

[PHS - 319] → Solid State Physics I

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SOLID STRUCTURE

Matter - Is anything that has mass and occupies space.
States of matter

- solid
- liquid
- gas
- plasma
- Amorphous solid

Solid structures can be classified into:
i) Crystalline Solid and ii) Amorphous Solid

Crystalline Solid → Are solid in which the components arrangement has long range order

Amorphous Solid → The components arrangement has short range order

N.B. i) Crystalline solid particles (or component) are arranged uniformly till infinity

ii) Amorphous solids can be obtained from crystalline solid

Crystal → Is a solid with periodic structure. The periodicity is represented by a Bravais Lattice

A Bravais lattice → Is an infinite array of discrete points with an arrangement and orientation that appear exactly the same from whichever of the points the lattice is viewed alternatively;

A Bravais lattice consists of all points with position vectors:

$$R = n \alpha \quad (1\text{-dimension})$$

E.g. of a Bravais lattice



(It continues infinitely)

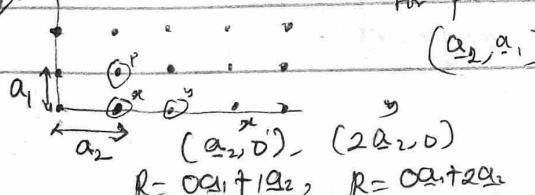
a → distance between any two close points

n → Is an integer

N.B. n could be +ve or -ve depending on the axis.

$$R = n_1 \alpha_1 + n_2 \alpha_2 \quad (2\text{-dimension})$$

Square lattice



For p

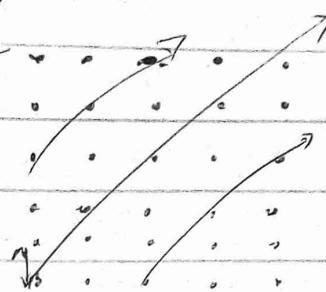
$$(\alpha_2, \alpha_1)$$

N.B. Every substances have their various lattice constant

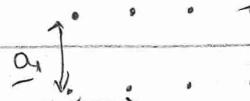
For a Square lattice;

$$\therefore |\alpha_1| = |\alpha_2| \text{ and } \theta = 90^\circ$$

Rectangular lattice

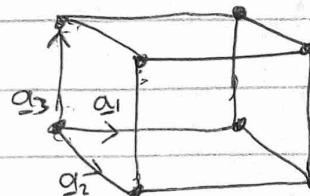


$$|\alpha_1| \neq |\alpha_2|, \theta = 90^\circ$$



Parallelogram lattice

$$|\alpha_1| = |\alpha_2|, \theta \neq 90^\circ$$



$$R = n_1 \alpha_1 + n_2 \alpha_2 + n_3 \alpha_3$$

N.B. n depends on the type of atom in consideration

Properties of Bravais Lattice

* Primitive Unit Cell; It is the volume (Surface area in 2-D) that when translated through all the vectors in a Bravais lattice just fills all space without overlapping or leaving voids. Note that, the choice of primitive unit cell is not unique.



A could be a primitive unit cell also

B could be a primitive unit cell hence they are not unique characteristics

* If usually contains one lattice point (this central lattice contributes $\frac{1}{4}$ to 4 places to form a whole primitive unit cell).

N.B atoms per bo

The central atom (lattice point) contributes $\frac{1}{4}$ for each in 4 places to give the whole face.

Atom on the face is shared by two faces

($\frac{1}{2}$)

Atom on the vertex ($\frac{1}{8}$)

Atom on the edge contributes ($\frac{1}{4}$)

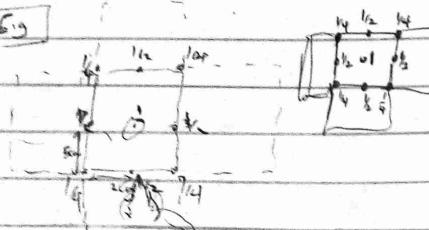
2) The volume of the primitive unit cell is

$$V = \frac{1}{n}$$

where n = density of points

$$n = \text{no. of points} \rightarrow n = \frac{V}{v}$$

$$V = \frac{1}{n} \quad n = 1 \text{ because we considered the lattice point.}$$



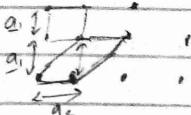
No. of atoms = 4 (only 1, 2, 3, 4 atoms are shown)

Volume = 40

$$\text{Density } n = \frac{4}{40} = 0.1 \text{ m}^{-3}$$

3) They do not sometimes have the full symmetry of the Bravais lattice. After rotation some might be symmetric while some might not.

4) The volume of all possible primitive unit cell are the same.



Conventional Unit Cell;

Face-Centred cubic lattice



there, the conventional unit cell is the cell containing $\frac{1}{8}$ each square.

N.B primitive cell only have one atom.

'Conventional unit cell' is usually bigger than the primitive cell in favour of preserving the symmetry of the broader lattice.

The volume of a conventional unit cell is equal to no. of points in the cell multiplied by volume of the primitive unit cell.



Conventional unit cell = $a_1 a_2 a_3$ × no. of atoms

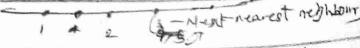
the primitive cell is a parallelogram

primitive cell area = $a_1 a_2$

$$\text{Conventional unit cell area} = \frac{\text{Area of box}}{2} \times \text{no. of atoms}$$
$$= \frac{a_1 a_2 a_3}{2} \times 2 = a_1 a_2$$

5) Coordination number:- These are the points in a Bravais lattice. The points in Bravais lattice that are closest to a given point are called its nearest neighbour. The no. of this nearest neighbour is called coordination number.

N.B. In 1-D, the coordination number is 2

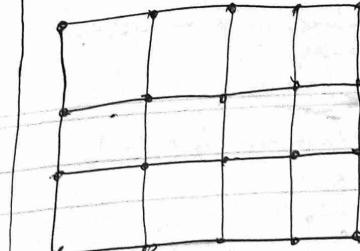


N.B. Nearest neighbour can change but the coordination number still remain the same.

3/2/2020 Differences between CUC & PUC

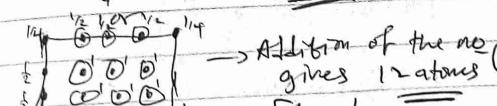
N.B. CUC = no. of points \times PUC

6) The primitive unit cell has one point while the conventional unit cell has many points.



There are 12 no. of atoms or points in the diagram above.

$$\text{N.B. } V = \frac{1}{n} \rightarrow 1 \times 12 (\text{boxes})$$
$$= 12 \text{ atoms}$$



7) Polyhedral Structure

If crystal structure is formed when basis (a fixed group of atoms) is attached to each lattice point.

N.B. Crystal = Bravais lattice + Basis structure

Bravais lattice \rightarrow Arrangement of point but this arrangement of point either when the point is replaced with atoms, it becomes crystal structure

Fundamental types of lattices

physicists used the symmetry of the unit cell to classify crystal structures and how they fill space. For 3-dimension, there are only five distinct lattices

Square

$$a_1 = |a_2|, \theta = 90^\circ$$

Rectangular

$$|a_1| \neq |a_2|, \theta = 90^\circ$$

Hexagonal

$$|a_1| = |a_2|, \theta = 90^\circ$$

Heptagonal

$$|a_1| \neq |a_2|, \theta \neq 90^\circ$$

Centered rectangular



Oblong

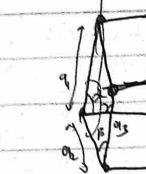


In 3-dimension, there are seven lattice system which give rise to 14 Bravais lattices.

The Seven Lattice systems are:

Lattice System	Number and types of Bravais lattices	Characteristics
Triclinic	It has only 1 Bravais lattice	* primitive Lattice $a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$

N.B. Primitive implies there are atoms at the vertices only!



→ Triclinic

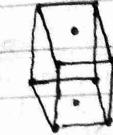
Monoclinic

They are primitive and Side-centered
 $\angle \beta = 90^\circ$

N.B. They are primitive and side-centered because they have atoms at the vertex, upper part and lower part

Primitive Monoclinic

Side-centered Monoclinic



Orthorhombic primitive, body centred, side centred face centred

$$a_1 = a_2 = a_3$$

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

^{NB} Body centred \rightarrow implies there is an atom at the center in addition of all the 8 vertices

Body centred orthorhombic



Faced centred \rightarrow 8 vertices + 6 face atoms
 $(\frac{1}{2} \times 8)$ atoms + $(\frac{1}{6} \times 6)$ atoms



- 5) No of next nearest neighbours
- 6) Next nearest neighbour distance
- 7) Atomic radius
- 8) Packing fraction

$$\text{No of points/unit cell} = \frac{1}{8} \times 8 = 1$$



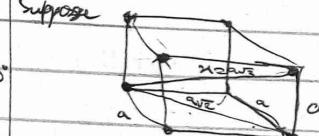
$$2) \text{Volume} = a_1 \cdot |a_2 \times a_3|$$

$$V = a_1 a_2 a_3 = a^3 \quad \text{since } a_1 = a_2 = a_3$$

$$|a_2 \times a_3| = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

$$\therefore \text{Volume of Unit cell} = a^3$$

3) No of nearest neighbours! - The shortest distance between two atoms is the distance between two atoms along any edge.



4) Tetragonal primitive and side centred

$$a_1 = a_2 = a_3$$

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

5) Cubic primitive, body centred

$$a_1 = a_2 = a_3$$

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

6) Trigonal primitive

$$a_1 = a_2 = a_3$$

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

7) Hexagonal primitive

$$a_1 = a_2 = a_3$$

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

$$\gamma = 120^\circ$$

^{NB} Hexagonal looks like a cylinder

Given a



The no of nearest neighbour = 6
 $\therefore 12 \times \frac{1}{2} = 6$

^{NB} Nearest point (or neighbour) is obtained when a line joining two points is noticed

Some Parameters

1) No of points or atoms per unit cell

2) Unit cell volume

3) No of nearest neighbour

4) No of next nearest neighbour distance

5) No of next nearest neighbour

Is $a\sqrt{2}$ \therefore
6) No of nearest neighbour is 12

7) Atomic radius $\rightarrow a$
i.e lattice constant divided by 2

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



8) Atomic Volume! - An atom is assumed to be spherical in shape.

$$\text{Atomic vol} = \frac{4}{3} \pi r^3 \Rightarrow \frac{4}{3} \pi (\frac{a}{2})^3$$

$$\therefore \text{Atomic vol} = \frac{1}{6} \pi a^3$$

9) Packing fraction! - Total area of atoms in a cell divided by volume

Packing fraction = $\frac{\text{No of atoms in a cell} \times \text{Atomic Volume}}{\text{Unit cell volume}}$

$$\text{Packing fraction} = \frac{1 \times \frac{1}{6} \pi a^3}{a^3} = \frac{1}{6} \pi$$

Body centred cubic

No of atoms per unit cell = 2

Unit cell volume = a^3

No of nearest neighbours = 8

One neighbor each in each 8 boxes



$$r = \sqrt{(a/2)^2 + (a/2)^2} = \sqrt{2a^2/4} = \sqrt{a^2/2}$$

$$\text{Nearest neighbour distance} = \frac{a}{\sqrt{2}}$$

$$\text{Next nearest neighbour distance} = \frac{a}{\sqrt{3}}$$

$$\text{No of next nearest neighbour} = 6$$



$$= 4r \text{ are inside the cube}$$

$$\text{here } 4 \times \frac{1}{8} \text{ (lattice constant)}$$

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

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

$$\text{Atomic Volume} = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi \left(\frac{\sqrt{3}}{4} a\right)^3 = \frac{1}{3} \pi \frac{a^3}{16}$$

$$\text{Packing fraction} = \frac{2 \times \frac{1}{6} \pi \frac{a^3}{16}}{a^3} = \frac{\pi \sqrt{3}}{8}$$

Assignment

Try for: Face Centred cubic

Try for:

(that) atoms in all the six faces and at the vertices \rightarrow This occurs in face-centred cubic

Solution to Assignment



$$\text{No of atoms per unit cell} = \left(\frac{1}{8} \times 8\right) + \left(\frac{1}{6} \times 6\right) = 1 + 3 = 4$$

Unit cell volume = a^3

Nearest neighbour distance = $a\sqrt{2}$

No of next nearest neighbour distance = 12

Next nearest neighbour distance = a

Number of next nearest neighbour distance = 6

^{NB} here, the lattice constant is $\frac{a\sqrt{2}}{2}$

$$\text{Atomic radius} = \frac{a\sqrt{2}}{2} = \frac{a\sqrt{2}}{4} \Rightarrow r = a\sqrt{2}/4$$

$$\text{Atomic volume} = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi \left(\frac{a\sqrt{2}}{4}\right)^3$$

$$\therefore \text{Packing fraction} = \frac{\text{No of atoms in a cell} \times \text{Atomic volume}}{\text{Unit cell volume}} = \frac{4 \times \frac{4}{3} \pi \left(\frac{a\sqrt{2}}{4}\right)^3}{a^3}$$

$$= \frac{4 \times \frac{4}{3} \pi \frac{a^3}{16}}{a^3} = \frac{4 \times \frac{1}{6} \pi \frac{a^3}{4}}{a^3} = \frac{1}{6} \pi$$

$$= \frac{4 \times \frac{1}{6} \pi \frac{a^3}{4}}{a^3} = \frac{1}{6} \pi$$

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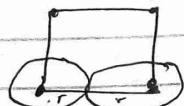
$$= \frac{4 \times \frac{1}{6} \pi \frac{a^3}{4}}{a^3} = \frac{1}{6} \pi$$

*) 17/02/2020

Face-centered cubic lattice (FCC)

N.B. If the angle between any two lines is not 90°
Then, unit cell volume = $a^3 - (b \times c)$

Along the line of nearest neighbours, the atom (in circular form) touches each other



$$\text{Here, } 2r = a \Rightarrow r = \frac{a}{2}$$

Packing fraction \rightarrow Is the percentage of the unit cell volume that the atoms occupy.

Atom on the edges are being shared by 4 cubes

N.B. If packing fraction = 80%
 $\Rightarrow \text{Void} = 20\%$

Packing fraction + Void fraction = 100%

CRYSTALLOGRAPHY DIRECTION AND PLANES

Crystalllography direction

1) A direction is usually taken to be the line from the origin to a given point.

2) Directions are usually indicated with a square bracket $[a b c]$

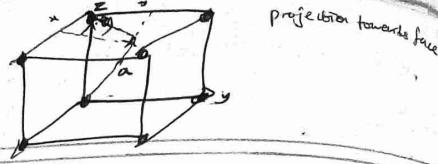
3) Parallel directions have the same value
E.g. $[111] = [222]$ i.e. lowest integer

E.g. $[444] = [111] -$

4) No fractions; convert to integers

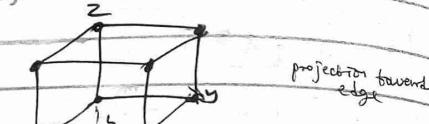
E.g. $[\frac{1}{2} 1 2]$ gives $[124]$

5) Negative directions has a top bar on the value of the axis that is negative



Intercept on x -axis = $\frac{1}{2}$
Intercept on y -axis = $\frac{1}{2}$
Intercept on z -axis = $\frac{1}{2}$
 $[1 \frac{1}{2} \frac{1}{2}]$

Direction of $a = [112]$



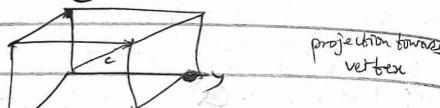
Intercept on $x = 1$

Intercept on $y = \frac{1}{2}$

Intercept on $z = 0$

Direction $[1 \frac{1}{2} 0]$

Direction of $b = [210]$



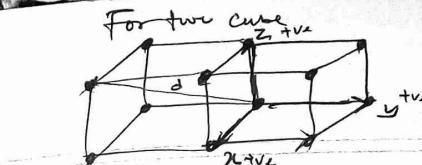
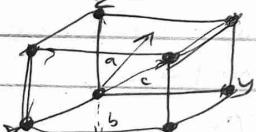
Intercept on $x = 1$

Intercept on $y = 1$

Intercept on $z = 1$

Direction $[111]$

Combining the three diagram



Direction of $d = [111]$

Direction of Planes (or crystallography plane)

i) Miller Indices which are reciprocal of the intersection of the plane with the z -axis's are used to indicate planes.

ii) The miller indices are placed in parentheses i.e. $(\cdot \cdot \cdot)$

iii) Properties (3), (4) and (5) have the same as direction crystallography.

iv) Parallel plane have the same value.

$$(111) = (222)$$

v) No fractions Convert to integers.

vi) Negative directions has a top bar on the value of the axis that is negative

Example ①



Reciprocal of the plane on x -axis = $\frac{1}{1} = 1$

" " " " " on y -axis = $\frac{1}{1} = 1$

" " " " " on z -axis = $\frac{1}{2} = \frac{1}{1} = 1$

Reciprocal of the plane on x -axis = $\frac{1}{1} = 0$
" " " " " on y -axis = $\frac{1}{1} = 1$
" " " " " on z -axis = $\frac{1}{6} = 0$

The plane direction (110)

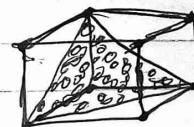


Intercept on $x = 1$
Intercept on $y = 1$
Intercept on $z = \infty$

Reciprocal of the plane on x -axis = $\frac{1}{1} = 1$
" " " " " on y -axis = $\frac{1}{1} = 1$
" " " " " on z -axis = $\frac{1}{6} = 0$

The plane direction (110)

Example 4
Find the Miller indices of



Intercept of the plane on x -axis = 1
" " " " " on y -axis = 1
" " " " " on z -axis = 1

Reciprocal of the plane on x -axis = $\frac{1}{1} = 1$
" " " " " on y -axis = $\frac{1}{1} = 1$
" " " " " on z -axis = $\frac{1}{1} = 1$

The plane direction (111)

Example 5



Intercept on x -axis = ∞
" " " " " on y -axis = 2
" " " " " on z -axis = ∞

Reciprocal on x -axis = $\frac{1}{\infty} = 0$
" " " " " on y -axis = $\frac{1}{2} = \frac{1}{1} = 1$
" " " " " on z -axis = $\frac{1}{\infty} = 0$

The plane direction is $(0 \frac{1}{2} 0)$
 $\Rightarrow (0 1 0)$

Q) learn about other place.

Crystal Binding

Inside a crystal, there are billions of atoms that binds together to form a solid. The force that binds atoms / ions together.

Magnetic, Electrostatic force, gravitational force

Gravitational force exists in the crystal (between any two charges or atom with masses).

Electrostatic force \rightarrow Exist between the ions

The force that binds atoms / ions together is dominated by electrostatic force, other forces such as magnetic or gravitational forces are negligible.

A crystal is more stable than a collection of ~~positive~~ free atoms that forms the crystal.

A system is more stable when the energy is low.

$$\text{Cohesive energy} = \text{Energy of the free atoms} - \text{Energy of the system}$$

24/01/2020

The amount of energy which is required to pull the crystal apart into a set of free atoms is called "the cohesive energy of the crystal".

Cohesive energy = Total energy of free atoms - Energy of the crystal

If the crystal energy is given per a given cell size (i.e primitive, or conventional unit cell) and there are 'n' atoms in the cell, then the cohesive energy will be given by;

$$\text{Cohesive energy} = \sum_{i=1}^n E_i - \text{Crystal energy}$$

$E_i \rightarrow$ Is the energy of free atoms

For a crystal with one type of atom

For two atom container

$$\text{Cohesive Energy} = \sum_{i=1}^n E_i + \sum_{j=1}^m E_j - \text{Crystal Energy}$$

or simply,

For one atom:

$$\text{Cohesive energy} = nE_i - \text{Crystal energy}$$

$$\text{For two different atoms} = nE_i + mE_j - \text{Crystal energy}$$

$$\text{For three atoms} = nE_i + mE_j + lE_k - \text{Crystal energy}$$

n = no. of atoms

For 'n' different atoms:

$$\text{Cohesive energy} = \sum_i^n nE_i - \text{Crystal energy}$$

Example (1) Energy of free atom of Ne = 136 eV

Ne gas crystallizes \Rightarrow FCC

Energy of Ne gas per fcc conventional cell

Solution

$$\text{Cohesive energy} = 4(136) - 520 \text{ eV}$$

$$= 544 - 520 \text{ eV} = 24 \text{ eV}$$

Example (2) The energy of Ne gas per primitive unit cell = 1/2 (in Example 1 above)

$$\text{Cohesive energy} = 136 - 1/2 = 24 \text{ eV}$$

Lattice Energy \rightarrow Is another quantity which is applicable to ionic crystal and is defined as the energy required to separate an ionic crystal component ions into free ions.



Lattice energy is the required energy to separate NaCl to Na^+ & Cl^-

A typical curve for the potential energy (Binding energy)

Representing interaction between two atoms is shown below

N.B.

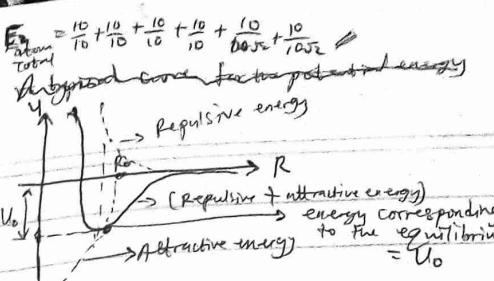
Suppose $E_{\text{2 atoms}} = \frac{10}{R}$

R = Distance between two atoms

Possible pair of atoms: (1,2), (2,3), (3,4), (1,4)

$$4C_2 = \frac{4!}{(4-2)!2!} = 6$$

$$(1,3), (2,4)$$



R \rightarrow Distance between two atoms

Equilibrium (minimum) energy or (Cohesive energy) = U_0

Equilibrium Lattice Constant = R_0

For $R > R_0$, $U \rightarrow 0$ as $R \rightarrow \infty$

For $R < R_0$, $U \rightarrow \infty$

U increases rapidly tending to ∞ at $R = 0$

Since the system tends to have the lowest possible energy at $R = R_0$ then it is most stable with the equilibrium interatomic crystal ($= R_0$)

N.B.) Stable configuration of a system is determined from the minimum energy.

The corresponding energy $U_0 \rightarrow$ is the cohesive energy

The interatomic force is determined by the gradient of the potential energy

$$F(R) = -\frac{\partial U}{\partial R}$$

For $R < R_0$

$$\Rightarrow F(R) = +U_R \quad (\text{because } \frac{\partial U}{\partial R} = -ve \text{ due to a negative slope graph})$$

Now the force, $F(R) \Rightarrow$ repulsive force.

From the curve, $F(R) < 0$ for $R > R_0$

this implies for large separation, the force is attractive. While for $R < R_0$ which implies that at small separation, the force is repulsive

(i) at $R = R_0 \Rightarrow F(R) = 0$

$$\text{i.e. } \frac{\partial U}{\partial R} = 0 \Rightarrow F(R) = 0$$

N.B.) If $F(R) = -10N$ at R_0 then, repulsive $F(R) = 10N$. The attractive interatomic forces reflects the presence of bonds between atoms in solid. There are five different types of bonding. These are;

1) Van der Waals (molecular)

2) Ionic

3) Covalent

4) Metallic

5) Hydrogen bonded.

The attractive energy is different in different solids. The origin of the repulsive energy is however similar in all solids. The repulsive force originates mainly due to the "Pauli Exclusion principle". It states that two electrons can not occupy the same orbital."

As atom ions approach each other close enough, the orbit of the electrons begin to overlap i.e. Some electrons attempt to occupy orbit already occupied by occupied by others.

This is however forbidden by Pauli exclusion principle. As a result, electrons are even excited to unoccupy higher energy state of the atom. Hence the electrons overlap increases the total energy of the system and gives the repulsive contribution to the interaction.

$$\begin{array}{c} 2 \\ \hline 2 \\ 2 \\ \hline 2 \\ \hline \end{array} \quad \begin{array}{c} E=2 \\ E=1 \\ E=0 \end{array} \quad E_T = (2 \times 0) + (2 \times 1) + (2 \times 2) \\ = 0 + 2 + 4 = 6$$

Now,

$$\begin{array}{c} 1 \\ \hline 1 \\ 1 \\ \hline 2 \\ \hline \end{array} \quad \begin{array}{c} E=3 \\ E=2 \\ E=1 \\ E=0 \end{array} \quad E_T = (2 \times 0) + (2 \times 1) + (1 \times 2) + (1 \times 3) \\ = 0 + 2 + 2 + 3 = 7$$

The above is repulsive contribution

The repulsive interaction is usually described by a central field for repulsive potential of the form;

$$U = \lambda r^{-n} \quad (\lambda \text{ and } n \text{ are constant})$$

or of the form;

$$U = \frac{A}{R^n} \quad (A \text{ and } n \text{ are constant})$$

$\Rightarrow U = \text{Repulsive component} + \text{Attractive component}$

Note: Attractive component is balanced by the crystal field.

$$\therefore U = \lambda e^{-r/p} + \frac{A}{r^2}$$

Repulsive energy is the same.

02/03/2020

Inert gases

They are characterized by van der waal's bonding. The electron distribution in such crystal is very close to that in free atoms (with filled electron shells). Hence the electrons are said to be spherically distributed.

Attractive force in van der waal forces

Repulsive force is due to pauli-exclusion principle

Consider two inert gas atoms (1 and 2) separated by a distance R

① ②

The average charge distribution in a single atom is spherically symmetric which implies that the average dipole moment of atoms 1 is zero i.e.,

$\langle d_1 \rangle = 0$
However at any moment of time, there may be non-zero dipole moment caused by fluctuations of the electronic charge distribution.

According to electrostatics, this dipole moment produces an electric field which induces the dipole moment in atom 2.

This dipole moment is proportional to the electric field, inversely which is in turn proportional to $\frac{1}{R^3}$ dipole moment.

$$d_2 \sim E \sim \frac{d_1}{R^3}$$

Dipole moment generated electric field \Rightarrow is due to fluctuation in electric charge distribution.

(The dipole moment of the two atoms interact with each other, the energy is therefore reduced due to this interaction.)

The energy of the interaction is proportional to the product of the dipole moment and inversely proportional to the cube of the distance between the atoms.

$$\text{i.e. } U \sim -\frac{d_1 d_2}{R^3} = \frac{d_1^2}{R^6} - \frac{d_1 \langle d_2 \rangle}{R^3}$$

$$= -\frac{d_1^2}{R^6}$$

N.B. If the shape of the atom is always spherical then its dipole moment is zero.

$$F = \frac{q_1 q_2}{r^3} \rightarrow -\frac{q_1 q_2}{r^3} = -ve \text{ (attractive)}$$

$$F = +ve \text{ (repulsive).}$$

Hence, the coupling between the two dipoles results in attractive force which is also called van der waal's force.

The time average potential is determined i.e. $\langle U \rangle_t = -\langle d_1 \rangle - \frac{d_1^2}{R^6}$

by the average value of $\langle d_1 \rangle$ which is not zero even though $\langle d_1 \rangle = 0$

$$\text{N.B. } 3, -3, 2, -2 \rightarrow \langle d_1 \rangle = \frac{-3 - 3 + 2 - 2}{4} = 0$$

$$\Rightarrow \langle d_1 \rangle = 0 \text{ but } \langle d_1^2 \rangle \neq 0$$

The attractive force is felt more only for a relatively large separation between atoms. At small separation or very strong repulsive force caused by the overlap of the inner electronic shell starts to dominate.

For inert gases, the repulsive force is adequately represented by the potential of the form:

$$U = \frac{B}{R^{12}} \rightarrow (B \text{ is a constant})$$

Hence, the total potential energy of two atoms at separation distance R

$$U_{ij} = 4\epsilon \left[\left(\frac{\sigma}{R_{ij}} \right)^{12} - \left(\frac{\sigma}{R_{ij}} \right)^6 \right]$$

$$\left[U = \frac{B}{R^{12}} - \frac{A}{R^6} \rightarrow \text{Repulsive } R^6 \rightarrow \text{Attractive} \right]$$

$$A = 4\epsilon \sigma^6, B = 4\epsilon \sigma^{12}$$

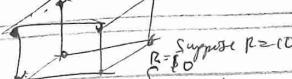
Generally,

$$U = \sum_{ij} U_{ij} = 4\epsilon \sum_{ij} \left[\left(\frac{\sigma}{R_{ij}} \right)^{12} - \left(\frac{\sigma}{R_{ij}} \right)^6 \right]$$

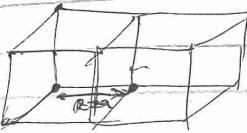
$$U = \frac{1}{2} N^2 4\epsilon \sum_{ij} \left[\left(\frac{\sigma}{R_{ij}} \right)^{12} - \left(\frac{\sigma}{R_{ij}} \right)^6 \right]$$

N.B. No of atoms
Repulsive force is short range
Attractive force is long range

N.B. Repulsive and attractive force acts on the nearest neighbour atom. But repulsive force is no more effect when one moves away from the nearest neighbour.



$$R = NN \quad \begin{cases} R = 10 \\ R = 0.8R \\ R = 2R \end{cases}$$



Nearest neighbour gives (6 nearest)

Next nearest neighbour gives (12 next nearest)

$$R_{ij} = P_{ij} R = \sqrt{2} R \quad ; \quad P_{ij} = \sqrt{2}$$

$$\text{Now: } U = \frac{1}{2} 4N\epsilon \sum_j \left[\left(\frac{\sigma}{P_{ij} R} \right)^{12} - \left(\frac{\sigma}{P_{ij} R} \right)^6 \right]$$

$R \rightarrow$ Nearest neighbour distance

For FCC (face centered cubic)

$$\text{For Nearest neighbour } P_{ij} = \frac{R}{\sqrt{2}}$$

$$\text{here: } R_{ij} = P_{ij} R = \left(\frac{\sqrt{2}}{2} \right) R$$

$$\Rightarrow P_{ij} = 1 \quad \Rightarrow R_{ij} = \frac{\sqrt{2}}{2} R = P_{ij} \frac{\sqrt{2}}{2} R \quad \Rightarrow P_{ij} = 1$$

$$\text{distance} = a = \frac{2}{\sqrt{2}} \left(\frac{\sqrt{2}}{2} a \right) = a$$

$$\text{hence: } P_{ij} = P_{ij} / 2 \Rightarrow P_{ij} = \frac{2}{\sqrt{2}}$$

$$\text{or say: } P_{ij} = \frac{2}{\sqrt{2}}$$

$$\text{opposite } R_{ij} = a = P_{ij} \left(\frac{\sqrt{2}}{2} a \right)$$

$$\Rightarrow P_{ij} = \frac{2}{\sqrt{2}}$$

Finally we get now;

$$\sum P_{ij}^{-12} = \left(\frac{1}{a} \right)^{12} + \left(\frac{2}{a} \right)^{-12}$$

$$= 12.13188$$

$$\text{also: } \sum P_{ij}^{-6} = \left(\frac{1}{a} \right)^6 + \left(\frac{2}{a} \right)^6$$

$$\sum P_{ij}^{-6} = 14.45392$$

$$\text{Given: } U = \frac{1}{2} 4N\epsilon \sum_j \left[\left(\frac{\sigma}{P_{ij} R} \right)^{12} - \left(\frac{\sigma}{P_{ij} R} \right)^6 \right]$$

$$\Rightarrow \frac{dU}{dR} = \frac{1}{2} 4N\epsilon \sum_j \left[-12 \frac{\sigma^{12}}{P_{ij}^{13} R^{13}} + 6 \frac{\sigma^6}{P_{ij}^7 R^7} \right]$$

$$\frac{dU}{dR} = \frac{1}{2} 4N\epsilon \sum_j \left(-12 \frac{\sigma^{12}}{R^{13}} \frac{P_{ij}^{-12}}{(12.13188)} + 6 \frac{\sigma^6}{R^7} \frac{P_{ij}^{-6}}{(14.45392)} \right)$$

$$\Rightarrow R_0 = 1.09 \text{ \AA}$$

$$U = 2.154N\epsilon$$

Cohesive energy is the minimum energy a crystal can possess

Note: From equation ①

$$0 = \frac{1}{2} 4N\epsilon \sum_j \left(-12 \frac{\sigma^{12}}{R^{13}} \frac{P_{ij}^{-12}}{(12.13188)} + 6 \times 10^{-6} \frac{P_{ij}^{-6}}{(14.45392)} \right)$$

$$\Rightarrow 12 \frac{\sigma^{12}}{R^{13}} \frac{P_{ij}^{-12}}{(12.13188)} = 6 \times 10^{-6} \frac{P_{ij}^{-6}}{(14.45392)}$$

$$\Rightarrow 2 \frac{\sigma^{12}}{R^{13}} \frac{1}{(12.13188)} = 14.45392$$

$$\Rightarrow P_{ij}^6 = \frac{2 \sigma^{12}}{14.45392} \frac{1}{(12.13188)}$$

$$\Rightarrow R_0 = \left(\frac{2 \sigma^{12}}{14.45392} \right)^{1/6} \text{ \AA} \Rightarrow R_0 = 1.09020$$

$$\Rightarrow P_{ij} \approx 1.09 \text{ \AA}$$

From equation ②

$$\Rightarrow 12 \frac{\sigma^{12}}{R^{13}} \frac{P_{ij}^{-12}}{(12.13188)} = \frac{6 \times 10^{-6} (P_{ij})^{-6}}{(1.09)^6 \text{ \AA}^7}$$

$$\Rightarrow U = \frac{1}{2} 4N\epsilon \left[-12 \frac{\sigma^{12}}{R^{13}} \frac{1}{(12.13188)} + \frac{6 \times 10^{-6} (14.45392)}{(1.09)^6 \text{ \AA}^7} \right]$$

$$U = 2.154N\epsilon$$

2)

9/03/2020 [SEMICONDUCTORS]

Semiconductors are materials that

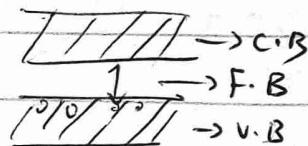
i) have properties between conductors and insulators.

- Conductors - have free electrons for conduction
- Insulators - have poor conductor of electricity and heat.

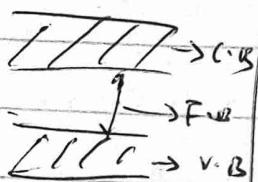
1,300 Amperes
of current
is present in
lightning
lightning

Conduction Band →
Forbidden Band →
Inert Valence band →

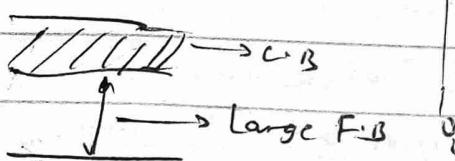
3) Conductors



Semiconductor



4) Insulators



Note: At large temperature, insulators conduct.

Semiconductors

- Pure Semiconductors → They are semiconductors without impurities e.g. silicon, germanium
- Impure Semiconductor - like Silicon Carbide / They are semiconductors with impurities. They are usually doped.

e.g. Silicon carbide (SiC), Silicon Germanium
Doping increases the characteristics of pure Sem. Semiconductor.

Impure Semiconductor

- N-type and P-type
- N-type has excess electrons (they are the majority carriers).

Electrons are particles, holes are bubbles (not particles)

5) Generation of

- Generation of Carriers is when electron moves from V.B. to C.B.
- Recombination is when electrons move from C.B. to V.B. due to withdrawal of energy
- N > P (For n-type), P > N (for p-type)
- P-type: Majority carries one hole.

1.3) For a pure semiconductor no. of $P_2 = \text{no. of Fermi-level}$

probability of a level being occupied by an electron is the Fermi-level (Refer CGP)

$$f(E) = \frac{1}{2}$$

Generally, $f(E) = \frac{1}{1 + \exp((E - E_F)/kT)}$

N.B. A simple cubic \rightarrow can be spanned by three mutually perpendicular primitive vectors of equal length.

N.B. A 2-D Bravais lattice is also known as a net

N.B. The vertices of a honeycomb do not form a bravais lattice (because structural and not orientational relations are identical when rotated through 180°) also, 3-D hexagonal close-packed lattice do not form a bravais lattice.

Infinite lattices and finite crystals

Since all points are equivalent, the Bravais lattice must be infinite in extent.

Infinite crystals have most points so far from the surface as to be unaffected by its existence (i.e. unaffected by surface effects)

The defects of the second definition of bravais lattice that give rise to $[R = n\mathbf{a}]$ is that:

- For any given Bravais lattice the set of primitive vectors is not unique.

Summary - continuation

A crystal structure \rightarrow is formed when a basis (a fixed group of atoms) is attached to each lattice point

$$\text{Crystal structure} \Rightarrow \text{Bravais lattice} + \text{Basis} \\ (\text{Arrangement}) \quad (\text{Atoms}) \\ \text{of point}$$

Fundamental types of lattices

For 2-D, there are 5 distinct lattices

- square, - rectangular, - hexagonal,
- centered rectangular, - oblique

For 3-D, there are 7 distinct lattice systems giving rise to 14 bravais lattices.

Bravais system \rightarrow It has only they are only primitive

2) Monoclinic \rightarrow primitive & side-centered

3) Orthorhombic \rightarrow primitive, body-centered, side-centered and face-centered.

4) Tetragonal \rightarrow primitive & side-centered

5) Trigonal \rightarrow primitive

6) Cubic \rightarrow primitive, body-centered, face-centered

7) Hexagonal \rightarrow primitive.

28/02/2020 (a) Primitive Unit Cell

No of points/unit cell along = 1

Nearest neighbour distance = a

No of nearest neighbour = 6

Next nearest neighbour distance = $a\sqrt{2}$

No of next nearest = 12

Body centered cubic

No of points atoms per unit cell = 2

Nearest neighbour distance = $a\sqrt{3}/2$

No of nearest " = 8

Next nearest neighbour distance = $a\sqrt{2}$

No of next nearest neighbour = 12

Face centered cubic = 6

No of atoms per unit cell = 4

Nearest neighbour distance = $a\sqrt{2}/2$

No of nearest neighbour = 12

Next nearest neighbour distance = $a\sqrt{3}/2$

No of next nearest neighbour = 6

[PT18 - 319] \rightarrow Solid State

Phys

29/02/2020

Summary Section

(a) Solid Structures \rightarrow Crystalline solid & Amorphous solid.

(b) Crystalline solid \rightarrow solid in which the components arrangement has long ranged order. Their particles are arranged uniformly till infinity.

(c) Amorphous solid \rightarrow solid in which the components arrangement has short ranged order. They can be obtained from crystalline solid.

(d) Crystal \rightarrow Is a solid with periodic structure represented by a bravais lattice.

(e) Bravais lattice \Rightarrow Is an infinite array or discrete point with an arrangement and orientation that appear exactly the same from whichever of the points the lattice is viewed. They consists of all points with position vector; $[R = n\mathbf{a}]$ where n integer.

$[R = n_1\mathbf{a}_1 + n_2\mathbf{a}_2] \rightarrow 2-D$ $[R = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3] \rightarrow 3-D$

N.B. n could be +ve or -ve depending on the axis.

n depends on the atom in consideration.

N.B. Every substances have their various lattice constant

(f) For square lattice, for rectangular lattice

$$|a_1| = |a_2|, \theta = 90^\circ$$

$$|a_1| \neq |a_2|, \theta = 90^\circ$$

parallellogram lattice;

$$|a_1| = |a_2|, \theta \neq 90^\circ$$

properties of bravais lattice

(g) Primitive unit cell: It is the volume (or surface if 2-D) that when translated through all the vectors in a bravais lattice just fills all the space without overlapping or leaving voids. N.B. \rightarrow The choice of primitive unit cell is not unique.

(h) It usually contains one lattice point \rightarrow volume of the primitive unit cell is

(i) The volume of the primitive unit cell is $V = \frac{1}{n}$ where $n =$ no of points

$$V \rightarrow \text{volume}$$

(j) The volume of all possible primitive unit cells are the same.

(k) They do not sometimes have the full symmetry of the bravais lattice.

(l) Conventional unit cell: - Is usually bigger than the primitive unit cell in favour of preserving the symmetry of the bravais lattice.

(m) The volume of conventional unit cell is equal to the no of points in the cell multiplied by volume of the primitive unit cell.

(n) Coordination number: - The points in a bravais lattice that are closest to a given point are called its nearest neighbour. No. of this nearest neighbour is called the coordination number.

N.B. In 1-D, the coordination no. of any point is 2

N.B. Nearest neighbour of any point can change but the coordination number still remain the same.

Solid state physics
Ashcroft and Mermin

CRYSTAL LATTICES

(o) Diamond, Metals, quartz, rocksalt

(p) The true test of crystallinity is to check whether on the microscopic level the ions are arranged in a periodic array.

N.B. Geometrical properties of periodic arrays in 3-D space are implicit in almost all the analysis one encounters throughout solid state physics.

Bravais lattice \rightarrow specifies the periodic array in which the repeated units of the crystal are arranged. The units may be single atoms, groups of atoms, molecules, ions etc. underlying periodic structure, regardless of what the actual units may be.

(q) Given: $R = \sum n_i \mathbf{a}_i$ \rightarrow \mathbf{a}_i are called primitive vectors and are said to generate or span the lattice.