Chapter 2

Crystallography

2.1 Crystal structure

The periodic three-dimensional array of atoms in a crystalline solid constitutes the crystal lattice of the substance. For monoatomic solids there are 14 distinct crystal structures, or Bravais lattices. Each of these is defined by a unit cell, a block of atoms which displays the crystallographic features of the lattice type and which, by translation alone (no rotation), can reproduce the entire crystal.

2.1.1 14 Bravais Lattice

An example of a primitive unit cell, since it effectively consists of only one atom. Although eight atoms are shown in the figure, each is shared equally by seven other unit cells adjacent to the one shown. Only $\frac{1}{8}$ of each atom belongs to the unit cell, in total, the unit cell consists of one atom in Fig. 2.1. Although the primitive unit cell is the most basic representation of each of the 14 fundamental lattice types, it may not be the most convenient. Three members of cubic lattices are SC, FCC, BCC (3 of 14 Bravais lattice system)

2.2 Miller indices for direction

A crystallographic direction is defined as a line between two points, or a vector. The following steps are utilized in the determination of the three directional indices. A vector of convenient length is positioned such that it passes through the origin of the coordinate system. Any vector may be translated throughout the crystal lattice

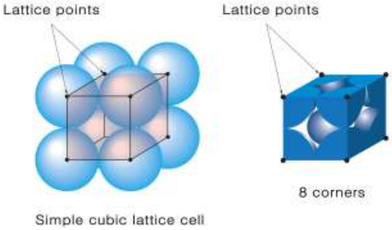
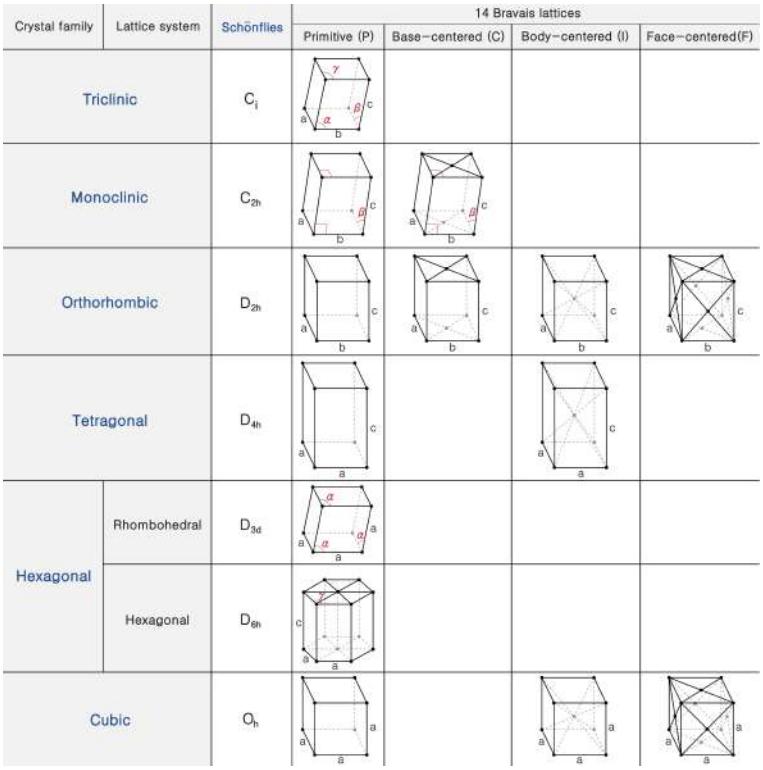


Figure 2.1: Crystal structure of simple cubic



Crystal family	Lattice system	Schönflies	14 Bravais lattices			
			Primitive (P)	Base−centered (C)	Body−centered (I)	Face−centered(F)
Triclinic		C_i	a, b, c, α, β, γ			
Monoclinic		C_{2h}	a, b, c, β	a, b, c, β		
Orthorhombic		D_{2h}	a, b, c	a, b, c	a, b, c	a, b, c
Tetragonal		D_{4h}	a, a, c		a, a, c	
Hexagonal	Rhombohedral	D_{3d}	a, a, a, α, α, α			
	Hexagonal	D_{6h}	a, a, c, γ			
Cubic		O_h	a, a, a		a, a, a	a, a, a

Figure 2.2: 14 Bravais lattices

without alteration, if parallelism is maintained. The length of the vector projection on each of the three axes is determined; these are measured in terms of the unit cell dimensions a, b, and c. These three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values. The three indices, not separated by commas, are enclosed in square brackets, thus: $[uvw]$. The u, v, and w integers correspond to the reduced projections along the x, y, and z axes, respectively. To represent the vector in Fig. 2.3,

1. We have projections along x, y, and z directions, $a/2$, b and $0c$.
2. Projections can be represented in terms of a, b and c, $1/2$, 1 and 0.
3. By reduction, we have 1, 2, 0 along x, y, and z directions
4. In enclosure form, we have [120]

Three components are sufficient to represent one vector in three-dimensional space, but the Hexagonal system uses the Miller-Bravais system, which uses four components conventionally in Fig. 2.4. n is a factor that may be required to reduce u, v, t, and w to the smallest integers.

$$[u'v'w'] \rightarrow [uvtw] \quad u = \frac{n}{3}(2u' - v') \quad v = \frac{n}{3}(2v' - u')$$

$$t = -(u + v) \quad w = nw'$$

To represent the green vector in Fig. 2.5, if you look at the basal plane from above, it is illustrated by Fig. 2.6, the project to $\mathbf{a}_1$ and $\mathbf{a}_2$ vectors, the lengths between

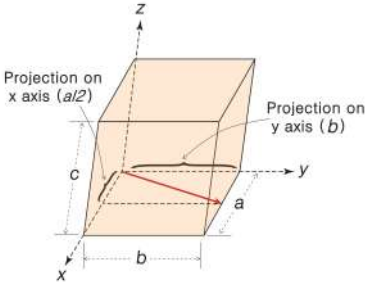


Figure 2.3: Illustration of direction using Miller-Bravais indices.

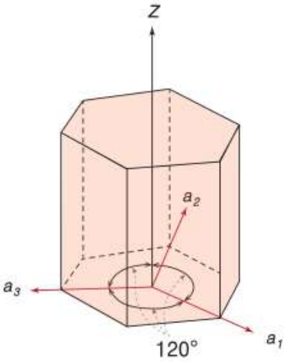


Figure 2.4: Miller-Bravais system of hexagonal system.

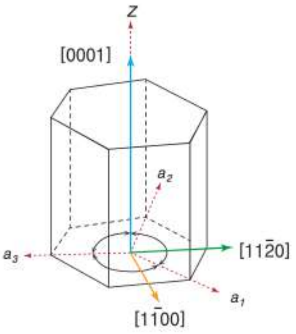


Figure 2.5: Miller-Bravais system of hexagonal system.

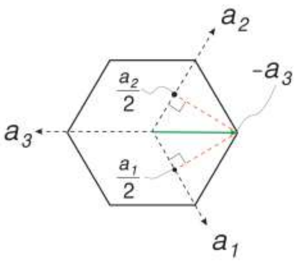


Figure 2.6: Projection to the basal plane of system in Fig. 2.5

the center to the foots of perpendicular are $a_1/2$ and $a_2/2$, and it is parallel to the $\mathbf{a}_3$ vector, so $1/2, 1/2, -1, 0$ and this can be expressed as $[11\bar{2}0]$ in enclousure form.

2.3 Miller indices for plane

he orientations of planes for a crystal structure are represented in a similar manner. In all but the hexagonal crystal system, crystallographic planes are specified by three Miller indices as (hkl). Any two planes parallel to each other are equivalent and have identical indices. The procedure employed in determination of the h, k, and l index numbers is as follows:

1. If the plane passes through the selected origin, either another parallel plane must be constructed within the unit cell by an appropriate translation, or a new origin must be established at the corner of another unit cell.

2. At this point the crystallographic plane either intersects or parallels each of the three axes; the length of the planar intercept for each axis is determined in terms of the lattice parameters a, b, and c.

3. The reciprocals of these numbers are taken. A plane that parallels an axis may be considered to have an infinite intercept, and, therefore, a zero index.

4. If necessary, these three numbers are changed to the set of smallest integers by multiplication or division by a common factor.

5. Finally, the integer indices, not separated by commas, are enclosed within parentheses, thus: (hkl).

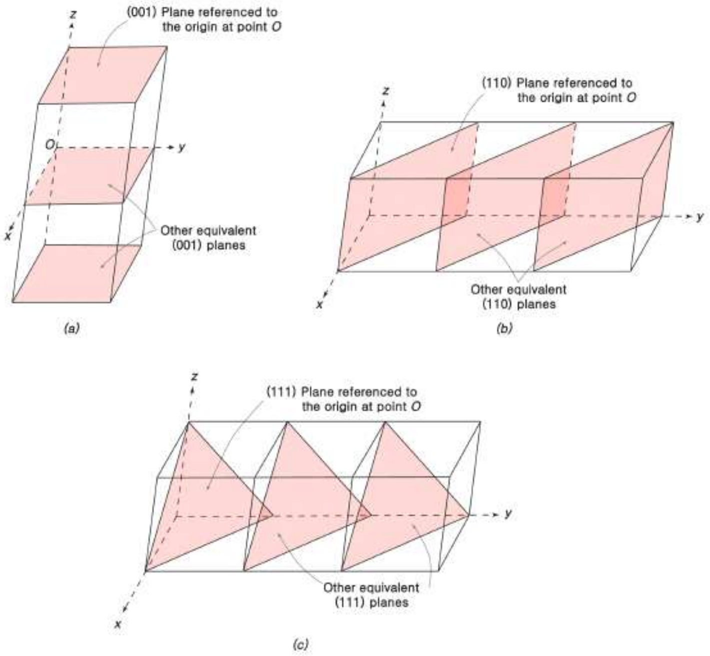


Figure 2.7: Miller indices of (001), (110) and (111) planes

To specify the plane in Fig. 2.8,

- Intercepts on x-axis: ∞a
- Intercepts on y-axis: $-b$
- Intercepts on z-axis: $c/2$
- Intercepts in terms of lattice parameters: ∞, -1, $1/2$
- Reciprocals 0, -1, 2
- In enclosure form, $(0\bar{1}2)$

2.4 Face Centered Cubic

The original unit cell is repeatedly set as the minimum unit that can compose the entire crystal, but in the case of FCC, it is slightly different from the conventional unit cell and primitive unit cell (minimum unit). Since it is more intuitive to interpret that there are atoms on each side of a cubic unit cell, the unit cell shown on the left is used more extensively. The coordinate number is 12 for FCC (Face Centered Cubic).

2.5 Body Centered Cubic

It is a form with one atom at the center of a simple cubic. In abbreviated form, we call it as BCC. The coordinate number is 8 for BCC.

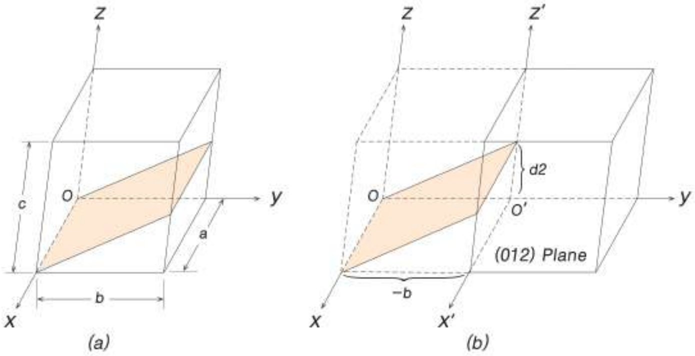


Figure 2.8: Miller indices of $(0\bar{1}2)$ plane.

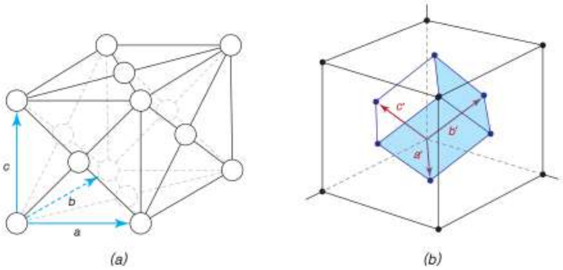


Figure 2.9: Primitive cell and unit cell of FCC.

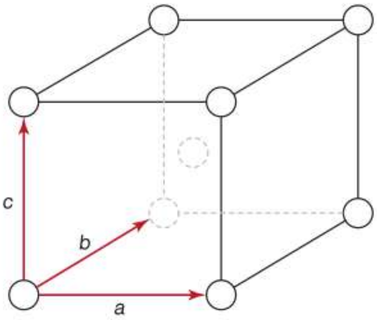


Figure 2.10: Unit cell of BCC.

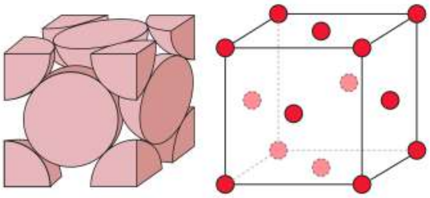


Figure 2.11: Unit cell of FCC.

2.6 Atomic Packing Factor

The fraction of volume in a crystal structure that is occupied by constituent particles. In Abbreviated form,

$$\mathrm{APF} = \frac{N_{\text{particle}} V_{\text{particle}}}{V_{\text{unit cell}}}$$

2.6.1 Simple cubic

APF for simple cubic is

$$\mathrm{APF} = \frac{N_{\text{particle}} V_{\text{particle}}}{V_{\text{unit cell}}} = \frac{\frac{4\pi r^3}{3}}{a^3} = \frac{4\pi r^3}{3a^3}$$

where $a = 2r$,

$$\mathrm{APF} = \frac{\pi}{6} \simeq 0.52$$

2.6.2 FCC

APF for FCC is

$$\mathrm{APF} = \frac{N_{\text{particle}} V_{\text{particle}}}{V_{\text{unit cell}}} = \frac{4 \times \frac{4\pi r^3}{3}}{a^3} = \frac{16\pi r^3}{3a^3}$$

where $\sqrt{2}a = 4r \rightarrow a = 2\sqrt{2}r$,

$$\mathrm{APF} = \frac{\pi}{3\sqrt{2}} \simeq 0.74$$

, APF is higher than the value for a simple cubic.

2.6.3 BCC

APF for BCC is

$$\mathrm{APF} = \frac{N_{\text{particle}} V_{\text{particle}}}{V_{\text{unit cell}}} = \frac{2 \times \frac{4\pi r^3}{3}}{a^3} = \frac{8\pi r^3}{3a^3}$$

where $\sqrt{3}a = 4r$,

$$\mathrm{APF} = \frac{\sqrt{3}\pi}{8} \simeq 0.68$$

, APF is higher than the value for a simple cubic and lower than the value for FCC.

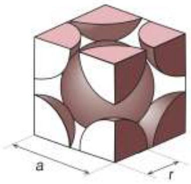


Figure 2.12: Unit cell of BCC.

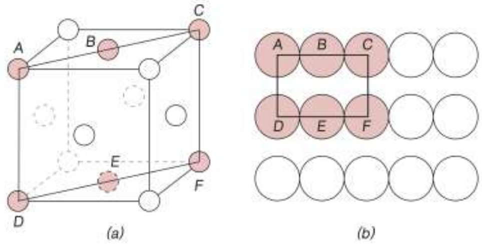


Figure 2.13: (110) plane of FCC structure.

2.7 Planar density

The planar density can be also defined. Assuming the hard sphere model, it is assumed that the center of the sphere is on the plane. The planar density of (110) plane of FCC structure illustrated in Fig. 2.13 is

$$\text{Planar density} = \frac{2\pi r^2}{\sqrt{2}a^2} \simeq 0.555$$

The planar density of (111) plane of FCC structure is

$$\text{Planar density} = \frac{\left(3 \times \frac{1}{6} + 3 \times \frac{1}{2}\right)\pi r^2}{\frac{\sqrt{3}}{2}a^2} \simeq 0.906$$

The planar density of (110) plane of BCC structure is

$$\text{Packing fraction} = \frac{2\pi r^2}{\sqrt{2}a^2} = \frac{3\sqrt{2}\pi}{16} \simeq 0.833$$

2.8 Family of planes

A family of planes contains all those planes that are equivalent—that is, having the same atomic packing and other many things; and a family is designated by indices that are enclosed in braces. In cubic crystal {111} family consists (111),($\bar{1}$11),(1$\bar{1}$1),(11$\bar{1}$), ($\bar{1}\bar{1}$1), ($\bar{1}$1$\bar{1}$), (1$\bar{1}\bar{1}$), ($\bar{1}\bar{1}\bar{1}$).

2.9 Hexagonal close packed

FCC and Hexagonal closed packed (HCP) system is all close packed system so APF is 0.74 and BCC is not close packed system. Sequence ABABAB $\cdots$ creates HCP structure and ABCABC $\cdots$ creates FCC structure.

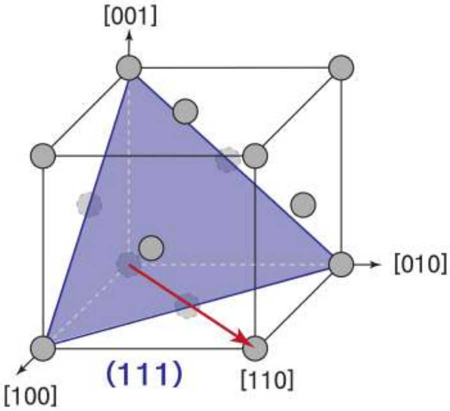


Figure 2.14: (111) plane of FCC structure.

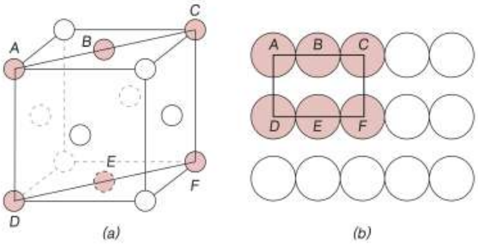


Figure 2.15: (110) plane of BCC structure.

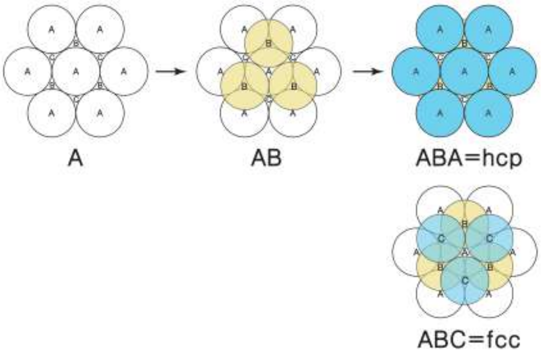


Figure 2.16: Atomic plane stacking for FCC and HCP structures.

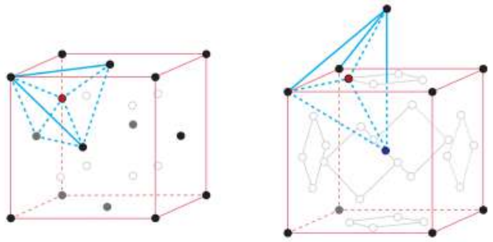


Figure 2.17: Tetrahedral sites of FCC and BCC structures.

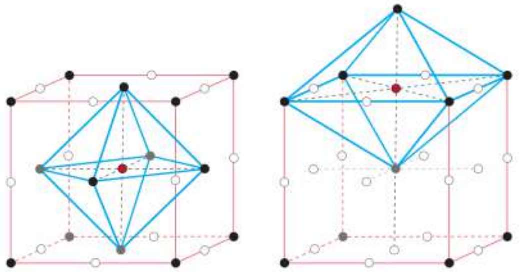


Figure 2.18: Octahedral sites of FCC and BCC structures.

2.10 Interstitial sites

The interstitial site means a site between packed atoms, and there are largely tetrahedral sites and octahedral sites. Since the APF of the FCC is usually higher than that of the BCC, it can be expected that there are more interstitial sites in the BCC rather than FCC.

2.10.1 Tetrahedral sites

A tetrahedron is made with atoms, and the center of gravity is the tetrahedral site. As shown in the Fig. 2.17, there are 8 of these sites in FCC and 12 in BCC, confirming again that there are more tetrahedral sites in BCC.

2.10.2 Octahedral sites

An octahedron is made with atoms, and the center of gravity is the octahedral site. As shown in the Fig. 2.18, there are 4 of these sites in FCC and 6 in BCC, confirming again that there are more octahedral sites in BCC.

2.11 Diamond structure

Group IV elements, such as Diamond (C), Si, Ge elements usually create covalent bonding between atoms. In the diamond structure, atoms are placed at FCC lattices and 1/2 tetrahedral sites. Each atom has four neighbors in tetrahedral coordination.

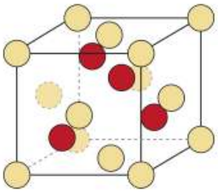


Figure 2.19: Diamond structure

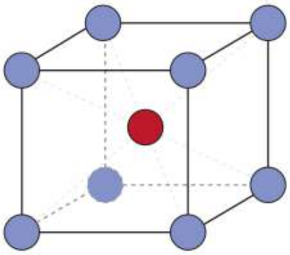


Figure 2.20: CsCl structure

2.12 Binary compounds

When two different atoms form the ionic compounds, there are many types of possibilities. The universally known binary compound structures are

- BCC substitutional: CsCl
- FCC interstitial(Octahedral): NaCl
- FCC interstitial(1/2 Tetrahedral): MgO, $\beta-$ZnS
- FCC interstitial (Tetrahedral): UO_2

The CsCl structure, also can be categorized by BCC substitutional, ratio between blue and yellow circles in Fig. 2.20 are 1:1. CsCl, CuZn(β) have those type of structure. When two atoms have similar atomic sized, it is possible to have CsCl structure. One cation is surrounded by the eight anions and an anion is surrounded by the eight cations, which minimizes the electrostatic interaction energy. The cation is placed at the octahedral site of the anion BCC structure.

There are many types of FCC interstitial structures. First type is FCC+All octahedral sites. All anions are placed at FCC lattice sites and cations placed at all octahedral sites in Fig. 2.22. NaCl structure has those type of the structure.

Another type of FCC interstitial structure is that anions place at FCC sites and cations are placed at 1/2 tetrahedral sites in Fig. 2.22. β-ZnS and MgO have the FCC + 1/2 tetrahedral sites structure.

Also all tetrahedral sites can be filled by cations, Fluorite structure described in Fig. 2.23. UO_2,CaF_2 have the Fluorite structure.

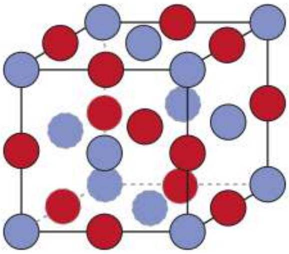


Figure 2.21: NaCl structure

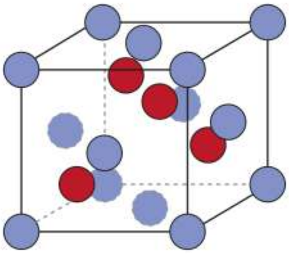


Figure 2.22: MgO structure

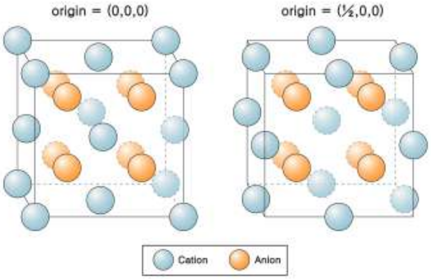


Figure 2.23: UO_2 structure