CHAPTER 2

CRYSTAL STRUCTURE

Contents

2.1 Introduction

Crystal is defined as a solid material whose constituent atoms, molecules, or ions are arranged in an ordered pattern extending in all three spatial dimensions. It is

- a word derived from the Greek word *Krystallos* meaning *frozen ice*.
- a misnomer for what we now know today as 'Quartz'

The scientific study of crystals and crystal formation is known as *crystallography*.

2.1.1 Characteristics

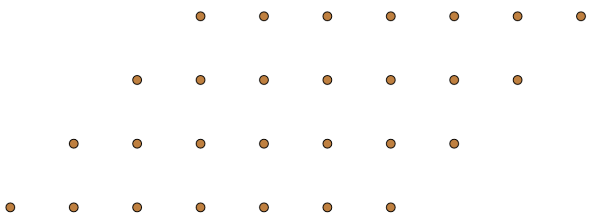
- They have a well defined shape.
- They show anisotropy with respect to physical properties.
- Some Crystals show polarization of light. (Ex. Sodium Chlorate ($NaClO_3$))
- Pleochroism, the effect when a material appears to have different colors when viewed in different directions.
- Fluorescence and Phosphorescence
- Magnetism

2.1.2 Occurrence

- found in nature (eg. diamond, graphite, quartz, etc)
- also grown in labs (eg. silicon, germanium, etc)

2.2 Space Lattice

A *space lattice* is a regular arrangement of geometrical points in space.



2.2.1 One Dimensional Lattice

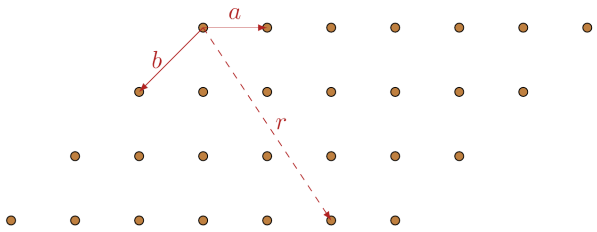
It is an array of points arranged such that the distance between any two successive points is a constant, a.

a is called the *lattice periodicity*. $\vec{a}$ is called the basis vector. Position vector of any lattice point with respect to an arbitrary origin is given as

$$\vec{r} = n \times \vec{a}; \qquad n \in \mathcal{Z}$$

2.2.2 Two Dimensional Lattice

An one dimensional lattice repeated at a regular interval b in a non-collinear direction gives a net of lattice points called the two dimensional lattice.



Position vector of any lattice point with respect to an arbitrary origin is given as

$$\vec{r} = p\vec{a} + q\vec{b}; \qquad p, q \in \mathcal{Z}$$

2.2.3 Three Dimensional Lattice

A two dimensional lattice repeated at a regular interval c in a non-coplanar direction gives rise to a three dimensional lattice.

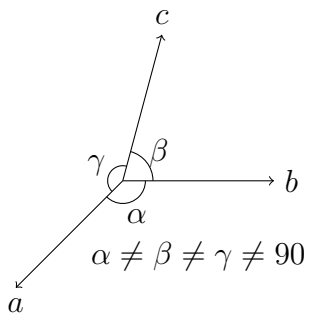
A 3-dimensional lattice will have three basis vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$.

Position vector of any lattice point with respect to an arbitrary origin is given as

$$\vec{r} = l\vec{a} + m\vec{b} + n\vec{c}; \qquad l, m, n \in \mathcal{Z}$$

2.3 Lattice Parameters

The crystal coordinate system is as shown. $\vec{a}$, $\vec{b}$ and $\vec{c}$ are cell axes; α, β and γ are the interaxial angles.

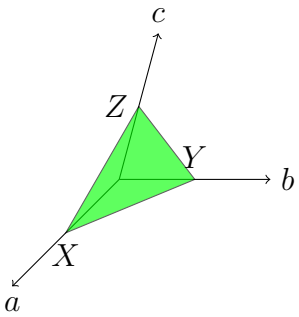


The coordinate system, in general, is *not orthogonal*

If a, b and c are the reference axes and X, Y and Z are the intercepts along the three axes respectively, then

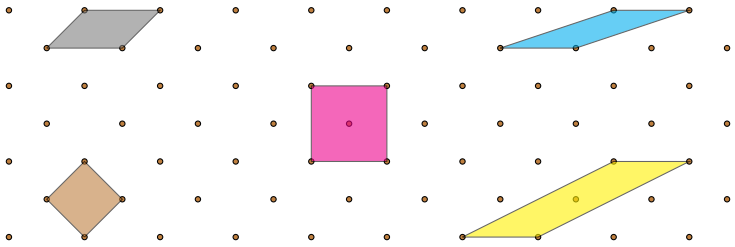
$$\frac{\vec{a}}{X} + \frac{\vec{b}}{Y} + \frac{\vec{c}}{Z} = 1$$

is the equation of the plane.



2.4 Unit cell and Primitive Cell

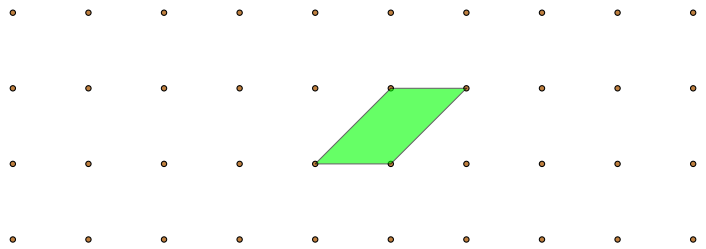
Given a lattice, the choice of a cell is arbitrary. Once can even choose a *centered* cell.



A cell with minimum area will generally be chosen unless the centered cell provides additional benefits.

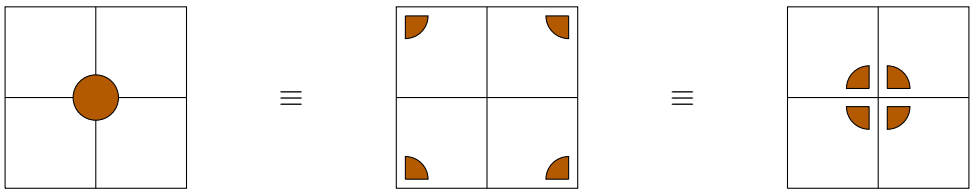
2.4.1 Lattice Points per Cell

When one considers a lattice and an unit cell, how many lattice points are associated with a cell?



One lattice point is associated with each cell.

An alternate view : Consider a lattice point as shown. It is shared between four cells. Contribution of the lattice point to each cell is 1/4. From the four corners, we have $4 \times 1/4 = 1$ lattice point per cell.



For a centered cell, it is $1 + 4 \times 1/4 = 2$ lattice points per cell.

2.4.2 Some definitions

Unit Cell A region of the crystal defined by three vectors, $\vec{a}$, $\vec{b}$ and $\vec{c}$, which when translated by any integral multiple of those vectors, reproduces a similar region of the crystal.

Primitive Cell A cell which has only one lattie point associated with it.

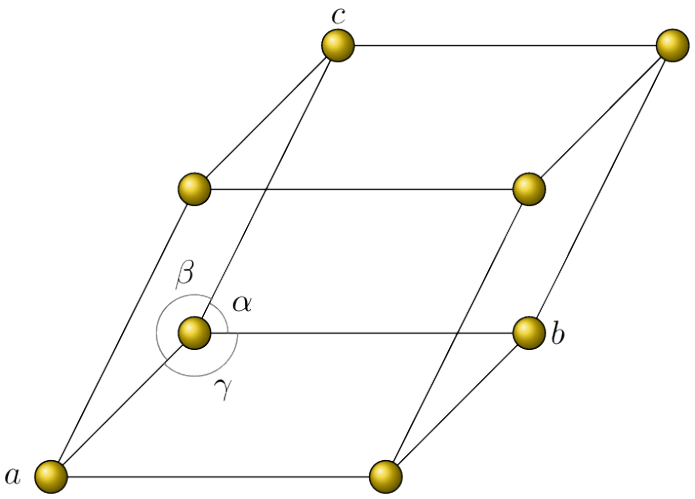
All primitive cells are unit cells, but all unit cells need not be primitive cells.

Basis Vector A set of linearly independent vectors, $\vec{a}$, $\vec{b}$ and $\vec{c}$,, which can be used to define a unit cell.

Lattice Parameters The basis vectors, along with the angle between the three vectors are called the lattice parameter.

2.5 Crytsal Systems

2.5.1 Triclinic

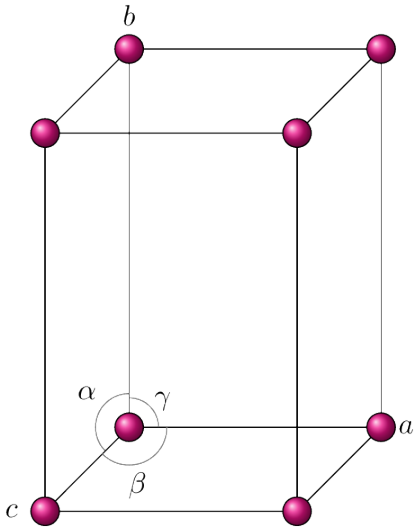


Cell Parameters

$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90°, 120°$

2.5.2 Monoclinic

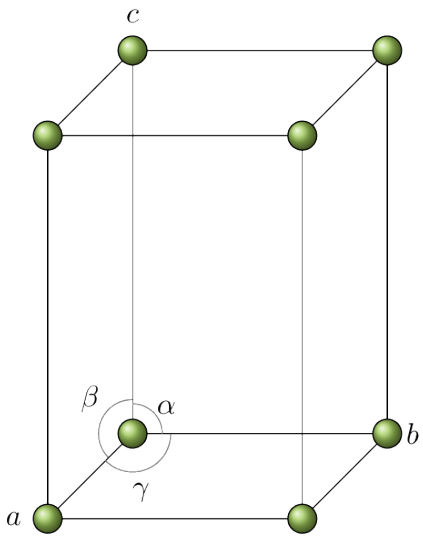


Cell Parameters

$a \neq b \neq c$

$\alpha = \gamma = 90, \beta \neq 90°, 120°$

2.5.3 Orthorhombic

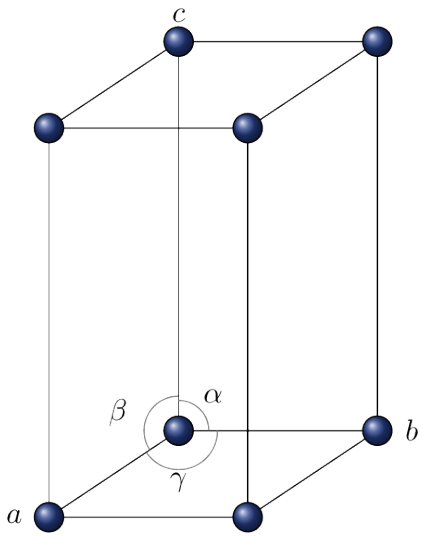


Cell Parameters

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

2.5.4 Tetragonal

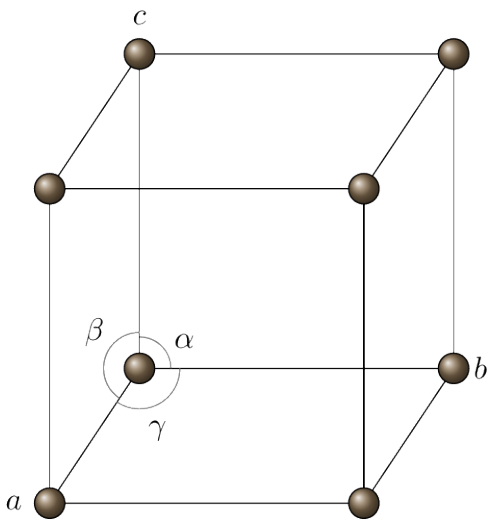


Cell Parameters

$a = b \neq c$

$\alpha = \beta = \gamma = 90°$

2.5.5 Cubic

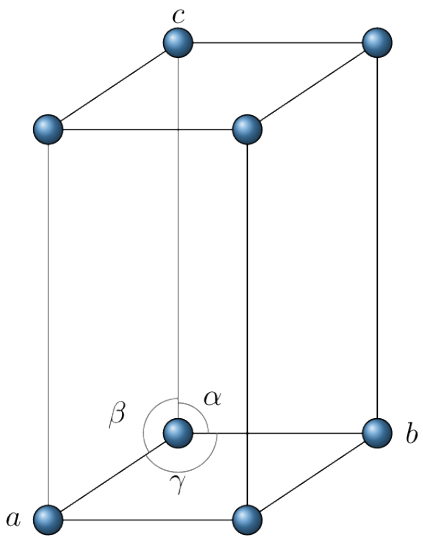


Cell Parameters

$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$

2.5.6 Hexagonal

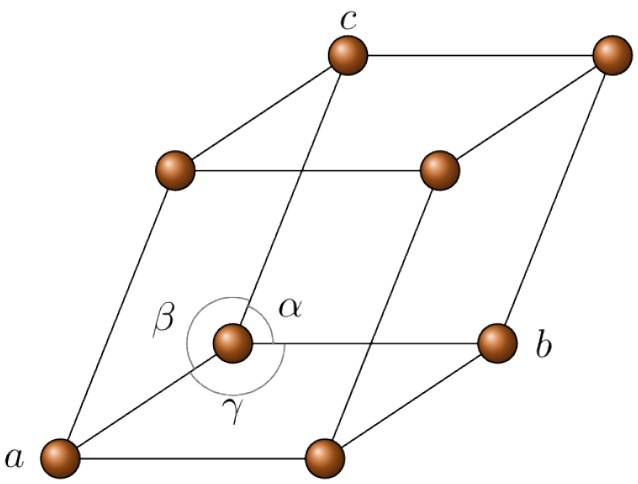


Cell Parameters

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ, \gamma = 120^\circ$$

2.5.7 Rhombohedral



Cell Parameters

$a = b = c$

$\alpha = \beta = \gamma \neq 90°, < 120°$

2.6 Bravais Lattice

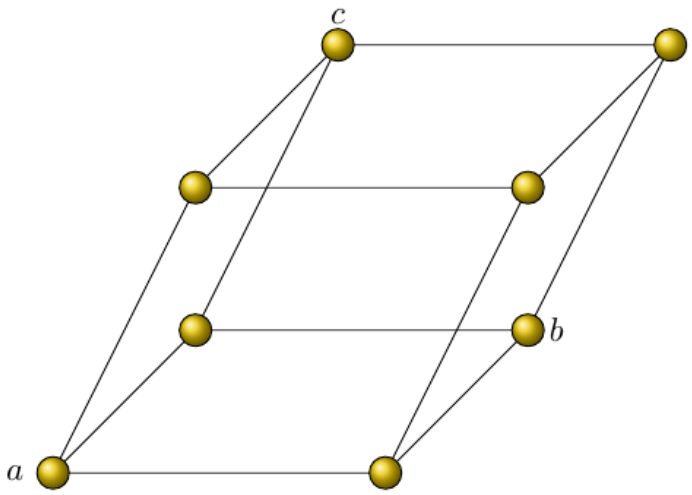
Auguste Bravais, a french physicist showed in 1845 that there are only 14 unique lattices in three dimensional crystallographic systems.

> "A Bravais lattice is an infinite set of points generated by a set of discrete translation operations."

The Bravais lattices are arrived at by combining one of the seven crystal systems with one of the lattice centerings.

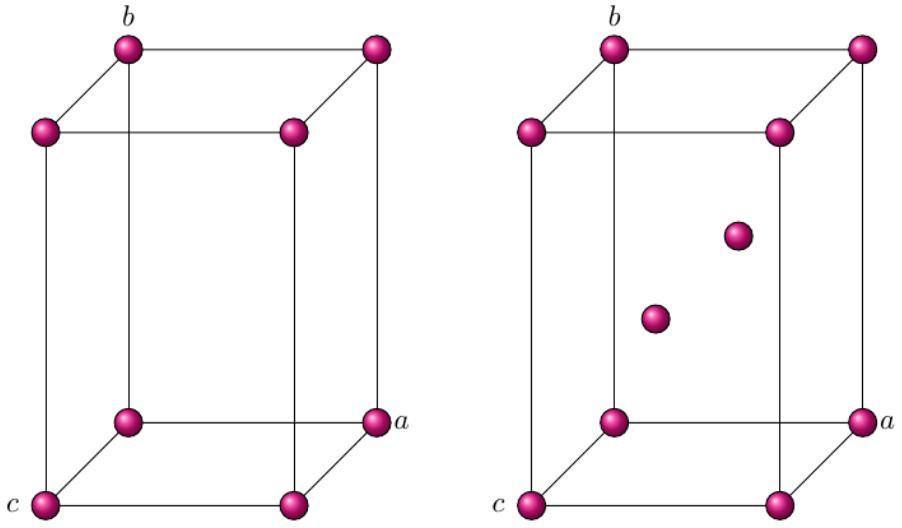
Primitive (P): Lattice points only at corners, or no centering.
Body Centered (I): P, with an additional point at the cell center.
Base Centered (C): P, with two additional points at the centers of opposite faces.
Face centered (F): P with one additional point at the centre of each face of the cell.

2.6.1 Triclinic Bravais Lattices



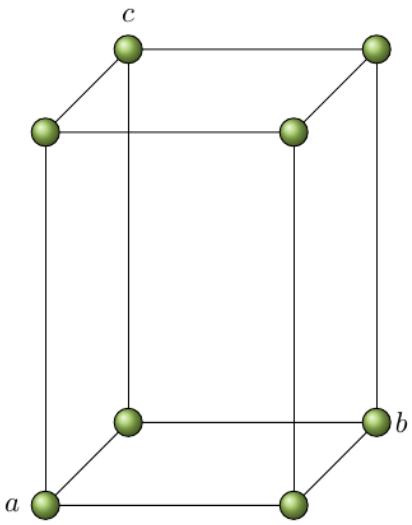
P

2.6.2 Monoclinic Bravais Lattices

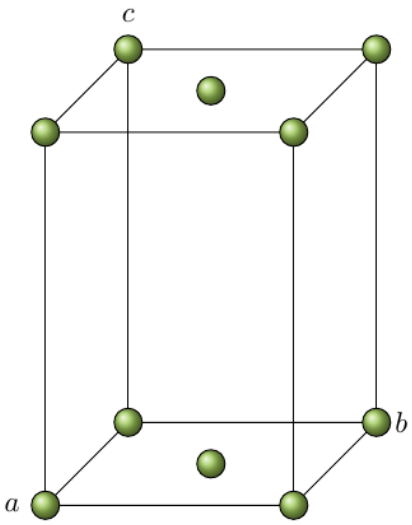


P *C*

2.6.3 Orthorhombic Bravais Lattices

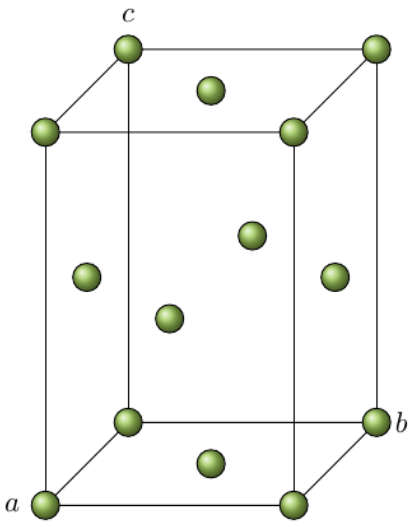


P

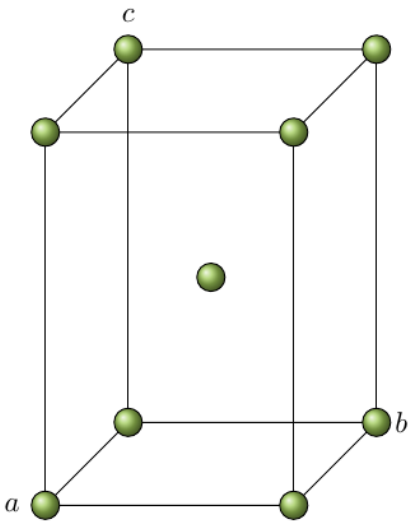


C

2.6.4 Orthorhombic Bravais Lattices

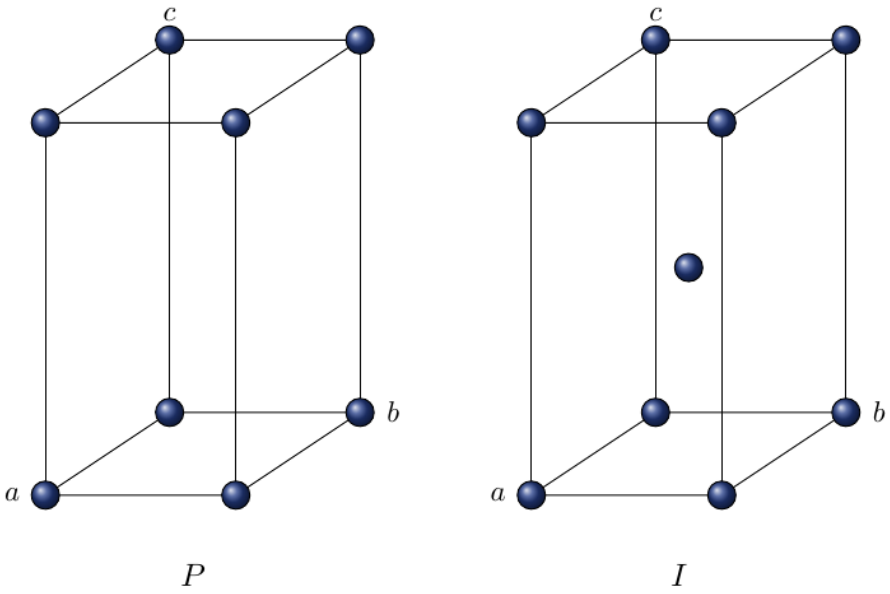


F

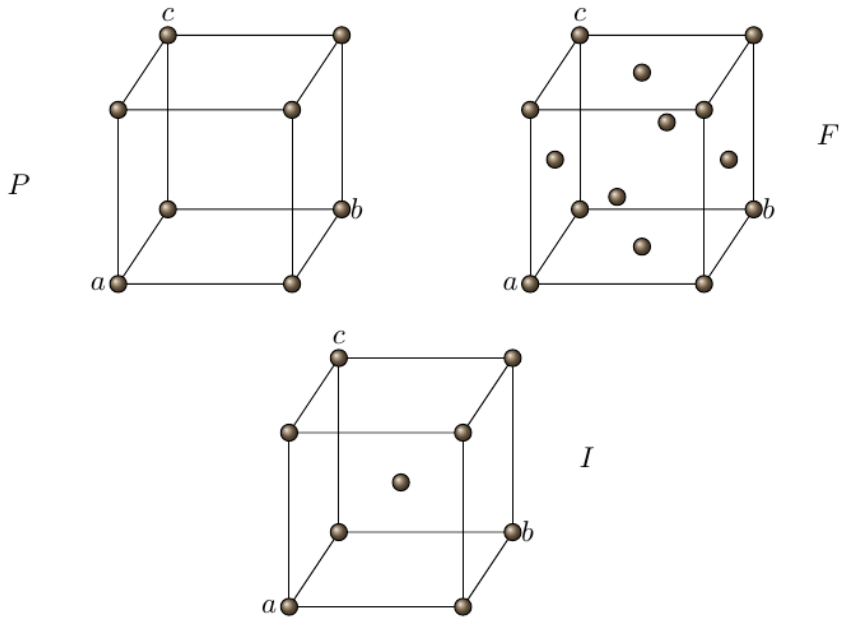


I

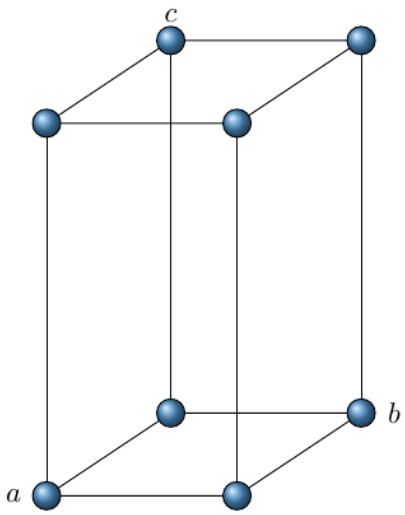
2.6.5 Tetragonal Bravais Lattices



2.6.6 Cubic Bravais Lattices

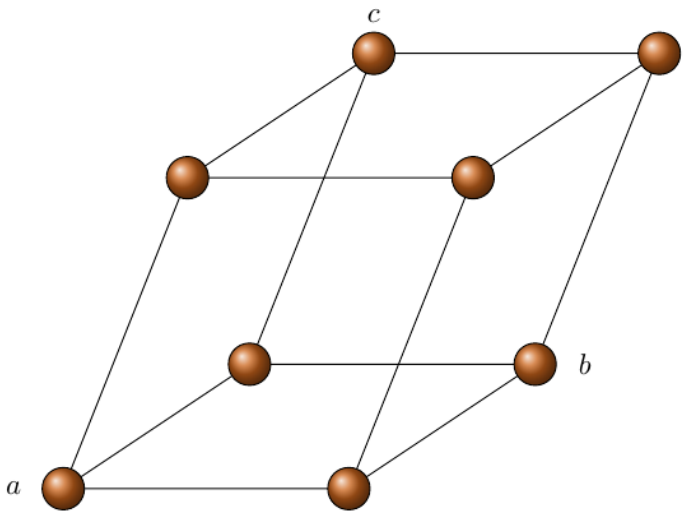


2.6.7 Hexagonal Bravais Lattices



P

2.6.8 Rhombohedral Bravais Lattices



P

2.7 Miller Indices

Miller indices may be defined as **a set of lowest three integers, whose ratio is taken in the order same as that of the reciprocals of the intercepts of the planes on the corresponding axes in the same order.**

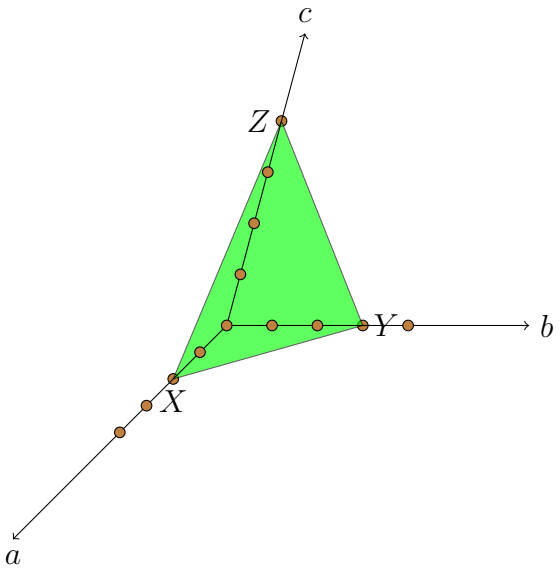
2.7.1 Calculating the Miller Indices

The 3 steps are

- Choose a convenient origin and set up a coordinate axes in the direction of the basis vectors.
- Find the intercepts of a plane belonging to the system, expressing them as integral multiples of the basis vectors along the crystal axes.
- Write the equation of the plane in intercept form and simplify to obtain the coefficients of a, b and c, namely h, k, and l as integers.

The quantity (hkl) is then the Miller indices of that system of planes.

2.7.2 Miller Indices: An example



1. We have drawn the coordinate axes
2. x-intercept: $2 \times \vec{a}$

   y-intercept: $3 \times \vec{b}$

   z-intercept: $4 \times \vec{c}$
3. Plane: $\frac{\vec{a}}{2} + \frac{\vec{b}}{3} + \frac{\vec{c}}{4} = 1$

   Simplify: $6\vec{a} + 4\vec{b} + 3\vec{c} = 12$
4. $\therefore$ Miller indices $\equiv (6\,4\,3)$

2.8 Planes in a cubic crystal

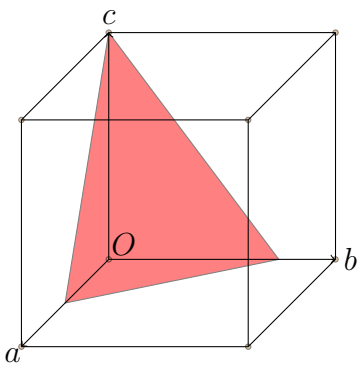
2.8.1 Drawing a plane

Drawing the plane represented by (643)

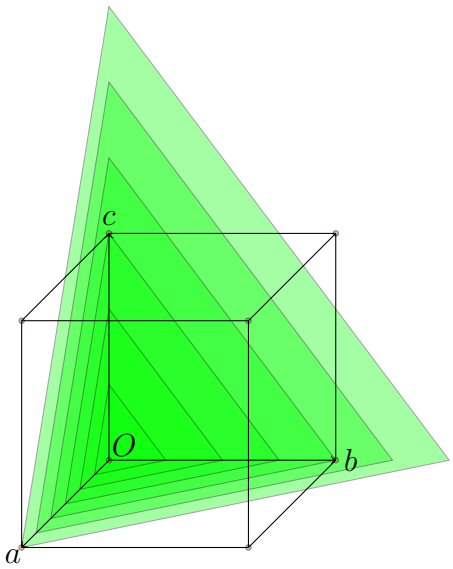
1. Draw the unit cell for a cubic crystal
2. Compute $\left(\frac{1}{h}, \frac{1}{k}, \frac{1}{l}\right)$

   $\equiv \left(\frac{1}{6}, \frac{1}{4}, \frac{1}{3}\right)$
3. Multiply by the lowest non-zero number among (h, k, l)

   $\left(\frac{1}{2}, \frac{3}{4}, 1\right)$

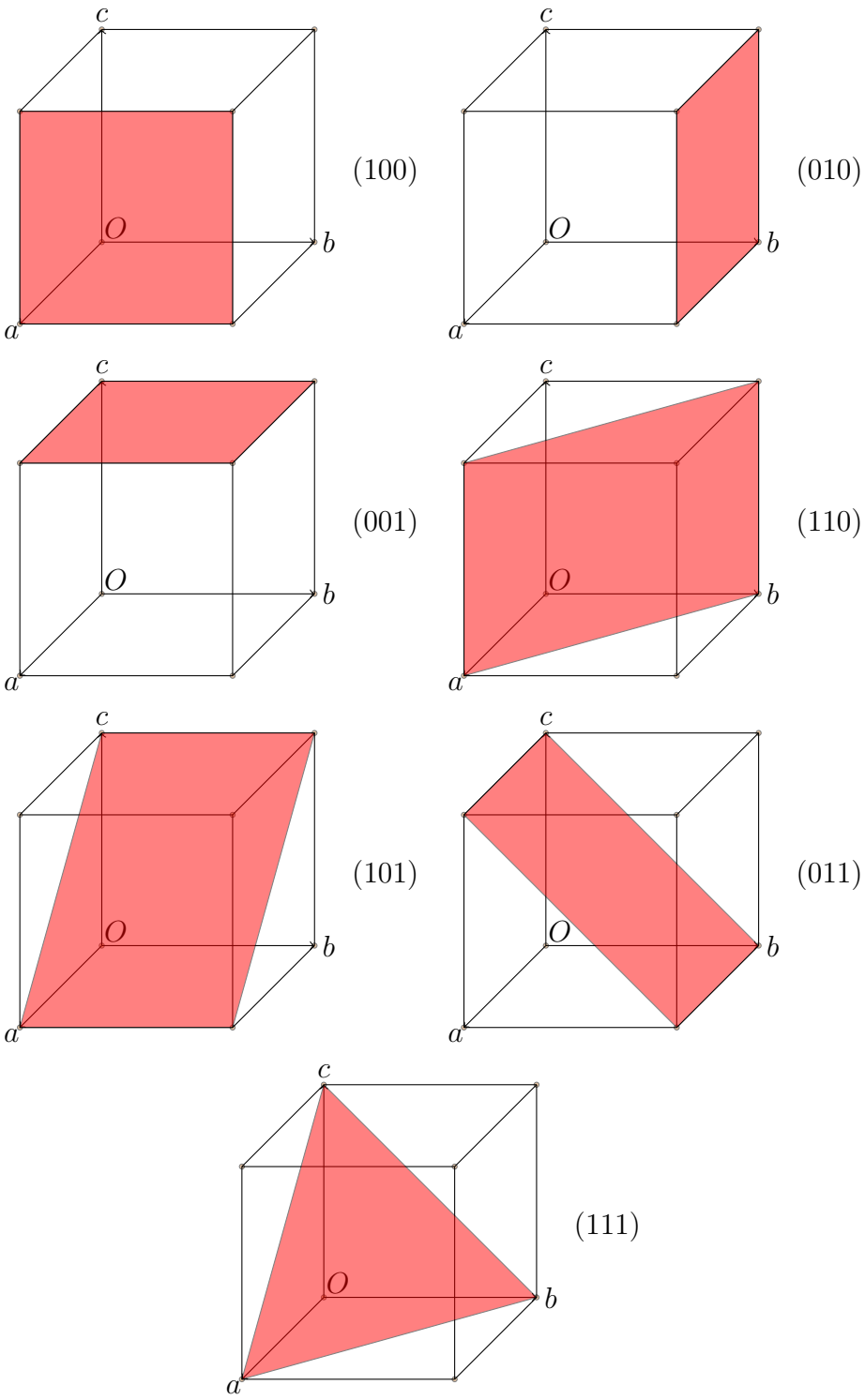


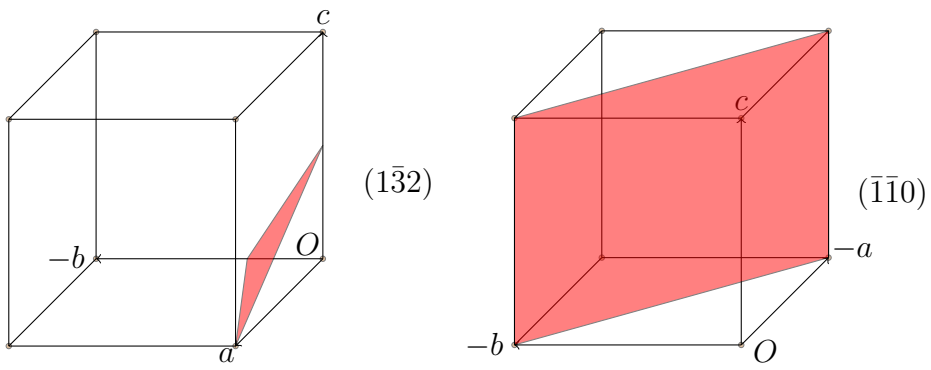
2.8.2 (643) family of planes



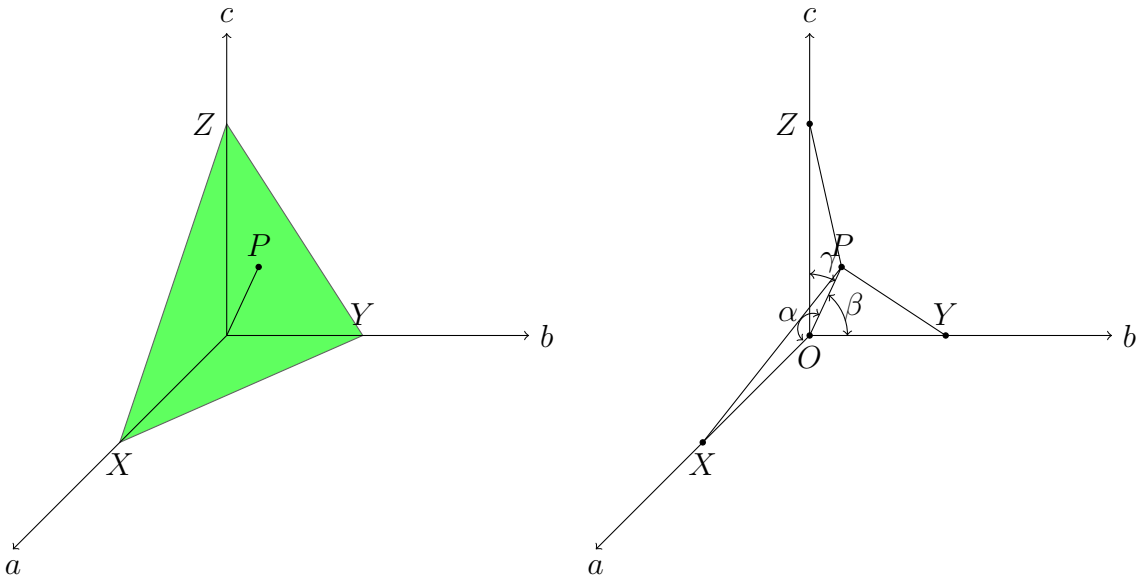
You can observe that the first 6 planes cut the a axis into 6 equal parts, the first 4 planes cut the b axis into 4 equal parts, the first 3 planes cut the c axis into 3 equal parts.

2.8.3 Planes in a cubic crystal





2.9 Interplanar distance, d_{hkl}



From $\triangle OPX$

- $\angle OPX = 90$
- $\angle POX = \alpha$
- $\Rightarrow OP = OX \cos\alpha$ OR
- $\cos\alpha = \dfrac{OP}{OX} = \dfrac{d_{hkl}}{OX}$

From $\triangle OPY$ and $\triangle OPZ$

$$\cos\beta = \frac{OP}{OY} = \frac{d_{hkl}}{OY}$$

$$\cos\gamma = \frac{OP}{OZ} = \frac{d_{hkl}}{OZ}$$

We know that, for an orthogonal coordinate system

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$$

Therefore,

$$\left(\frac{d_{hkl}}{OX}\right)^2 + \left(\frac{d_{hkl}}{OY}\right)^2 + \left(\frac{d_{hkl}}{OZ}\right)^2 = 1$$

Also,

$$\frac{1}{OX} = \frac{h}{a},\ \frac{1}{OY} = \frac{k}{b},\ \frac{1}{OZ} = \frac{l}{c}$$

This give us,

$$d_{hkl}^2\left(\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2\right) = 1$$

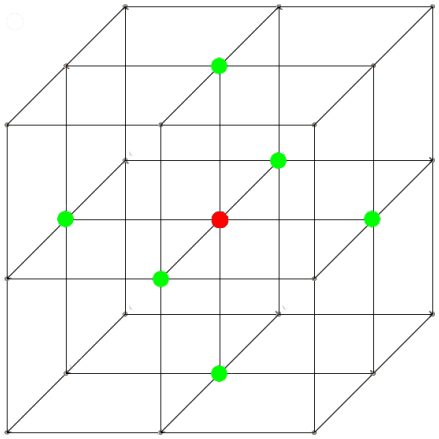
or

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}}$$

2.10 Coordination Number

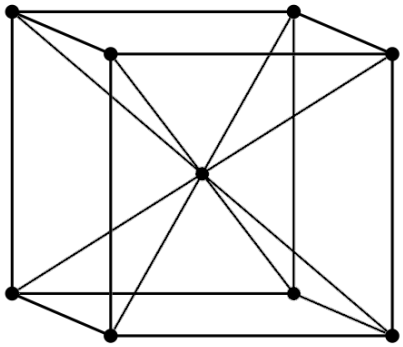
Coordination Number is defined as the number of nearest neighbors of the given atom.

2.10.1 Simple Cubic



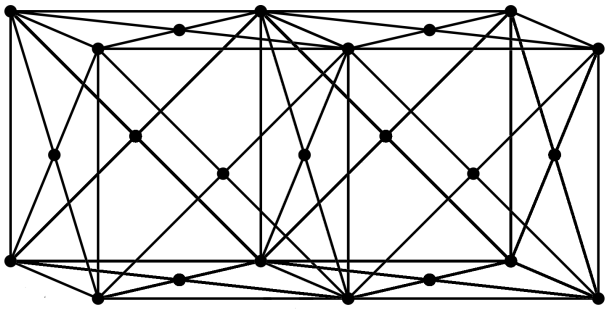
Coordination number = 6

2.10.2 Body Centered Cubic



Coordination number = 8

2.10.3 Face Centered Cubic



Coordination number = 12

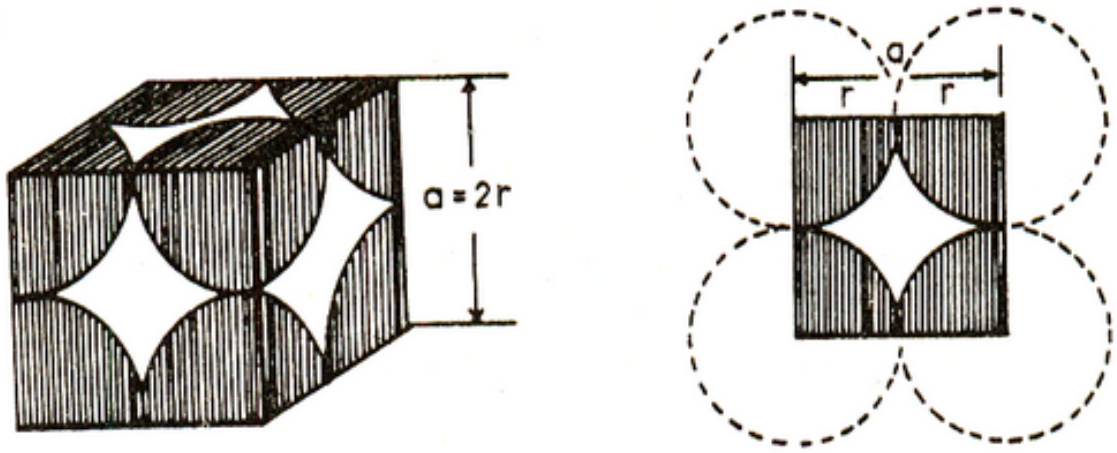
2.11 Atomic Packing Factor

APF is defined as the ratio of the volume of all the atoms in the unit cell to that of the unit cell. Mathematically,

$$APF = \frac{n \times \frac{4}{3}\pi r^3}{a^3}$$

2.11.1 Simple Cubic

- Number of atoms per unit cell = 1
- Volume of one **atom** $= \frac{4}{3}\pi r^3$

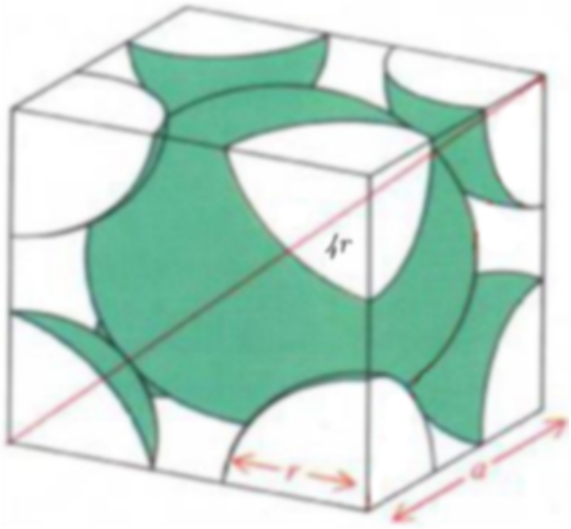


- Volume of one **cube** $= a^3$ In terms of r, it is

$$a = 2r$$

$$A.P.F = \frac{1 \times \frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

2.11.2 Body Centered Cubic



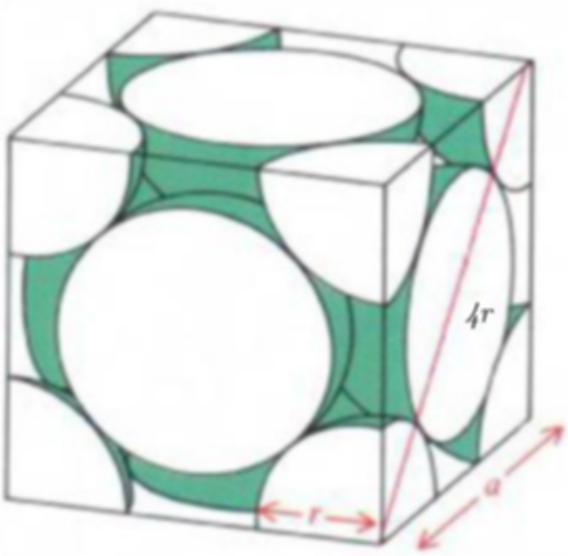
- Number of atoms per unit cell = 2
- Volume of one **atom** $= \frac{4}{3}\pi r^3$

- Volume of one **cube** $= a^3$ In terms of r, it is

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

$$A.P.F = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}}{8}\pi$$

2.11.3 Face Centered Cubic



- Number of atoms per unit cell $= 4$
- Volume of one **atom** $= \frac{4}{3}\pi r^3$
- Volume of one **cube** $= a^3$ In terms of r, it is

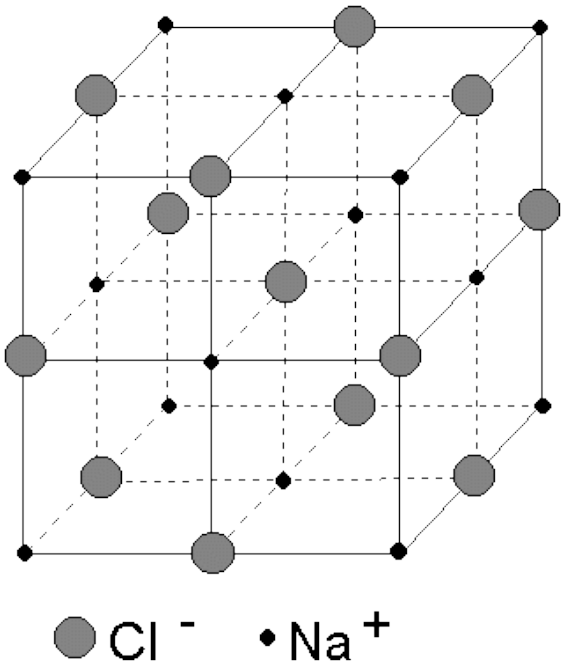
$$a = 2\sqrt{2}r$$

$$A.P.F = \frac{4 \times \frac{4}{3}\pi r^3}{(2\sqrt{2}r)^3} = \frac{1}{3\sqrt{2}}\pi$$

2.12 NaCl Structure

In solid sodium chloride, each ion is surrounded by six ions of the opposite charge as expected on electrostatic grounds. The larger chloride ions are arranged in a cubic array whereas the smaller sodium ions fill all the cubic gaps between them.

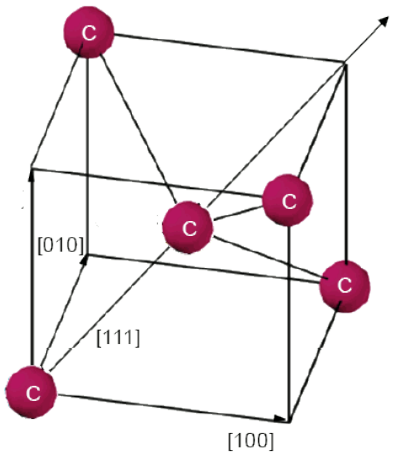
It can be represented as a face-centered cubic (fcc) lattice with a two-atom basis or as two interpenetrating face centered cubic lattices. The first atom is located at each lattice point, and the second atom is located half way between lattice points along the fcc unit cell edge.

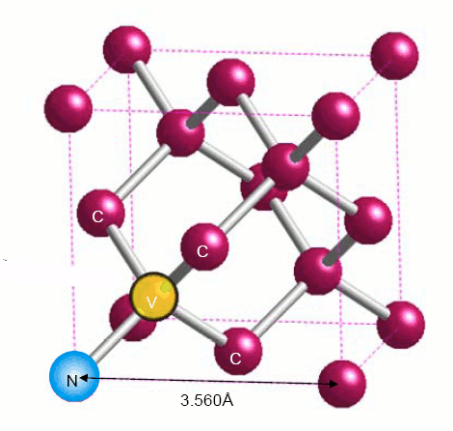


2.13 Diamond Structure

Diamond cubic follows the face-centered cubic bravais lattice. The lattice describes the repeat pattern; for diamond cubic crystals this lattice is "decorated" with a motif of two tetrahedrally bonded atoms in each primitive cell, separated by 1/4 of the width of the unit cell in each dimension.

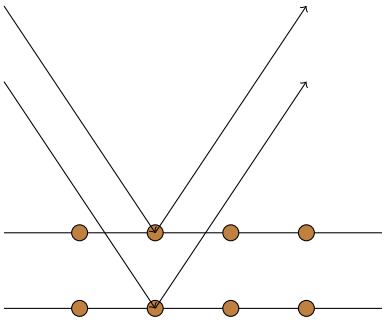
The atomic packing factor of the diamond cubic structure is $\frac{\pi\sqrt{3}}{16} \approx 0.34$, significantly smaller (indicating a less dense structure) than the packing factors for the face-centered and body-centered cubic lattices.





2.14 Bragg Law

W L Bragg considered diffraction as reflection from a set of parallel planes. A beam not reflected at the top level is reflected at a deeper level. The two beams will have a phase difference. Beams reflected off the same plane have no phase difference.



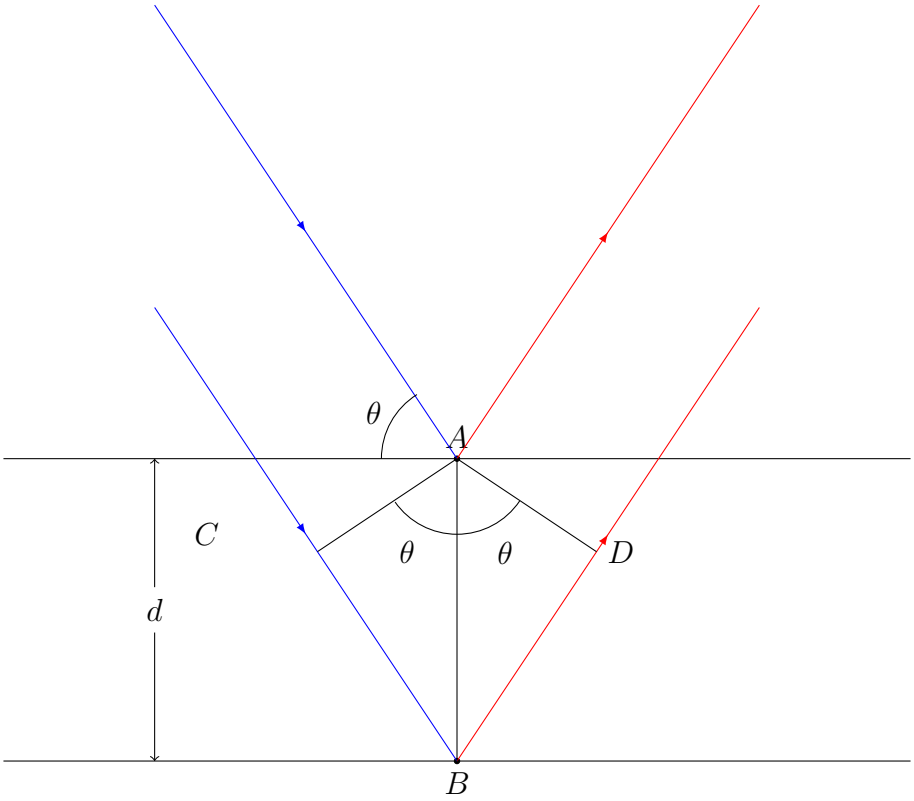
2.14.1 Derivation of Bragg's Law

The path difference, δ, is the extra path $CB + BD$ the second ray travels.

$$\delta = CB + BD$$

From the $\triangle ABC$ and $\triangle ABD$, we have

$$BC = AB \sin\theta = d \sin\theta$$
$$BD = AB \sin\theta = d \sin\theta$$



Therefore,

$$\delta = d\sin\theta + d\sin\theta = 2d\sin\theta$$

We know that, there is constructive interference only when the path difference is an integral multiple of the wavelength. That would mean that

$$\begin{aligned} \delta &= n\lambda \\ &or \\ n\lambda &= 2d\sin\theta \end{aligned}$$

where, n is the order of diffraction.

2.15 Bragg's X-ray Spectrometer

2.15.1 Construction

- Bragg's X-ray Spectrometer consists of three parts
    1. A source of X-rays (X-ray tube)

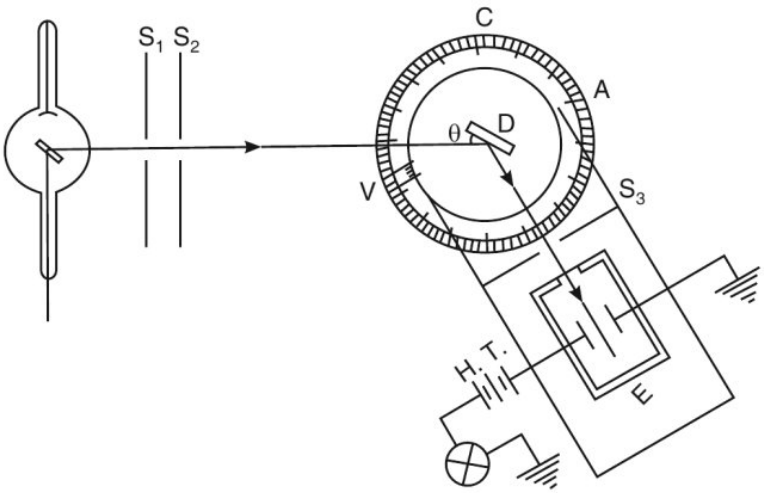


Figure 2.1: Bragg's X-Ray Spectrometer

2. A crystal held on a graduated circular turntable
3. A detector (ionization chamber)

- X-rays from an x-ray tube collimated by two narrow slits S_1, and S_2 are allowed to fall upon the crystal D.
- The crystal is mounted on the turn table which can rotate about a vertical axis and its position can be determined from the graduations.
- The table is provided with a radial arm which carries the ionization chamber which acts as the detector.
- The ionization chamber is connected to an electrometer to measure the ionization current.
- The crystal table and the detector are mounted in such a way that when the crystal turns through an angle θ, the detector rotates through an angle of 2θ.

2.15.2 Working

- To begin with the glancing angle θ is kept very small and corresponding ionization current is noted.
- The glancing angle is increased in equal steps and in each case, ionization current is noted down.
- The ionization current is plotted against the glancing angle.
- This graph is called x-ray spectrum.
- The peaks in the graph occur whenever Bragg's law is satisfied.

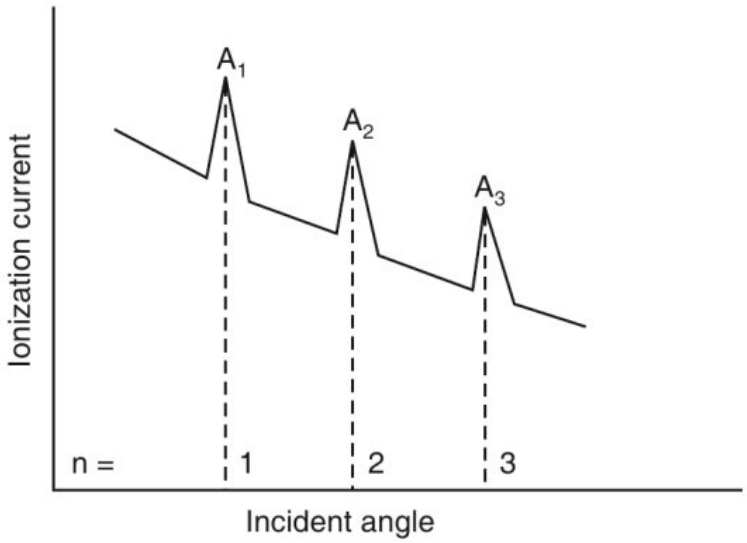


Figure 2.2: X-Ray Spectrum

2.15.3 Wavelength measurement

- To measure the wavelength we use a crystal of known lattice constant, say, NaCl.
- Then from the X-ray spectrum, we can obtain the angle θ and the order n.
- From the Bragg's law, we can obtain λ as

$$\lambda = \frac{2d}{n} \sin\theta$$

2.15.4 d_{hkl} measurement

- To measure the interplanar spacing we perform the spectrometry using x-rays of known wavelength.
- Then from the X-ray spectrum, we can obtain the angle θ and the order n.
- From the Bragg's law, we can obtain d as

$$d = \frac{n\lambda}{2\sin\theta}$$

References

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