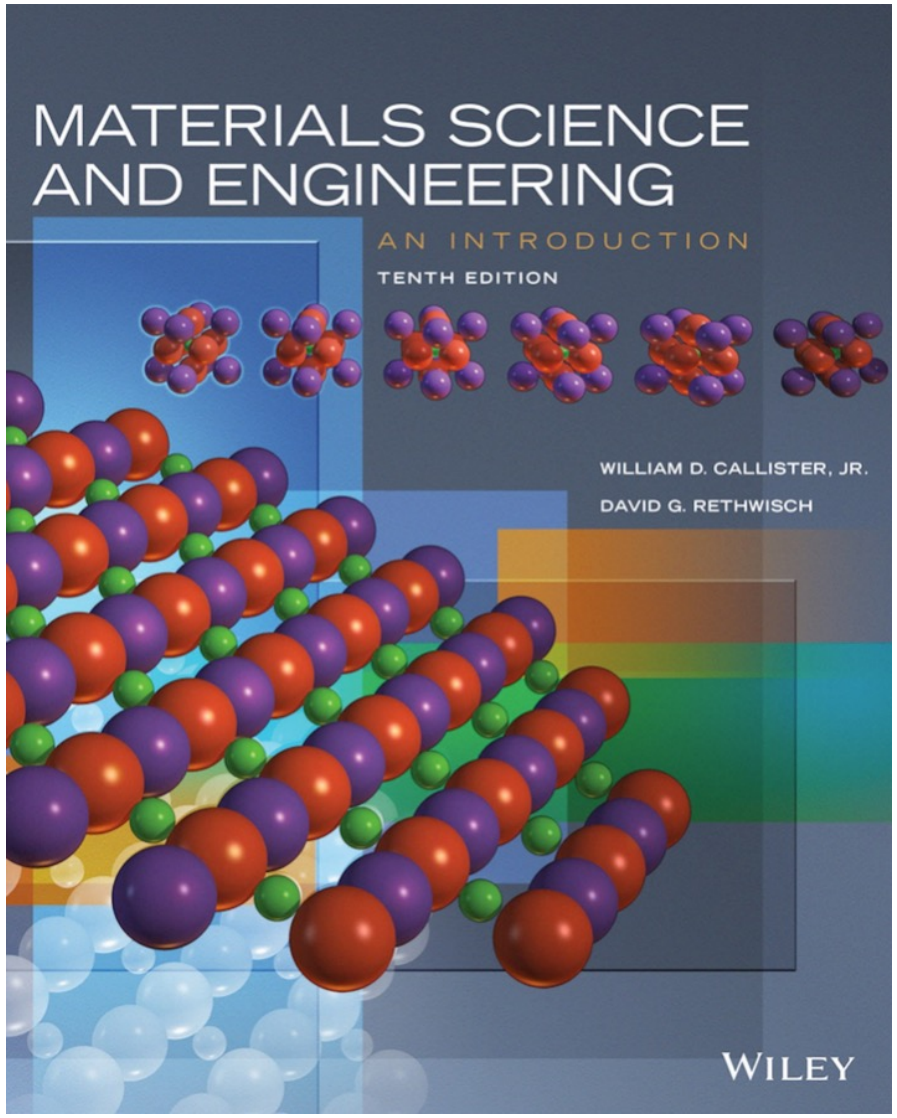
Lecture 2:
The Structure of Crystalline Solids

Prof. Nathan Szymanski
nszymanski@seas.ucla.edu
Department of Materials Science & Engineering

Reading for this subject



Chapter 3 The Structure of Crystalline Solids

This discussion will closely follow **Chapter 3** of Callister, **pages 48-91** of the 10th edition. This is a ***very important chapter*** – it forms a foundation for the rest of the course

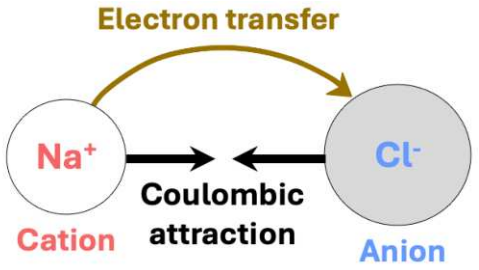
Supplementary Texts:

- *Chemical Structure and Bonding* by DeCock
- *Solid-State Materials Chemistry* by Woodward
- *Ceramic Materials* by Carter

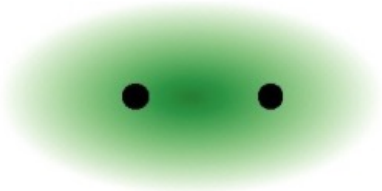
Some review from last time

Types of interatomic bonding:

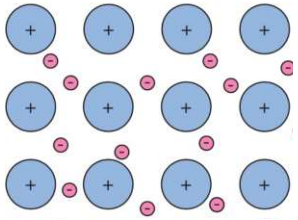
1) **Ionic**



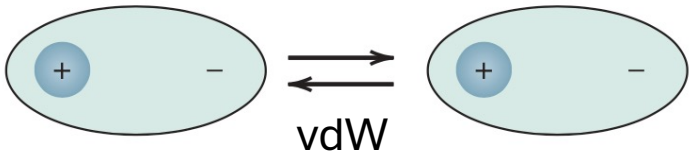
2) **Covalent**



3) **Metallic**



4) **Secondary**

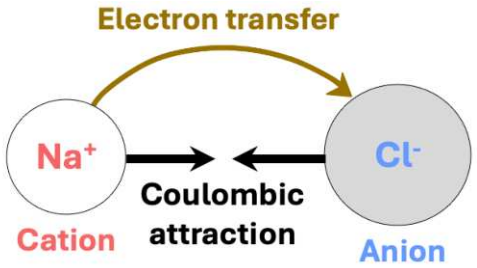


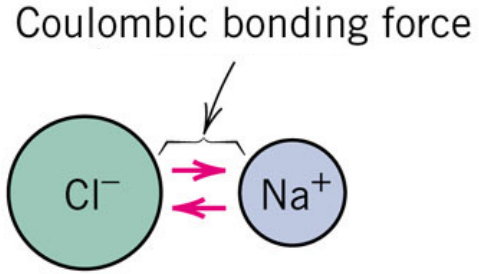
We mostly discussed these in the context of **2-atom bonds**...But how do these bonds give rise to **entire materials ($\sim 10^{23}$ atoms)?**

Materials are just a sum of many atoms and bonds

Types of interatomic bonding:

1) **Ionic**



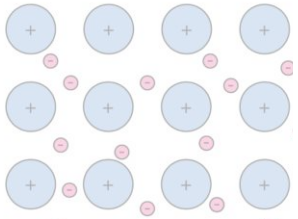


Start with a simple pair: cation + anion

2) **Covalent**



3) **Metallic**



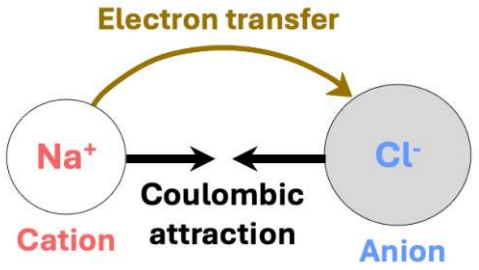
4) **Secondary**

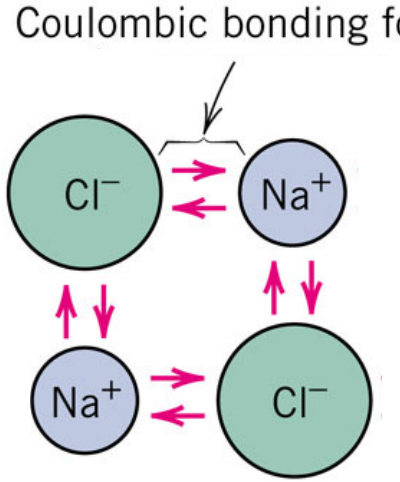


Materials are just a sum of many atoms and bonds

Types of interatomic bonding:

1) **Ionic**



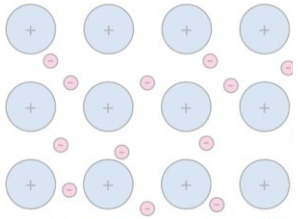


Add another pair, now we have attractions among all 4 ions

2) Covalent



3) Metallic



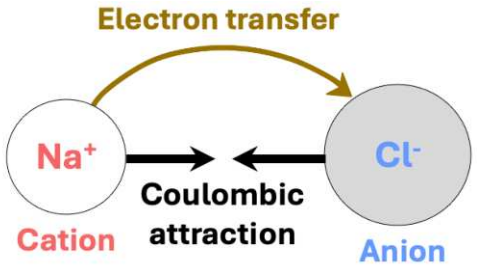
4) Secondary

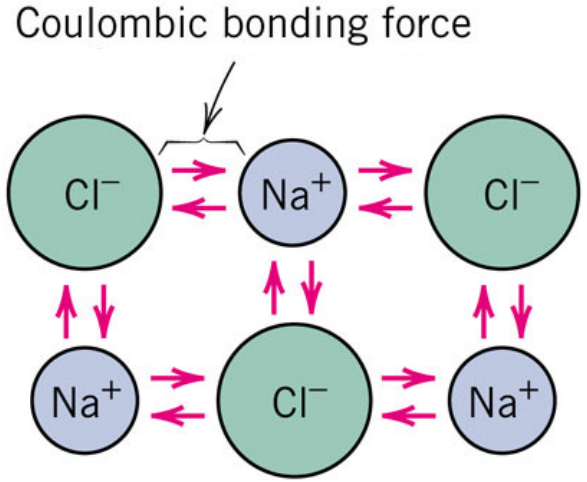


Materials are just a sum of many atoms and bonds

Types of interatomic bonding:

1) **Ionic**



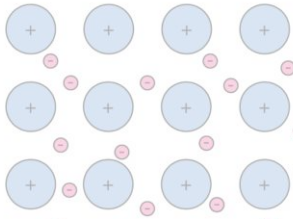


And another…

2) **Covalent**



3) **Metallic**



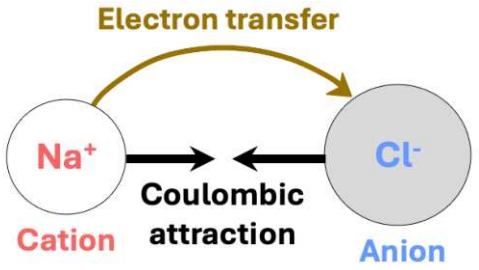
4) **Secondary**



Materials are just a sum of many atoms and bonds

Types of interatomic bonding:

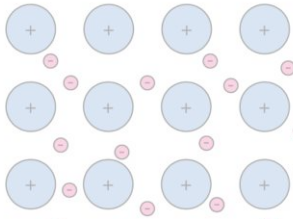
1) Ionic



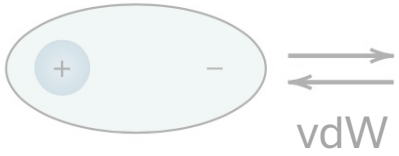
2) Covalent

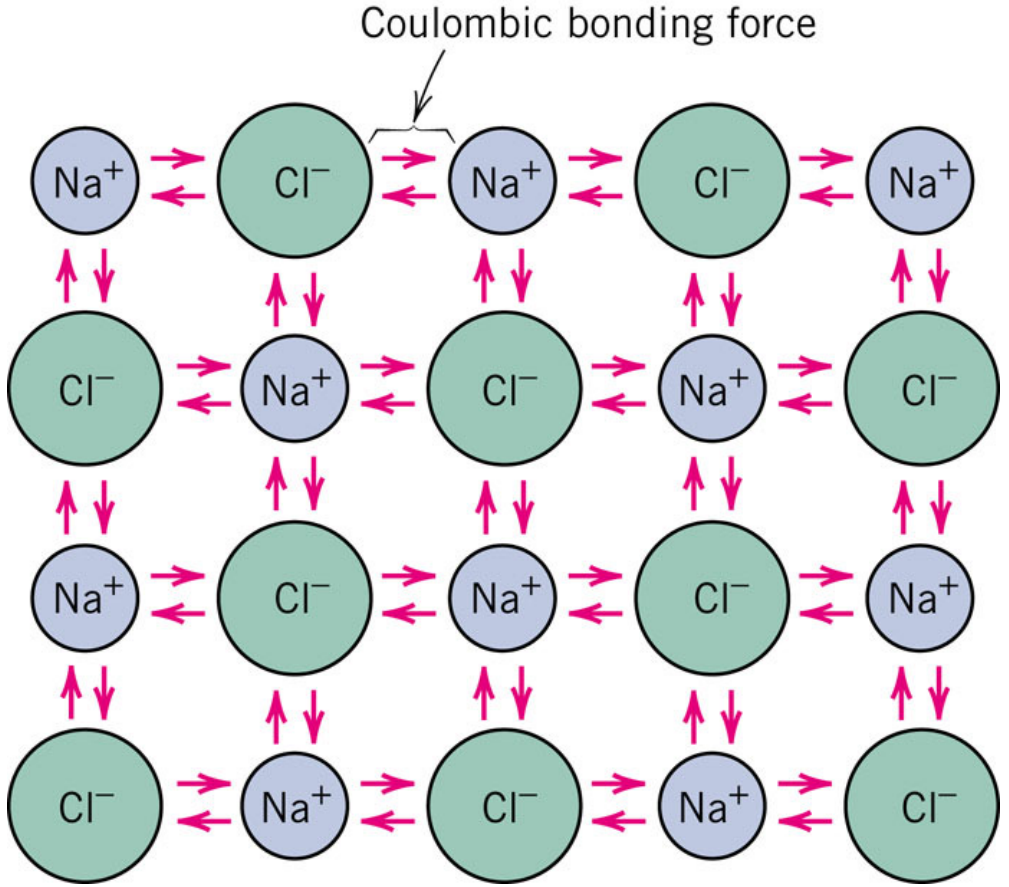


3) Metallic



4) Secondary



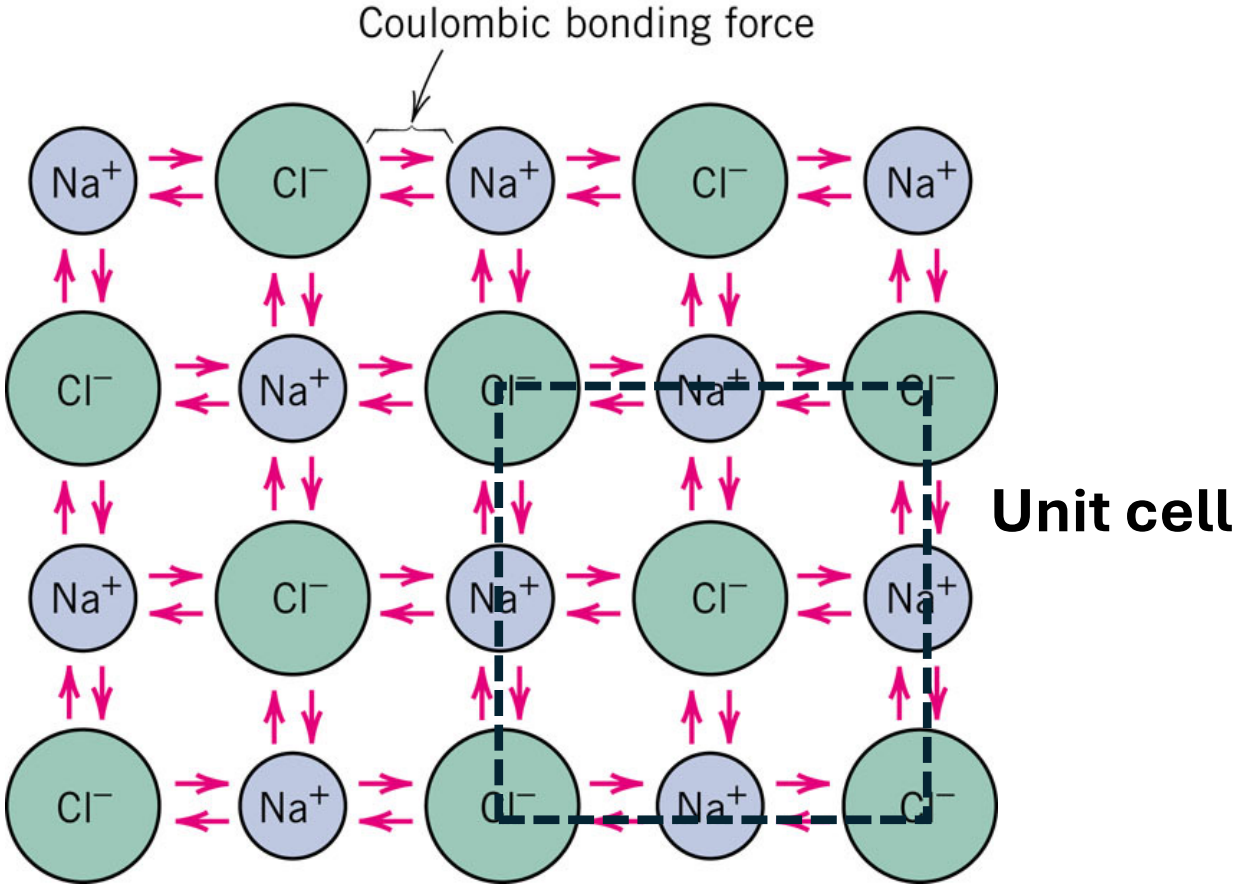


And so on, until we form a complete solid

Crystalline materials are composed of repeating units (unit cells)

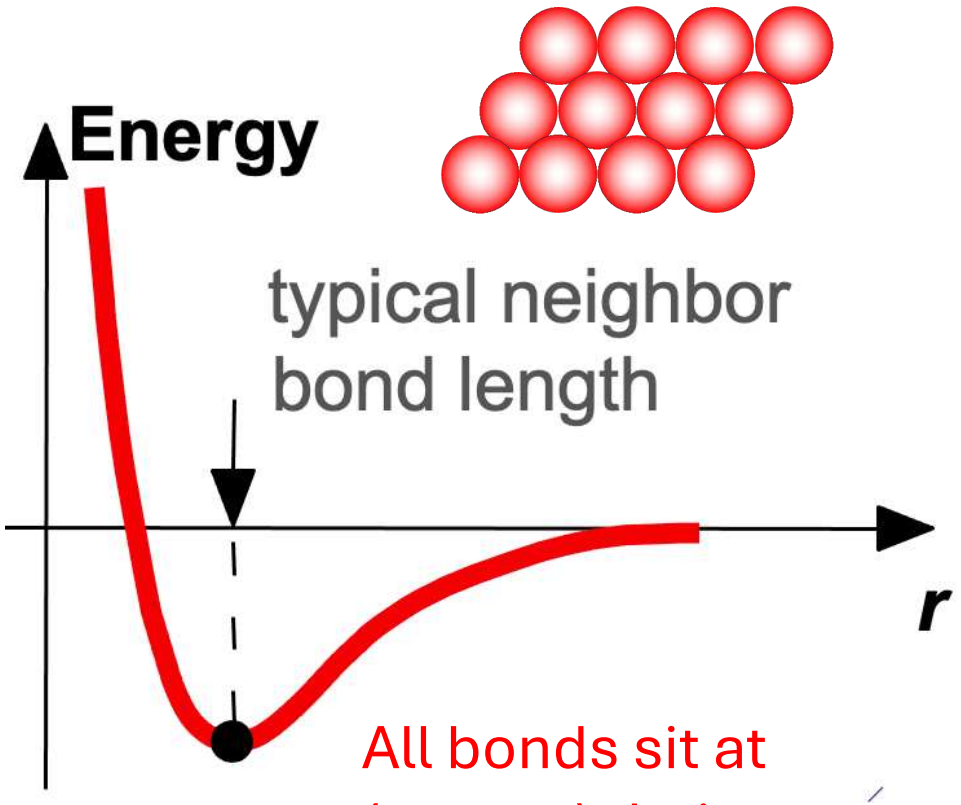
Notice the nice ***periodicity*** of this arrangement – we've unknowingly formed a ***crystal***

Is this how materials form in reality?



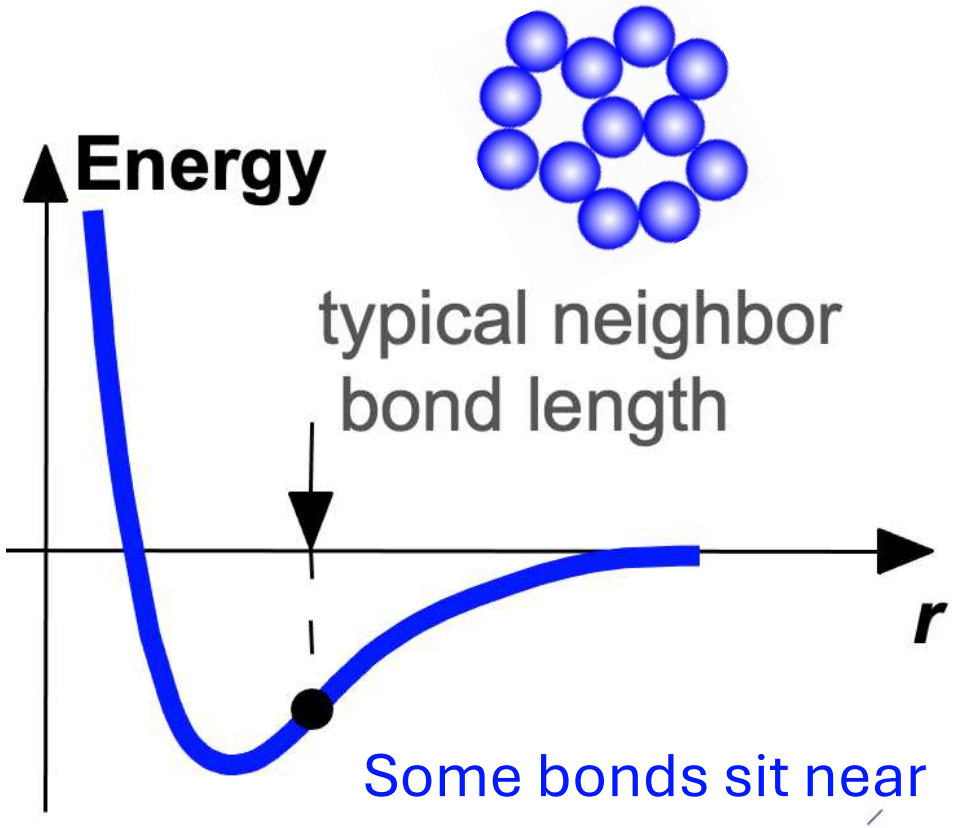
Crystals provide a low-energy arrangement

Dense, ordered packing in a periodic (**crystalline**) structure



All bonds sit at (or near) their energy minimum

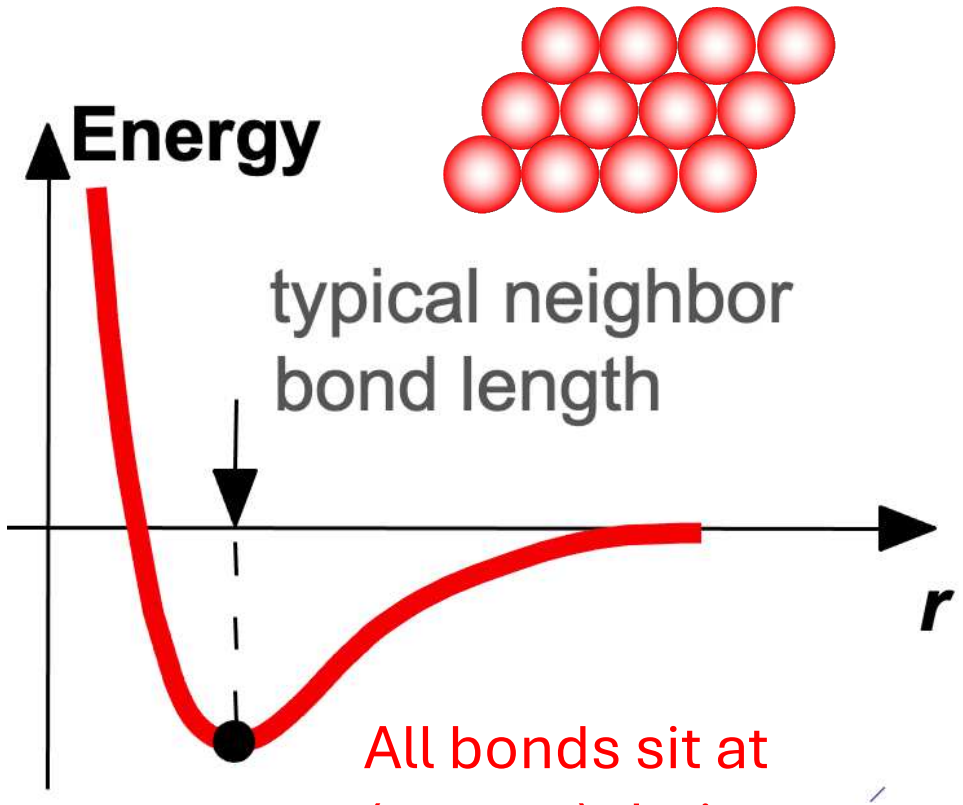
Loose, random packing in an ***amorphous*** structure



Some bonds sit near their energy minimum, but many *do not*

Crystals provide a low-energy arrangement

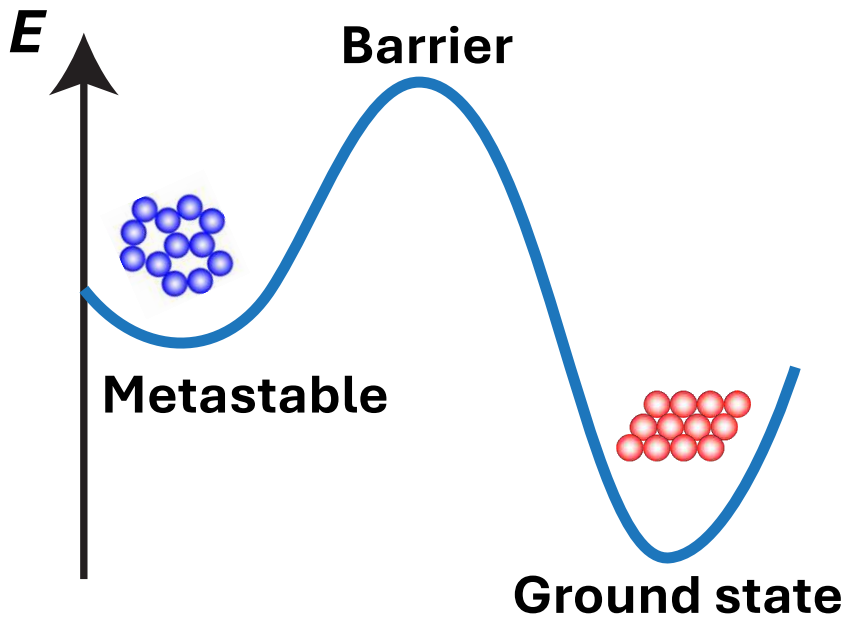
Dense, ordered packing in a periodic (**crystalline**) structure



All bonds sit at (or near) their energy minimum

Atoms *always* prefer to form a regular arrangement at low temperature…

If they have sufficient time and energy to get there

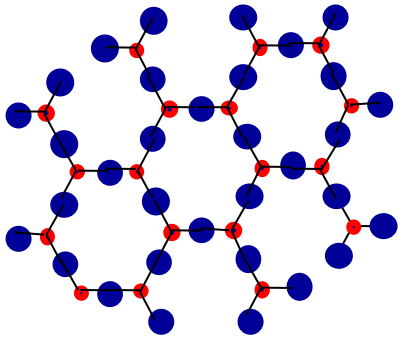


Materials fall into one of two categories

Crystalline materials

- Atoms arranged in periodic 3D arrays composed of repeating unit cells
- Typical for **metals** and most **ceramics**, some **polymers**

Here, the unit cell is a hexagon



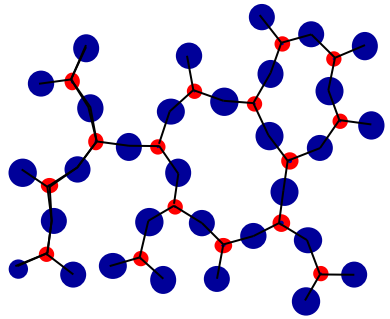
Si

Oxygen

Crystalline SiO_2

Non-crystalline (amorphous) materials

- Atoms have no periodic arrangement or long-range order
- Locally, they may have some preferred arrangement (short-range order)
- More rare: some ceramics & polymers



No unit cell

Noncrystalline SiO_2

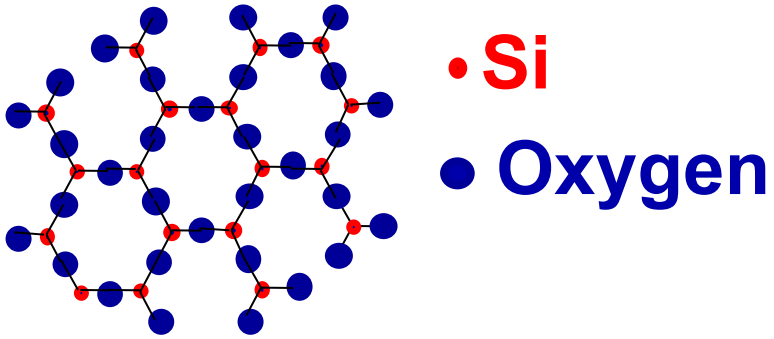
Materials fall into one of two categories

Crystalline materials

- Atoms arranged in periodic 3D arrays composed of repeating unit cells
- Typical for **metals** and most **ceramics**, some **polymers**

For now, we'll focus on crystalline materials given they are much more prevalent

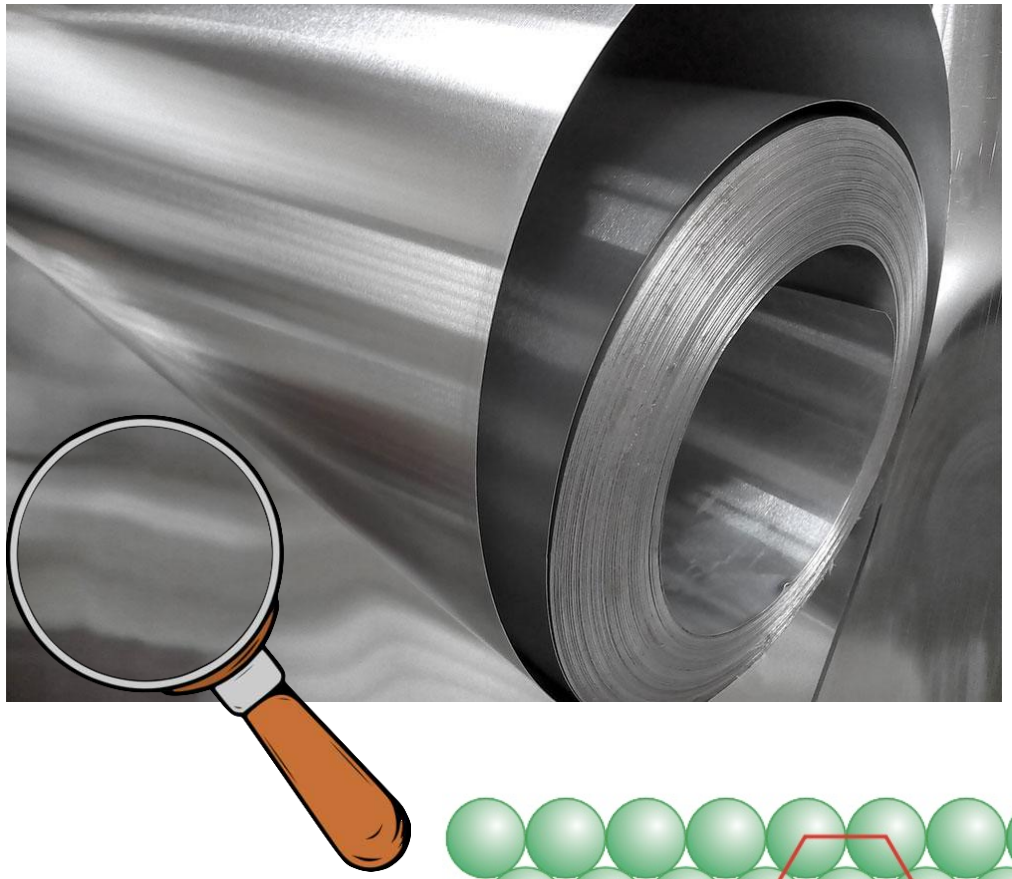
Here, the unit cell is a hexagon

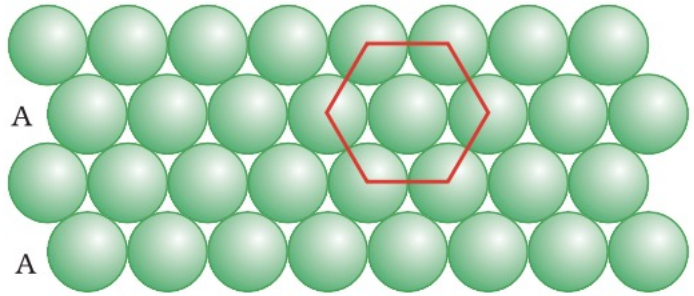


Crystalline SiO_2

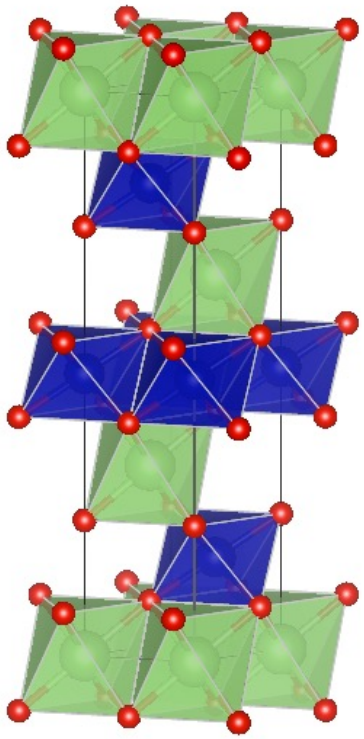
“Crystals”

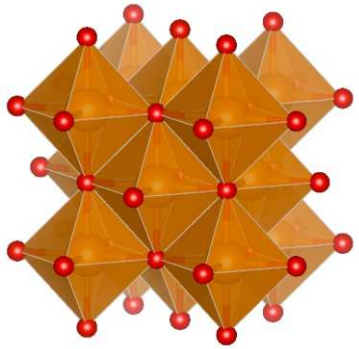


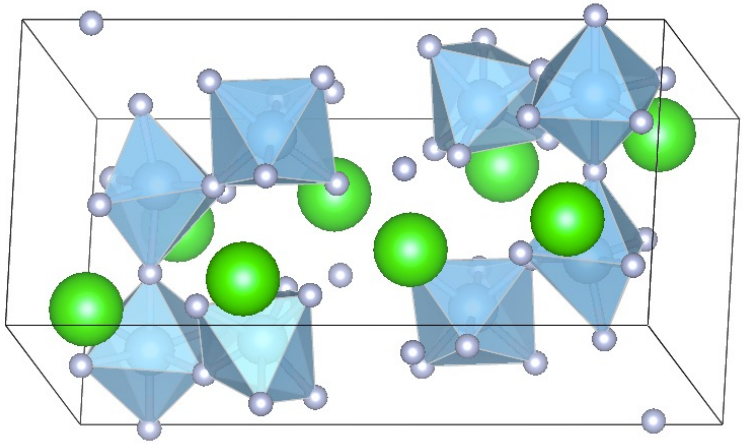


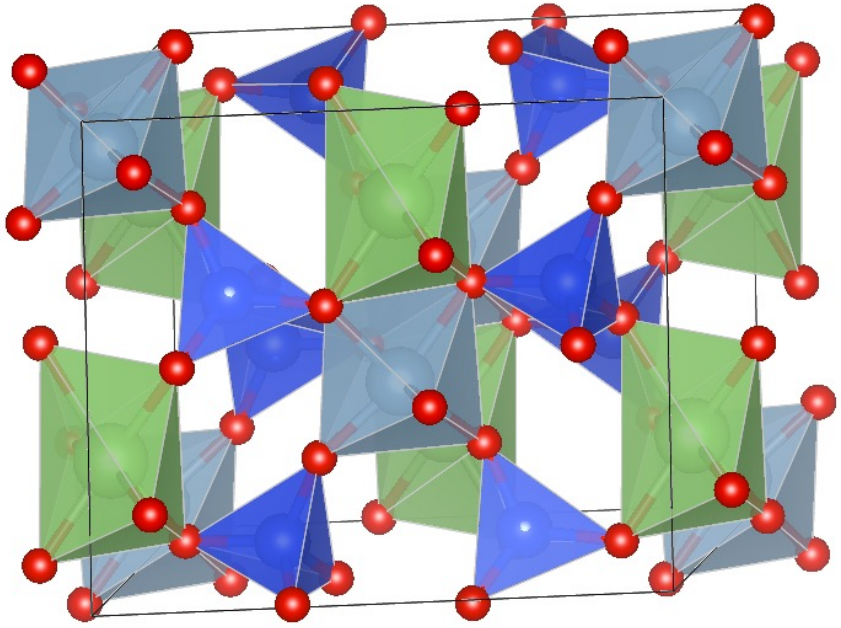


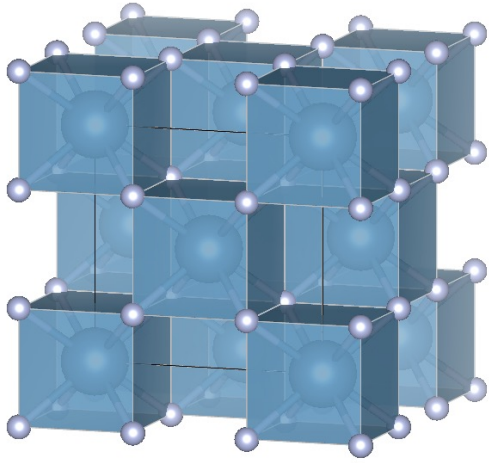
There are *many* arrangements that can be formed



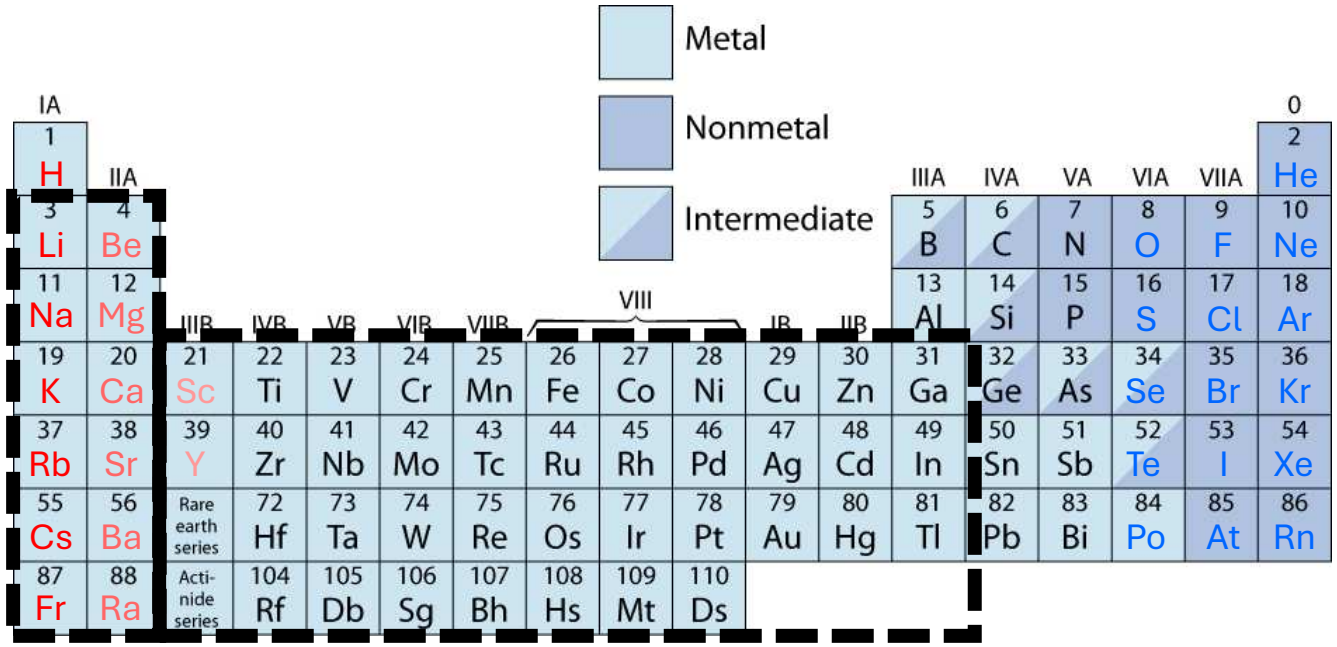








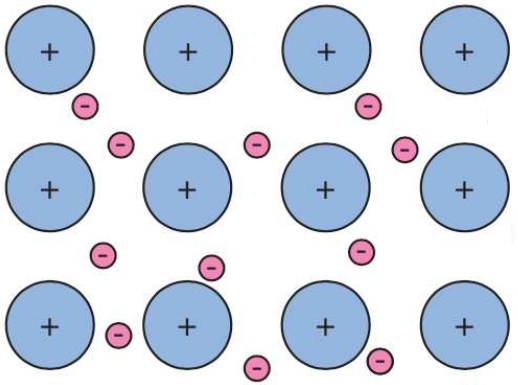
Let’s start simple: metals with a single element



Metals:

Na, Mg, Fe, Co, Ni, …

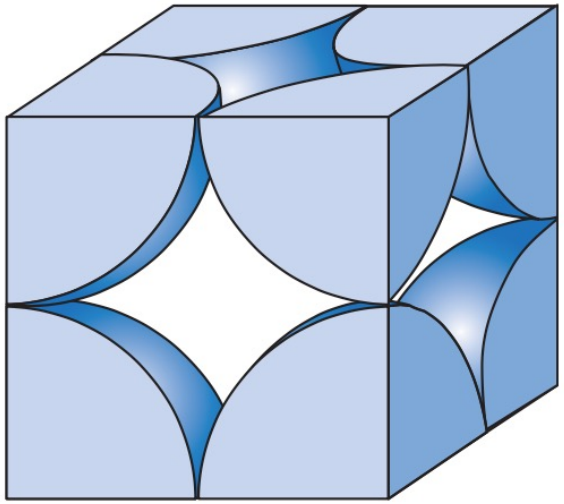
What does their atomic structure look like?

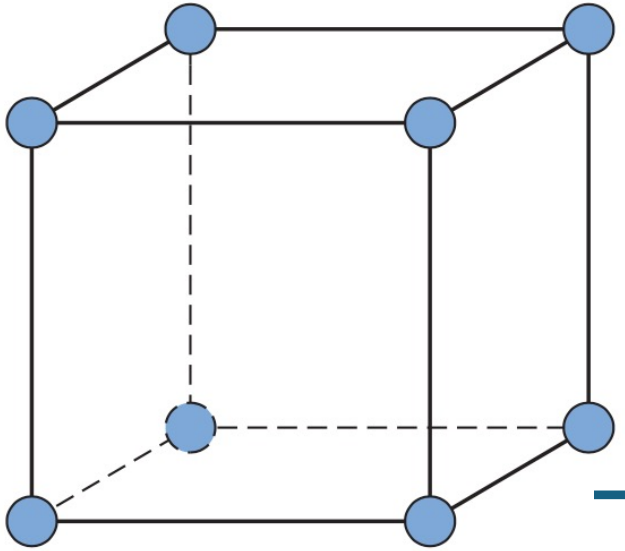


Recall: metals contains positively charged ion cores in a negatively charged electron sea

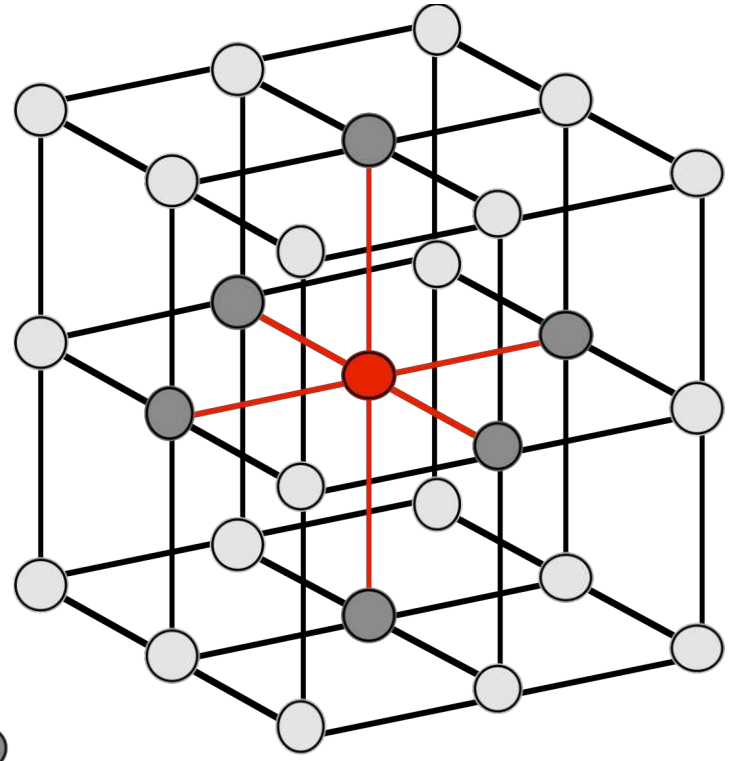
- This bonding is highly **non-directional** (think of **spheres**)
- Energy is lowest when atoms are **packed densely**

One possible arrangement: Simple Cubic (SC)

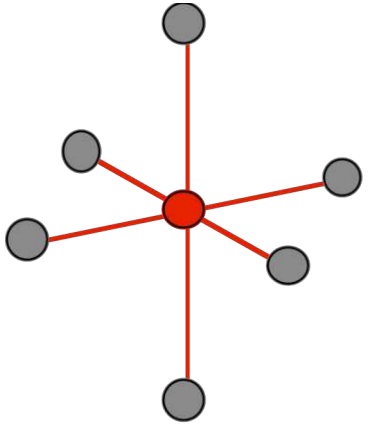




Take this cubic cell and repeat in all three dimensions



Centers of atoms are located at the eight corners of a cube



Coordination number of 6

Some quick definitions

Coordination Number: the number of nearest neighbors, or the number of "touching atoms" in the hard sphere model

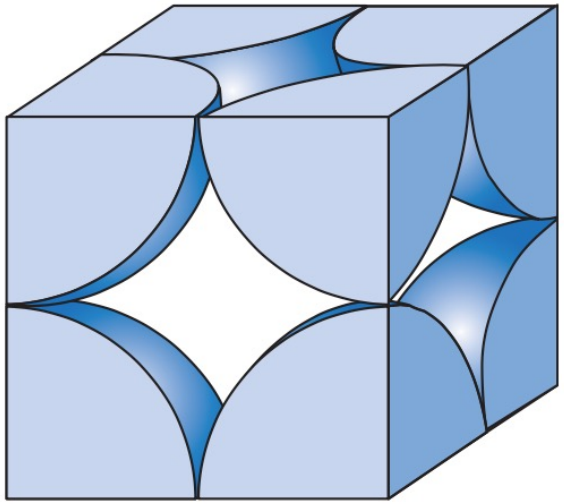
Atomic packing factor: measures how dense a structure is, or more precisely, what fraction of space is filled by atoms

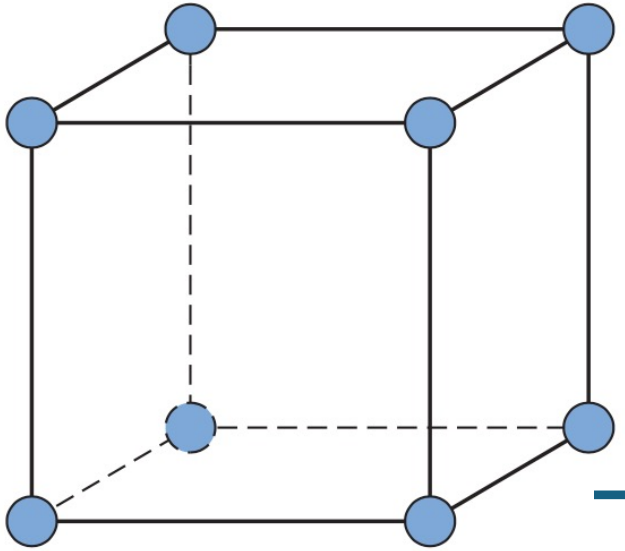
$$\text{APF} = \frac{\text{Volume of atoms in unit cell*}}{\text{Volume of unit cell}}$$

*assume hard spheres

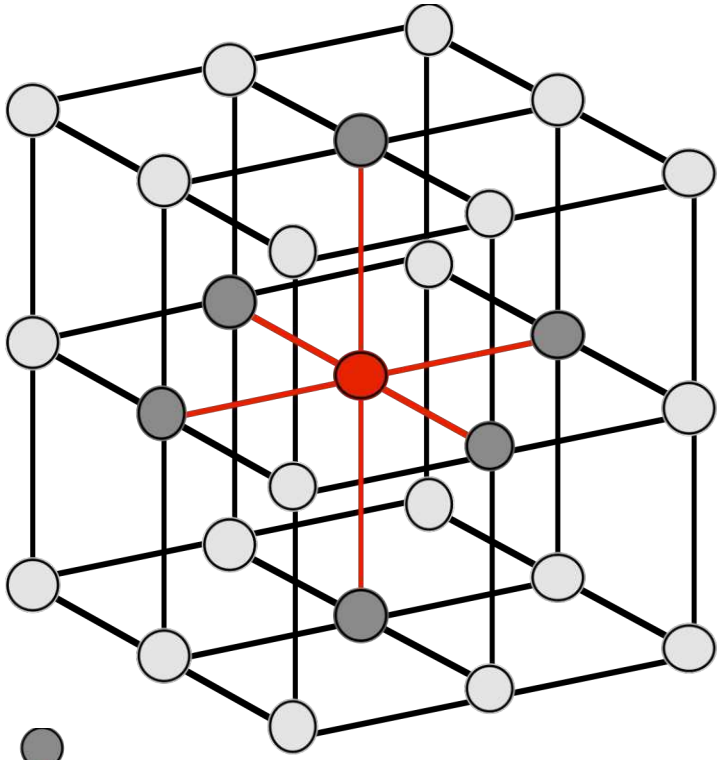


One possible arrangement: Simple Cubic (SC)



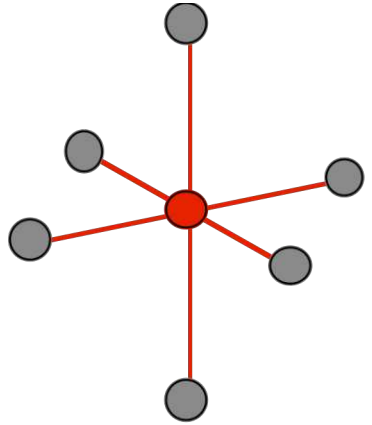


Take this cubic cell and repeat in all three dimensions



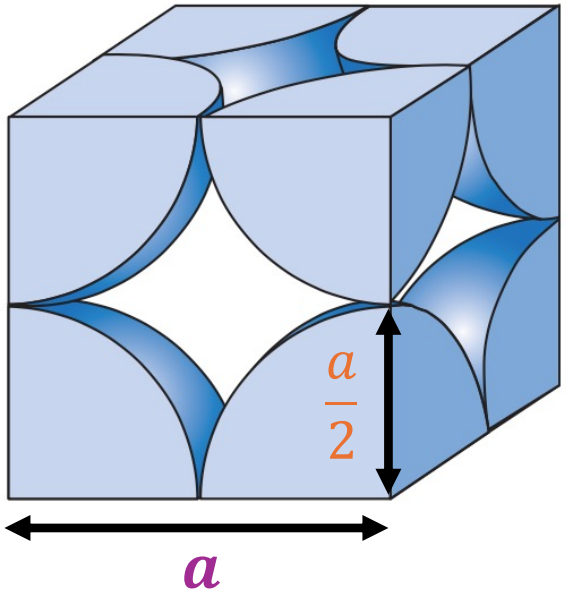
Centers of atoms are located at the eight corners of a cube

Notice the gap in the middle of the cube. This structure is **not very dense**, and is therefore **rare** (*e.g.*, Po)



Coordination number of 6

Simple Cubic (SC) Atomic Packing Factor (APF)



lattice constant

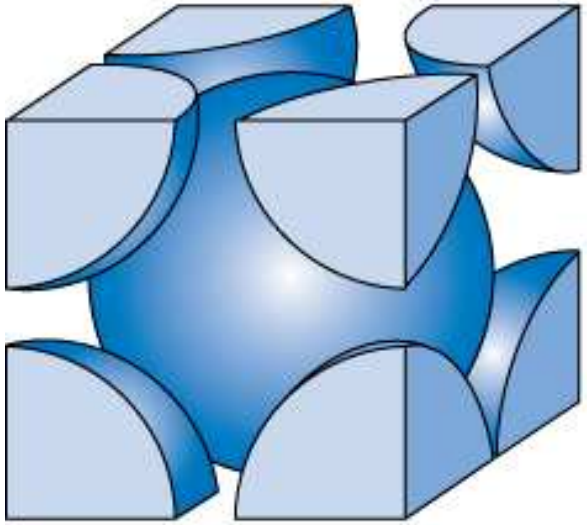
Radius of atoms: $r = a/2$

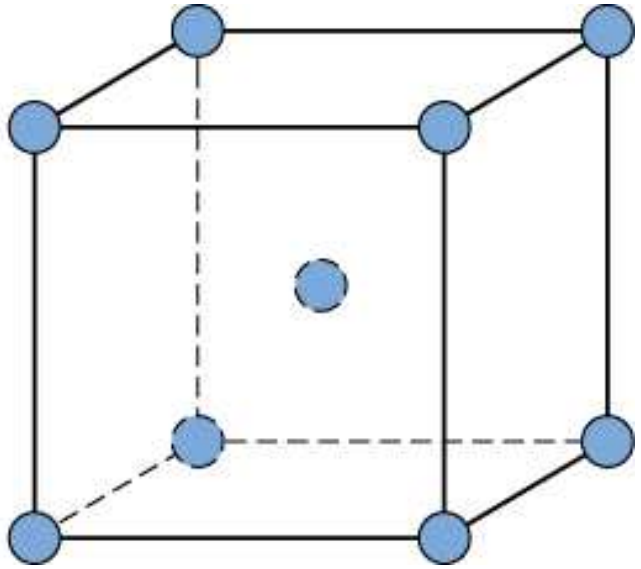
$$\text{APF} = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}}$$

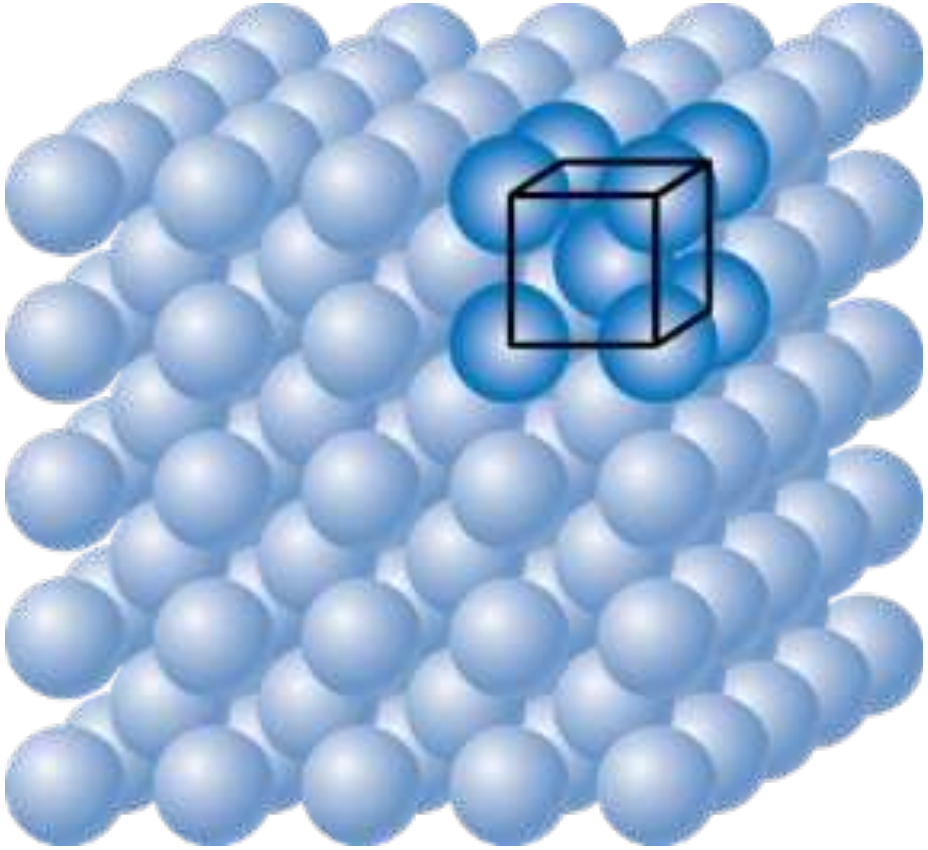
$$\text{APF} = \frac{\overbrace{(8 \text{ atoms})}^{\text{Corners per cube}} \times \overbrace{\left(\frac{4}{3}\pi\left(\frac{a}{2}\right)^3\right)}^{\text{Sphere volume}} \times \overbrace{(1/8)}^{\text{Only 1/8 of each sphere is in the cube}}}{\underbrace{a^3}_{\text{Cube volume}}}$$

APF ≈ 0.52 Not very dense! We can do better...

Fill in the center: Body-Centered Cubic (BCC)







Centers of atoms are located at the **eight corners** of a cube ***and*** **at the "body" center of the cube**

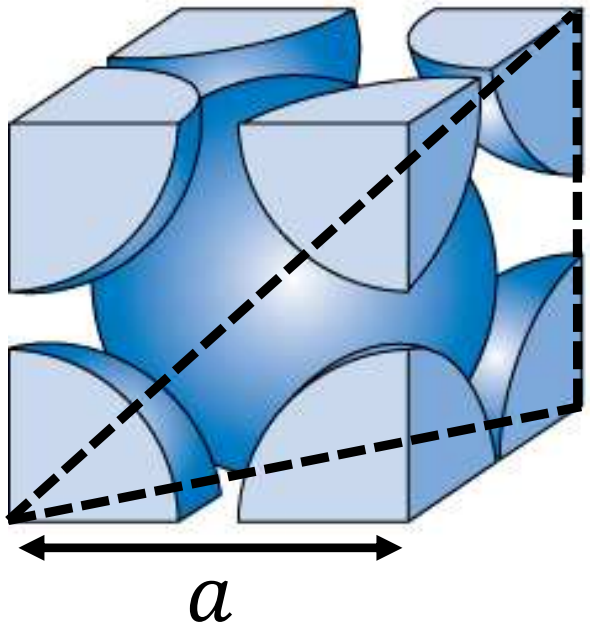
This structure is clearly denser* and also quite common:

Fe, Cr, W, Mo, Ta

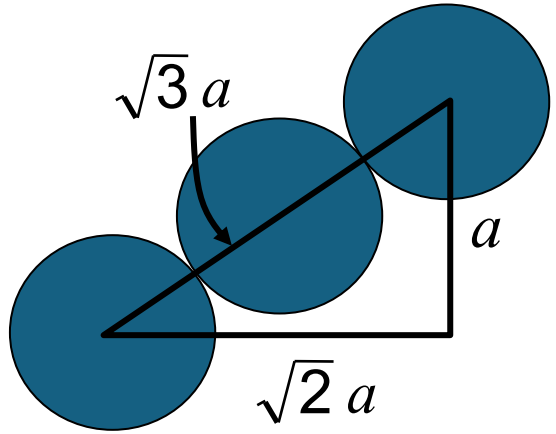
*by how much?

Coordination number = 8

Body-Centered Cubic (BCC) atomic packing factor



The **close-packed direction** (where spheres are touching) is from corner-to-corner through the body center

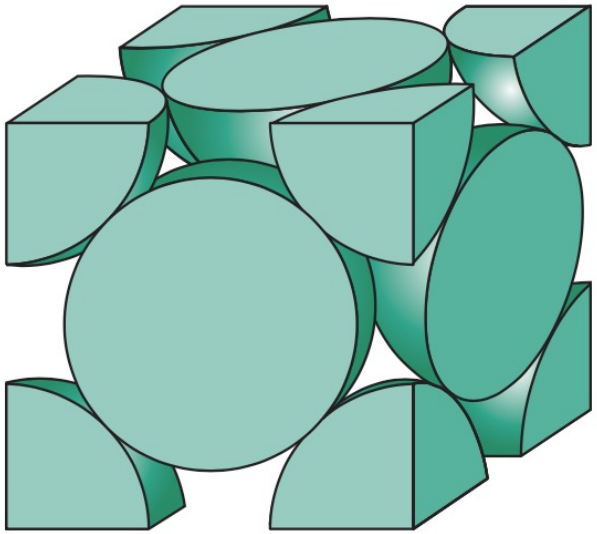


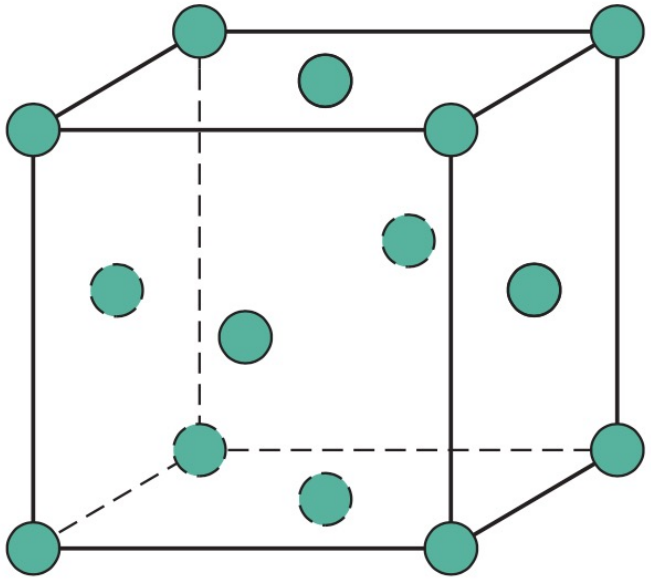
$$r = \frac{a\sqrt{3}}{4}$$

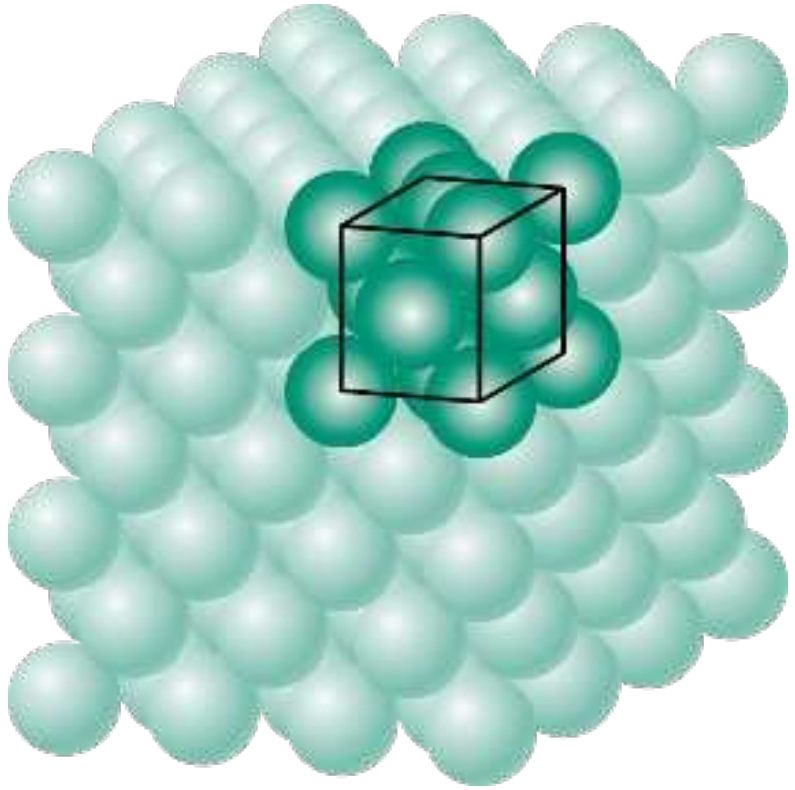
$$\text{APF} = \frac{\text{Volume of atoms}}{\text{Volume of cell}} = \frac{\overbrace{\left(8\frac{1}{8}+1\right)}^{\text{Spheres in cell}} \times \overbrace{\left(\frac{4}{3}\pi\left(\frac{a\sqrt{3}}{4}\right)^{3}\right)}^{\text{Sphere volume}}}{\underbrace{a^{3}}_{\text{Cube volume}}} \approx 0.68$$

Better! Can we get even denser?

The densest structure: Face-Centered Cubic (FCC)







Centers of atoms are located at the **eight corners** of a cube ***and*** **at the "face" centers of the cube**

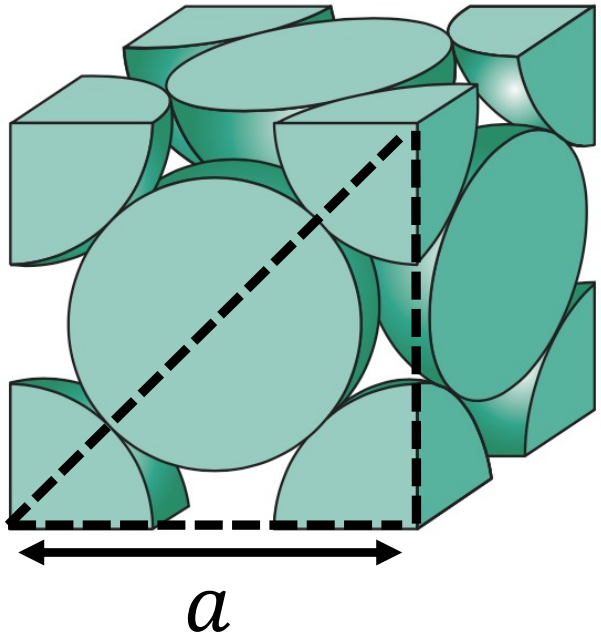
This structure is ***closed-packed***, meaning it is the densest arrangement possible.

Coordination number = 12

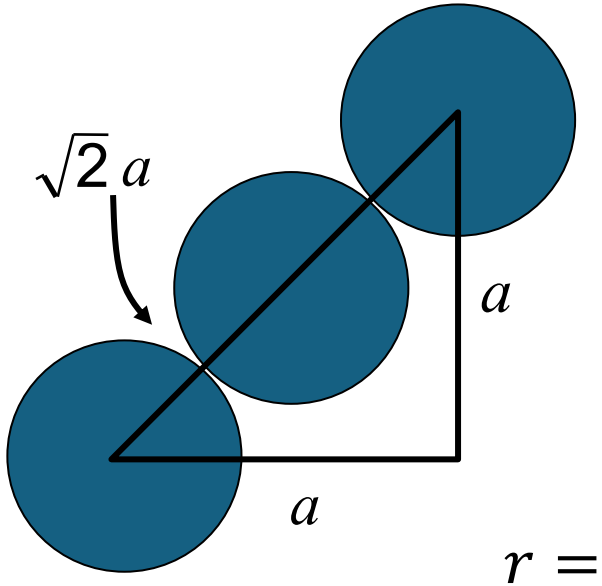
Most common structure for metals: Al, Cu, Au, Pb, Ni, Pt, Ag, …

DEMO

Face-Centered Cubic (FCC) atomic packing factor



The **close-packed direction** (where spheres are touching) is from corner-to-corner through the *face* center

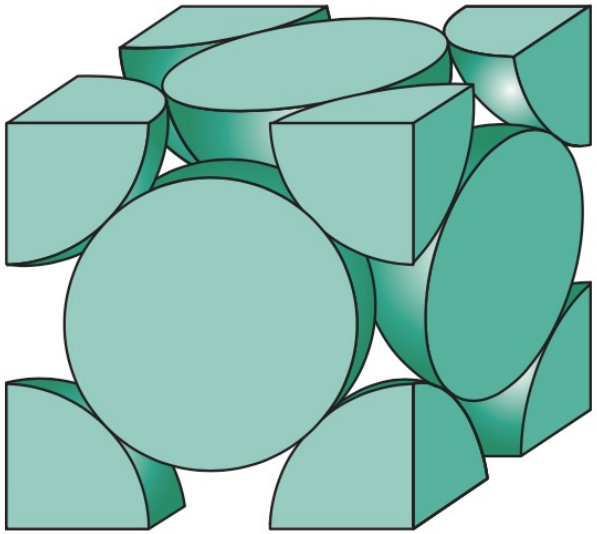


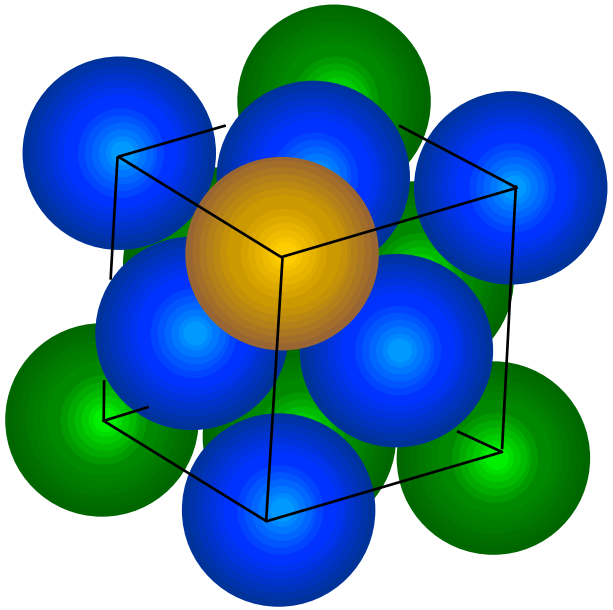
$$r = \frac{a\sqrt{2}}{4}$$

$$\text{APF} = \frac{\text{Volume of atoms}}{\text{Volume of cell}} = \frac{\overbrace{\left(8\frac{1}{8} + 6\frac{1}{2}\right)}^{\text{Spheres in cell}} \times \overbrace{\left(\frac{4}{3}\pi\left(\frac{a\sqrt{2}}{4}\right)^3\right)}^{\text{Sphere volume}}}{\underbrace{a^3}_{\text{Cube volume}}} \approx \mathbf{0.74}$$

Max possible APF

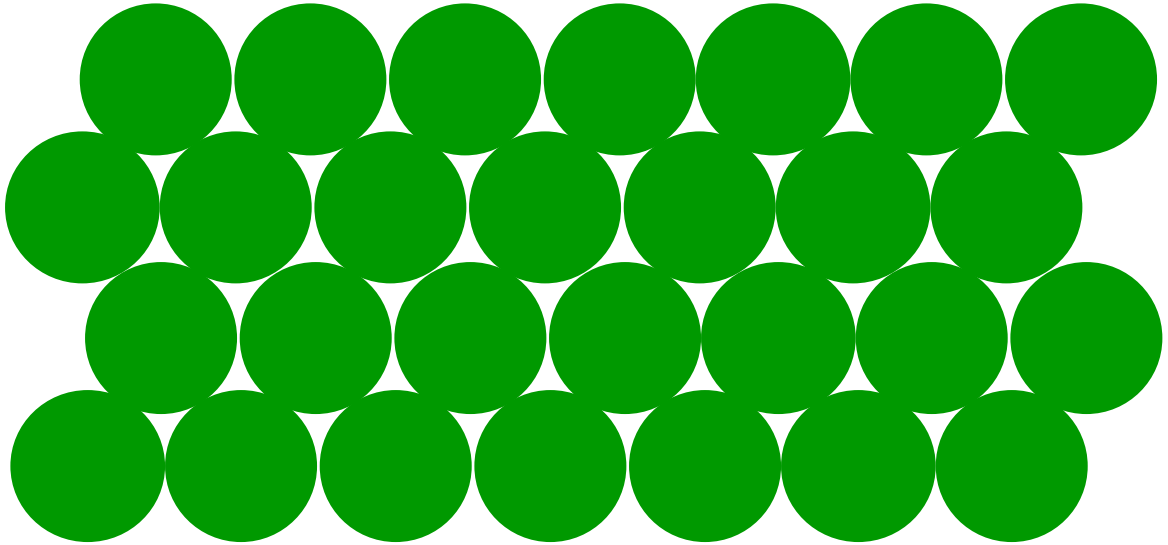
Stacking sequence in the FCC structure



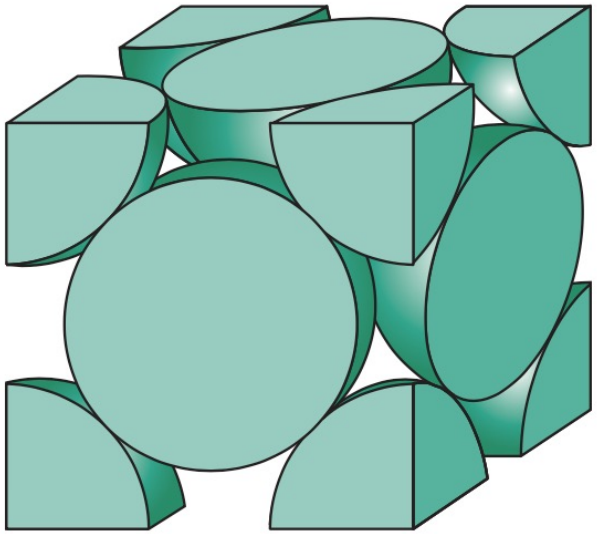


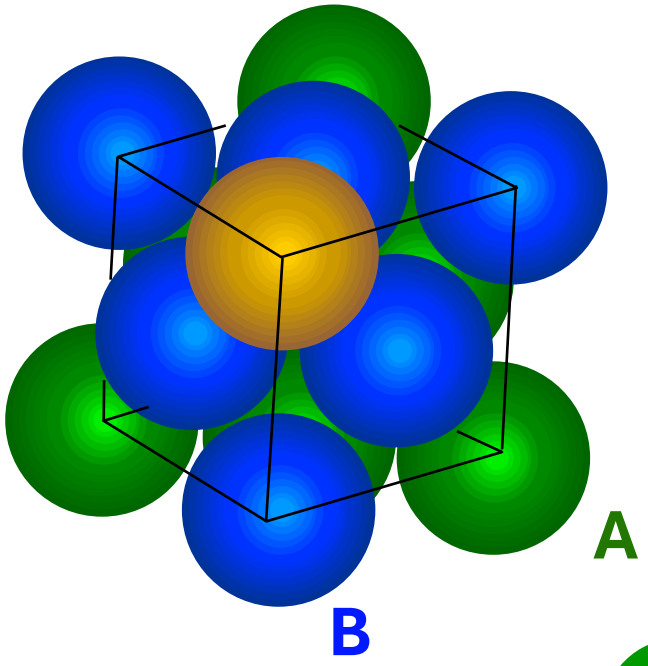
You can think of the FCC structure as a series of close packed planes

This is the densest arrangement of spheres in 2D – so how do we stack these planes in 3D to achieve max volume density?



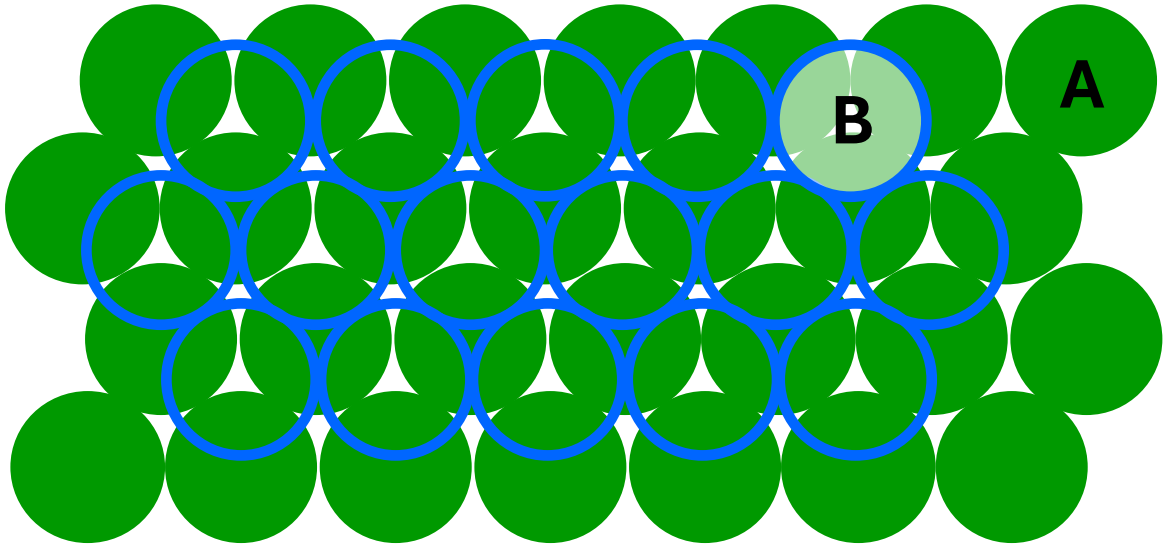
Stacking sequence in the FCC structure



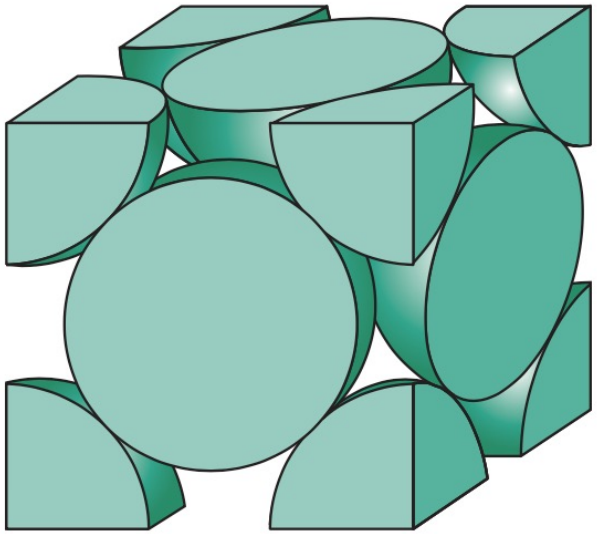


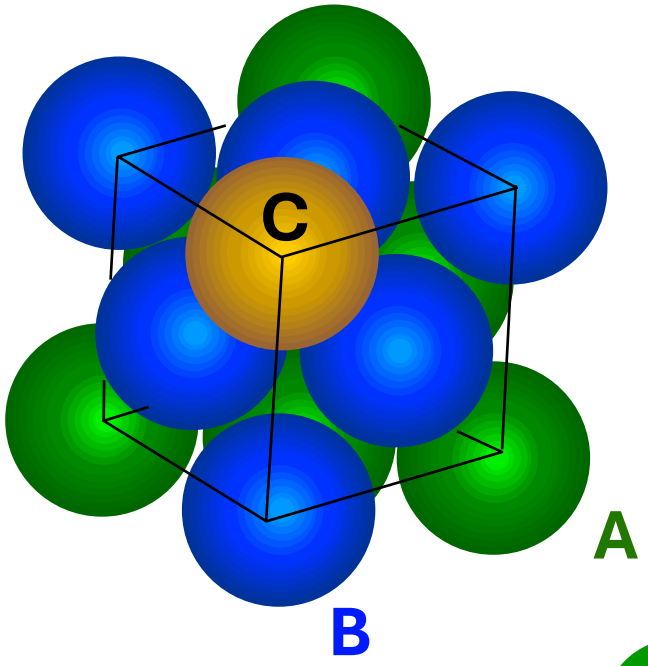
You can think of the FCC structure as a series of close packed planes

This is the densest arrangement of spheres in 2D – so how do we stack these planes in 3D to achieve max volume density?



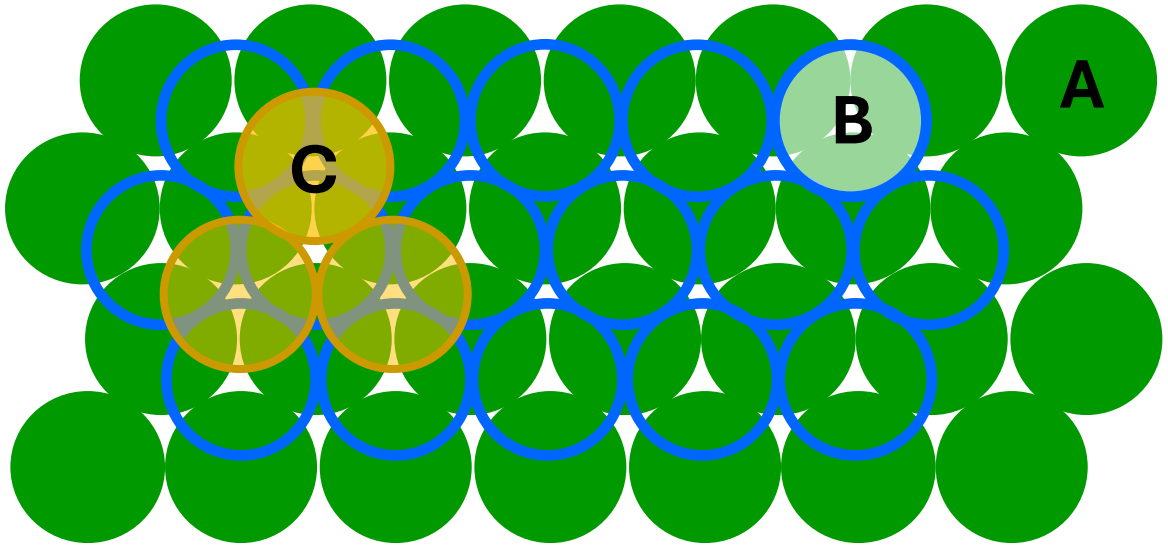
Stacking sequence in the FCC structure





You can think of the FCC structure as a series of close packed planes

This is the densest arrangement of spheres in 2D – so how do we stack these planes in 3D to achieve max volume density?

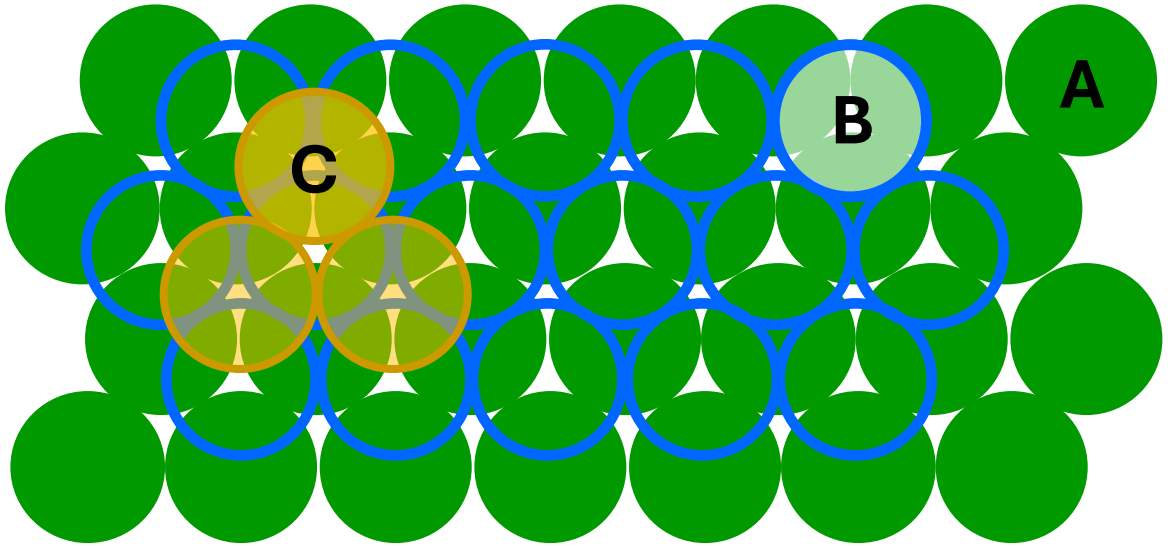


Stacking sequence in the FCC structure

Then it repeats! Again and again…FCC has a stacking sequence:

ABC**ABC**ABC…

Notice that **atoms in the A and C layers do *not* overlap…**



Stacking sequence in the FCC structure

Then it repeats! Again and again…FCC has a stacking sequence:

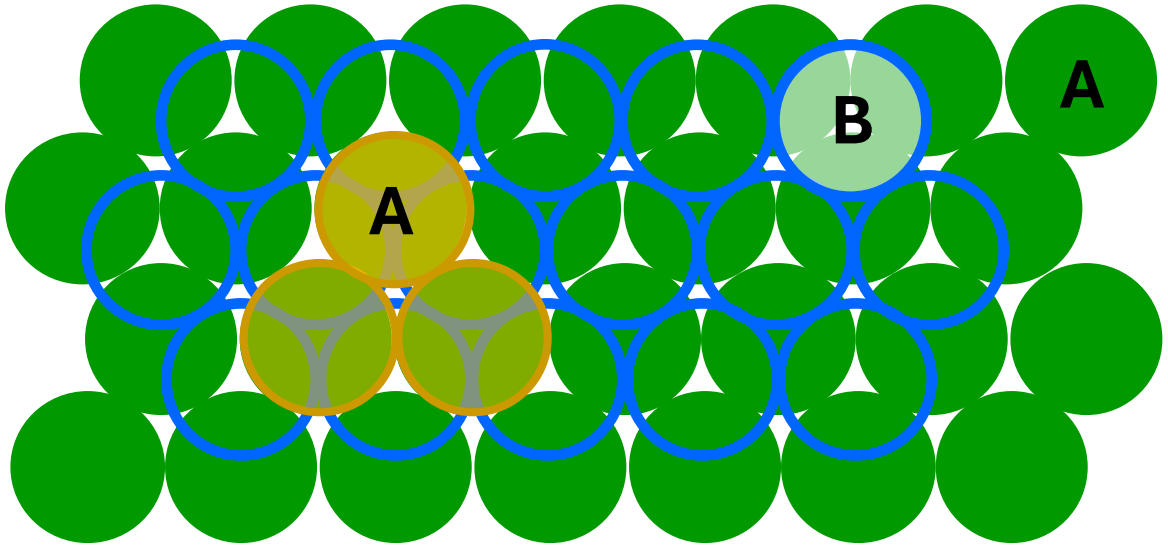
ABC**ABC**ABC…

Notice that **atoms in the A and C layers do *not* overlap…**
But they could! This would not affect the density (APF)

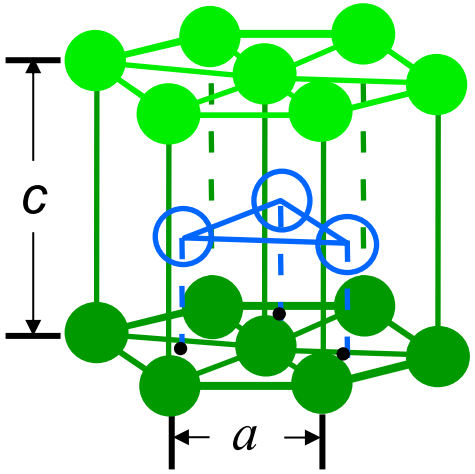
This is a different stacking sequence:

AB**AB**AB…

→ **Hexagonal close packed (HCP)**



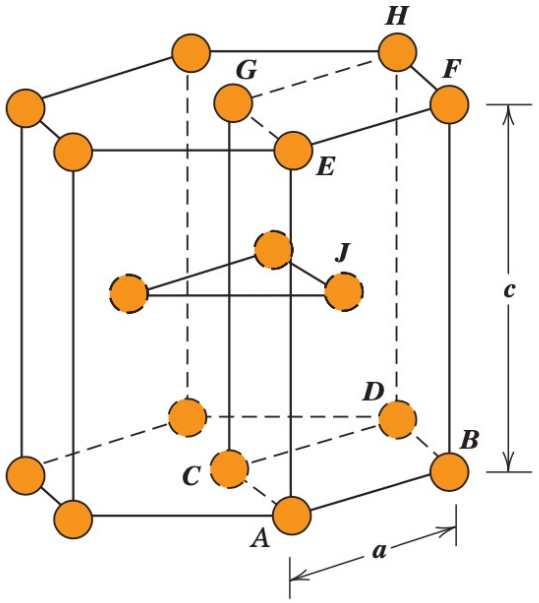
Hexagonal closed packed (HCP) structure

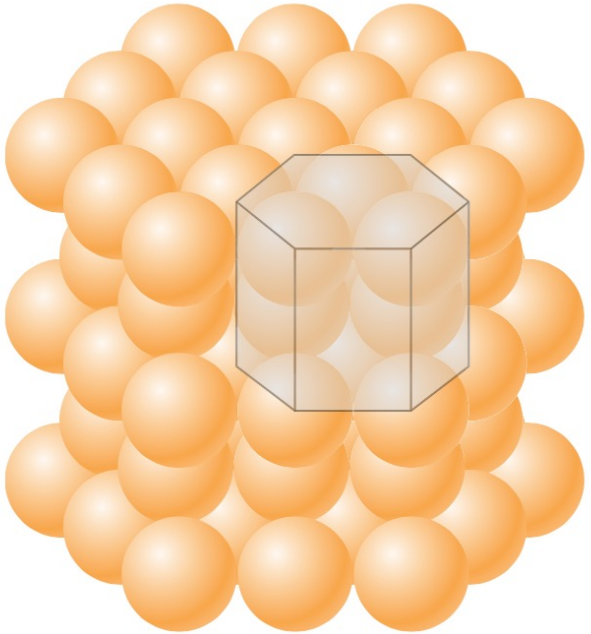


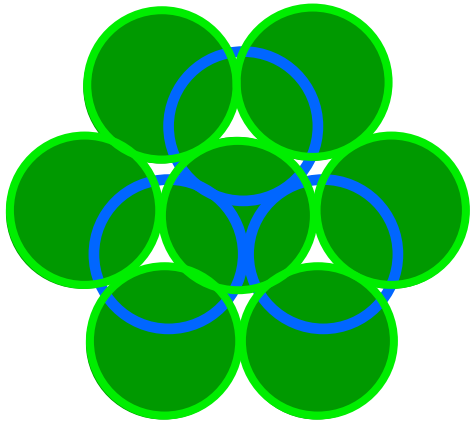
A sites

B sites

A sites







Top layer

Middle layer

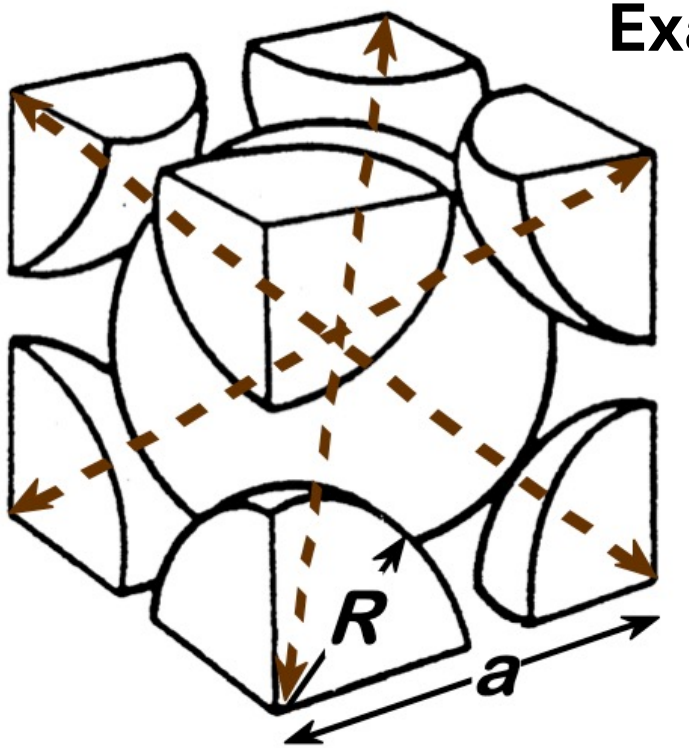
Bottom layer

- Coordination number = 12 (same as FCC)
- APF = 0.74 (same as FCC)
- Differs only in *next* nearest neighbors
- Common structure for metals:
  Mg, Ti, Zn, Cd

Computing (mass) densities of some metals

$$\text{Density } (\rho) = \frac{\text{Mass of atoms in unit cell}}{\text{Volume of the unit cell}} = \frac{nA}{V_C N_a}$$

n = number of atoms/unit cell
A = atomic weight
V_C = Volume of unit cell = a^3 for cubic
N_A = Avogadro's number
= 6.023×10^{23} atoms/mol



Example: Cr (BCC)

A = 52.00 g/mol
R = 0.125 nm
n = 2

$a = 4R/\sqrt{3} = 0.2887$ nm

$$\rho = \frac{\frac{\text{atoms}}{\text{unit cell}} \times \frac{\text{g}}{\text{mol}}}{\frac{\text{volume}}{\text{unit cell}} \times \frac{\text{atoms}}{\text{mol}}} = \frac{2 \times 52.00}{a^3 \times 6.023 \times 10^{23}}$$

$\rho_{theoretical}$	= 7.18 g/cm^3
ρ_{actual}	= 7.19 g/cm^3

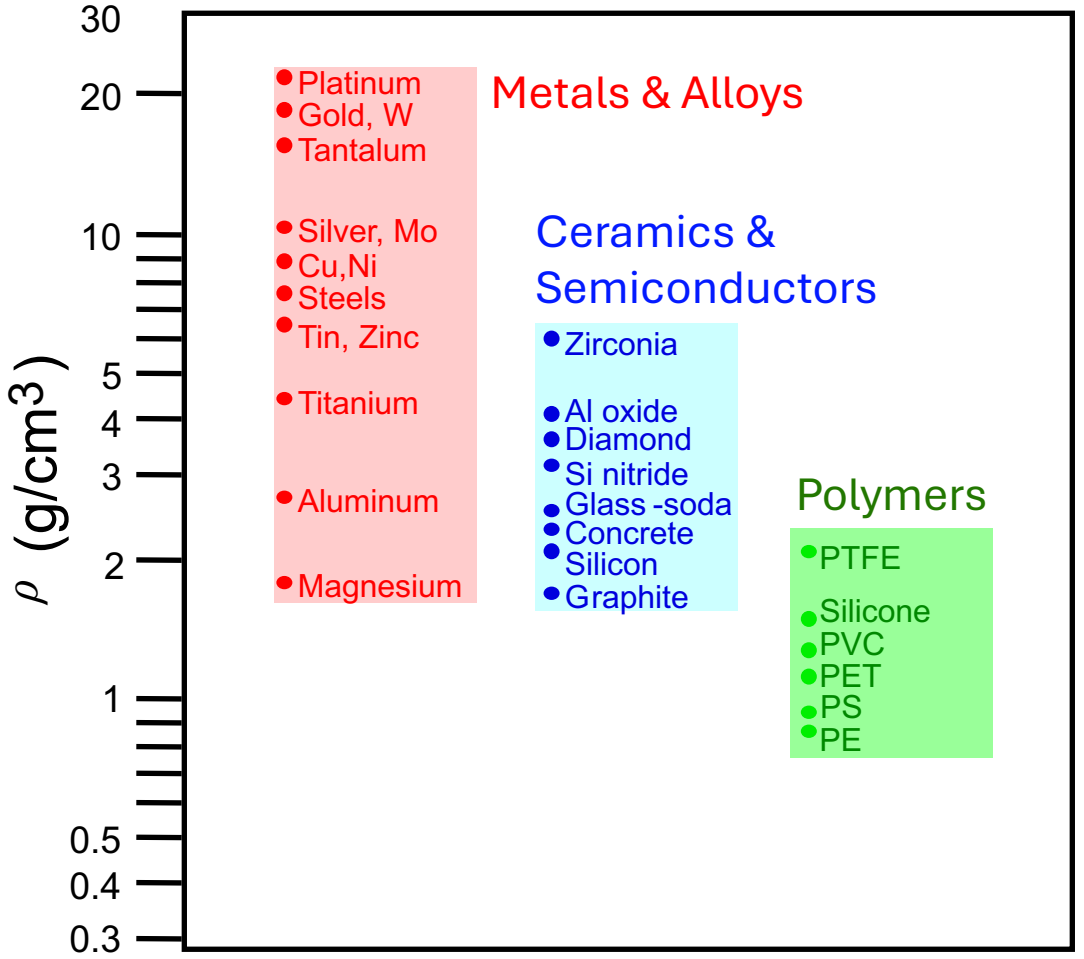
Comparing densities among different materials

In general:

$\rho_{metals} > \rho_{ceramics} > \rho_{polymers}$

Why?

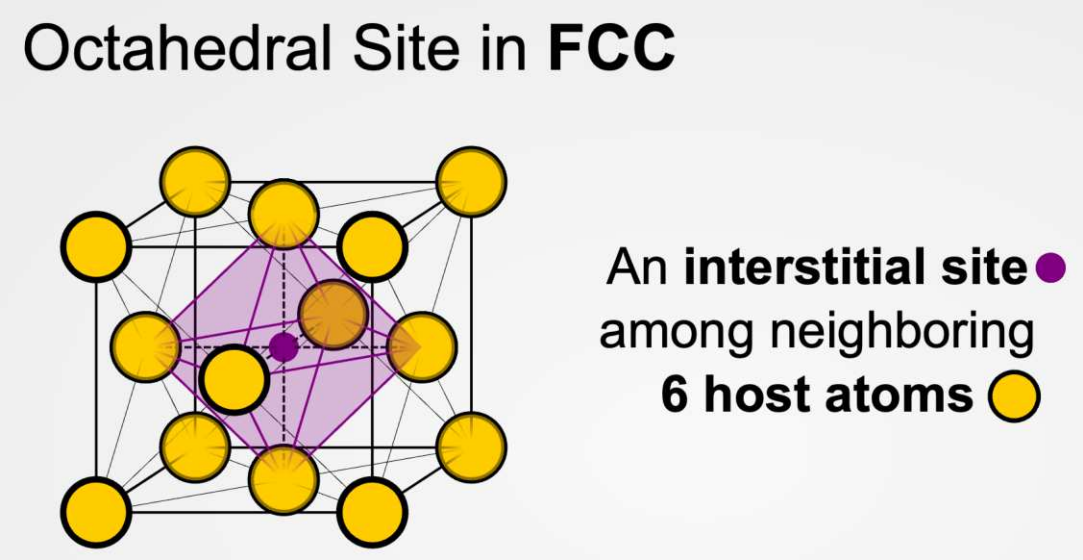
- **Metals** have **close-packed** structures and often contain heavy elements
- **Ceramics** generally adopt "open" structures with much **lower packing densities**
- **Polymers** have low packing densities *and* contain **light elements (C, H, O, …)**



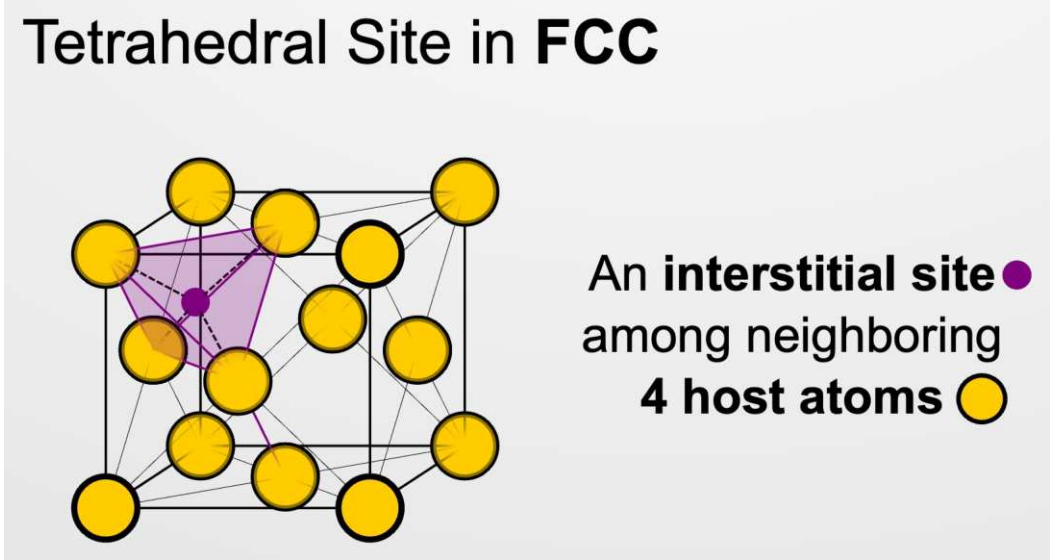
A brief note on the structures of ceramics

These few simple structures (FCC, BCC, HCP) serve as the basis for many others.

Ionic/covalent structures are often viewed a having **close-packed structures (anions)** + new **atoms (cations) place at the interstitial sites (voids)**



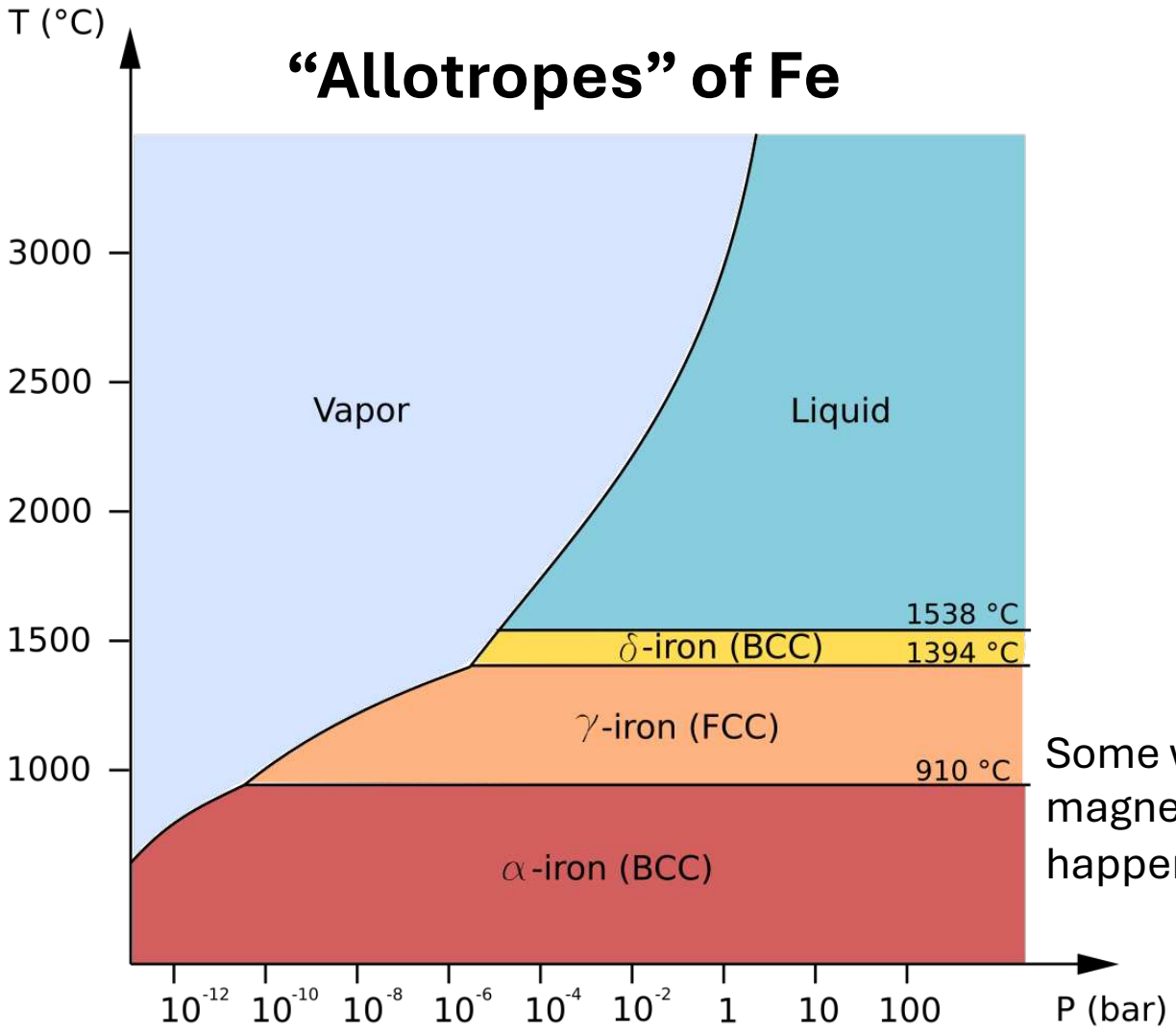
Filling of *octahedral* sites creates the "**rocksalt structure**." Common for ionic materials **(NaCl, MgO, …)**



Filling of ½ *tetrahedral* sites creates the "**zincblende structure**." Common for covalent materials **(GaAs, ZnS, …)**

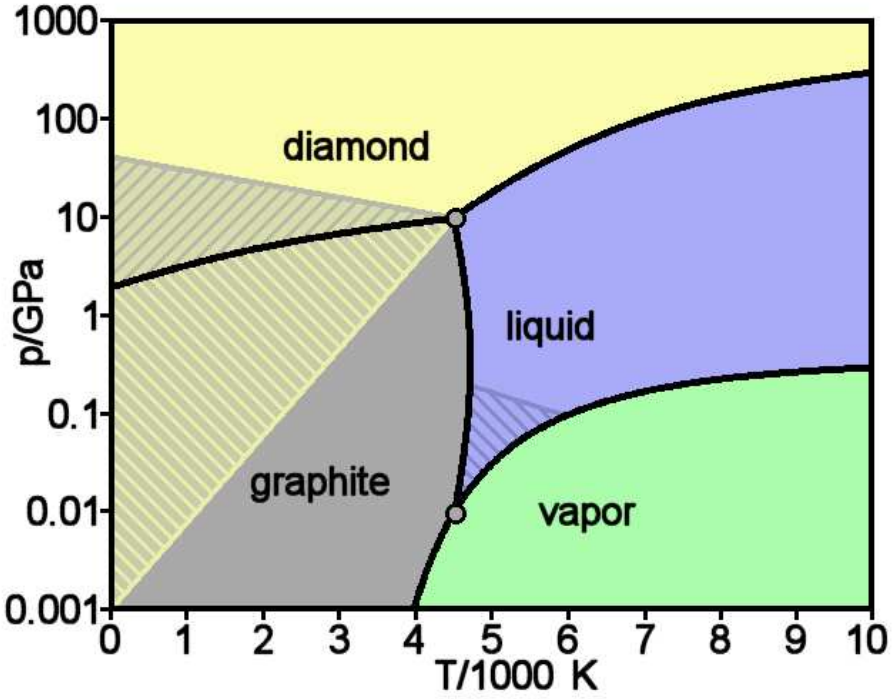
Polymorphism: some compositions adopt > 1 structure

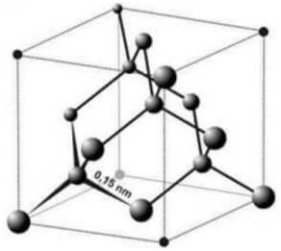
“Allotropes” of Fe

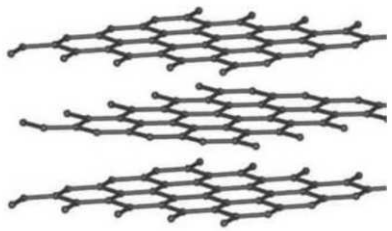


Some weird magnetic stuff happens with Fe

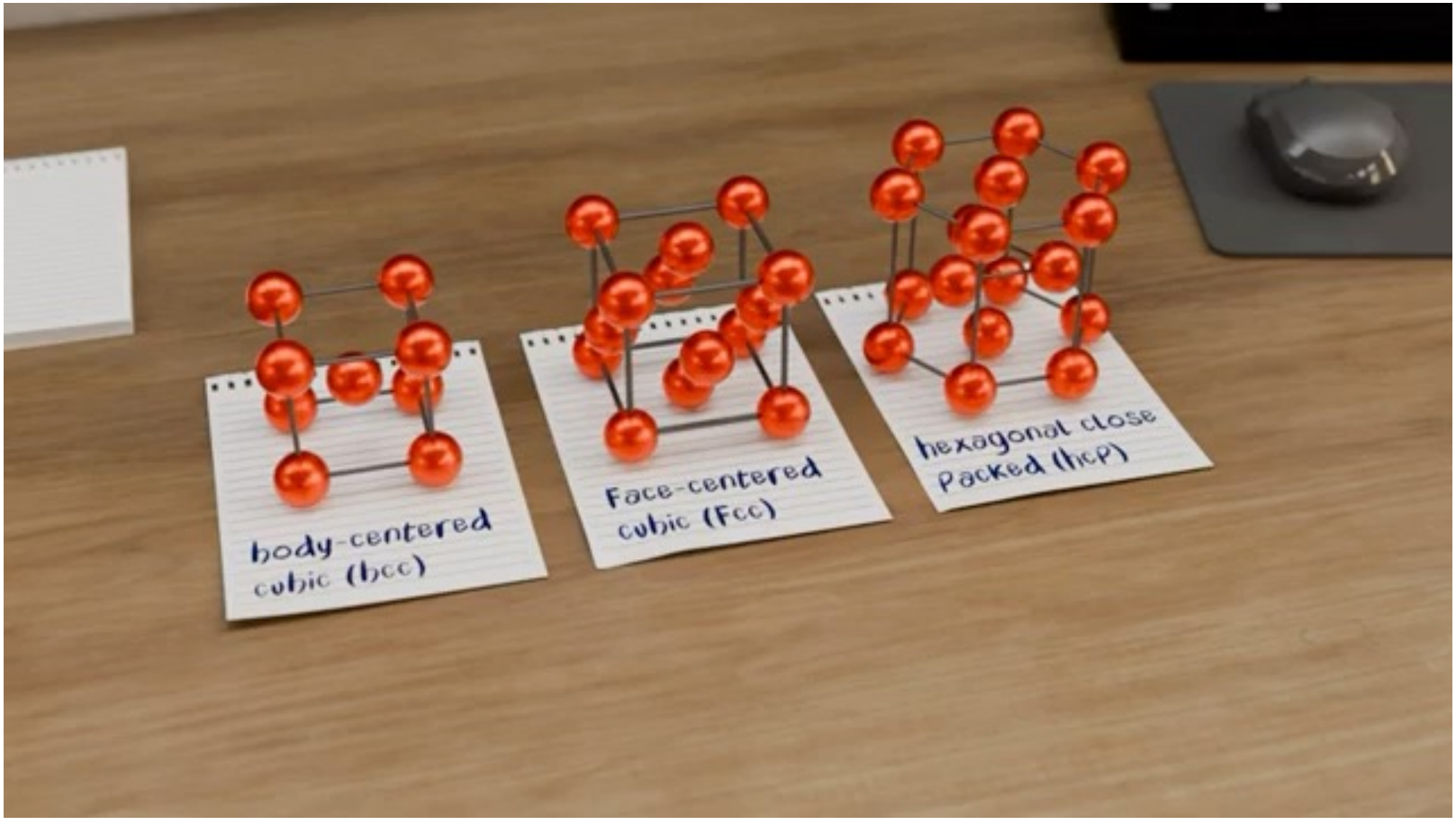
Carbon: diamond vs graphite





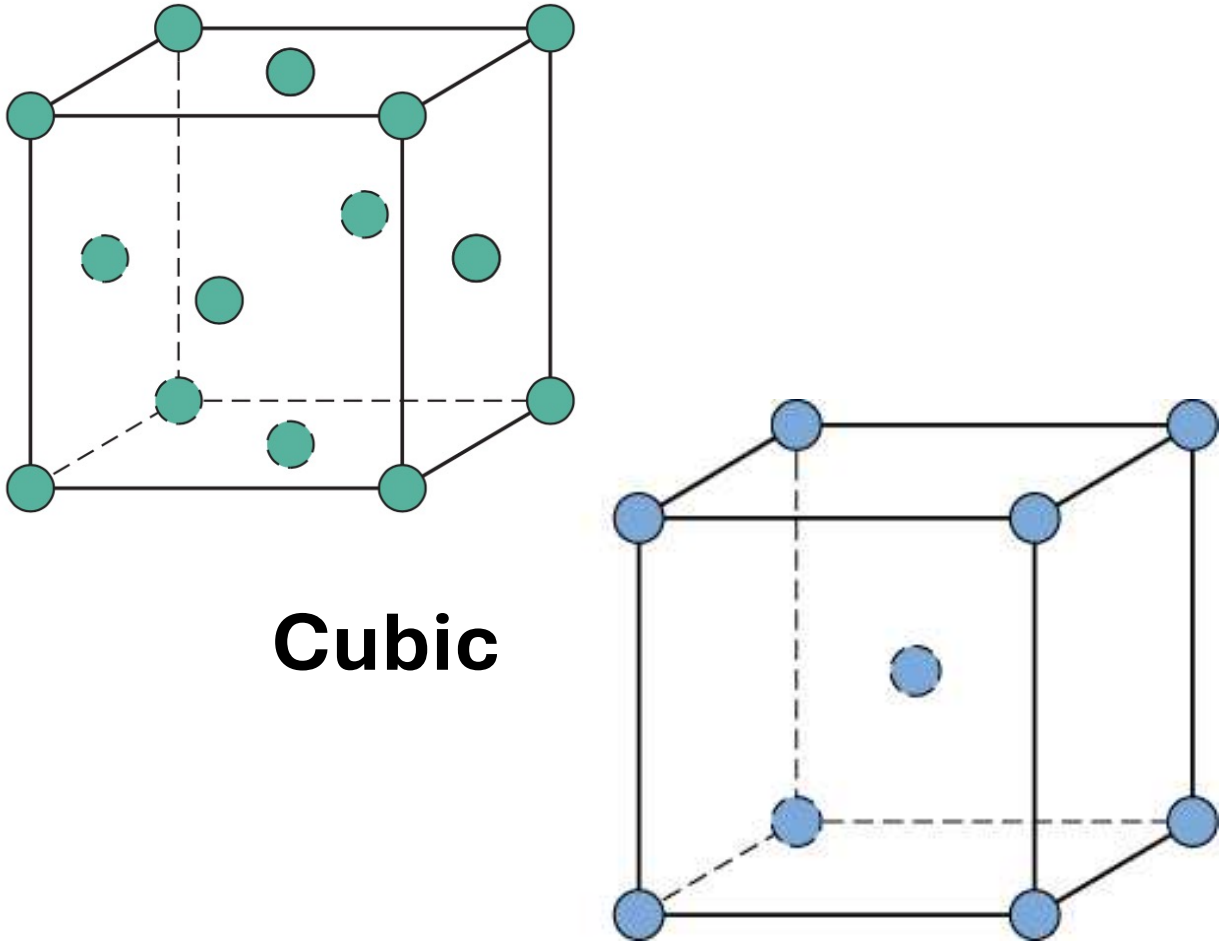


https://www.youtube.com/watch?v=zuu_tcdcje0&t=247s

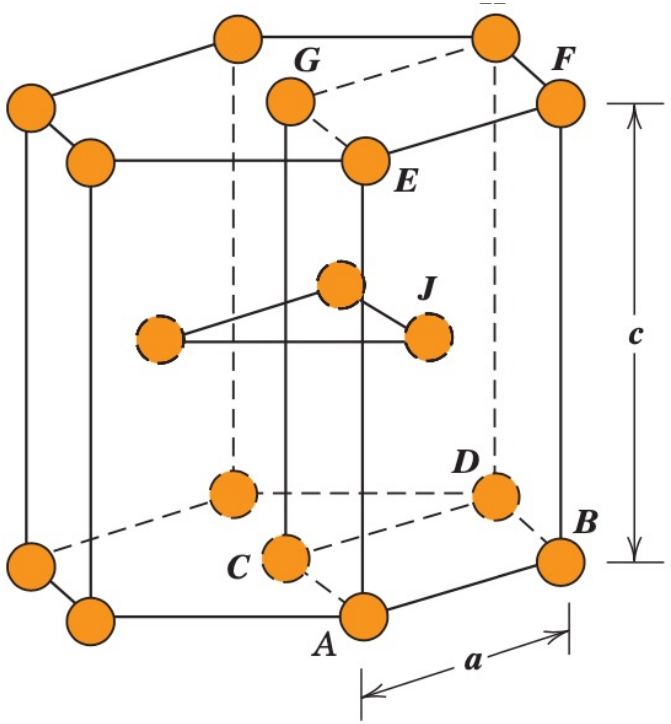


Other types of crystal systems

We have so far discussed two **crystal systems: cubic and hexagonal.** These are defined by their **unit cell shapes**



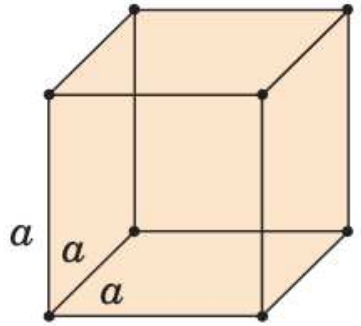
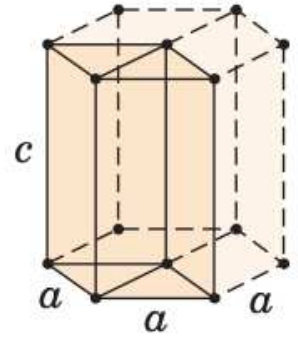
Cubic



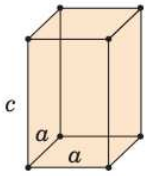
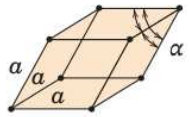
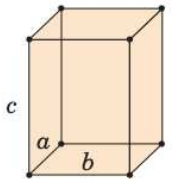
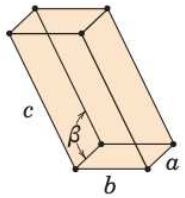
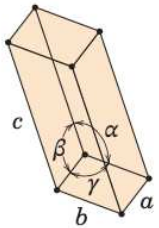
Hexagonal

Other types of crystal systems

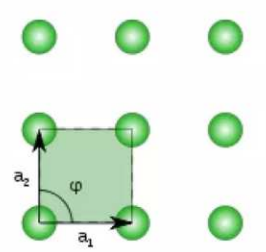
We have so far discussed two **crystal systems: cubic and hexagonal.**
These are defined by their **unit cell shapes → Lattice parameters**

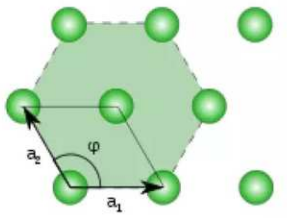
Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	

There are 5 more (7 total) crystal systems

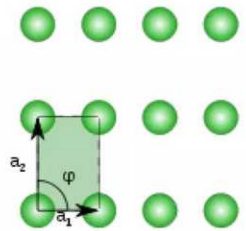
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

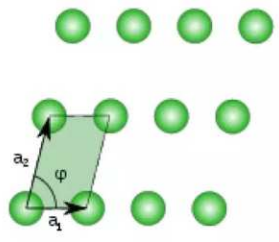
These are the *only* 3D unit cell shapes that can be used to **fill space by translation**





2D examples

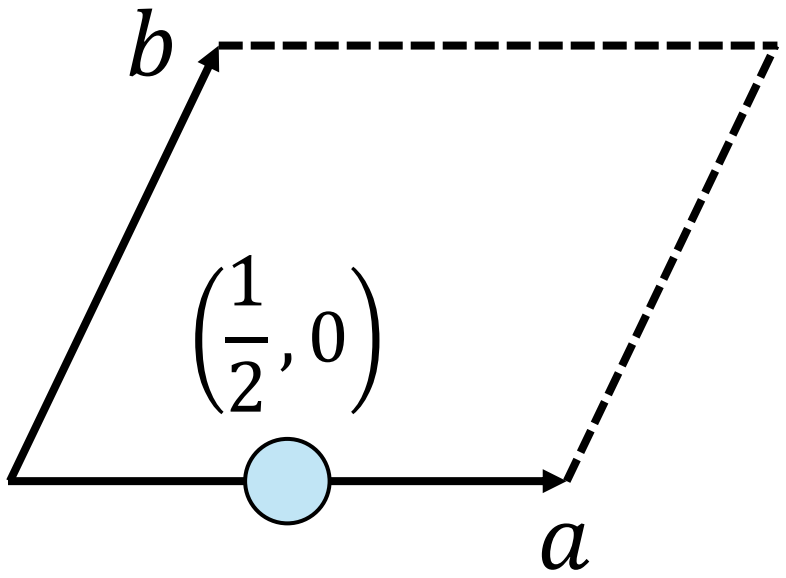




Describing structures: point coordinates

Unit cells are “building blocks” for the crystal structure. Now we will specify the **positions of atoms within those unit cells** using **point coordinates**.

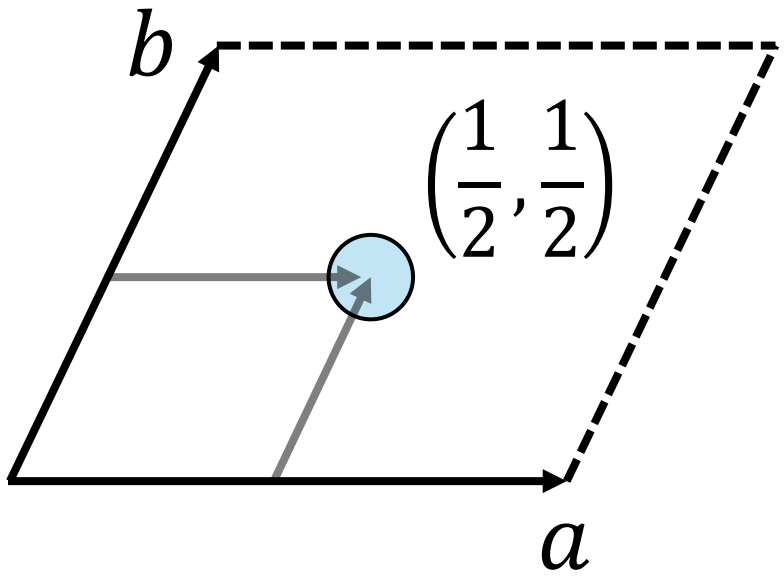
Example in 2D:



Describing structures: point coordinates

Unit cells are “building blocks” for the crystal structure. Now we will specify the **positions of atoms within those unit cells** using **point coordinates**.

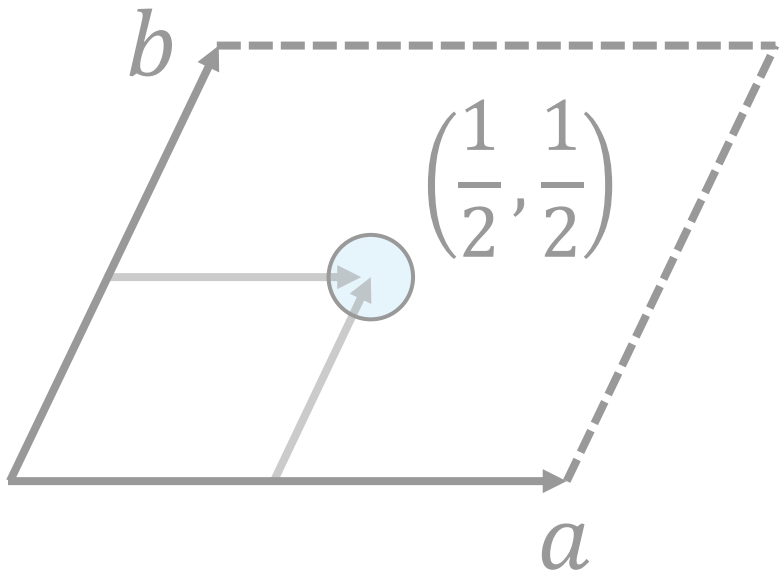
Example in 2D:



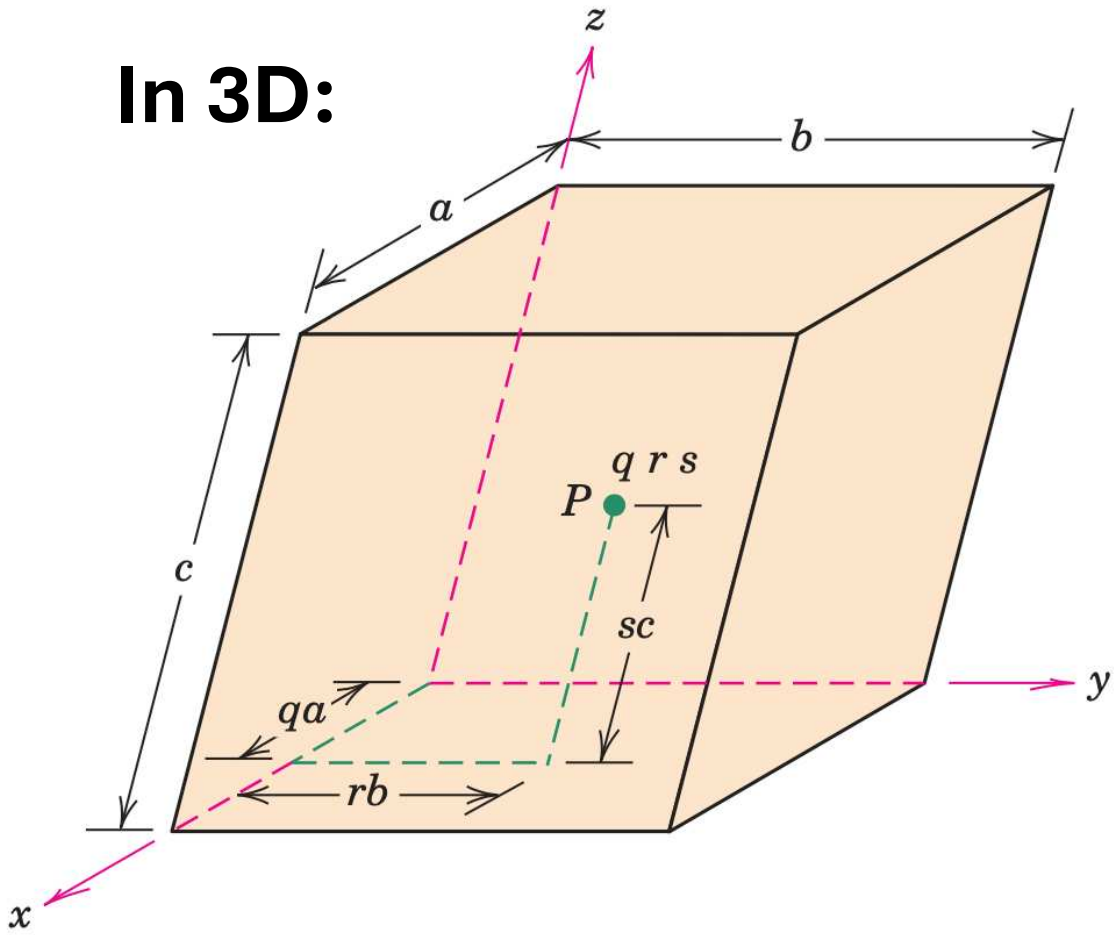
Describing structures: point coordinates

Unit cells are “building blocks” for the crystal structure. Now we will specify the **positions of atoms within those unit cells** using **point coordinates**.

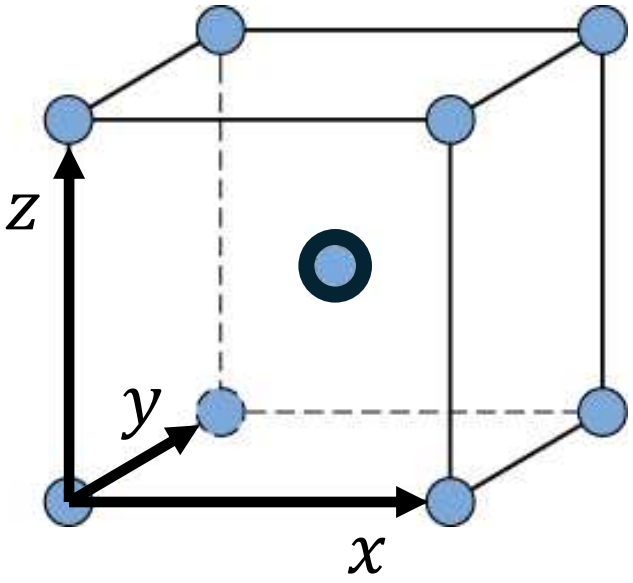
Example in 2D:



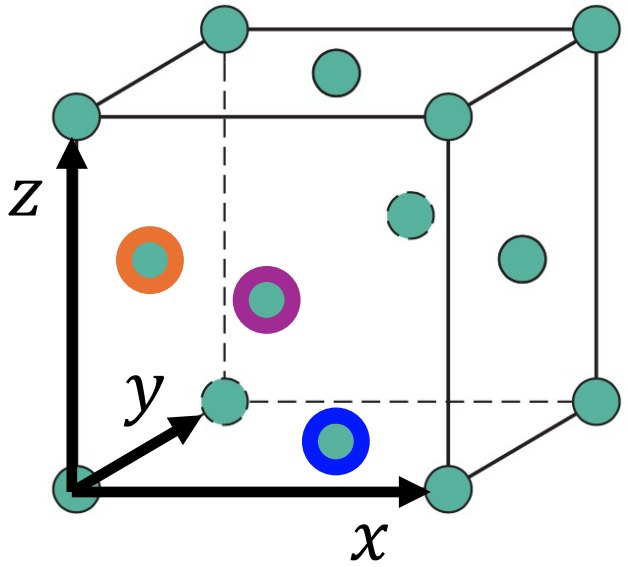
In 3D:



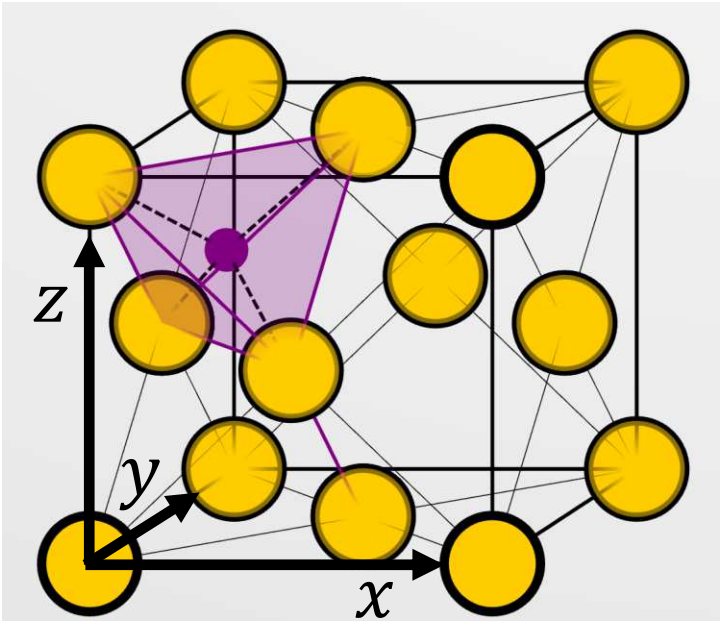
Examples of point coordinates



The body-center atom sits at:
(0.5, 0.5, 0.5)



The face-center atoms sit at:
(0.5, 0.5, 0.0)
(0.5, 0.0, 0.5)
(0.0, 0.5, 0.5)

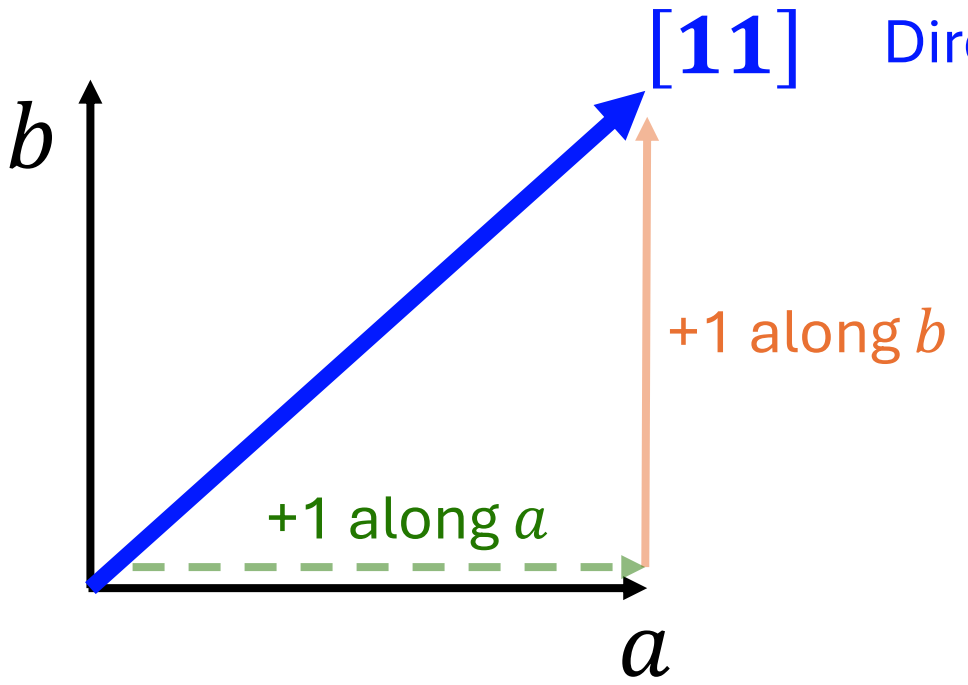


The tetrahedral interstitial shown to the left sits at:
(0.25, 0.25, 0.75)

Describing structures: crystallographic directions

It is sometimes useful to **specify directions** rather than positions.
These are also defined relative to the unit cell lattice parameters.

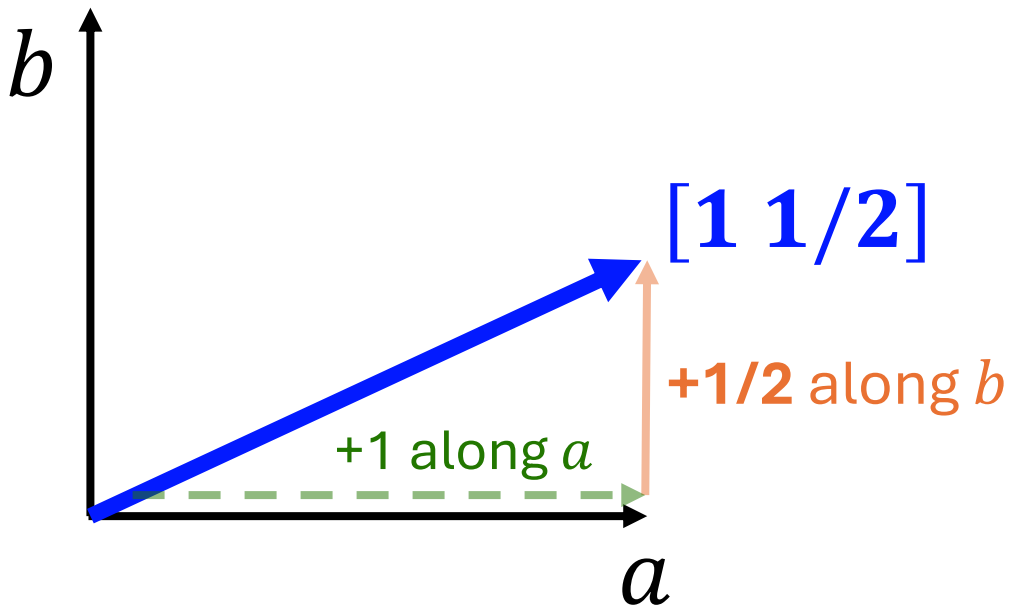
Example in 2D:



Describing structures: crystallographic directions

It is sometimes useful to **specify directions** rather than positions.
These are also defined relative to the unit cell lattice parameters.

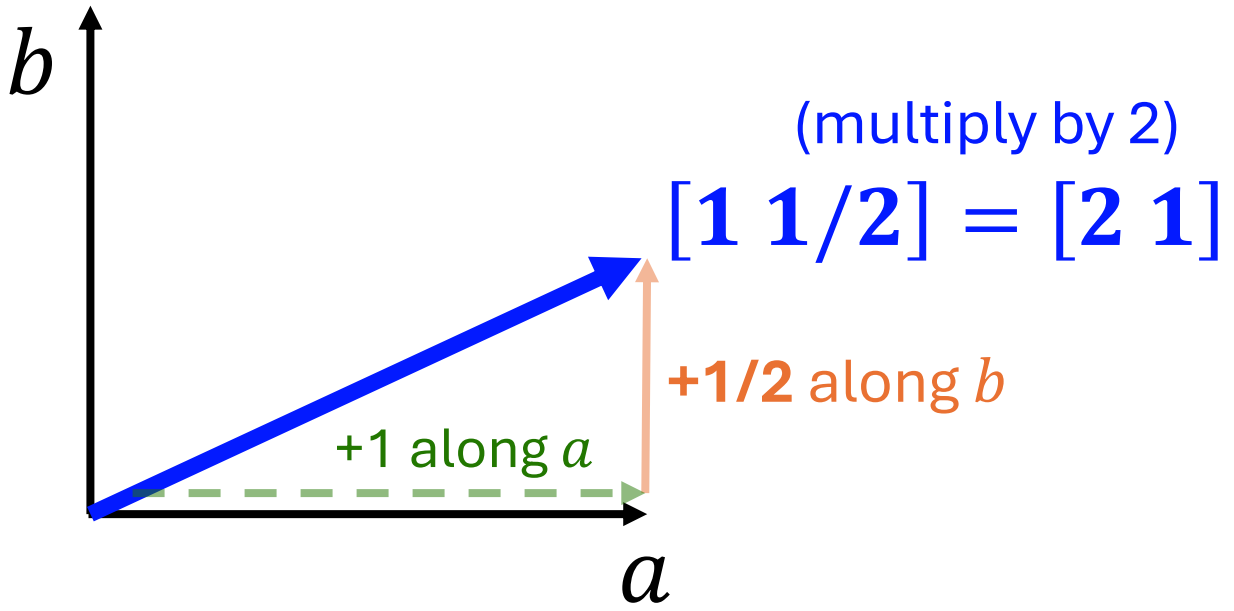
Example in 2D:



Describing structures: crystallographic directions

It is sometimes useful to **specify directions** rather than positions.
These are also defined relative to the unit cell lattice parameters.

Example in 2D:



(multiply by 2)

$$[1\ 1/2] = [2\ 1]$$

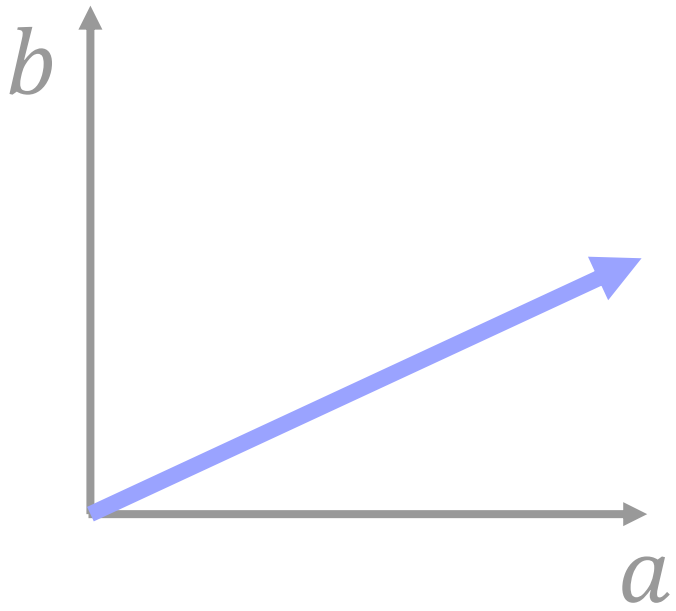
Multiply the the smallest number to make **all values integers**

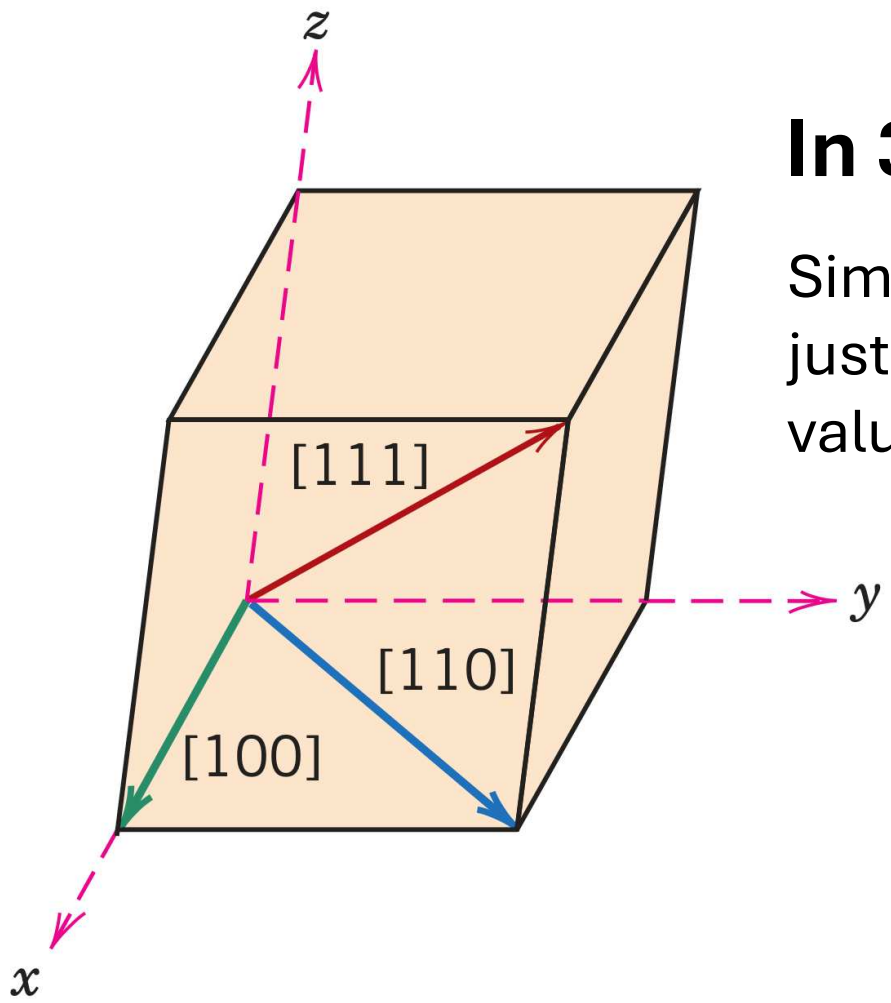
This just makes the vector longer. It doesn't change direction

Describing structures: crystallographic directions

It is sometimes useful to **specify directions** rather than positions.
These are also defined relative to the unit cell lattice parameters.

Example in 2D:





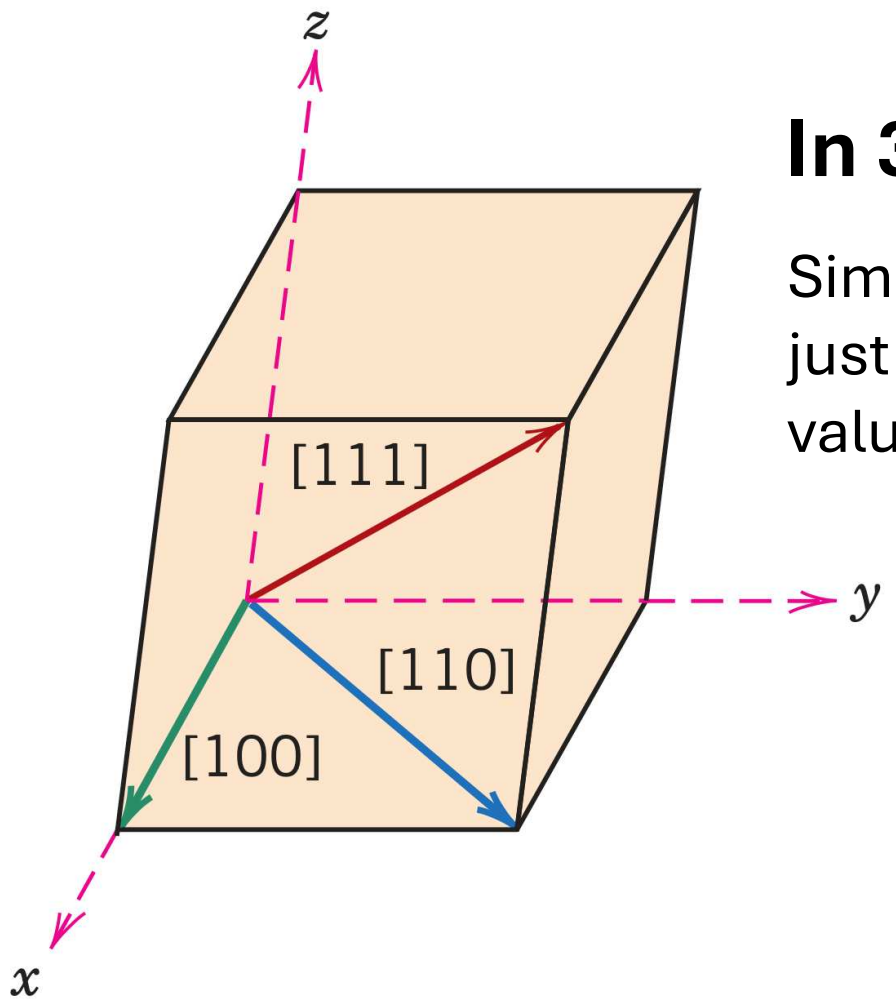
In 3D

Similar idea, just an extra value

Describing structures: crystallographic directions

It is sometimes useful to **specify directions** rather than positions.
These are also defined relative to the unit cell lattice parameters.

These assume (0, 0, 0) is the origin but we can **generalize to other vectors by subtracting the tail from the head**

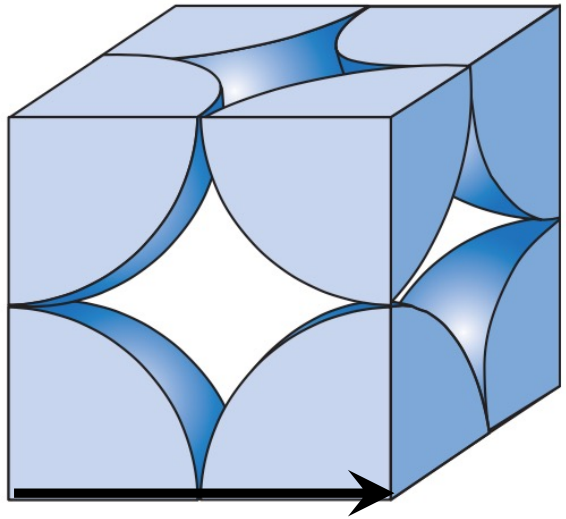


In 3D

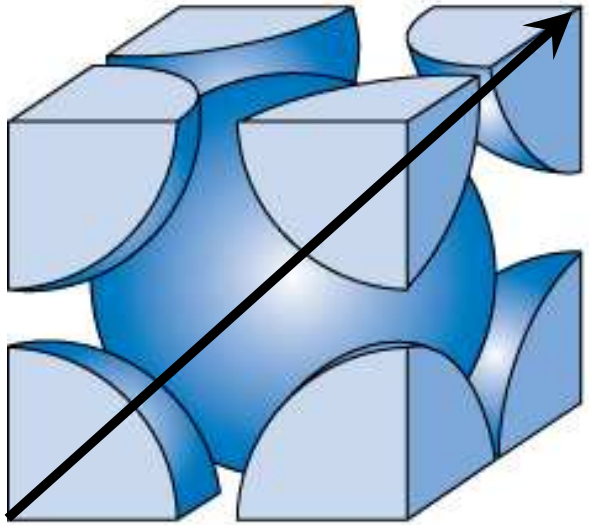
Similar idea, just an extra value

Examples of crystallographic directions

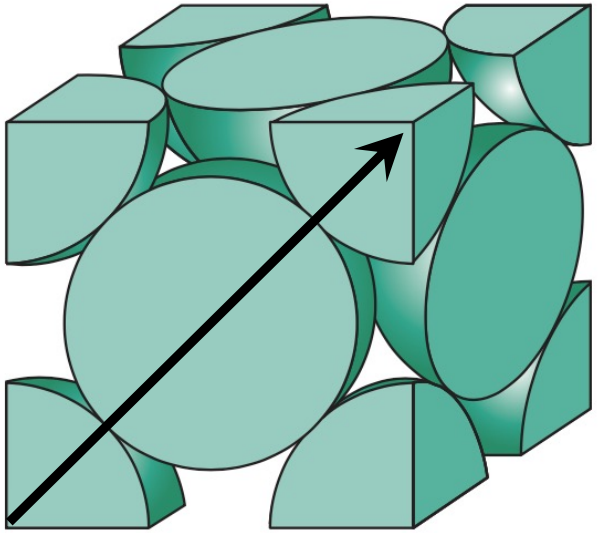
Identify the **close-packed direction** in each cubic structure



[100]



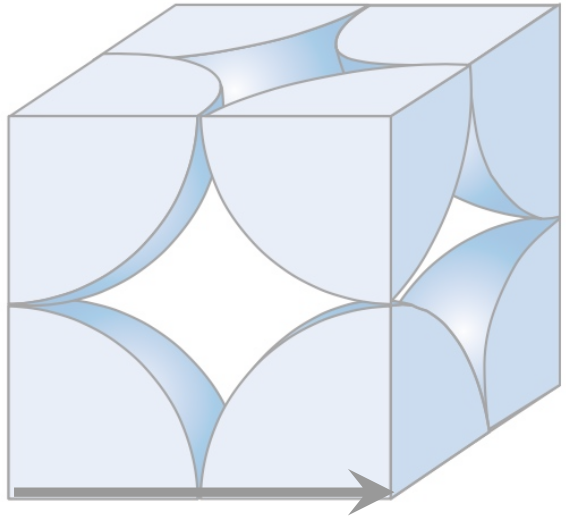
[111]



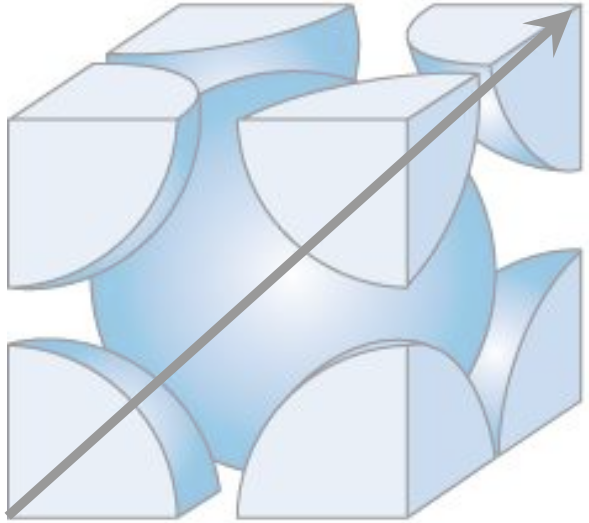
[101]

Examples of crystallographic directions

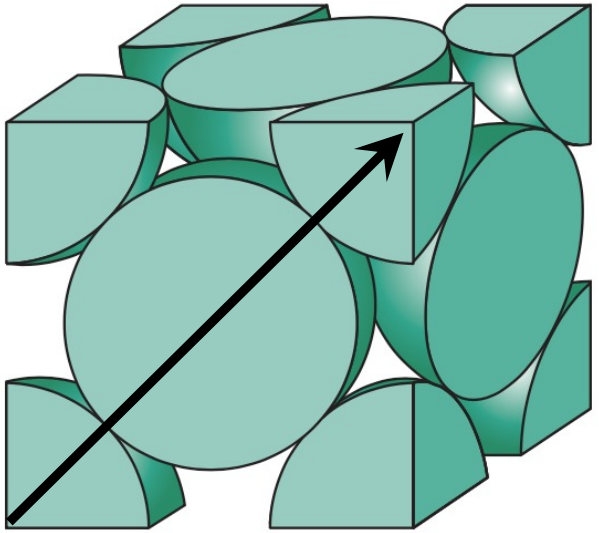
Identify the **close-packed direction** in each cubic structure



[100]



[111]



[101]

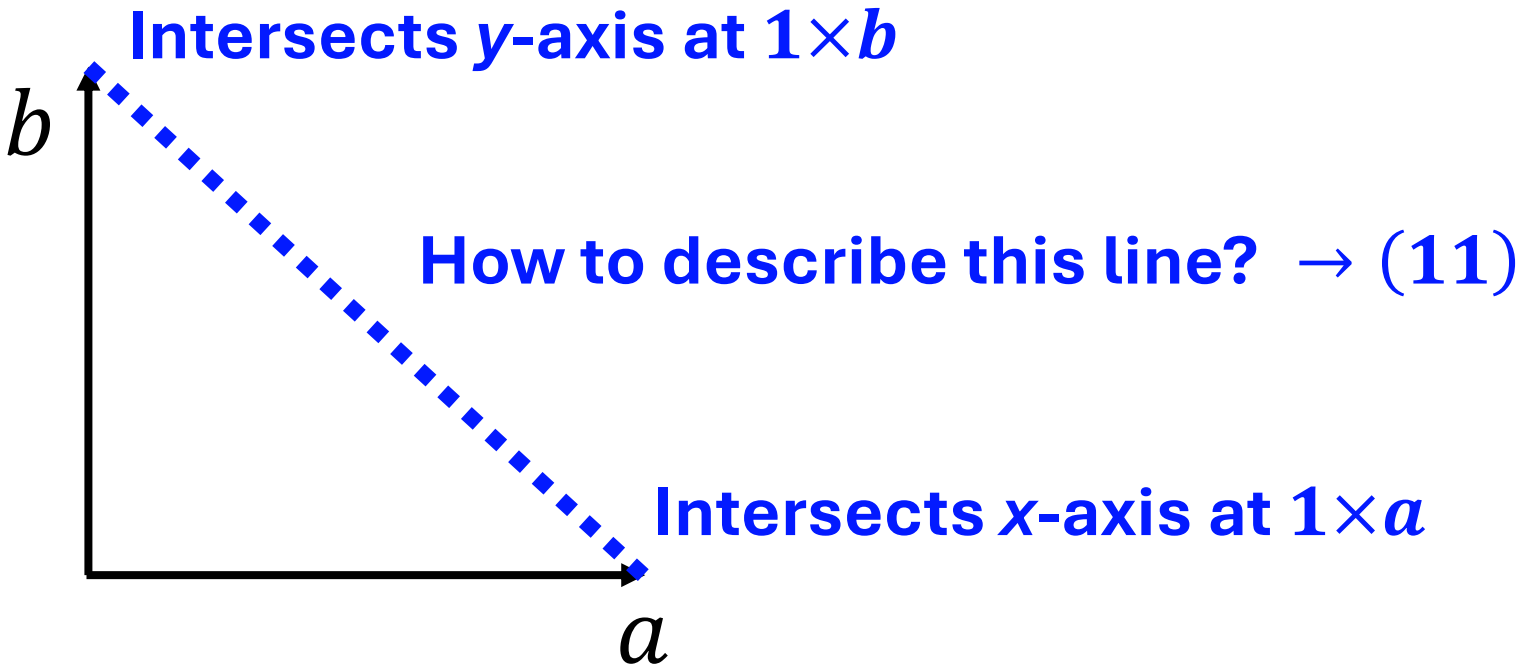
Notice: we could just have well named [110] or [011] as the close-packed directions for FCC

This is **a family: ⟨110⟩**

Describing structures: crystallographic planes

In addition to positions and directions, we can also specify **entire planes**

Example in 2D:

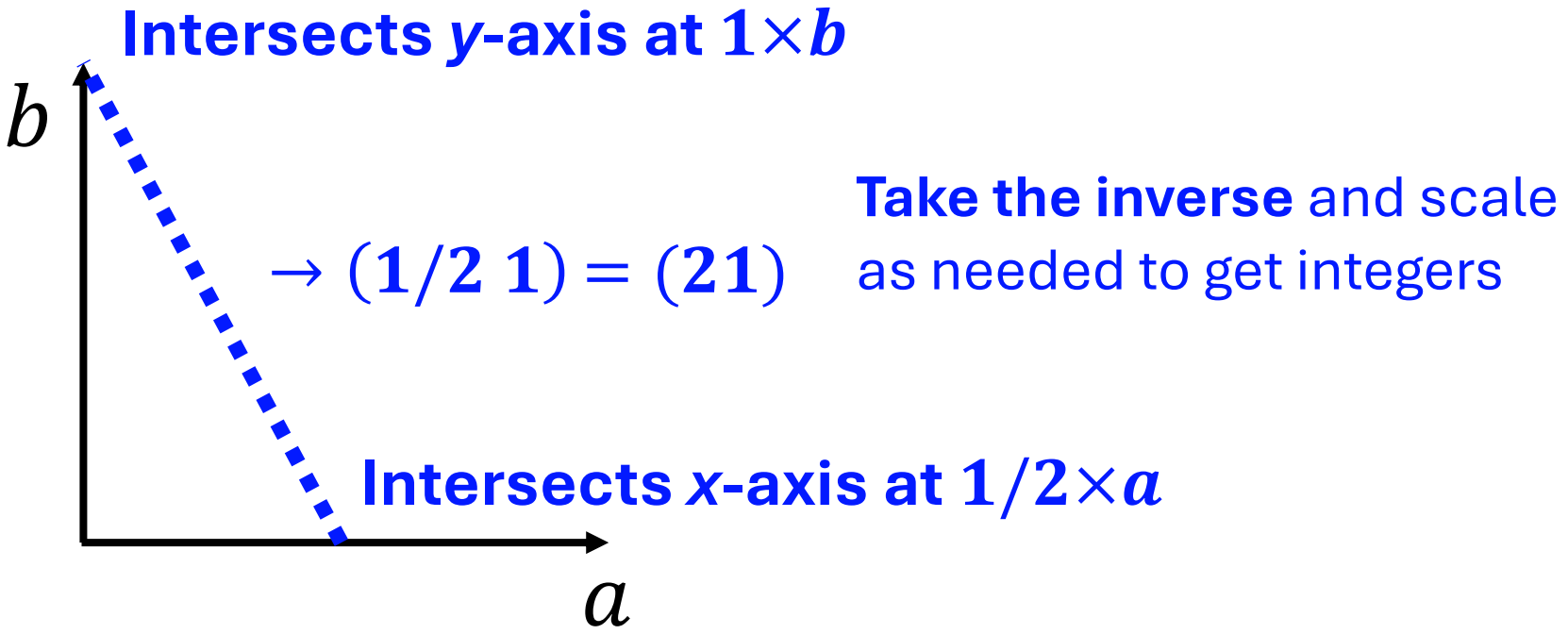


These are the *inverses* of the **axis intersections**
Planes are specified by ***parentheses*** (hkl)
These are referred to as **Miller indices**

Describing structures: crystallographic planes

In addition to positions and directions, we can also specify **entire planes**

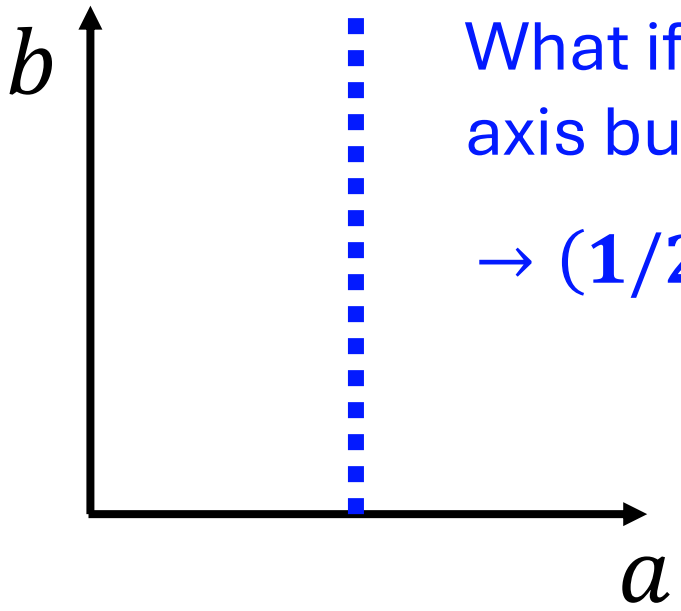
Example in 2D:



Describing structures: crystallographic planes

In addition to positions and directions, we can also specify **entire planes**

Example in 2D:



What if it ***never*** **intersects** an axis but is instead **parallel** to it?

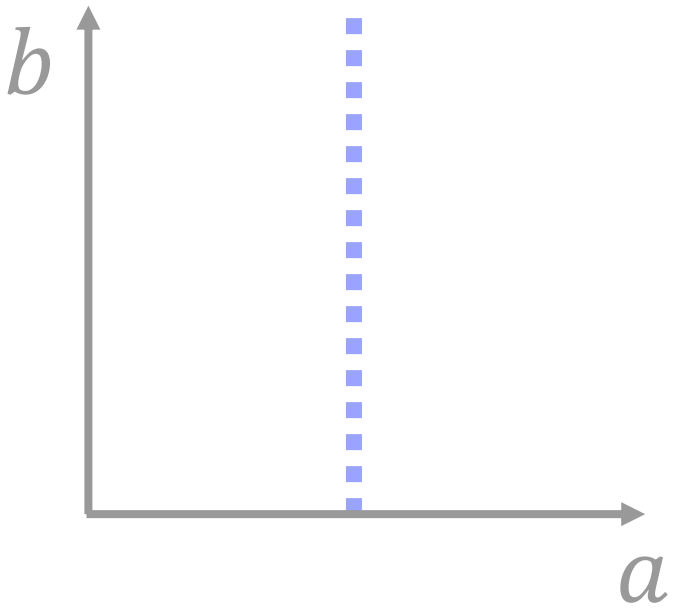
$\rightarrow (\mathbf{1/2}\ \infty) = (\mathbf{2}\ \mathbf{0})$ **Set that index = 0**

(Divide by ∞)

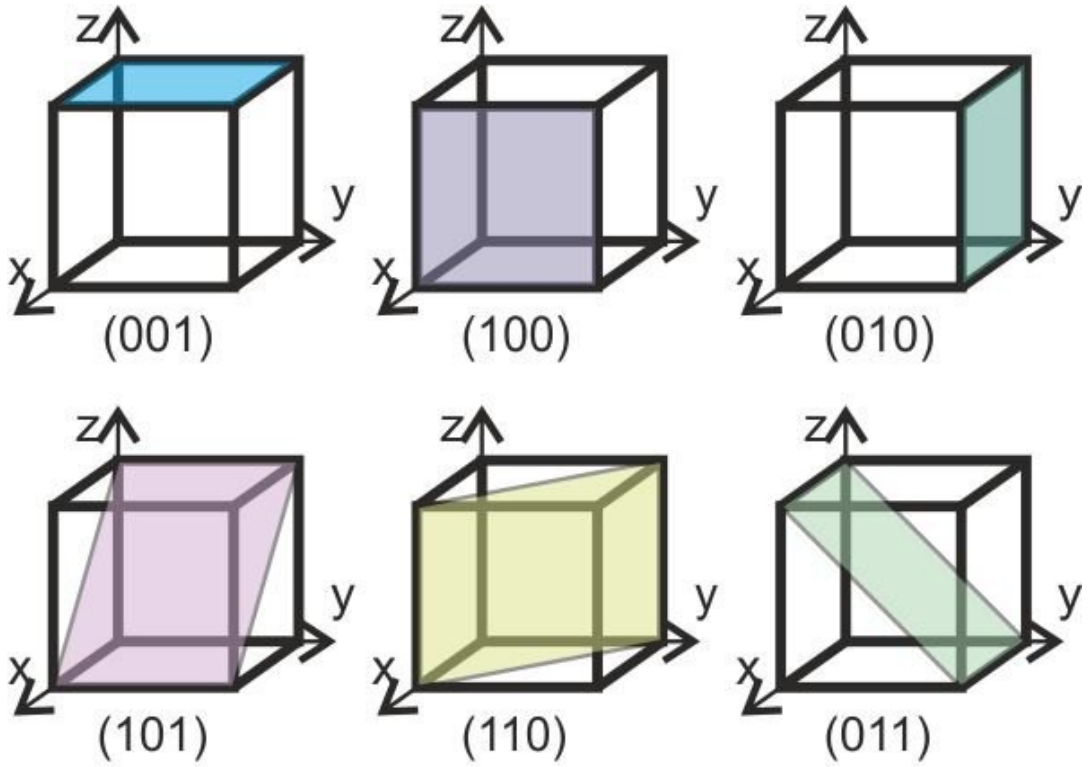
Describing structures: crystallographic planes

In addition to positions and directions, we can also specify **entire planes**

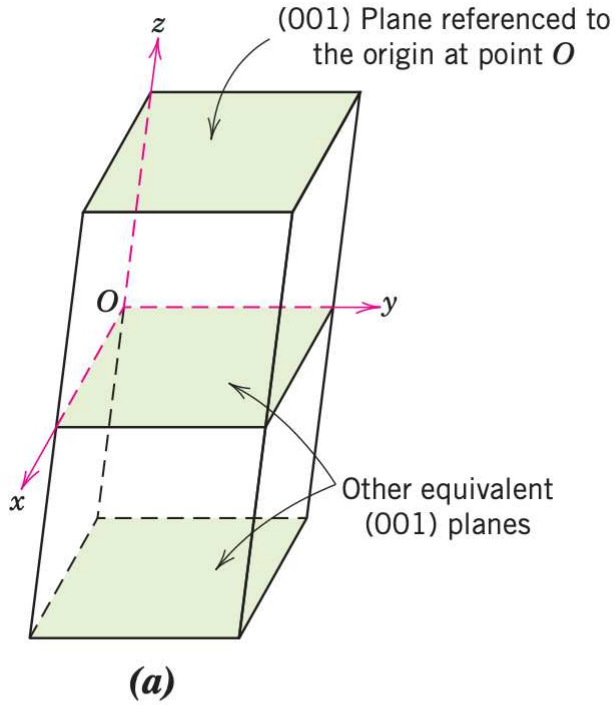
Example in 2D:



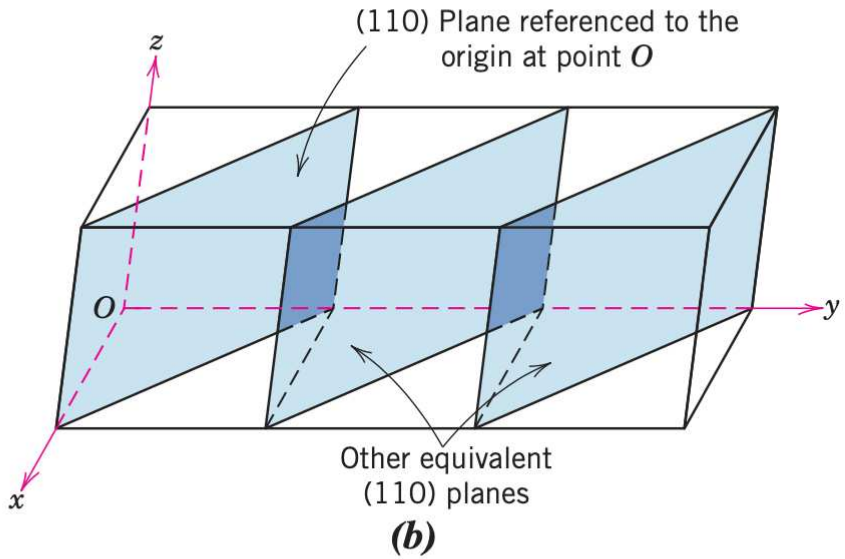
In 3D: Similar idea, extra value



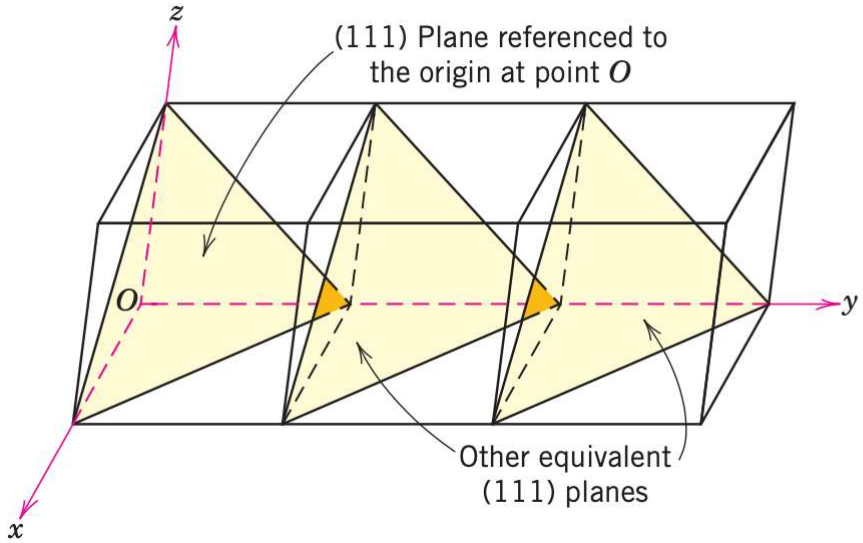
These planes repeat every unit cell



(a)

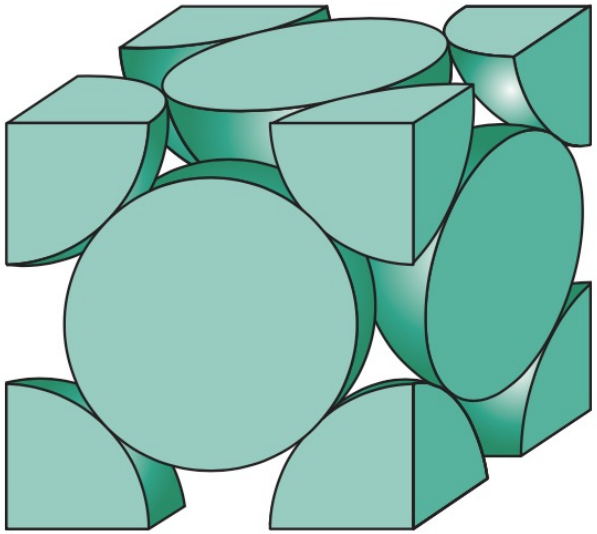


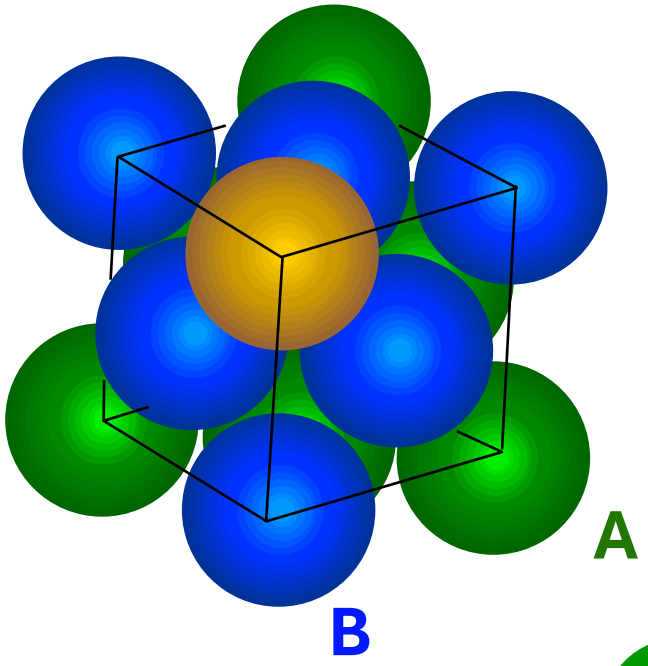
(b)



(c)

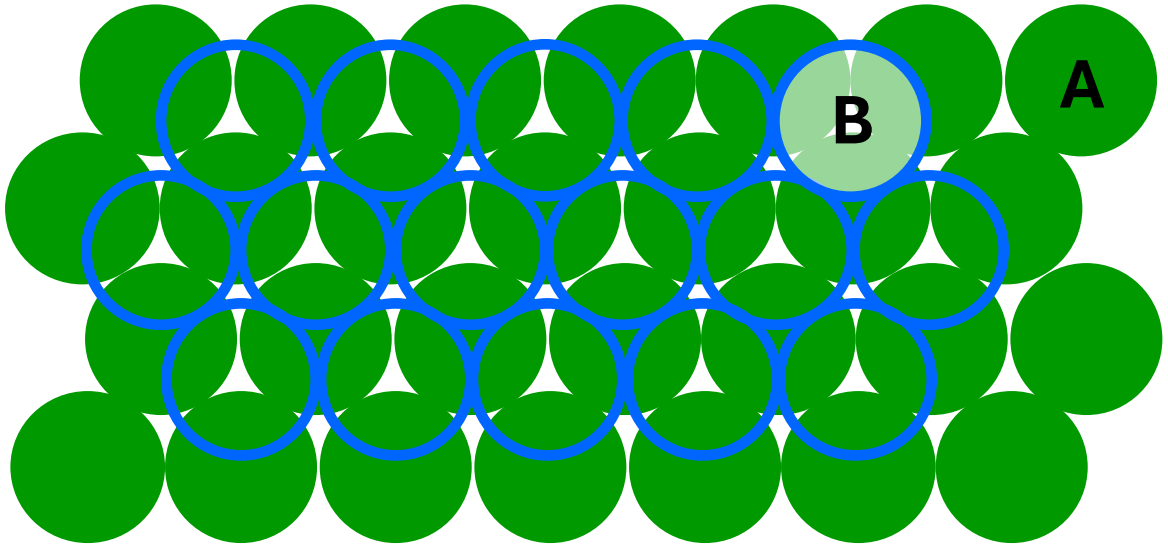
Examples of Miller indices





Recall: when discussing FCC, we identified by **close-packed plane**

This is known as the {**111**} **family** of planes, specified by brackets



Computing linear and planar densities

Linear density (LD):

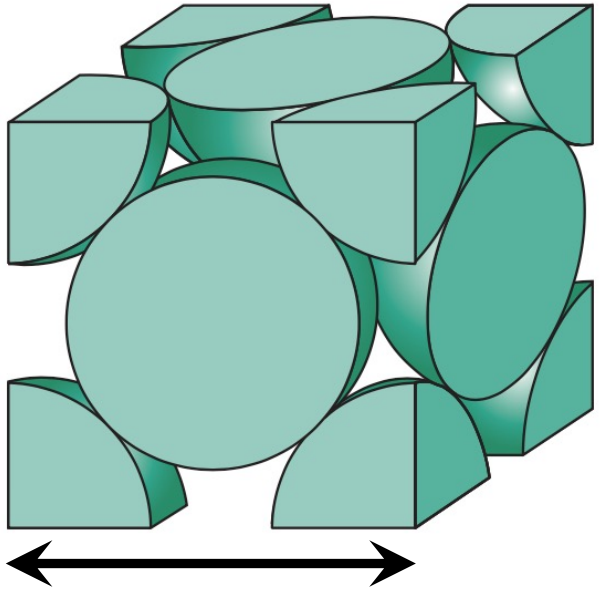
$$\mathrm{LD} = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}}$$

Planar density (PD):

$$\mathrm{PD} = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}}$$

Computing linear and planar densities

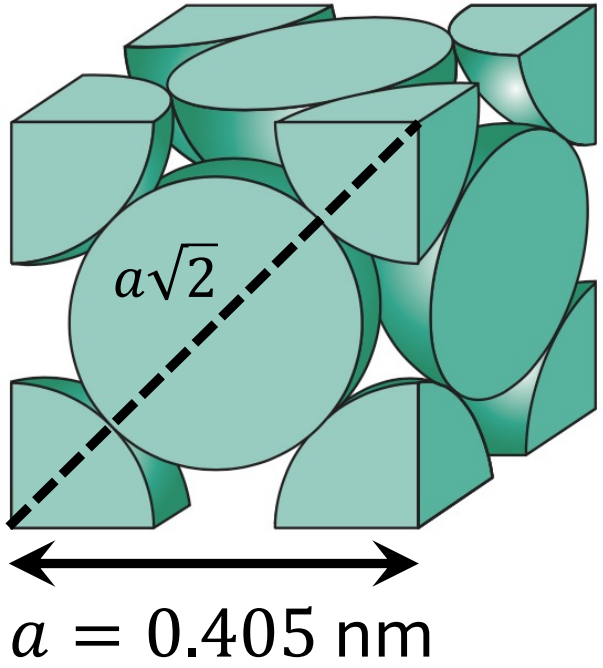
Example: what is the **linear density** of Al (FCC) along the **[110] direction**?



$a = 0.405$ nm

Computing linear and planar densities

Example: what is the **linear density** of Al (FCC) along the **[110] direction**?



There are 2 half atoms and 1 full atom along this vector
= 2 atoms in total

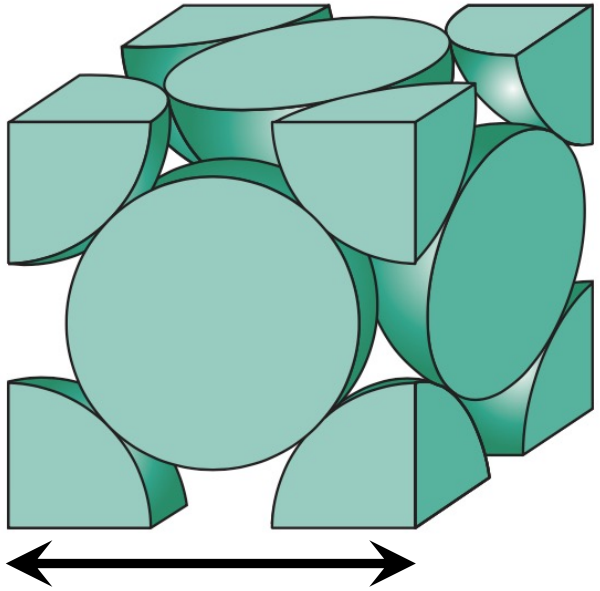
atoms

$$LD = \frac{2}{\sqrt{2}a} = \frac{2}{\sqrt{2}\ (0.405\ \text{nm})} = 3.5\ \text{nm}^{-1}$$

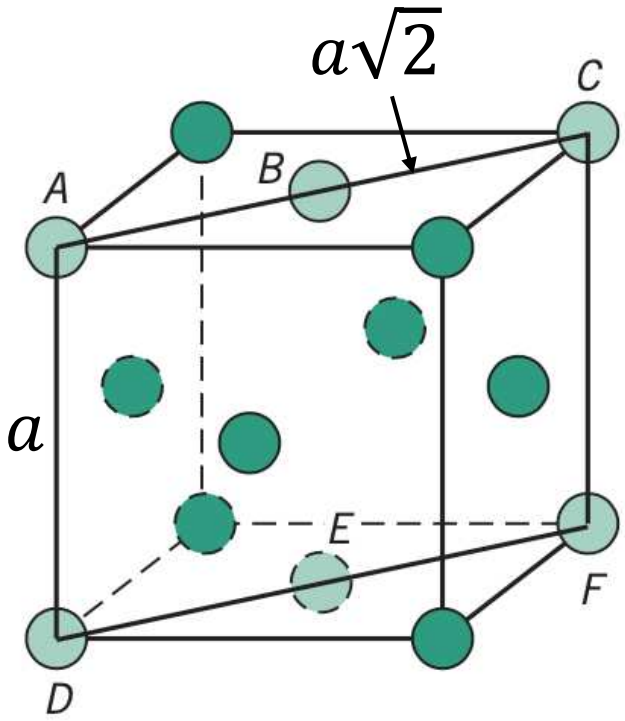
length

Computing linear and planar densities

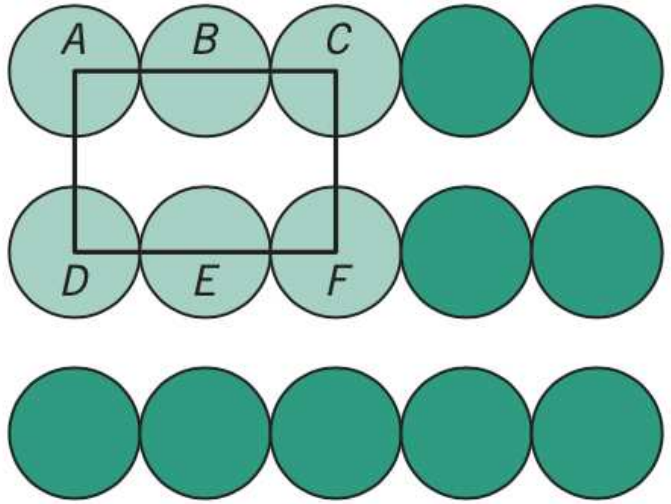
Example: what is the **planar density** of Al (FCC) along the **(110) plane**?



$a = 0.405$ nm



2 atoms per cell

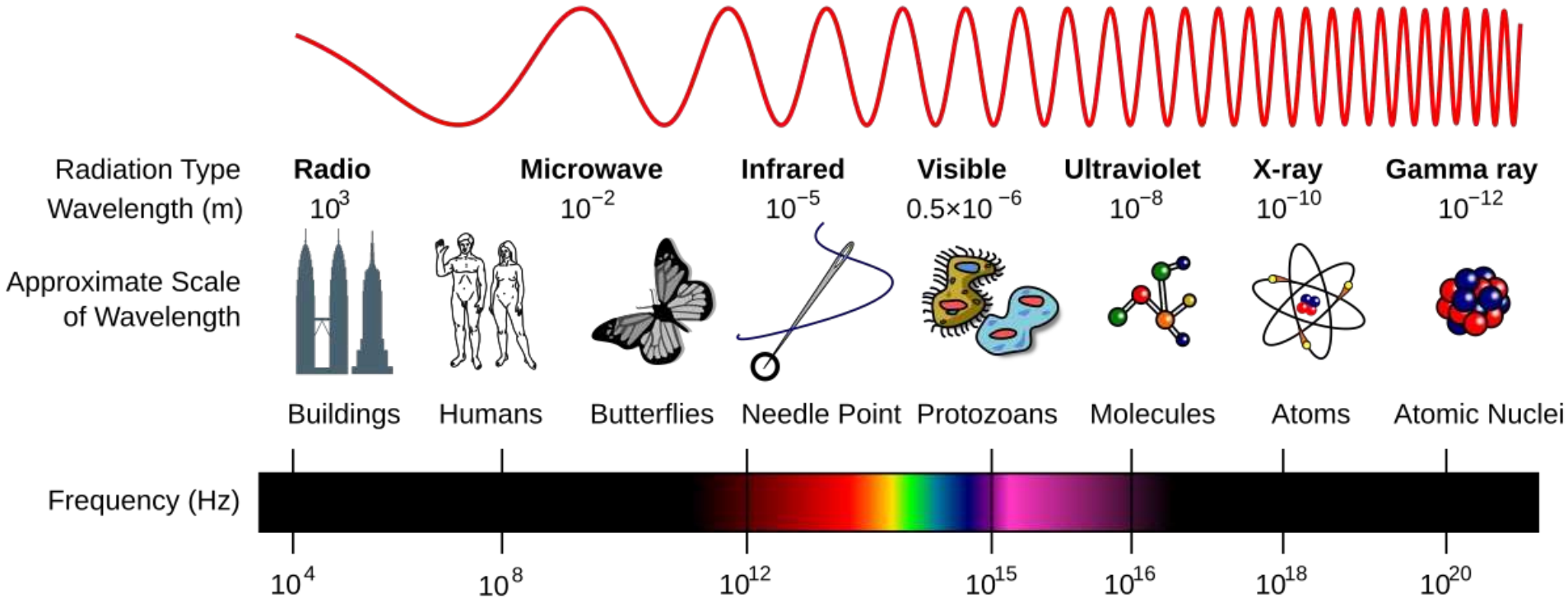


$$\mathrm{PD}_{110} = \frac{2 \text{ atoms}}{a^2\sqrt{2}} = \frac{2 \text{ atoms}}{(0.405 \text{ nm})^2\sqrt{2}}$$

Quick pause. Any questions?

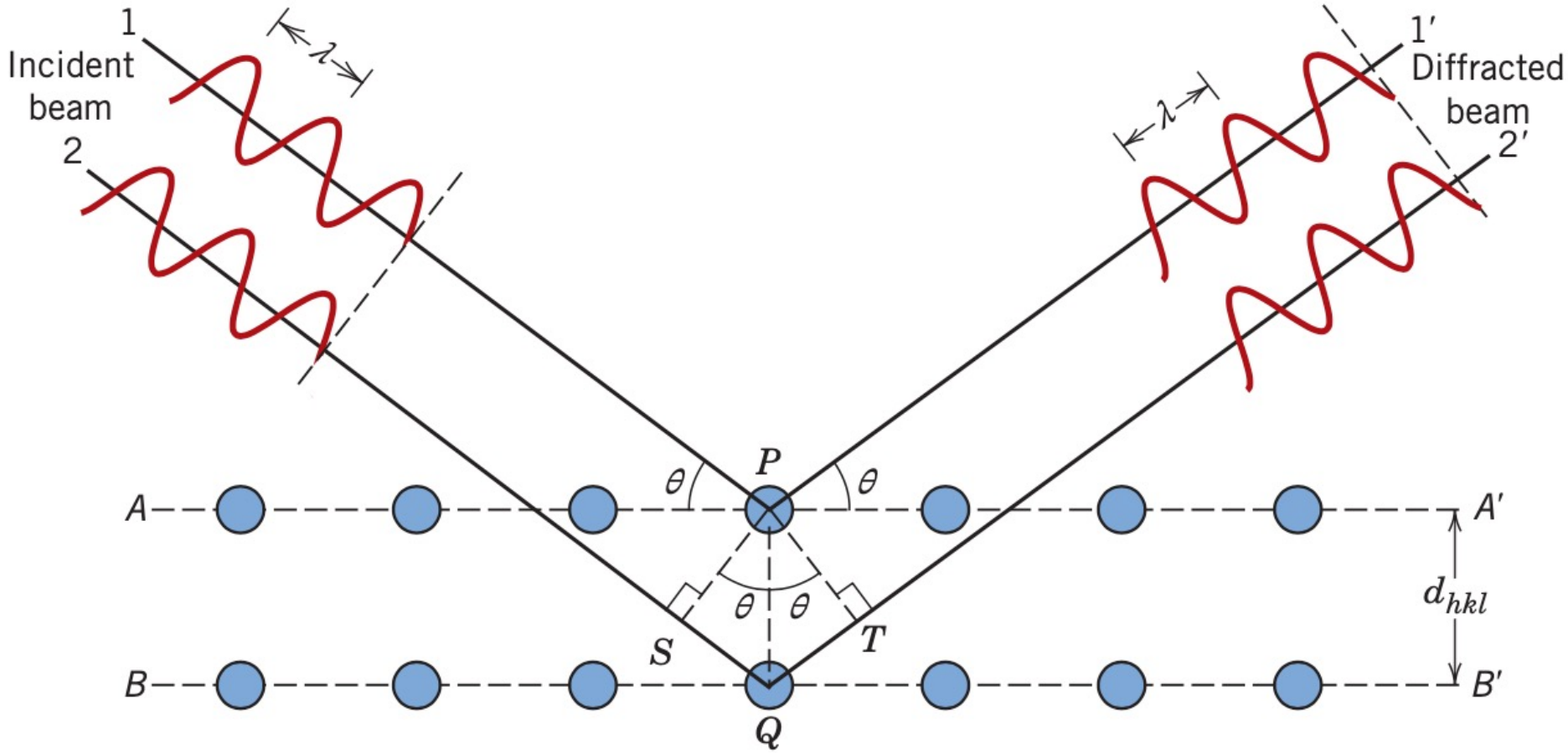
How do we *characterize* these structures?

X-ray diffraction (XRD): We shoot electromagnetic radiation (**X-rays**) at our sample and observe how it bounces back (**diffraction**) at various angles



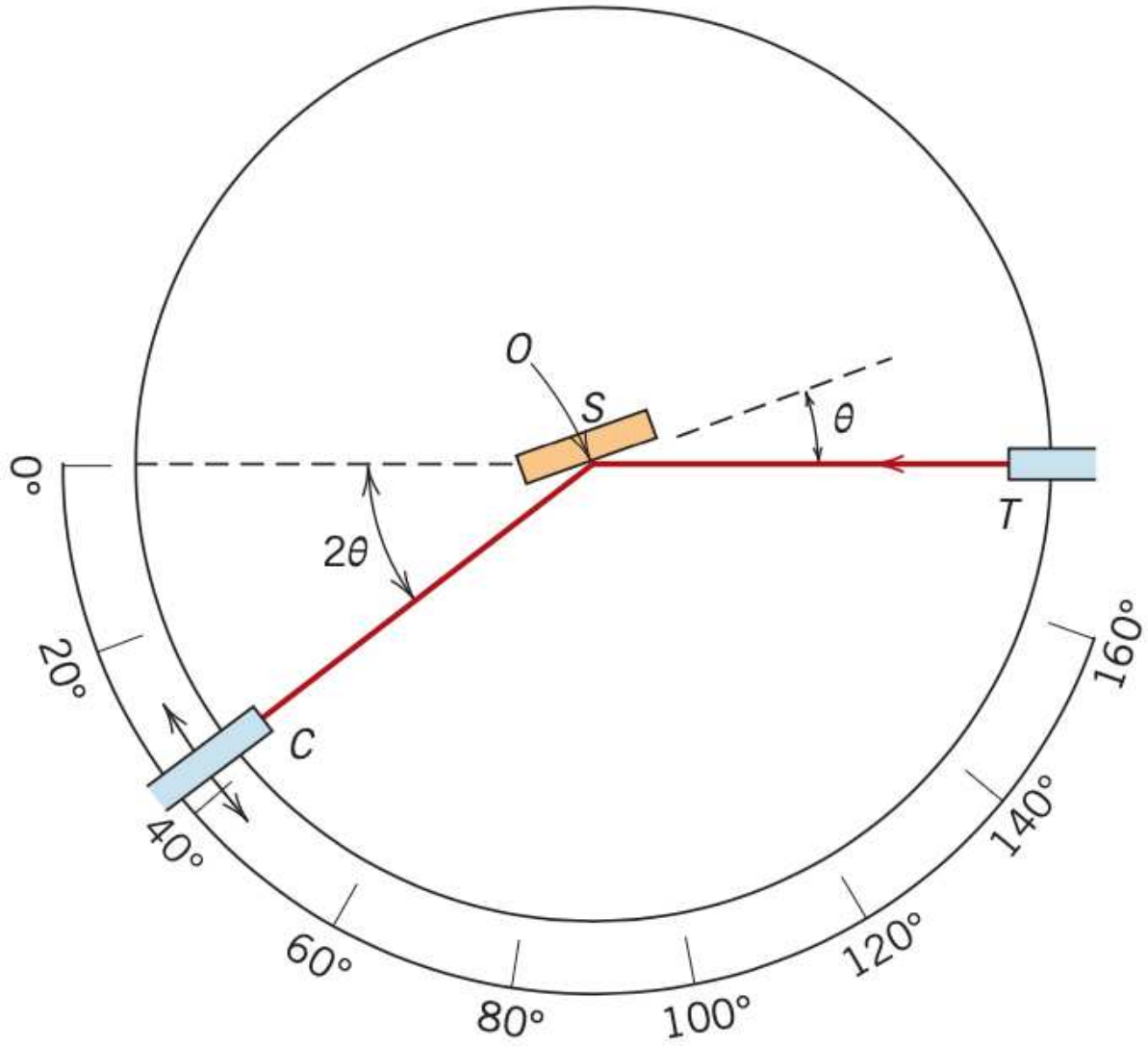
X-rays have a **comparable wavelength to atomic structure (nanometers)** → ensures they can interact

Principles of X-ray diffraction

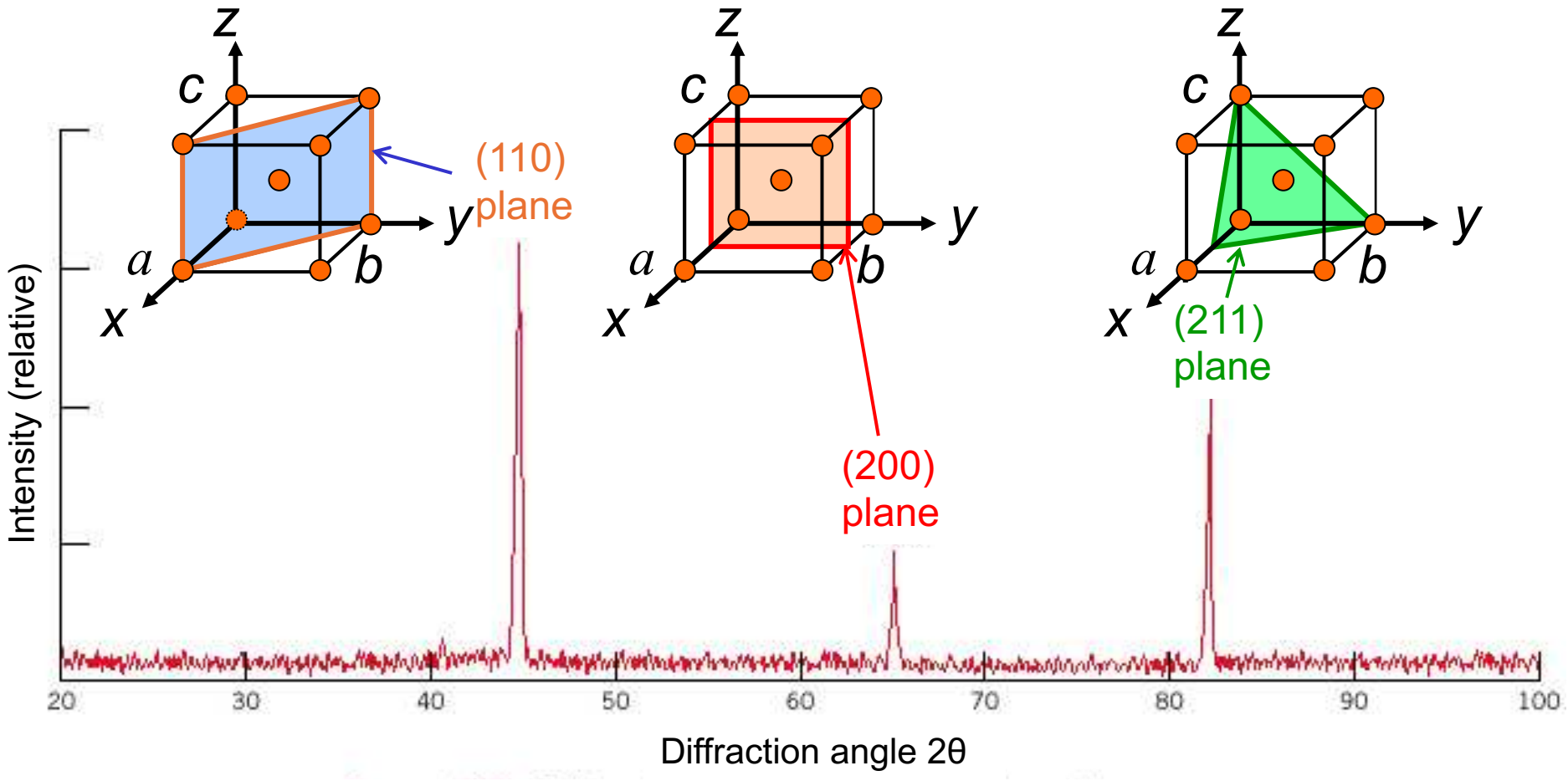


DEMO

Principles of X-ray diffraction



An example: XRD pattern from BCC Fe



Where these peaks are (2θ) and how tall they are (I) gives us insight into structure

Bragg's law

$$n\lambda = 2d_{hkl} \sin \theta$$

X-ray wavelength (fixed, usually 0.154 nm)

Spacing of planes with Miller indices (hkl) in the crystal

Angle between X-rays and sample – we control this

If we are at an angle where Bragg's law is not satisfied for some plane (hkl), then constructive interference will **not** occur

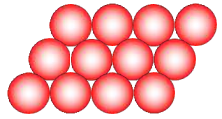
→ No signal in the diffraction pattern

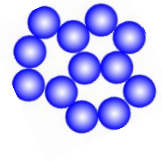
But if it *is* satisfied, bright signal (a peak) will be observed at θ



Summary

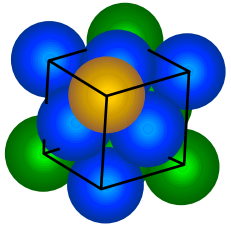
- Atoms may assemble into crystalline or amorphous structures.

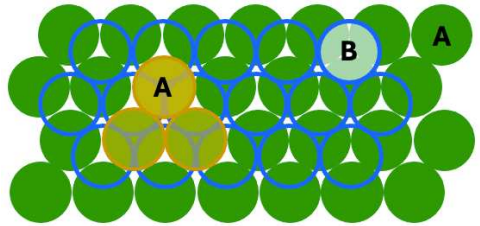




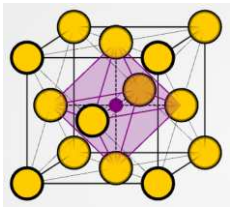
- Metals often adopt close-packed crystal structures: FCC, HCP, BCC

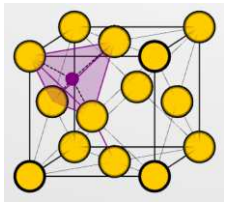
Describe using unit cells, atomic positions, crystallographic directions and planes





- Ceramics often adopt low-density structures by filling interstitial sites





- Characterize these structures using X-ray diffraction (XRD)

