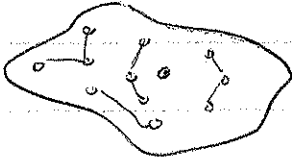
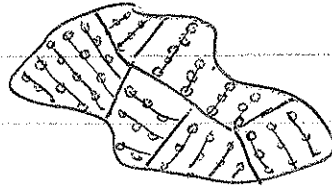


ii. Crystals

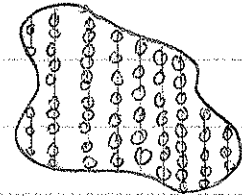
The atomic arrangement within solids falls into one of three broad classifications, namely



a) Amorphous
No recognizable
long-range order



b) Polycrystalline
Completely ordered
in segments



c) Crystalline
Entire solid is made
up of atoms in orderly
array

Overwhelming majority of semiconductor materials in common usage is crystalline.

2.1 The unit cell concept

A unit cell is a small portion of a crystal that could be used to reproduce the crystal.

Note: A unit cell must not necessarily be unique



Def. A unit cell comprising only 1 lattice point is called a primitive cell. not identical with # of atoms

Common choice: "Wigner-Seitz cell"

Region within the lattice that is closer to a particular lattice point than to any other point in the lattice

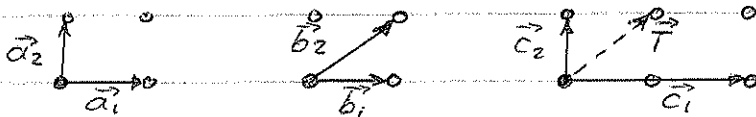
A crystal lattice is defined by three fundamental translation vectors \vec{a}_1 , \vec{a}_2 and \vec{a}_3 such that the atomic arrangement looks the same in every respect when viewed from any point \vec{r} as when viewed from the point

$$\vec{r}' = \vec{r} + n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

where n_1 , n_2 and n_3 are integer numbers.

The shortest three translation vectors are known as the primitive vectors.

e.g. (2-dimensional lattice)



All pairs of vectors are translation vectors, but

\vec{c}_1 and \vec{c}_2 are not primitive since

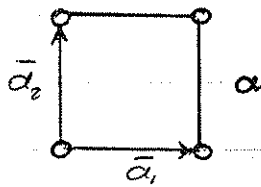
$$\vec{r} = n_1 \vec{c}_1 + n_2 \vec{c}_2$$

cannot connect any two lattice points for integer numbers of n_1 and n_2

primitive translation vector

e. g. 2-dimensional lattices

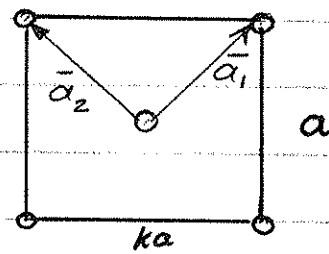
a)



square

$$\vec{a}_1 = \bar{x} \cdot a \quad \vec{a}_2 = \bar{y} \cdot a$$

b)

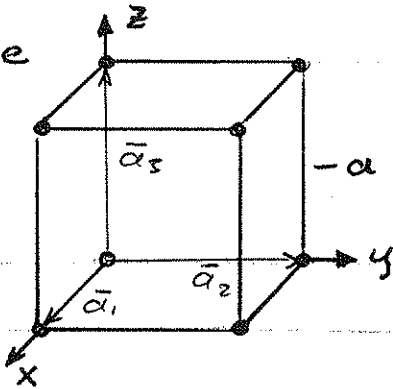


centered rectangular

$$\vec{a}_1 = a \frac{1}{2} (k\bar{x} + \bar{y}) \quad \vec{a}_2 = a \frac{1}{2} (-k\bar{x} + \bar{y})$$

3-dimensional lattices

a) cube

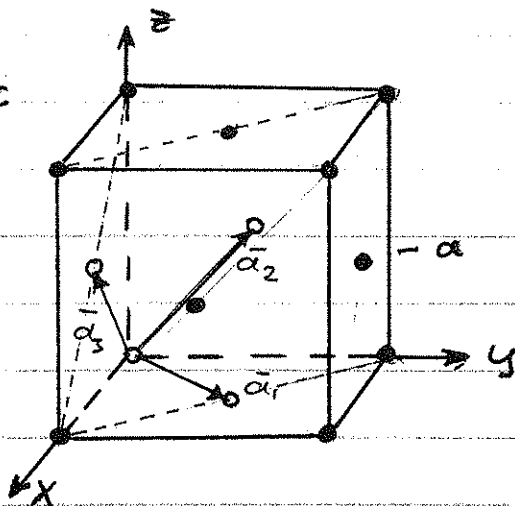


$$\vec{a}_1 = a \cdot \bar{x}$$

$$\vec{a}_2 = a \cdot \bar{y}$$

$$\vec{a}_3 = a \cdot \bar{z}$$

b) fcc



$$\vec{a}_1 = a \frac{1}{2} (\bar{x} + \bar{y})$$

$$\vec{a}_2 = a \frac{1}{2} (\bar{y} + \bar{z})$$

$$\vec{a}_3 = a \frac{1}{2} (\bar{x} + \bar{z})$$

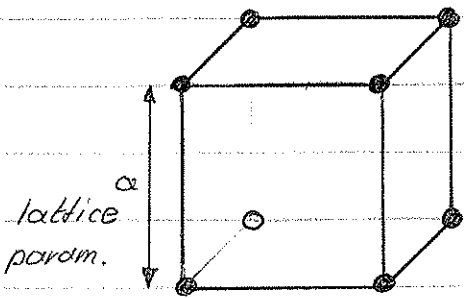
Note, Each lattice point can comprise a group of atoms. These groups are called Basis

Thus: Crystal structure = Lattice + Basis

2.2 Crystal Structures

In the 3-dimensional space, there exist 14 distinct lattice types \rightarrow "Bravais Lattices"

4 important crystal structures:



cubic

atoms

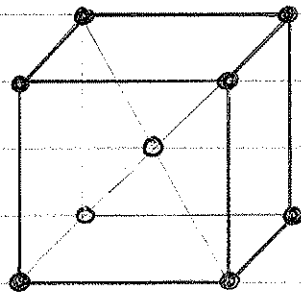
$$8 \cdot \frac{1}{8} = 1$$

each atom has

6 nearest neighbors

at distance a

Po, CsCl



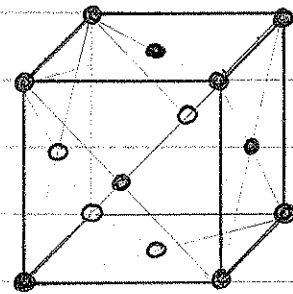
bcc

$$8 \cdot \frac{1}{8} + 1 = 2$$

8 nearest neighbors

at distance $a \frac{\sqrt{3}}{2}$

Na, Rb



fcc

$$8 \cdot \frac{1}{8} + 6 \cdot \frac{1}{2} = 4$$

12 nearest neighbors

at distance $a \frac{\sqrt{2}}{2}$

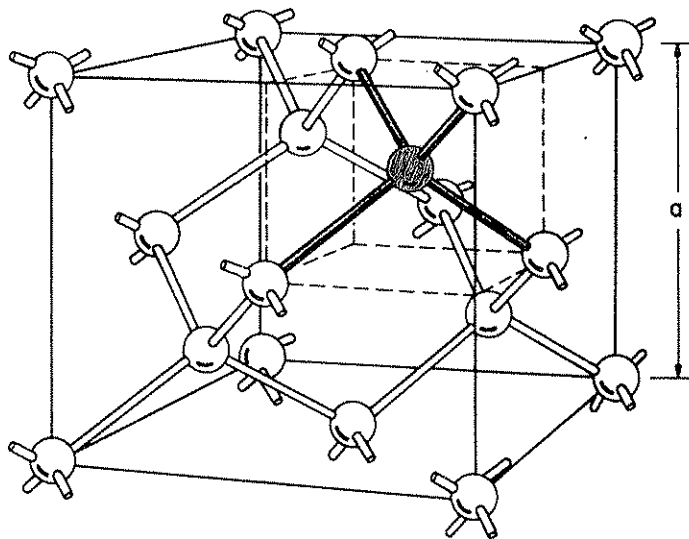
Al, Cu

e. g. Si

$\alpha = 5.43 \text{ \AA}$

atoms:

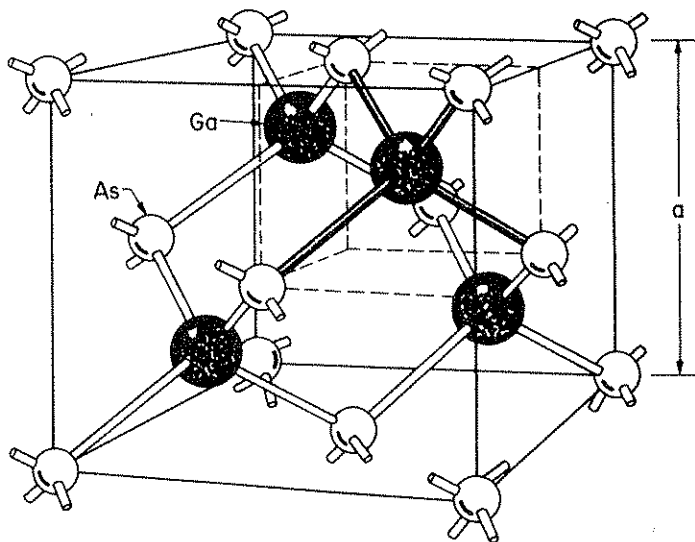
$8 \cdot \frac{1}{8} + 6 \cdot \frac{1}{2} + 4 = 8$



(a)

e. g. GaAs

$\alpha = 5.63 \text{ \AA}$



(b)

(a) Diamond lattice. (b) Zincblende lattice.

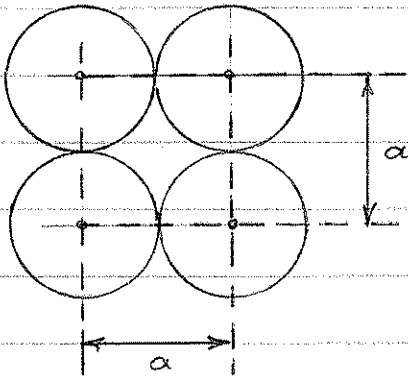
2.3 Atomic density in Crystals

To determine the density of atoms in a particular crystal structure, it is necessary to know the dimensions of the unit cell (lattice parameter a) and the number of atoms in a unit cell. The dimensions of unit cells can be determined by x-ray diffraction techniques.

Simplification:

To calculate the density of atoms, we assume that the atoms are rigid spheres and two nearest neighbors are touching each other.

e.g. simple cubic lattice



$$\begin{aligned} \text{Volume of unit cell: } & a^3 \\ \text{" " " 1 atom: } & \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 \end{aligned}$$

$$\begin{aligned} \text{rel. Volume occupied} & \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 \\ \text{by the atoms:} & \frac{\quad}{a^3} = \frac{\pi}{6} \approx 52\% \end{aligned}$$

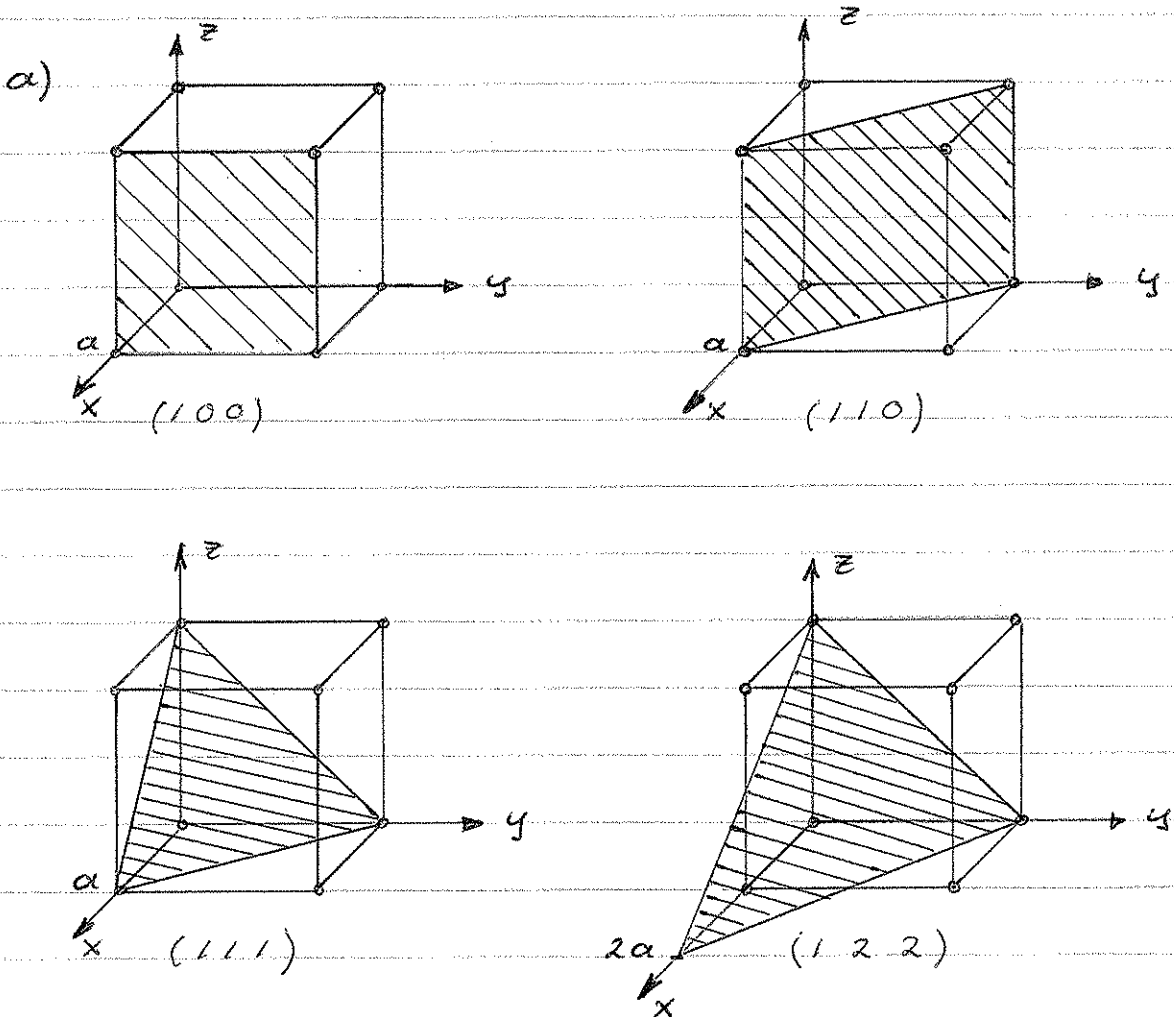
↑
fraction of unit cell that is occupied by rigid atoms

2.4 Miller Indices

Miller indices are used to identify planes and directions within a crystal.

Note: The orientation of a crystal is an important parameter, since crystalline materials often exhibit different properties when viewed from different directions.

example: cubic unit cell



Indexing Procedures:

1. Set up coordinate axes along the edges of the unit cell and note where the plane to be indexed intercepts the axes.
2. Divide each intercept value by the unit cell length along the respective coordinate axis (normalization) and record them in the order x, y, z .
3. Invert the intercept values.
4. Convert these values to the smallest possible set of whole numbers and enclose them in curvilinear brackets.

Note: If the plane to be indexed is parallel to a coordinate axis, the intercept along that axis is taken to be at infinity.

If the plane to be indexed has an intercept along the negative portion of a coordinate axis, a (-) is placed over the corresponding index number.

Miller indices enclosed within square brackets, $[]$, are used to designate directions within a crystal.

$$\bar{i} - 6a$$

Bx Given simple cubic unit cell $a = 3.54 \text{ \AA} \rightarrow (P_0)$
Calculate the density of atoms for the following
crystallographic planes:

a) (100)

b) (110)

c) (111)

Solutions:

a) (100) plane \Rightarrow 4 corner atoms, each of which
has $\frac{1}{2}$ inside the front face of
the cube

$$\Rightarrow \frac{\text{Atoms}}{\text{Area}} = \frac{4 \times \frac{1}{2}}{(3.54 \times 10^{-10})^2} \text{ m}^{-2} = 8.96 \times 10^{18} \text{ m}^{-2} \quad || \\ = 8.96 \times 10^{14} \text{ cm}^{-2} \quad ||$$

b) (110) plane 4 corner atoms, each of which $\frac{1}{4}$
inside area of $a \times a\sqrt{2}$

$$\Rightarrow \frac{\text{Atoms}}{\text{area}} = \frac{4 \times \frac{1}{4}}{a^2 \sqrt{2}} = 6.34 \times 10^{18} \text{ m}^{-2} \quad || \\ = 6.34 \times 10^{14} \text{ cm}^{-2} \quad ||$$

c) (111) plane 3 corner atoms, each of which $\frac{1}{6}$
inside Δ with $a\sqrt{2}$ sidelength

$$\Rightarrow \frac{\text{Atoms}}{\text{area}} = \frac{3 \times \frac{1}{6}}{a^2 \sqrt{3}/4} = 5.18 \times 10^{18} \text{ m}^{-2} \quad || \\ = 5.18 \times 10^{14} \text{ cm}^{-2} \quad ||$$

For the cubic class of crystals, an $[hkl]$ direction is normal to the corresponding (hkl) plane.

e.g. x-axis $\rightarrow [100]$
 $[0\bar{1}0]$ \rightarrow neg. y-axis

The angle θ between two crystallographic directions denoted by $[h_1 k_1 l_1]$ and $[h_2 k_2 l_2]$ is given for a cubic lattice by

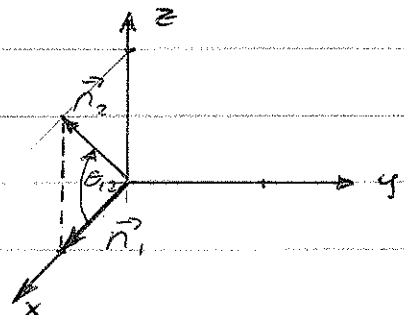
$$\cos \theta_{12} = \frac{[h_1 k_1 l_1] \cdot [h_2 k_2 l_2]}{\sqrt{[h_1 k_1 l_1]^2} \cdot \sqrt{[h_2 k_2 l_2]^2}}$$

$$= \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)}}$$

e.g. $h_1 = 1$ $h_2 = 1$
 $k_1 = 0$ $k_2 = 0$
 $l_1 = 0$ $l_2 = 1$

$$\cos \theta_{12} = \frac{1+0+0}{\sqrt{1 \cdot 2}} = \frac{1}{\sqrt{2}}$$

$$\Rightarrow \underline{\underline{\theta_{12} = 45^\circ}}$$



2.5 Reciprocal Lattices

We consider the set of translation vectors

$$\vec{T} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

that generate a distinct lattice in "direct" position space and a plane wave

$$\Psi(\vec{r}) = A \exp[i \vec{k} \cdot \vec{r}] \quad \vec{k}: \text{wave vector}$$

We are looking for some particular $\vec{k} \equiv \vec{G}$ such that the wave and the lattice have the same periodicity

Thus

$$\exp[i \vec{G} \cdot \vec{T}] = 1$$

or

$$\vec{G} \cdot \vec{T} = n \cdot 2\pi$$

The primitive transl. vectors of the reciprocal lattice are given by

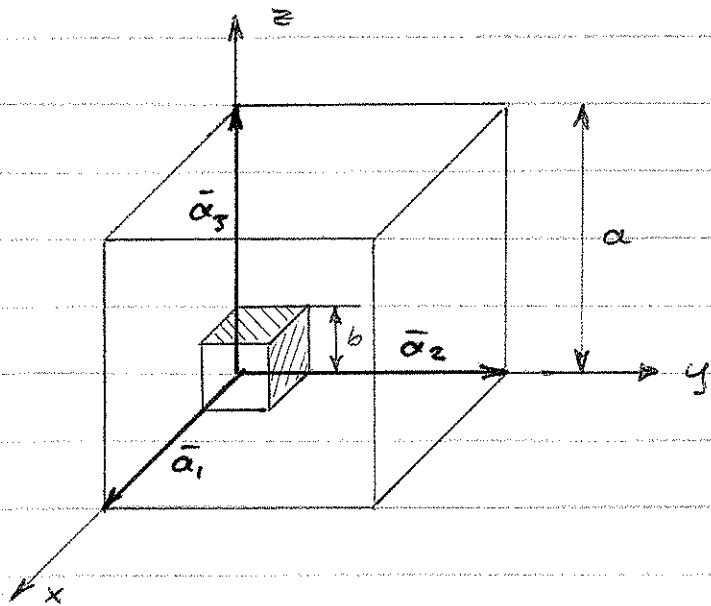
$$\vec{b}_i = 2\pi \frac{\vec{a}_j \times \vec{a}_k}{\vec{a}_i \cdot (\vec{a}_j \times \vec{a}_k)}$$

Thus the reciprocal lattice is generated by the set of translation vectors

$$\vec{G} = h \vec{b}_1 + k \vec{b}_2 + l \vec{b}_3$$

EX reciprocal lattices

a) simple cube



$$\vec{a}_1 = a \cdot \vec{x}$$

$$\vec{a}_2 = a \cdot \vec{y}$$

$$\vec{a}_3 = a \cdot \vec{z}$$

$$\vec{r} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

$$\vec{G} = h \vec{b}_1 + k \vec{b}_2 + l \vec{b}_3$$

$$\vec{b}_1 = \frac{2\pi (\vec{a}_2 \times \vec{a}_3)}{a_1 (\vec{a}_2 \times \vec{a}_3)}$$

$$= \frac{2\pi (\vec{y} \times \vec{z})}{a \vec{x} (\vec{y} \times \vec{z})} = \frac{2\pi}{a} \frac{\vec{x}}{\vec{x} \cdot \vec{x}} = \frac{2\pi}{a} \vec{x}$$

$$\vec{b}_2 = \frac{2\pi (\vec{z} \times \vec{x})}{a_2 (\vec{z} \times \vec{x})} = \frac{2\pi}{a} \frac{\vec{y}}{\vec{y} \cdot \vec{y}} = \frac{2\pi}{a} \vec{y}$$

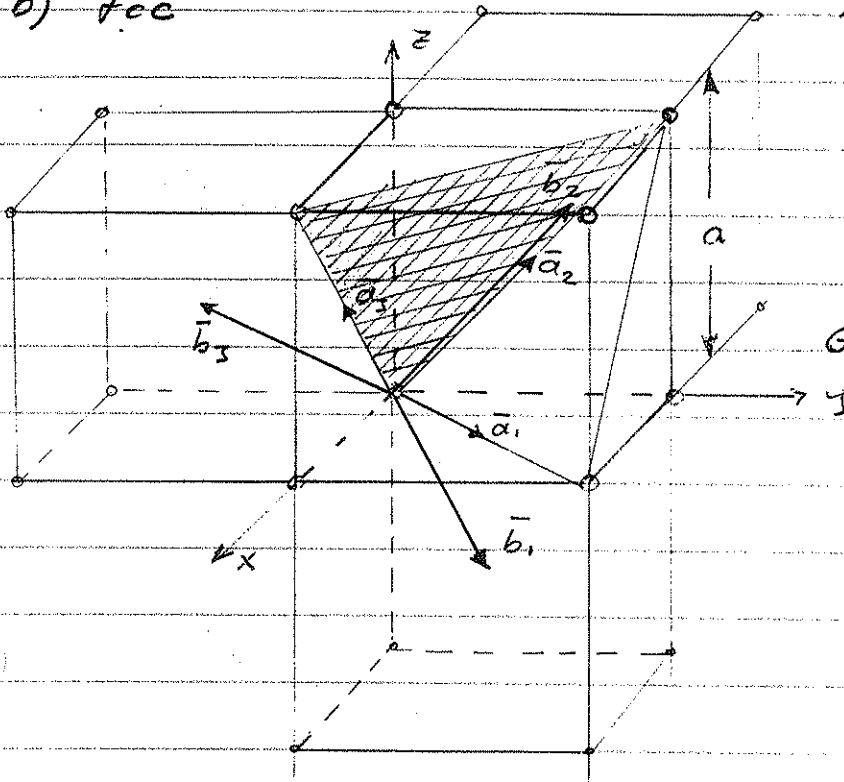
$$\vec{b}_3 = \frac{2\pi (\vec{x} \times \vec{y})}{a_3 (\vec{x} \times \vec{y})} = \frac{2\pi}{a} \frac{\vec{z}}{\vec{z} \cdot \vec{z}} = \frac{2\pi}{a} \vec{z}$$

Reciprocal lattice of simple cube is also a simple cube.

Side length of reciprocal lattice cube:

$$b = \frac{2\pi}{a}$$

b) fcc



$$\vec{r} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

$$\vec{b}_1 = \frac{2\pi}{a_1} \frac{\vec{a}_2 \times \vec{a}_3}{(\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{G} = h \vec{b}_1 + k \vec{b}_2 + l \vec{b}_3$$

Side of reciprocal lattice cube,

$$\left| \frac{2\pi}{a} = \frac{2\pi}{a} \cdot 2 = b \right|$$

Note: $|\vec{a}_1 \times \vec{a}_2| = |\vec{a}_1| \cdot |\vec{a}_2| \cdot \sin \phi_{\vec{a}_1, \vec{a}_2}$

$$|\vec{a}_1 \cdot \vec{a}_2| = |\vec{a}_1| \cdot |\vec{a}_2| \cdot \cos \phi_{\vec{a}_1, \vec{a}_2}$$

$$\vec{b}_1 = \frac{2\pi}{a^{\frac{3}{2}}} \frac{(\bar{y} + \bar{z}) \times (\bar{x} + \bar{z})}{(\bar{x} + \bar{y}) [(\bar{y} + \bar{z}) \times (\bar{x} + \bar{z})]} = \frac{2\pi}{a^{\frac{3}{2}}} \frac{\bar{y} \times \bar{x} + \bar{y} \times \bar{z} + \bar{z} \times \bar{x} + \bar{z} \times \bar{z}}{(\bar{x} + \bar{y}) [\dots]}$$

$$= \frac{2\pi}{a} (\bar{x} + \bar{y} - \bar{z})$$

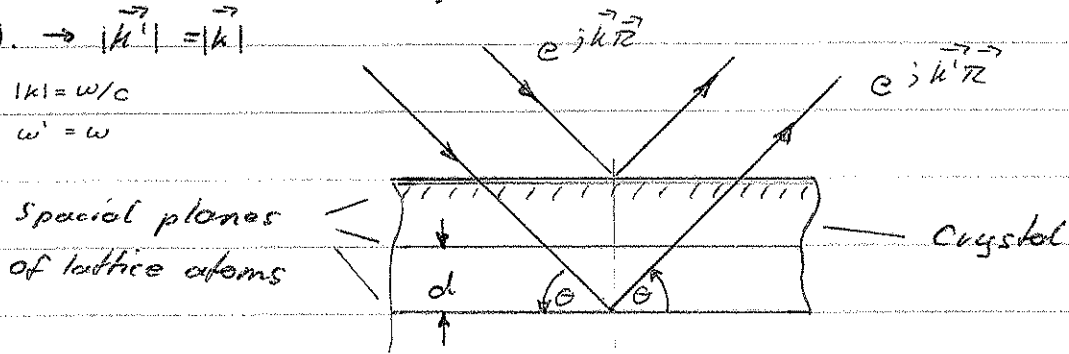
$$\vec{b}_2 = \frac{2\pi}{a} (-\bar{x} + \bar{y} + \bar{z}) \Rightarrow \underline{bcc}$$

$$\vec{b}_3 = \frac{2\pi}{a} (\bar{x} - \bar{y} + \bar{z})$$

2.6 Bragg Reflection

A wave of periodicity $\exp[i\vec{k}(\vec{r}+\vec{r}')]]$ is incident on the lattice and is elastically scattered (i.e. without energy loss). $\rightarrow |\vec{k}'| = |\vec{k}|$

since $|\vec{k}| = \omega/c$
and $\omega' = \omega$



Constructive interference

\Rightarrow "Bragg Reflection"

$$\vec{k} \cdot \vec{r} = \vec{k}' \cdot \vec{r} + 2\pi \cdot n$$

$$(\vec{k} - \vec{k}') \cdot \vec{r} = 2\pi \cdot n$$

Recall

$$\vec{G} \cdot \vec{r} = 2\pi \cdot n$$

$$\Delta \vec{k} = \vec{G}$$

or

$$\underline{\underline{2\vec{k} \cdot \vec{G} = G^2}}$$

Thus, x-ray diffraction patterns unambiguously determine the special lattice structure by identifying the reciprocal lattice structure

Distance between two nearest planes (h k l)

$$\underline{\underline{d = \frac{2\pi}{|\vec{G}|}}}$$

where $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$

or derived geometrically:

$$2d \sin \theta = n \cdot \lambda$$

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

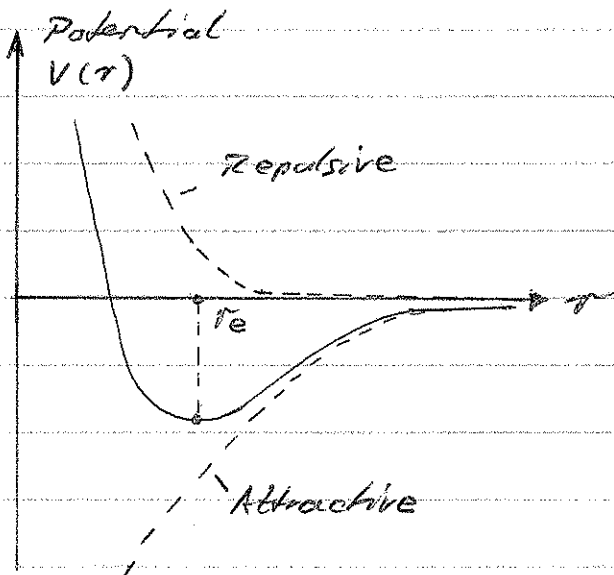
$$n = 1, 2, \dots$$

2.7 Crystal Binding

Crystals form because it is energetically favorable for them to do so.

Atoms in close proximity to each other experience both attractive and repulsive forces that are functions of the distance between them.

If the repulsive potentials are inversely proportional to a higher power of r than the attractive potentials, a local minimum of energy occurs at a certain distance r_e .



Mathematically formulated

$$V(r) = -\frac{A}{r^m} + \frac{B}{r^n} \quad n > m$$

$$\Rightarrow \underline{\underline{r_e = \left(\frac{n}{m} \frac{B}{A} \right)^{\frac{1}{n-m}}}}$$

Repulsive forces:

Forces attributed to the Pauli exclusion principle (overlapping electrons with parallel spins have to enter higher energy states \rightarrow system energy is lowered by increased interatomic distance.)

Attractive forces:

These forces can have different origins

1. Van der Waal interaction ($\sim r^{-6}$)

Binds crystals of "inert" gases by induced dipole moments

2. Metallic Binding

Valence electrons are shared by many ionic cores (reduces system energy) \rightarrow "electronic gas"

Special case: Covalent Bonding e.g. Si-crystal (e.l. between specific pairs of atoms are shared)

3. Electrostatic Forces (strongest attractive binding)

Binds ionic crystals. Requires that crystal must consist of at least two types of atoms (e.g. $\text{Na}^+ + \text{Cl}^-$)

Summary Chapter II

1. unit cells

we considered:	simple cubic	1 lattice site \rightarrow primitive cell
	bcc	2
	fcc	4
	diamond	8

crystal structure: Basis + lattice

lattice: defined by translation vector

$$\vec{r} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

$$\vec{r}_p = \vec{a}_1 + \vec{a}_2 + \vec{a}_3 \quad \text{primitive tr. vector}$$

2. Reciprocal lattice

Def.

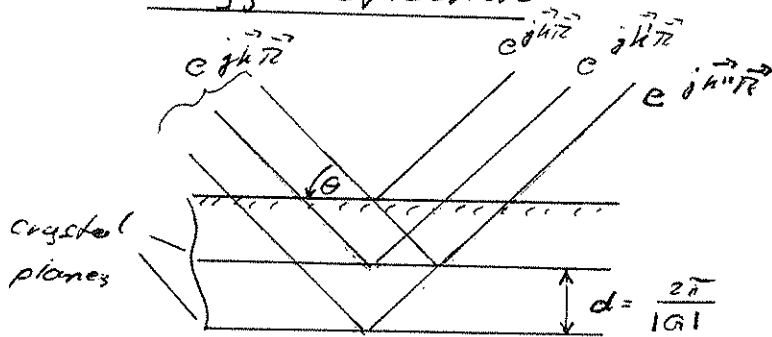
$$\vec{G} \cdot \vec{r} = 2\pi$$

$$\vec{G} = h \vec{b}_1 + k \vec{b}_2 + l \vec{b}_3$$

$$\vec{G}_p = \vec{b}_1 + \vec{b}_2 + \vec{b}_3 \quad \text{pr. tr. vector of recipr. l.}$$

$$\vec{b}_i = 2\pi \frac{(\vec{a}_j \times \vec{a}_k)}{\vec{a}_i \cdot (\vec{a}_j \times \vec{a}_k)}$$

3. Bragg reflection



for constructive interference:

$$\vec{k}\cdot\vec{r} = \vec{k}'\cdot\vec{r} + 2\pi \quad (\text{equal phase})$$

or

$$(\vec{k} - \vec{k}')\cdot\vec{r} = 2\pi$$

$$\Delta\vec{k}\cdot\vec{r} = 2\pi$$

$$\vec{G}\cdot\vec{r} = 2\pi \quad \text{if } \Delta\vec{k} = \vec{G}$$

We have constructive interference if

$$\Delta\vec{k} = \vec{G}$$

$$\text{or } k'^2 = (k - G)^2$$

$$\text{since } k'^2 = k^2$$

$$2kG = G^2$$

other formulation

$$2d \sin \theta = n\lambda$$

$$\text{Thus } \lambda_{\min} = 2d \sin \theta$$

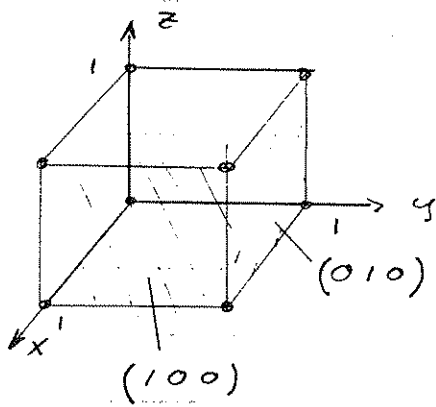
d is in the order of 1\AA

$\Rightarrow \lambda$ must also be in this order

\Rightarrow X-rays

4. Miller indices

They describe planes in the crystal lattice



- Miller indices are obtained by
1. Calculating intercepts of the plane with coordinate axis
 2. Inverting the values of the intercepts
 3. Converting the reciprocal values to the smallest triplet of whole numbers

Note: Directions perpendicular to a certain plane (n_1, n_2, n_3) are marked by $[n_1, n_2, n_3]$

The distance between two nearest parallel planes is given by

$$d = \frac{2\pi}{|\bar{a}|}$$

where \bar{a} is the reciprocal lattice vector normal to the direct lattice plane (n_1, n_2, n_3)

e.g. cubic lattice $\bar{r}_p = a(\bar{x} + \bar{y} + \bar{z})$

$$\bar{a}_p = \frac{2\pi}{a}(\bar{x} + \bar{y} + \bar{z})$$

plane (1 2 3)

$$\bar{a} = \frac{2\pi}{a}(1\bar{x} + 2\bar{y} + 3\bar{z})$$

$$d = \frac{2\pi}{2\pi} a \frac{1}{\sqrt{1^2 + 2^2 + 3^2}} = a \frac{1}{\sqrt{14}}$$