

Summary Chapter 1

We learned in chapter 1 that there is order in most solid materials, i.e. the atoms are not arranged arbitrary, solid materials show order and consist of crystals. An ideal crystal is constructed by the infinite repetition of identical groups of atoms. A group is called the basis. The set of mathematical points to which the basis is attached is called the lattice. The lattice may be defined by three translation vectors, \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 . The arrangement of atoms looks the same from any point \mathbf{r}' where \mathbf{r}' differs from \mathbf{r} by an integral multiple of the translation vectors, i.e.

$$\mathbf{r}' = \mathbf{r} + u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3 \quad \text{so } u_1, u_2, \text{ and } u_3 \text{ are integers}$$

The space defined by \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 is called the unit cell. The definition of unit cell is not unique. If any two points for which the atomic arrangement looks the same satisfies above equation with suitable choice of integers u_1 , u_2 , and u_3 we identify the lattice as primitive. For a primitive lattice the volume of the unit cell, i.e. $\vec{a}_1 \bullet \vec{a}_2 \times \vec{a}_3$ is minimum. The corresponding translation vectors are referred to as primitive translation vectors. Note that the primitive unit cell is not unique. Conventional unit cells are defined by non-primitive axes. A primitive unit cell contains one lattice point per cell.

A special type of primitive lattice cell is the Wigner-Seitz cell. This cell is bounded by planes that intersect the lines between neighboring lattice points right in between both lattice points. We will see in chapter 2 that the Wigner-Seitz cell is very relevant to understand diffraction effects.

The basis is defined by one or more atoms positioned within the unit cell. The position of the atoms in the unit cell is defined with respect to the associated lattice point, i.e.

$$\mathbf{r}'_j = \mathbf{r} + x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3$$

where x_j , y_j , and z_j define the position of the j th atom with the unit cell and are numbers between 0 and 1.

In addition to the translational symmetry discussed above, crystal lattice may have rotational symmetry. Some lattices have one, two, three, four or six-fold rotation axes. A crystal with a three-fold rotation axis for example will look the same when rotated over $2\pi/3$. Although molecules with other rotation symmetries do exist, a periodic infinite lattice cannot have for example a fivefold rotation axis.

In two-dimensions the oblique lattice as depicted in figure 3 is only invariant under rotation of π and 2π . A rectangular 2D lattice is also invariant under the mirror operation. A square 2D lattice is also invariant under a rotation of $\pi/2$ and $3\pi/2$. The other two Bravais lattices in 2D are the hexagonal lattice and the centered rectangular lattice. Note that each Bravais lattice is defined by a number of symmetry operations.

In 3D the triclinic lattice is the most general lattice. There are 13 special lattices in 3D: cubic, tetragonal (one side different length), orthorhombic (all sides different length), monoclinic (all sides different length and one angle unequal to 90 degrees), trigonal (all sides equal and all angles equal but unequal to 90 degrees), hexagonal (two sides equal and two angles 90 degrees and one angle 120 degrees). Note

that for some of these lattice types there are different centering, i.e. body centered, face centered, simple cubic, or base centered.

We looked to four different crystal structures more carefully, i.e. the simple cubic, the body centered cubic, the face centered cubic, and the Hexagonal closed packed crystal structures. The HCP and FCC structures have the largest packing fraction while the SC structure has the lowest packing fraction. Materials with ionic bonds often crystallize in a closed packed structure. Good examples are the metal oxides where the oxygen forms an FCC crystal structure. The much smaller positive ions fill the voids in between the large oxygen ions. For an FCC structure two types of voids exist: (1) tetrahedral voids (two for each atom); (2) octahedral voids (one for each atom). Tetrahedral voids have a coordination number of 4 while octahedral voids have a coordination number of 6. For FCC the octahedral voids are the largest. If all octahedral voids are filled up we will get the NaCl structure also often referred to as the rocksalt structure: the Cl⁻ ions form a fcc structure and the small Na⁺ ions fill the octahedral voids. For the fcc structure the octahedral voids have a radius of 0.414 times the radius of the negative ion radius and the tetrahedral voids have a radius of 0.225 times the radius of the negative ion radius. For atoms that form covalent bonds the coordination number of the void might be more important than the size of the void. For example in SiC both atoms have a valence of four and want to be surrounded by 4 neighbors. If one considers an fcc structure built up from Si atoms, half of the tetrahedral voids are filled up with Carbon atoms. This results in the ZnS crystal structure drawn on page 18 of the text.

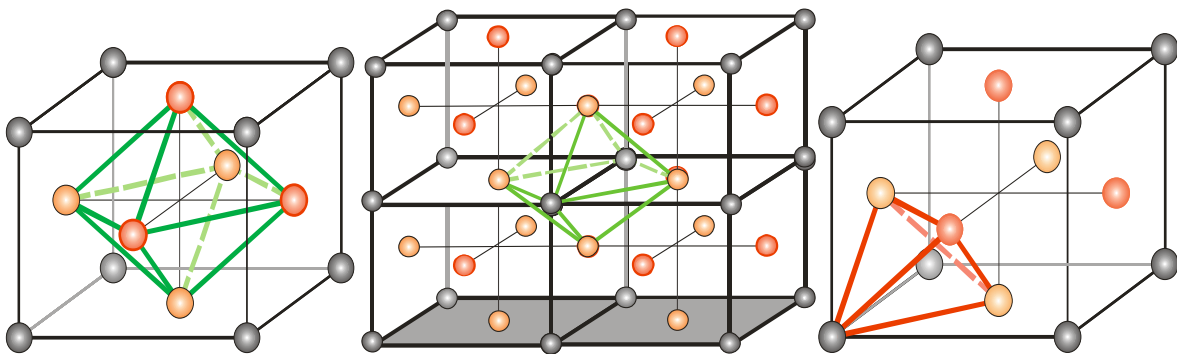


Fig. 1: (a) Octahedral voids in center of conventional unit cell of fcc structure (note that this void is solely owned by the conventional unit cell); (b) Octahedral void at the edge of the conventional and only counts for $\frac{1}{4}$. For each line of the cube there is one octahedral void which adds up to $12/4=3$ octahedral voids at the edge of the conventional unit; (c) tetrahedral void in conventional unit cell (there is one at each corner of the cube, i.e. 8 tetrahedral voids per conventional unit cell or 2 tetrahedral voids per atom).

Note that in a SC crystal the atoms have a coordination number of 6. This crystal structure has a small packing fraction. There is only one element that crystallizes in the SC structure. The voids for the simple cubic structure is depicted in Fig. 2. The void is large, i.e. 0.732 times the radius of the negative ions that are situated at the corners of the cube. The coordination number of the central void is 8. Considering a SC crystal structure of chloride ions, a positive ion fits easily in the center void. Filling the void with Cs⁺ ion will result in the CsCl crystal structure shown on page 14 of Kittel.



Fig 2: central void in center of simple cubic crystal structure.

For a BCC crystal the coordination number for each atom is 8. One can find 3 octahedral voids and 6 tetrahedral voids in the conventional bcc unit cell as depicted in Fig. 3 below. The octahedral voids in the bcc are the smallest voids, i.e. 0.155 times the radius of the negative ions. The tetrahedral voids are a little larger i.e. 0.29 time the radius of the negative ions that build up the bcc lattice. Note that the tetrahedral and octahedral voids of the bcc structure are distorted.

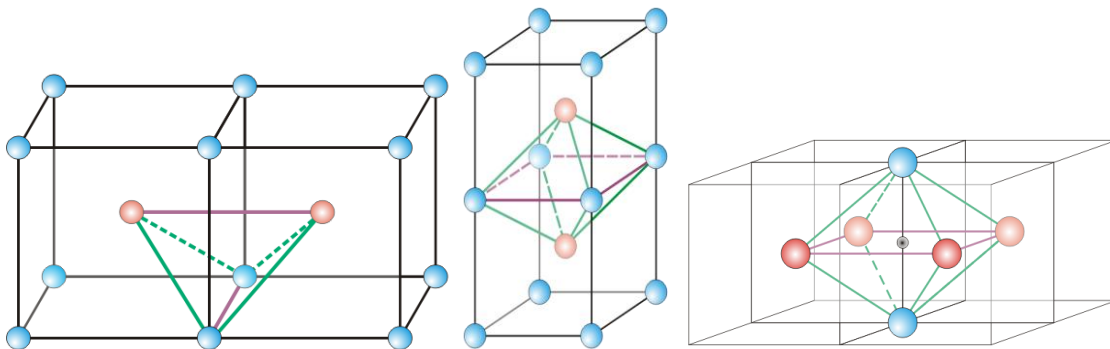


Fig. 3: (a) tetrahedral void bcc structure, i.e. two for each line of the cube so $2 \times 12 / 2 = 12$; (b) octahedral void on each plane so $6 / 2 = 3$; (c) other octahedral void, one on each line so $12 / 4 = 3$.

The hcp and fcc crystal structure are very similar if one compares the (111) planes of the fcc structure with the (001) plane of the hcp structure. Both planes are close packed, i.e. each atom is surrounded by 6 neighbors. Stacking atom layers on top of these closed packed planes allows for two different methods. One can stack every third layer of atoms exactly above the first layer. This will result in a stacking sequence ABABABAB etc. This corresponds to an hcp crystal structure. It is also possible to put the third layer shifted with respect to the first two layers, so now you will get a stacking ABCABCABC. This stacking corresponds to an fcc crystal structure. The difference between both structures is depicted in the figure below.

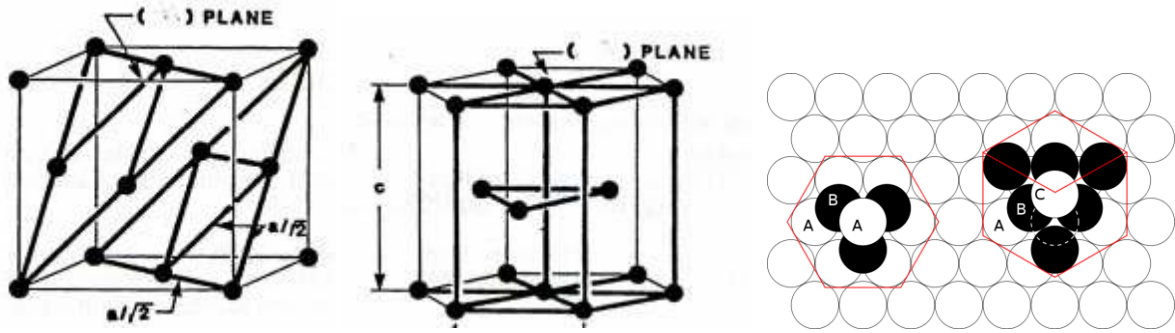


Fig. 4: (111) planes of fcc structure on the left and (001) planes of hcp structure in the middle; difference between hcp and fcc crystal structure on the right.

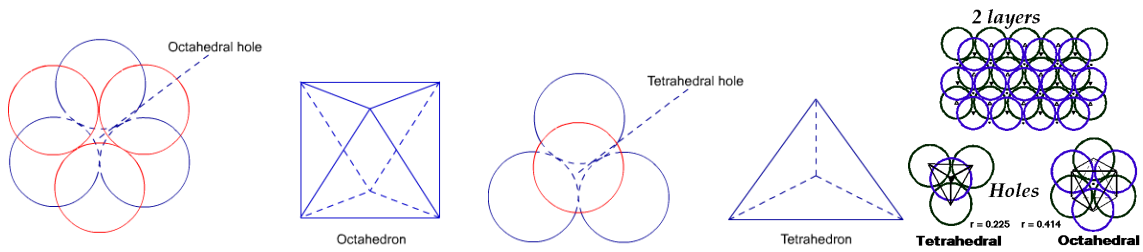


Fig. 5: Octahedral voids on the left and tetrahedral void in the middle for fcc or hcp structures; tetrahedral and octahedral voids on far right.

The voids for an hcp crystal structure are very similar to the voids for an fcc structure. For each atom we expect two tetrahedral voids, i.e. one above the atom and one below the atom in the (001) direction. One octahedral voids can be expected per atom for the hcp crystal structure.