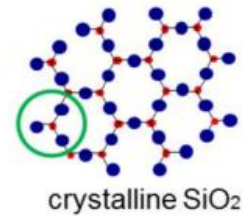


Crystal structure

Crystalline materials...

- atoms pack in dense periodic, 3D arrays
- typical of:
 - metals
 - many ceramics
 - some polymers



Noncrystalline materials...

- atoms have no periodic packing
- occurs for:
 - complex structures
 - rapid cooling

"Amorphous" = Noncrystalline



Materials fall into two different categories

First are the Crystalline materials – where the atoms pack in dense, periodic 3D array. For example, all metals, many ceramics and some polymers fall into this category.

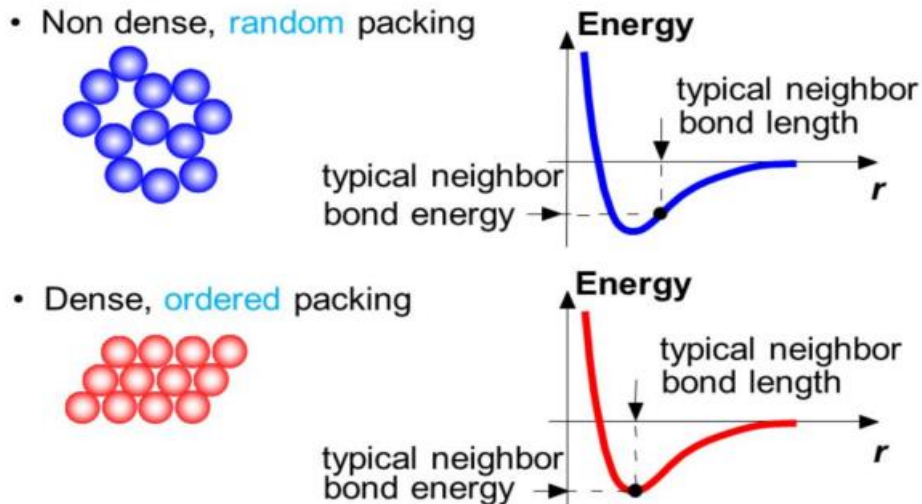
Shown here is an example of crystalline silicon dioxide. Note that each silicon atom is surrounded by three oxygen atoms in a dense, periodic array. For Non-crystalline materials – the atoms have no periodic packing. This occurs for complex structures and under conditions of rapid cooling. Sometimes the term amorphous is used as a substitute for non crystalline.

In the second example shown here, for non crystalline silicon dioxide, each silicon atom is still surrounded by three oxygen atoms, but in a this time in a random manner

Energy & Packing

So now let's look at the relationship between the atomic packing and the interatomic energies within materials. Shown in blue here is an example of a non dense, randomly packed, non crystalline material. On the right is a plot of the interatomic energy vs distance of separation between the atoms. For non crystalline materials, there is no 3d periodic arrangement of the atoms and therefore the typical neighbor bond energy will not be at the bottom of the energy trough, as shown here. However, when we look at dense, ordered packing the

atoms are now arranged as close as possible to each other and therefore, the neighbour bond energy will fall at the bottom of the energy trough. How does this influence the properties of the material, for example, the melting temperature? As a general rule, crystalline materials have higher melting temperatures than non-crystalline materials, as more energy is required to separate the atoms.



Basic concepts

Crystal structure: The manner in which atoms, ions, or molecules are spatially arranged within the unit cell.

There are extremely large number of different crystal structures.

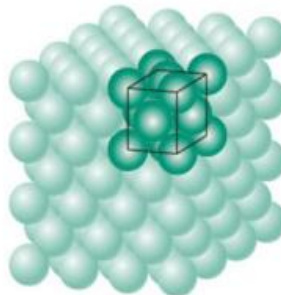


Fig. 3.01 Callister & Rethwisch 8e.

Can be relatively simple as in metals to exceedingly complex ones, as displayed by some of the ceramic and polymeric materials.

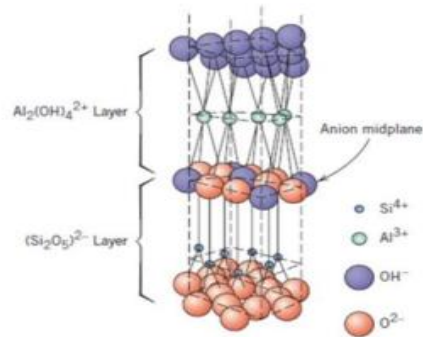
Some basic concepts about the Crystal structure. Crystal structure is defined as the manner in which atoms, ions or molecules are spatially arranged within the unit cell. There are a very large number of different crystal structures possible and

in this lecture summary we will discuss four. Crystal structures can be relatively simple, as for metals, but can also be extremely complex, as for some ceramic and polymeric materials.

Crystal lattice: Three-dimensional array of points coinciding with atom positions.

Atomic hard sphere model:
Atoms are represented by spheres.

Nearest-neighbour atoms touch one another.



The structure of kaolinite clay

Some more basic concepts. Crystal lattice is defined as the three-dimensional array of points coinciding with atomic positions within the crystal. Atomic structure is usually represented by the atomic hard sphere model, and in this model the atoms are represented as spheres. Nearest neighbor atoms can touch each other, but not overlap. The example on screen now shows a hard sphere representation of the structure of kaolinite clay.

Unit cell: Smallest repetitive entity in the crystal.

The **unit cell** is the **basic structural unit** or building block of the crystal structure.

The **unit cell** defines the **crystal structure** by virtue of its geometry and the atom positions within.

a, b, c – edge lengths
(lattice constants)

α, β, γ – interaxial angles

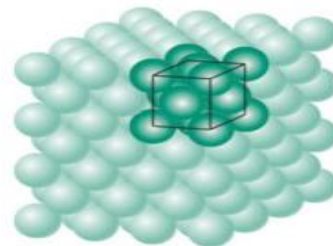


Fig. 3.01 Callister & Rethwisch 8e.

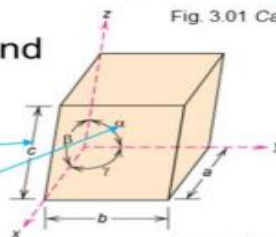


Fig. 3.04 Callister & Rethwisch 8e.

The unit cell is the smallest repetitive entity in the crystal and is therefore the basic structural unit or the basic building block of the crystal structure. An example of a unit cell is shown in green on the right. The unit cell defines the crystal structure by virtue of its geometry and the atomic positions within it. The unit cell is defined by its edge lengths, a , b and c , also known as lattice constants, and also by the inter-axial angles, α , β and γ . Metals tend to be densely packed and there are a number of reasons for this. Typically metals are made up of only one type of element, and therefore all the atomic radii are the same. Metallic bonding is also non-directional. Nearest neighbor distances tend to be small, in order to lower bond energy between the atoms, and the electron clouds shield the cores from each other. Metals have very simple crystal structures, and in this lecture summary we will discuss four examples.

Metals tend to be densely packed.

Reasons for dense packing:

Typically, only one element is present, so all atomic radii are the same.

Metallic bonding is non-directional.

Nearest neighbor distances tend to be small in order to lower bond energy.

Electron cloud shields cores from each other.

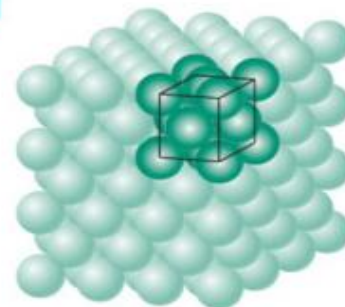


Fig. 3.01 Callister & Rethwisch 8e.

Metals have the simplest crystal structures.

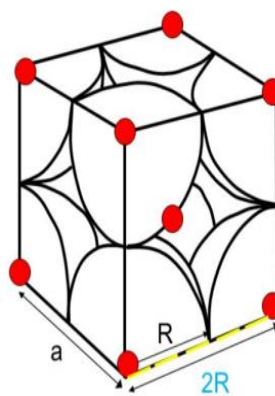
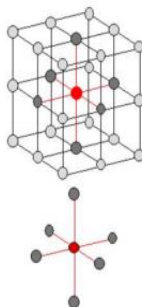
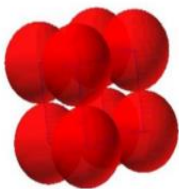
Simple Cubic Structure(Sc)

Here we start with the simplest crystal structure possible. This is the simple Cubic Structure. It consists of eight atoms, which are arranged into a cube. This structure is not common due to its low packing density. In fact, only one element, polonium, has this crystal structure. An important characteristic for all crystal structures is the coordination number, which is defined as the number of atoms, or nearest touching atoms, within the crystal. If we consider the atom in red, here on the right, we can see that it has six nearest neighboring atoms and the coordination number for the simple cubic structure is therefore six. Let's now look at some other important parameters of the simple cubic unit cell. The length of the cell edge, or lattice parameter a , is equal to two times the atomic radius. You can see this in the illustration on screen. This edge length is also the close packed direction for the simple cubic cell, that is, the direction within the cell in which the atoms are touching. As this is a cubic unit cell, the volume of the cell is given by a^3 . A second important parameter is the number of atoms within the unit cell. The simple cubic structure contains eight atoms, each shared eight ways with other surrounding unit cells. $8 \times 1/8$ gives us the equivalent of one atom within the cell.

Rare due to low packing density (only Po has this structure)

Coordination Number = 6

(the number of nearest neighbors or touching atoms)



a is equal to $2R$

Unit cell volume = $a^3 = (2R)^3$

How many atoms are in a simple cubic unit cell?

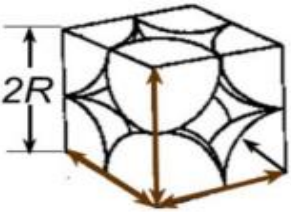
$8 \times \frac{1}{8}$ atoms = 1 atom

Atomic Packing Factor

Another important characteristic of crystal structure is the Atomic Packing Factor. The atomic packing factor gives you the density, or how close the packing of the atoms is in the crystal. The packing factor is defined as the volume of the atoms in the unit cell, divided by the volume of unit cell. So to determine the atomic packing factor, we need to know the dimensions of the unit cell, and the number of complete atoms within the unit cell. So for the simple cubic structure, the atomic packing factor is given by the number of atoms within the unit cell, which is one, multiplied by the volume of each atom. As we are modelling the atoms as hard spheres, this is just the usual equation for volume of a sphere, where the radius is the atomic radius. These are then divided by the total volume of the unit cell. For a simple cubic structure, this comes out to be 0.52, which is relatively low.

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

**assume hard spheres*



Adapted from Fig. 3.24, Callister & Rethwisch 8e.

$$APF = \frac{\text{atoms unit cell} \times \text{volume atom}}{\text{volume unit cell}}$$

$$APF = \frac{1 \times \frac{4}{3}\pi(0.5 \times a)^3}{(2R)^3}$$

Volume of sphere: $\frac{4}{3}\pi r^3$

$$APF \text{ for a simple cubic structure} = 0.52$$

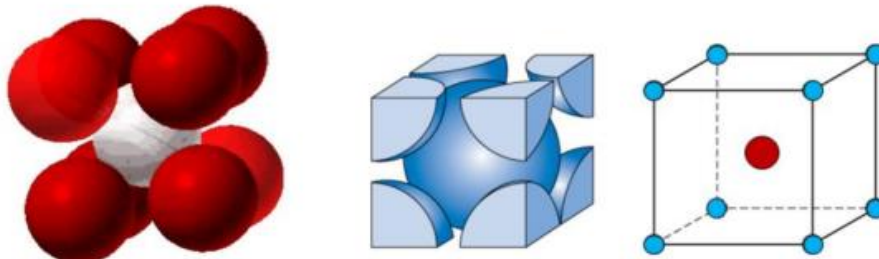
Body Centered Cubic Structure (Bcc)

The next more complex structure for metals is the body centered cubic structure. In this cubic structure, the atoms touch each other along the diagonal of the unit cell. This crystal structure is typical for several elements, including chromium, tungsten, iron, tantalum and molybdenum. To determine the coordination number of the body centered cubic structure, if we now look at the atom in red it is

surrounded by the eight blue atoms at the corners of the unit cell, and the coordination number is therefore 8.

Atoms touch along cube diagonals.

ex: Cr, W, Fe (α), Tantalum, Molybdenum

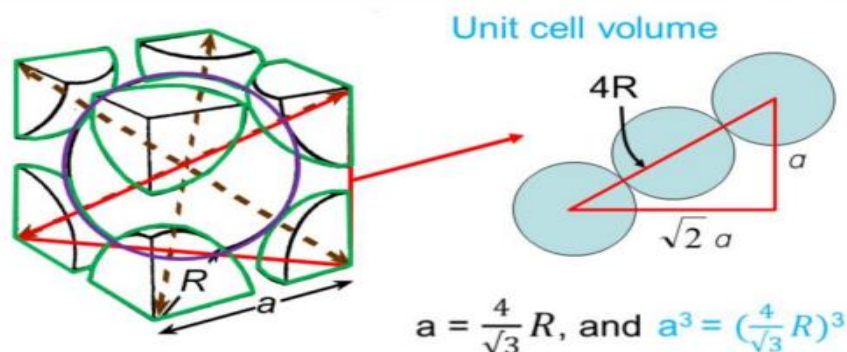


Adapted from Fig. 3.02, Callister & Rethwisch 8e.

(Note: All atoms are identical; the center atom is shaded differently only for ease of viewing).

- Coordination No = 8

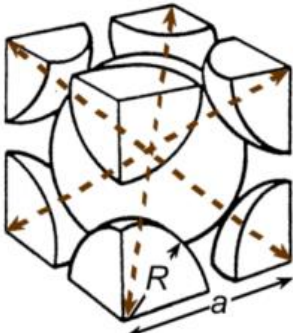
We'll now look at the close packed directions and unit cell volume for the body centered cubic structure. The schematic on screen shows the unit cell, with a right angled triangle making up one of the edge lengths and two diagonals across the bottom face, and the center of the cell. As the atoms touch along the central diagonal, we know that the distance of this line is 4 times the atomic radius. We can use this information along with Pythagoras' theorem, to get a value for a in terms of r , the atomic radius. The result is a equals 4 divided by the square root of 3, multiplied by r . The unit cell volume is given by cubing this result.



How many atoms are in a BCC unit cell?

$(8 \times \frac{1}{8})$ corner + 1 centre = 2 atoms

We'll now look at the close packed directions and unit cell volume for the body centered cubic structure. The schematic on screen shows the unit cell, with a right angled triangle making up one of the edge lengths and two diagonals across the bottom face, and the center of the cell. As the atoms touch along the central diagonal, we know that the distance of this line is 4 times the atomic radius. We can use this information along with Pythagoras' theorem, to get a value for a in terms of r , the atomic radius. The result is a equals 4 divided by the square root of 3, multiplied by r . The unit cell volume is given by cubing this result. Next we consider how many atoms are within the unit cell. In the center of the cell we have one complete atom, shown in blue, whereas in the corners we have eight atoms shared eight ways with neighboring cells. These are highlighted here in green. When we account for their contribution, we end up at a total of 2 atoms per unit cell.



Adapted from Fig. 3 pg 50, Callister & Rethwisch 8e.

$$\text{APF} = \frac{\text{atoms per unit cell} \times \text{volume of one atom}}{\text{volume of unit cell}}$$

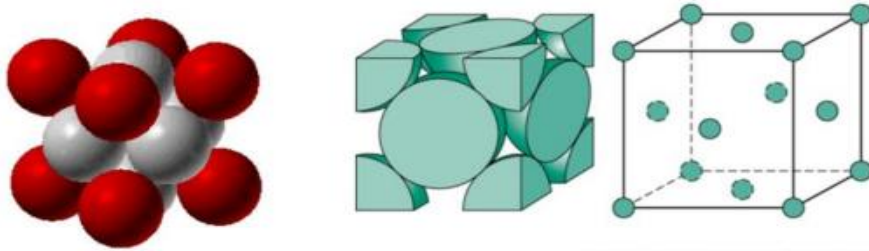
atoms per unit cell: 2
 volume of one atom: $\frac{4}{3}\pi R^3$
 volume of unit cell: $\left(\frac{4}{\sqrt{3}}R\right)^3$

$$\text{APF for a body-centered cubic structure} = 0.68$$

We can now determine the atomic packing factor for the BCC structure. There are two atoms per unit cell, and the volume of a sphere is $\frac{4}{3}\pi r^3$, as before. This is divided by the volume of the unit cell to give an atomic packing factor of 0.68.

Atoms touch along face diagonals.

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

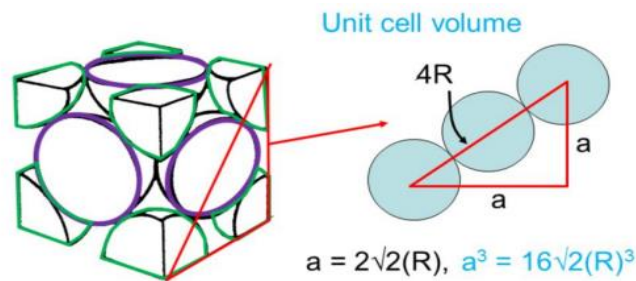


Adapted from Fig. 3.02, Callister & Rethwisch 8e.

[Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.]

- Coordination No = 12

The next crystal structure is face centered cubic. In this crystal structure, the atoms touch each other along the face diagonals. This crystal structure is again typical for several elements, such as aluminum, copper, gold, lead, nickel, platinum and silver. The coordination number for this crystal structure is 12.



How many atoms are in a FCC unit cell?

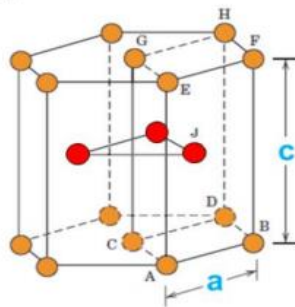
$$(8 \times \frac{1}{8}) \text{ corner} + (6 \times \frac{1}{2}) \text{ face} = 4 \text{ atoms}$$

As the atoms in a face centered cubic structure touch along the face diagonals, we can construct a right angled triangle with a diagonal equal to 4 time the radius of the atom, and two sides equal to a , the lattice parameter. Using Pythagoras theorem, we can determine a value for a in terms of r , and this is two time the

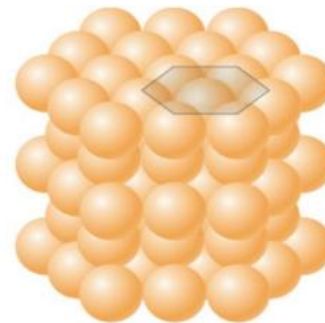
square root of 2 times r . Cubing this value gives us the unit cell volume. Now we'll determine how many atoms are in a face centered cubic cell. We have half atoms at each of the six faces, highlighted here in purple, plus eight corner atoms, shown in green. This gives us a total of 4 atoms per unit cell. So again, we now determine the atomic packing factor, this time for a face centered cubic structure. We already know that the number of atoms per unit cell this time is 4, and this is multiplied by the volume of each atom, and again divided by the volume of the unit cell. The result is an atomic packing factor of 0.74. This is actually the highest possible or maximum achievable atomic packing factor for materials.

Cadmium,
Cobalt, Zinc,
Titanium

Fig. 3.03, Callister &
Rethwisch 8e.



c/a ratio is 1.633
6 atoms per unit cell



Coordination number = 12
APF = 0.74

The last crystal structure that we will discuss is the hexagonal close packed crystal structure. This structure is typical for cadmium, cobalt, zinc and titanium. It consists of two planes of atoms on the top and the bottom, each with six atoms arranged in a regular hexagon, surrounding one atom in the center. In between these two planes there are three atoms, as highlighted here. The edge length ratio for this crystal structure, the distance c divided by a , is typically 1.633. We have six atoms per unit cell and the coordination number is 12. The atomic packing factor is the same as for the face centered cubic structure, 0.74.