Atomic Arrangement of Atoms

[Introduction to Structures](https://virginiatech.sharepoint.com/sites/AdaptiveLearning/Shared%20Documents/General/Intro%20Structures.docx?web=1)

Structure can be described at 4 levels (or length scales).

1. Atomic Structure
   1. Bonding
   2. Electron configuration
2. **Atomic Arrangement**
   1. **Crystalline Solids**
   2. Semi-Crystalline & Amorphous Solids
3. Microstructure
   1. Polycrystalline
   2. Crystal structure changes
   3. Compositional changes
4. Macrostructure
   1. Presence of stress concentrators
   2. Overall design

**Lesson Summary (key points) - SLO**

**Lesson Terminology**

**Lattice:**

**Crystal system:**

**Unit cell:**

**Crystalline solid:**

**Allotropes:**

**APF:**

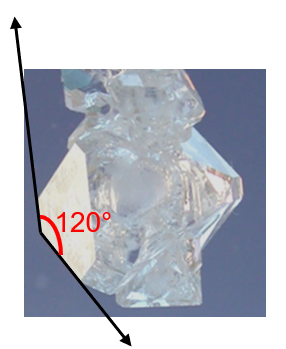
**Lattice constants:**

**Close-packed structure:**

Crystalline Solids

Prerequisite knowledge: **Bonding**

**Principle: Material properties are determined by structure; structure can be modified in predictable ways through processing.**

Further study: shape memory alloys, Phase Diagrams

Previous lesson: [Introduction to Structures](https://virginiatech.sharepoint.com/sites/AdaptiveLearning/Shared%20Documents/General/Intro%20Structures.docx)

Next lesson: [Semi-Crystalline & Amorphous Solids](https://virginiatech.sharepoint.com/sites/AdaptiveLearning/Shared%20Documents/General/Semi-Crystalline%20and%20Amorphous%20Structures.docx)

**Introduction**

The atoms in crystalline solids (most metals and ceramics (except glasses) and some simple polymers) arrange themselves in a highly ordered periodic structure. Notice the well-defined angles between edges of the alum crystals. The edges may change in length but the angles between edges remain the same. The angles are specific to the type of crystalline material and imply an underlying ordered structure of atoms. For alum crystals shown in the figure, the most prevalent angle is 120 degrees.

# Grow your own Alum Crystals

To grow these crystals, you will need:

1/2 cup hot tap water

2-1/2 tablespoons Alum

A close-up of a container

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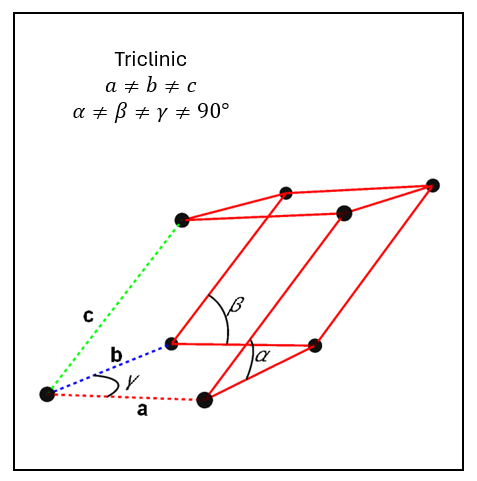
There are a limited number of ways atoms can be arranged periodically to fill space. This can be demonstrated in 2D if you try to completely fill space with regular pentagons versus regular hexagons. The hexagons (as well as parallelograms, squares, rectangles, and triangles) can be arranged to fill a plane without gaps, but the pentagons cannot as shown in figure #.

If we extend this concept to 3D, we find that only 7 crystal systems can be uniquely identified to fill space. Some systems can have further subclassifications, giving us the 14 Bravais lattices. In this course, we will focus on the cubic crystal system and briefly introduce the hexagonal crystal system.

A hexagon shaped object

Description automatically generatedA blue hexagon shaped object

Description automatically generated

Monoclinic 
p = 90 
Primitive 
Body-centered 

a 
Primitive 
Orthorhombic 
900 
Base-centered 
Body-centered 
Face-centered 

a 
Tetragonal 
900 
Primitive 
Body-centered а 
нехадопа[ 
р = 90,у 1200 
ь 
о 
90 
а. 
с; 
2 

A diagram of different shapes

Description automatically generatedRhombohedral 
p = 900 

Figure #: 7 Crystal systems and 14 Bravais Lattices

**Lattice Parameters**

A diagram of a triangle with lines and dots

Description automatically generatedThe 7 crystal systems (and hence a given crystalline material) are described by a set of lattice parameters composed of 3 edge lengths: a, b, c and 3 angles: α, β, γ. The lattice parameters (a, b, c, α, β, γ) and their relations to one another are shown below. For the triclinic system, the sides are unequal and the angles are unequal and not equal to 90 degrees.

Figure 1: Triclinic system showing the relation between lattice parameters

For a cubic system, the edge lengths are all equal a=b=c and the angles are all 90 degrees. We would write this as (a, a, a, 90, 90, 90). The hexagonal system would be (a, a, c, 90, 90, 120).

A cube with lines and dots

Description automatically generated90 
a 
120 Figure 2: Primitive Cubic Unit Cell Figure 3: Primitive Hexagonal Unit Cell

The table below gives some common crystalline materials along with their lattice parameters.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Material** | **Crystal System (Bravais)** | **a b c** | **α, β, γ** | **Common Use** | **refs** |
| Po, polonium | Cubic (P) |  |  |  |  |
| Au, gold | Cubic (F) |  |  |  |  |
| Fe, iron | Cubic (I) |  |  |  |  |
| Cu, copper |  |  |  |  |  |
| Al, aluminum |  |  |  |  |  |
|  |  |  |  |  |  |
| Zn, zinc |  |  |  |  |  |
| NaCl, sodium chloride |  |  |  |  |  |
| Pb, lead |  |  |  |  |  |
| Hg, mercury |  |  |  |  |  |
| TiC, titanium carbide | cubic |  |  |  |  |
| WC, tungsten carbide | hexagonal |  |  |  |  |
| Fe3C, iron carbide | orthorhombic |  |  |  |  |
| polyethylene |  |  |  |  |  |
| C, graphite | hexagonal |  |  |  |  |
| C, diamond | cubic |  |  |  |  |
| Si, silicon |  |  |  |  |  |
| Ge, germanium |  |  |  |  |  |
| TiO2, titanium dioxide |  |  |  |  |  |

\*P=primitive (simple), I = body centered, C = base centered, F = face centered

**Mini-lesson 1: Cubic Crystal System (a, a, a, 90, 90, 90)**

**Cubic:** Notice that the cubic system has 3 Bravais lattices. By associating 1 atom (hard sphere) with each lattice point, we can generate 3 distinct cubic structures as shown below. Notice the directions in which the atoms touch (along edges, body diagonal, or faces). The number of atoms in each unit cell increases as we move from the simple cubic, to the body-centered and finally to the face-centered cell. The size of the unit cell also increases but not as much as we might expect just from counting the number of atoms. This is because the packing density of atoms increases. The simple cubic lattice is 50% space and 50 % atom. The body-centered is 68% atom and the face-centered is 74% atom. This is usually expressed in fractional form as the atomic packing factor or APF. We would say that the face-centered cubic structure has an APF of 0.74.

|  |  |  |  |
| --- | --- | --- | --- |
|  | A yellow and green cubes  Description automatically generated  Figure 4: Hard sphere model of atom arrangement on Bravais lattice. | | |
|  | Simple (P) | Body-centered (I) | Face-centered (F) |
| APF | 0.5 | 0.68 | 0.74 |
| atoms/unit | 1 | 2 | 4 |
| Edge length |  |  |  |
| Atoms touch along | Cube edges | Body diagonal | Face diagonal |
| Avg. Volume / atom | 8 R3 | 6.16 R3 | 5.66 R3 |

Concept check: We have 3 samples labeled A, B, and C. All contain the same 1 million atoms but sample A has the simple cubic crystal structure; sample B is body-centered cubic; and sample C is face-centered cubic. If they were all in the shape of a cube, which sample would be the largest? Smallest? Which material would weigh the greatest?

**Face-centered cubic lattice (FCC):** There are three common views used in this course to describe crystal structures as shown below. They are the space filled model, unit cell model, and the exploded view model, respectively. The first is the space filled model which shows full atoms associated with the crystal lattice. The second view shows the unit cell with atoms filling space but only shows that part of the atom that is contained within the unit cell. The last view is called an exploded view where the atoms are shown but the lattice is expanded so that it is easier to see all atoms throughout the volume. The unit cell model is the view necessary to make calculations of such parameters as the edge lengths, number of atoms per unit cell, and the atomic packing factor (APF).

A cube with red and yellow circles

Description automatically generated

Figure 5: The face-centered cubic lattice represented by the (a) space filled model, (b) unit cell model, and (c) exploded view model. The coloring is used to make it easier to distinguish the face positions (red) from the cell corners (yellow).

Notice that atoms are touching along face diagonals for the FCC lattice as well as from one face center to an adjacent face center. In the primitive or simple cubic lattice, the atoms touch along edges. In the BCC lattice, the atoms touch along the body diagonal (from one corner of the cubic cell to the opposite corner).

**Body-centered cubic lattice (BCC):** The body-centered cubic lattice is shown below.

A yellow and yellow cube

Description automatically generated

Figure 6: The body-centered cubic lattice represented by the (a) space filled model, (b) unit cell model, and (c) exploded view model. Notice that the atoms do not touch along cube edges but touch along the cube diagonal.

The unit cell model (Fig 5 (b)) is shown here repeated five times so you can see how the crystal structure is built up from this unit. If you consider the atom in the center (red), you can see that each corner piece is 1/8 of a full atom.

A yellow and red cubes

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A red and yellow cube with circles

Description automatically generated with medium confidence

**Worked Example: Calculation of the APF for BCC**

A colorful cube with a red and yellow ball inside

Description automatically generatedNotice that the atoms at the corners of the BCC unit cell are not completely contained within this cell but as shown are only 1/8 of a full atom. We have 8 corners each with 1/8 of an atom so the corners contribute 1 full atom worth of volume to the unit cell. The body center atom is completely contained within the unit cell and so the cell has a total of 2 atom volumes.

**Number of atoms per unit cell:** 8 corner atoms x 1/8 + 1 body center atom = **2 atoms**

The volume of a sphere is given by:

A red sphere with yellow circles and a cube

Description automatically generatedA diagram of a mathematical equation

Description automatically generated**Edge length, , of the BCC unit cell:** From the figure below, we can see that atoms touch along the body diagonal. The body diagonal is equal to if we simply count the number of radii along its length (1R at the starting corner + 2R as we move along the diameter of the center atom + 1 R for the last corner atom). The body diagonal is also equal to (see Method 1 or 2 below). Equating these two relations we have that or  **.**

The atomic packing factor is then:

A black and white triangle with dotted lines

Description automatically generatedA drawing of a cube

Description automatically generated**A black line with a square in the corner

Description automatically generated with medium confidenceMethod 1 for length of body diagonal:** From triangle (1) we get the face diagonal is and from triangle 2 we find the body diagonal:

A diagram of a red sphere and a cube with a red circle and yellow circles

Description automatically generated

**Method 2 for length of body diagonal:**  Consider a cube of edge length =. If we start at one corner (0,0,0) and draw the body diagonal as a vector, , to the opposite corner, , then the body diagonal length is given by the magnitude of this vector: .

**Math aside: Dot products** We can find the magnitude of a vector starting with the definition of the dot product between two vectors, and forming an angle, . now if vector 1 is equal to vector 2 then the angle between them is zero degrees and we have: or since . Finally, we get

**Questions**

1. FCC – calculate edge length, volume, density, APF
2. We have 3 samples labeled A, B, and C. All contain the same 1 million atoms but sample A has the simple cubic crystal structure; sample B is body-centered cubic; and sample C is face-centered cubic. If they were all in the shape of a cube, which sample would be the largest? Smallest? Which material would weigh the greatest?
3. Same as 2 but give numbers and have the student calculate the size of samples A, B, and C.
4. Give a structure and ask which direction atoms touch I.e. along edges, faces or through the body diagonal.

**Deep Dive (Optional): Miller Indices**

**Point Coordinates**

**Directions**

**Planes**

**Angles & Distances using Point Coordinates and the Dot Product (Cubic System)**

**Worked Example: size of tetrahedral site in fcc lattice**

The easiest way to handle these problems is to use our point coordinates along with the definition of the dot product. The tetrahedral site using point coordinates is located at position (¼, ¼, ¼) relative to the neighboring corner at (0,0,0). The length of the vector connecting these two points is equal to R + r where R is the radius of the atoms occupying the fcc lattice points and r is the radius of the largest atom that can just fit into the tetrahedral site. We get where .

**Questions**

1. Size of octahedral site in fcc
2. Size of octahedral site in bcc type 1 and type 2

**Mini-lesson 2: Hexagonal Close-Packed (a, a, c, 90, 90, 120)**

**Hexagonal:** space filled model vs exploded view, atoms within unit cell, packing density (APF), edge length for close-packed structure. Packing of closest-packed planes versus FCC.

**Worked Example: Ideal c/a ratio using point coordinates.**

(stress that we are treating atoms as hard spheres)

**Fascinating Aside: Crystal structure affects mechanical behavior. FCC / HCP packing, Ductile/Brittle; white vs grey tin**

Blister on Pipe Organ

**A close-up of a skin cancer

Description automatically generated**A close-up of a metal piece

Description automatically generated**** by A. Eckert****

Question: Why does it form a blister? Hint: think about the difference in atom packing between white and grey tin.

**Questions**

1. Which of the following materials do you expect to be more ductile. FCC vs BCC, FCC vs HCP
2. Many hcp materials such as… do not have c/a ratios equal to … What does that suggest about the atoms in some hcp materials (think about our assumptions in the worked example).

**Deep Dive (Optional): Miller Indices for hexagonal system**

 Crystalline Solids (part 2)

Previously, we discussed BCC and FCC structures in their closest packed form. The atoms “want” to touch. This is typical of metals because of the metallic bond… nondirectional, delocalized. In some solids, especially the ceramics (ionic and covalent bonding), the atoms only want to touch opposite signed neighbors (ionic) or at specific angles (covalent). This means the unit cell contains much more space (less dense) than their metallic counterparts. Let’s take a look at some examples.

--- start with image of SC metallic structure then change ions to Cl-, but chloride ions repel each other and we need to balance the charge so let’s add Cs+ to the center. Cs is larger than space in center for SC structure so we need to expand the lattice a bit which makes the Cl- happier. Notice ratio of Cs to Cl is 1:1. Charge balance.

--- now what if instead of Cs the positive ion is much smaller, say Na+… try it in SC structure and show lattice doesn’t expand so look for another structure where the sites between Cl- are smaller e.g. fcc structure.

--- consider purely covalent bond – Carbon – wants 4 neighbors at specific angles. Fcc structure is compatible with this if we expand lattice and place more carbon atoms in tetrahedral sites… diamond

Principle: balance charge, ion ratio size avoid like sign atoms touching.