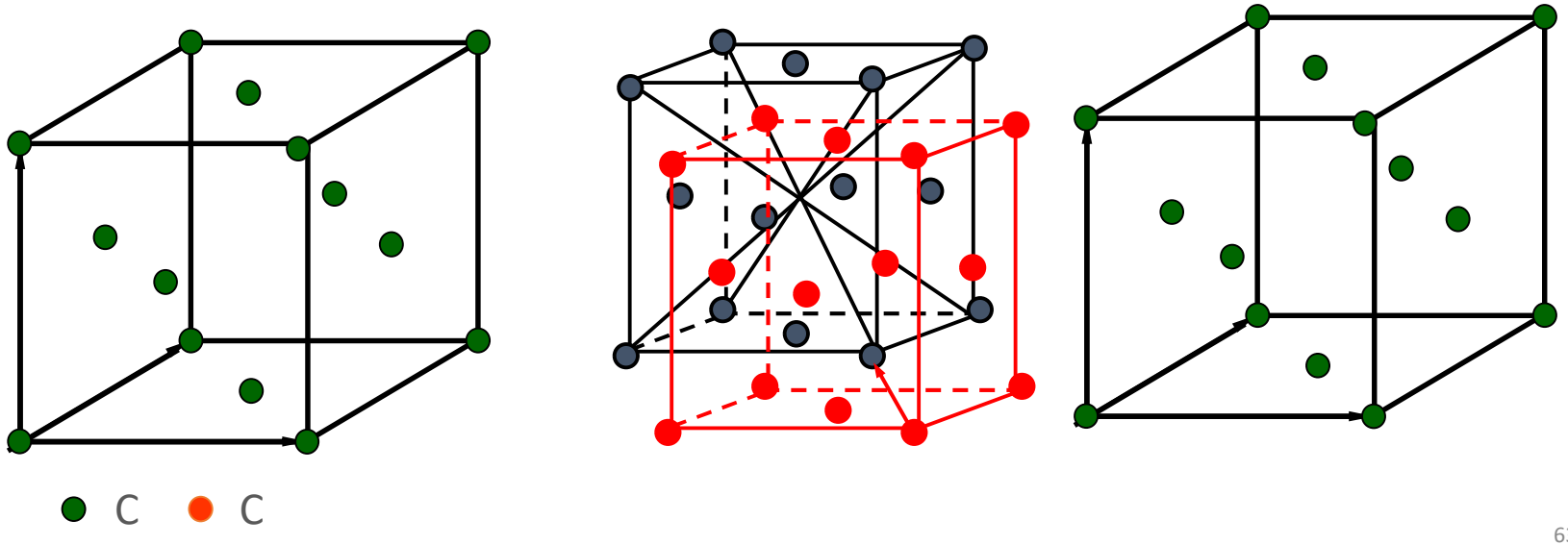
- Silicon has three main orientations, [111], [100], and [110].

Diamond Structure



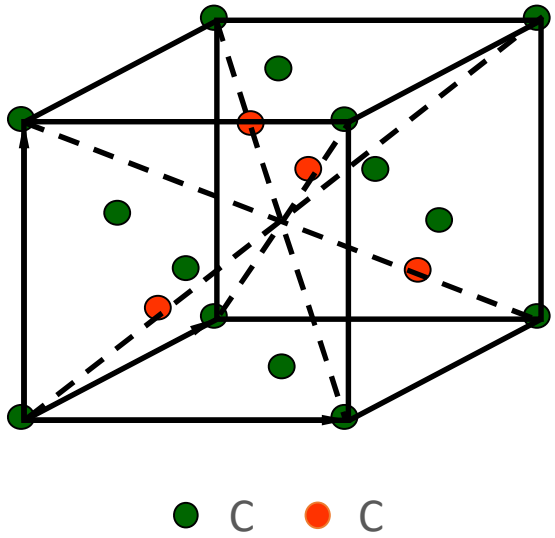
Diamond Structure

- The diamond structure is composed of two face-centred cubic sublattices with one-fourth of the diagonal displacement along the volume, and its Bravais lattice is face-centred cubic (FCC);
- Each unit cell contains 4 lattice points and 8 atoms.



Diamond Structure

- The diamond structure is face-centred cubic. Each unit cell contains 4 lattice points, and each primitive cell contains 1 lattice point. The basis is composed of two carbon atoms, which locate at (000) and $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$.



Imaging of Silicon Crystal Planes

- Images below are taken by scanning tunnelling microscopy (STM) on silicon crystal planes. Atomic arrangement can be clearly observed.

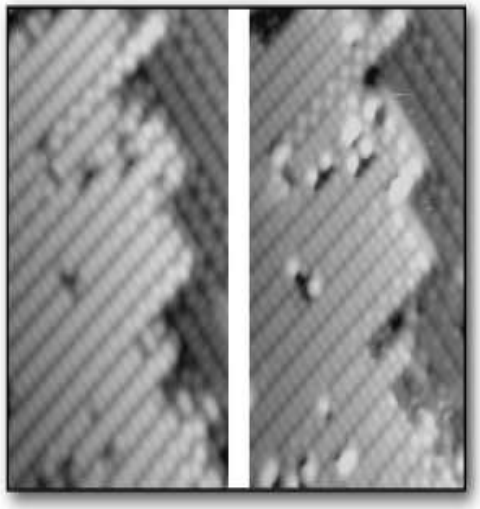


Image of Atomic Structure of Silicon Crystal along the {100} plane
[image from Dept. of Synchrotron Radiation Research, in Lund]

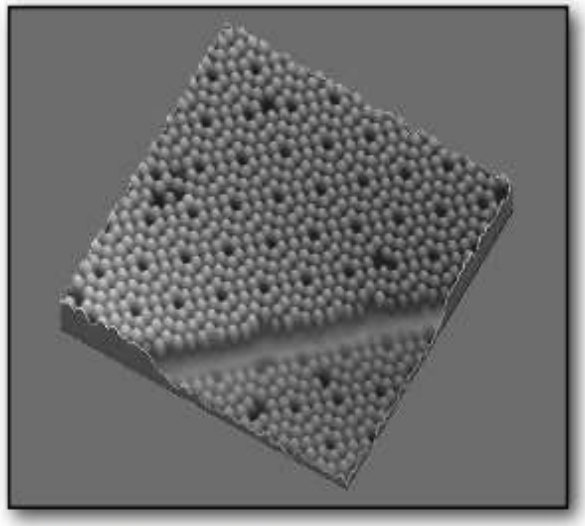


Image of Atomic Structure of Silicon Crystal along the {111} plane
[image from Dept. of Synchrotron Radiation Research, in Lund]