Inorganic Chemistry I (CH331)
Solid-state Chemistry II

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Text books :

1. D.F. Sheiver, P.W. Atkins & C.H. Langford "Inorganic Chemistry" 2nd Edition (1994), Oxford University Press

2. Alan G. Sharpe "Inorganic Chemistry" 3rd edition (1992), Longman

3. R.B. Heslop & P.L. Robinson "Inorganic Chemistry : A Guide to Advance Study" 3rd edition (1967), Elsevier

4. F.A. Cotton & G. Wilkinson "Advanced Inorganic Chemistry: A Comprehensive Text" (1964), Interscience Publishers

5. K.M. Mackay & R.A. Mackay "Introduction to Modern Inorganic Chemistry" 2nd Edition (1972), Intertext Books

Contents

1. **Strength of Solids / Compounds**
   - Lattice Enthalpy
   - Born-Haber cycle / Born-Haber Equation

2. **Band Structure**

3. **Imperfections in Solids**

1. Strength of Solids / Compounds

Lattice Enthalpy $\Delta H_L^{\ominus}$

- standard enthalpy change accompanying the formation of a gas of ions from the solid:

$$MX_{(s)} \rightarrow M^+_{(g)} + X^-_{(g)} \qquad \text{Lattice enthalpies are always +}$$
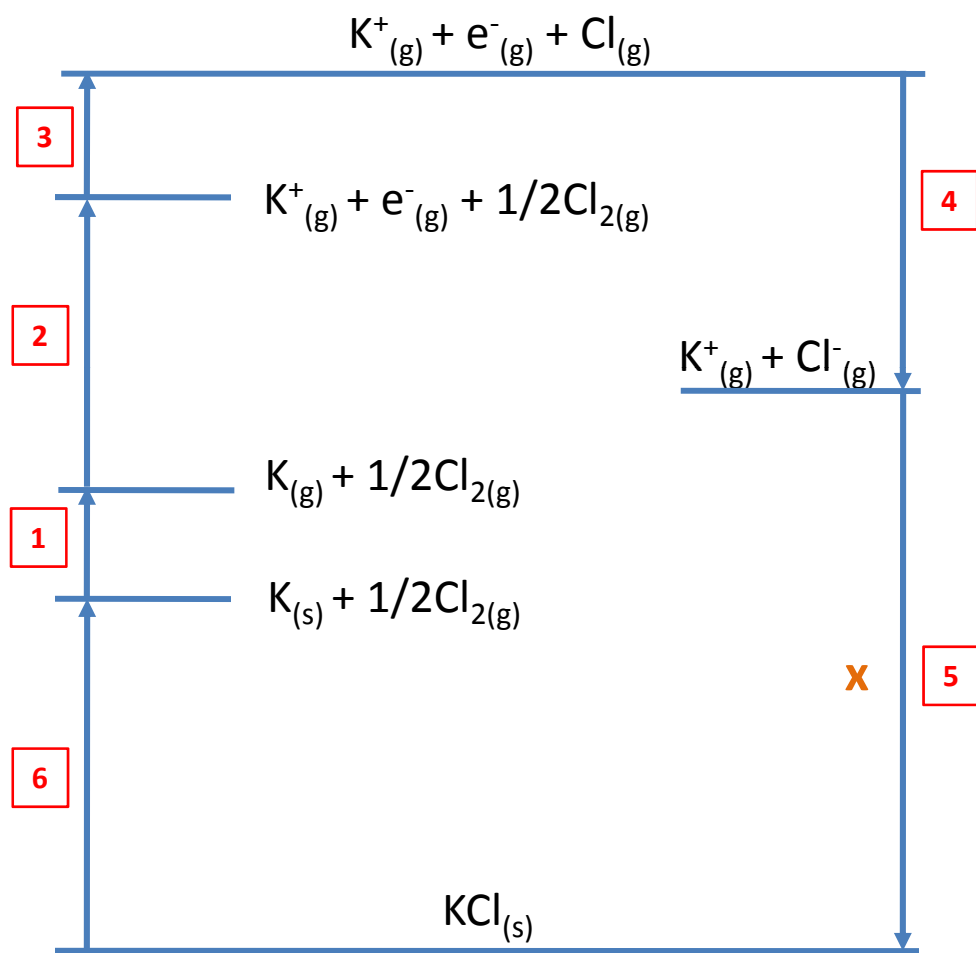
- greatest lattice enthalpy ➔ the most stable crystal

- there are many ways to calculate or consider the lattice enthalpy, e.g. equation involving Madelung constant (previous lecture);

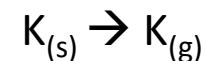$$\Delta U = \frac{NMZ_+Z_-}{r_0}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\left(1 - \frac{\rho}{r_0}\right)$$

-Using Born-Haber cycle

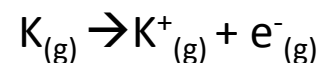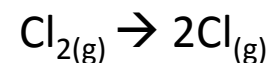Born-Haber cycle is a thermodynamic cycle including all steps of crystal formation.

$K^+_{(g)} + e^-_{(g)} + Cl_{(g)}$

3

$K^+_{(g)} + e^-_{(g)} + 1/2Cl_{2(g)}$

4

2

$K^+_{(g)} + Cl^-_{(g)}$

$K_{(g)} + 1/2Cl_{2(g)}$

1

$K_{(s)} + 1/2Cl_{2(g)}$

X **5**

6

$KCl_{(s)}$

Reactions involves

- Atomisation or sublimation **1**

$K_{(s)} \rightarrow K_{(g)}$

- ionisation **2**

$K_{(g)} \rightarrow K^+_{(g)} + e^-_{(g)}$

- dissociation **3**

$Cl_{2(g)} \rightarrow 2Cl_{(g)}$

- Electron attachment **4**

$Cl_{(g)} + e^-_{(g)} \rightarrow Cl^-_{(g)}$
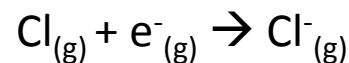
-X = Lattice Enthalpy **5**

-Decomposition **6**

$KCl_{(s)} \rightarrow K_{(s)} + 1/2Cl_{2(g)}$
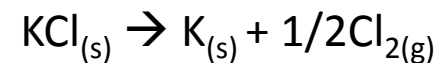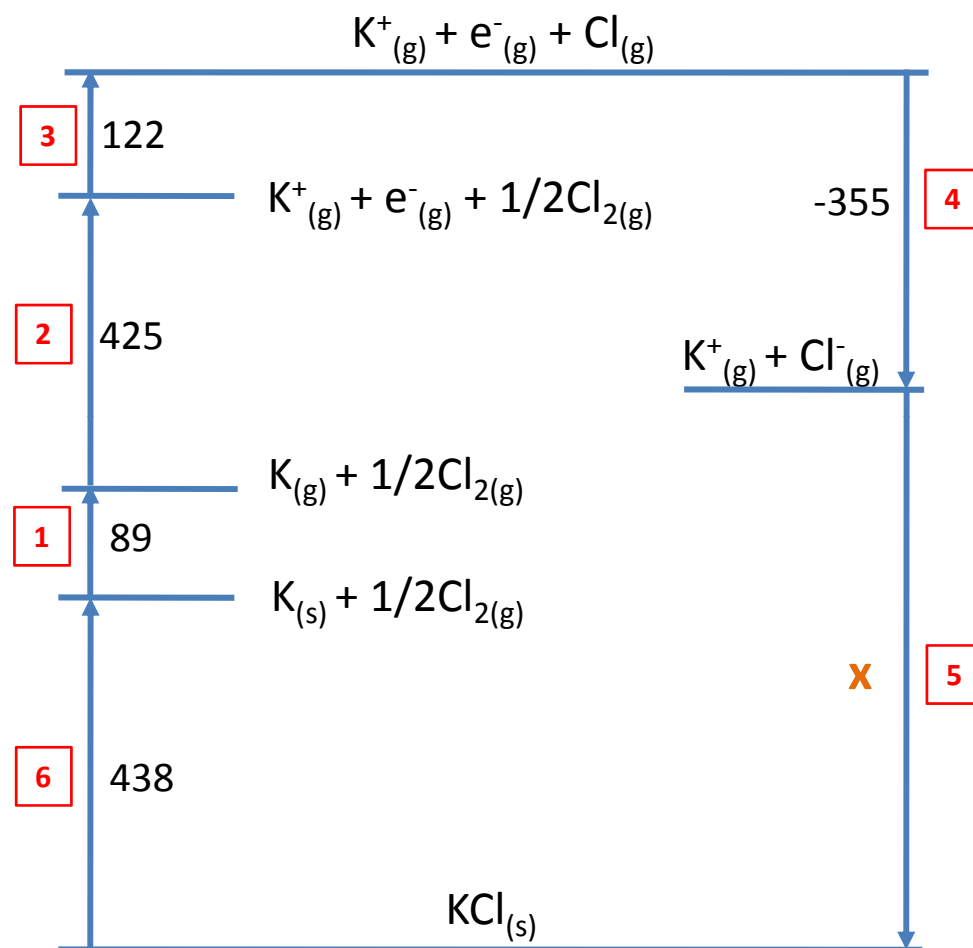
** Sum of the enthalpy changes in the cycle is ZERO (0).

Exercise : Calculate the lattice enthalpy of KCl(s) from following information of the standard enthalpy change

	$\Delta H^{\ominus}/(kJ\ mol^{-1})$
Sublimation of K(s)	+89
Ionization of K(g)	+425
Dissociation of $Cl_2(g)$	+244
Electron gain by Cl(g)	−355
Formation of KCl(s)	−438

ANS : 719 kJ mol^{-1}

$K^+_{(g)} + e^-_{(g)} + Cl_{(g)}$

3 122

$K^+_{(g)} + e^-_{(g)} + 1/2Cl_{2(g)}$ −355 **4**

2 425

$K^+_{(g)} + Cl^-_{(g)}$

$K_{(g)} + 1/2Cl_{2(g)}$

1 89

$K_{(s)} + 1/2Cl_{2(g)}$

**X** **5**

6 438

$KCl_{(s)}$

Other than those lattice enthalpy calculations (i.e. using Madelung Equation and Born-Haber Cycle), there are other ways that the scientists used to explain lattice enthalpy.

1. **Considering coulombic contribution**
    - charges of ions and electrons are involved, thus the term of potential energy (V) of the crystal is somehow considered.

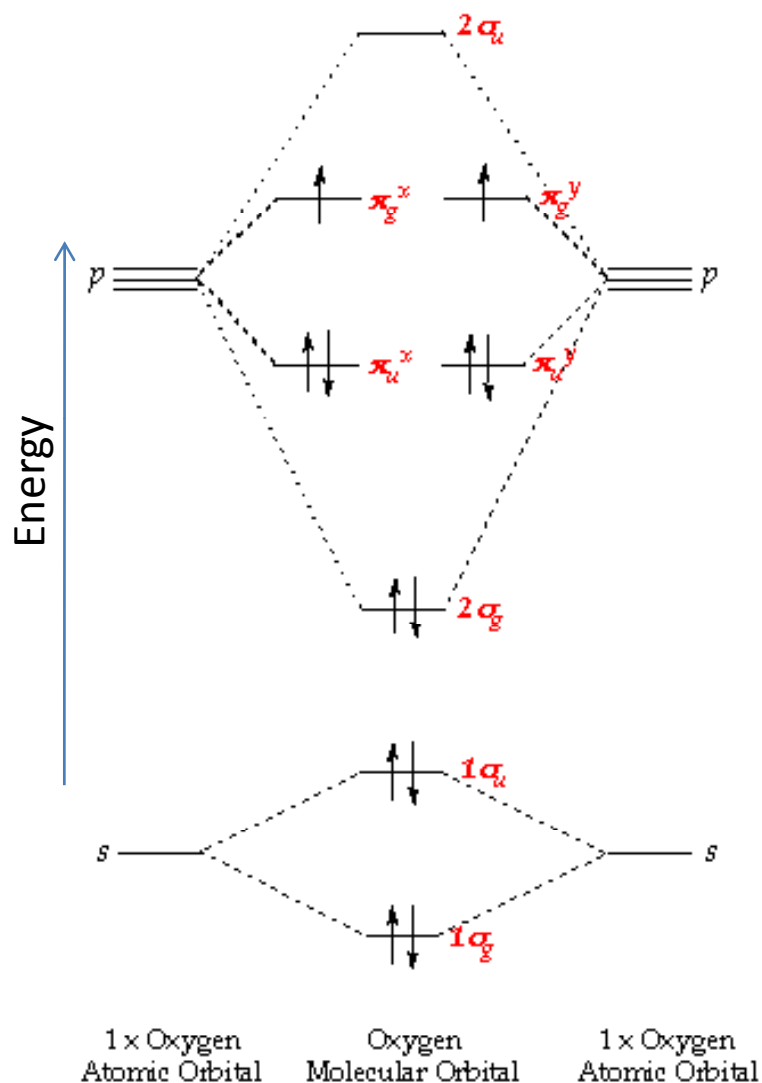$$V_{AB} = \frac{(z_A e)(z_B e)}{4\pi\varepsilon_0 r_{AB}}$$

2. Considering Repulsive and Attractive force between ion
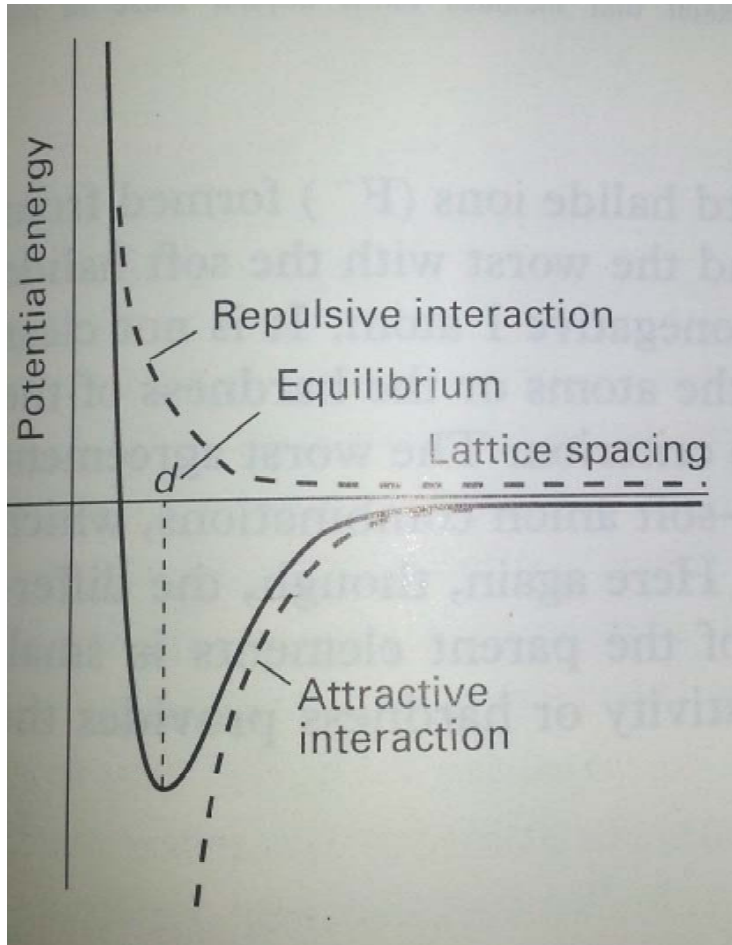
Born-Haber Equation

$$V = \frac{N_A(z_A z_B e^2)}{4\pi\varepsilon_0 d}\left(1 - \frac{d^*}{d}\right)A$$

2. Band Structure

2σ_u
π_g^x   π_g^y
p   p
π_u^x   π_u^y

Energy

2σ_g

1σ_u

s   s

1σ_g

1 x Oxygen   Oxygen   1 x Oxygen
Atomic Orbital   Molecular Orbital   Atomic Orbital

http://www.ch.ic.ac.uk/vchemlib/course/mo_theory/

- According to the bonding of atoms forming a molecule containing two atoms, the energy levels of molecular orbitals (MO) are split into a lower energy level and higher energy level. The number of these molecular orbitals are depending on the valence orbital of an atom involved.

-In solid, where there are a large number of atoms are involved (not only 2 atoms), resulting in a large number of molecular orbitals, resulting in a **band** like structure containing all molecular orbitals.
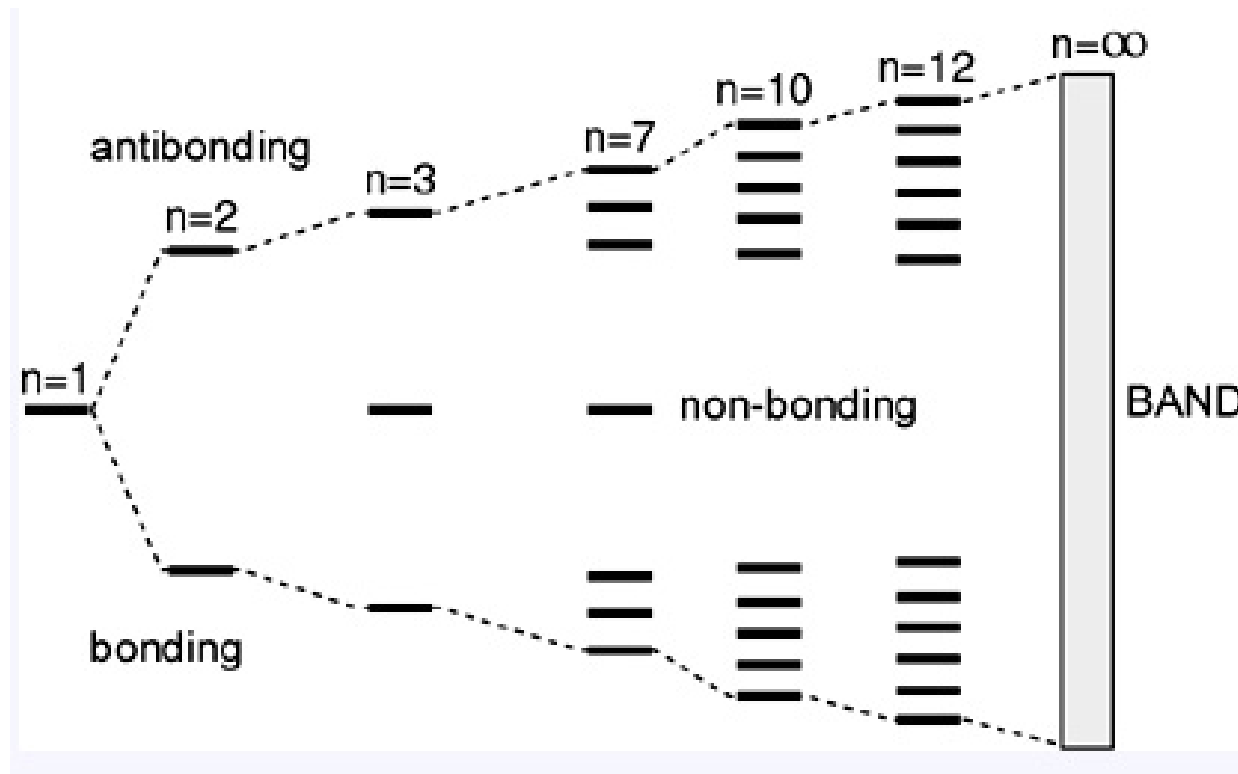
-There are two types of bands, which are

1. Conduction band; where there is no electron filled in this range of energy level. → *Vacant States in the picture*

2. Valence band; where the electrons is placed.
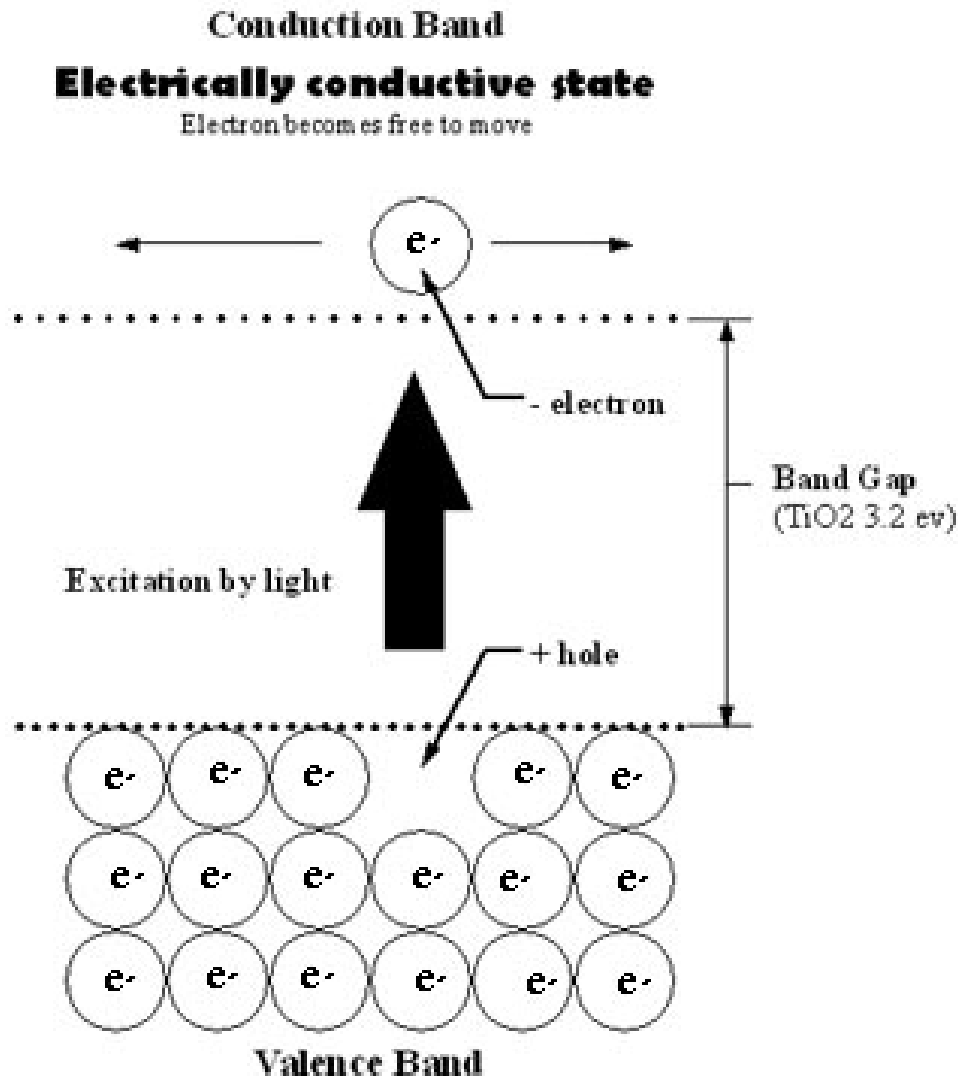→ *Occupied States in the picture*
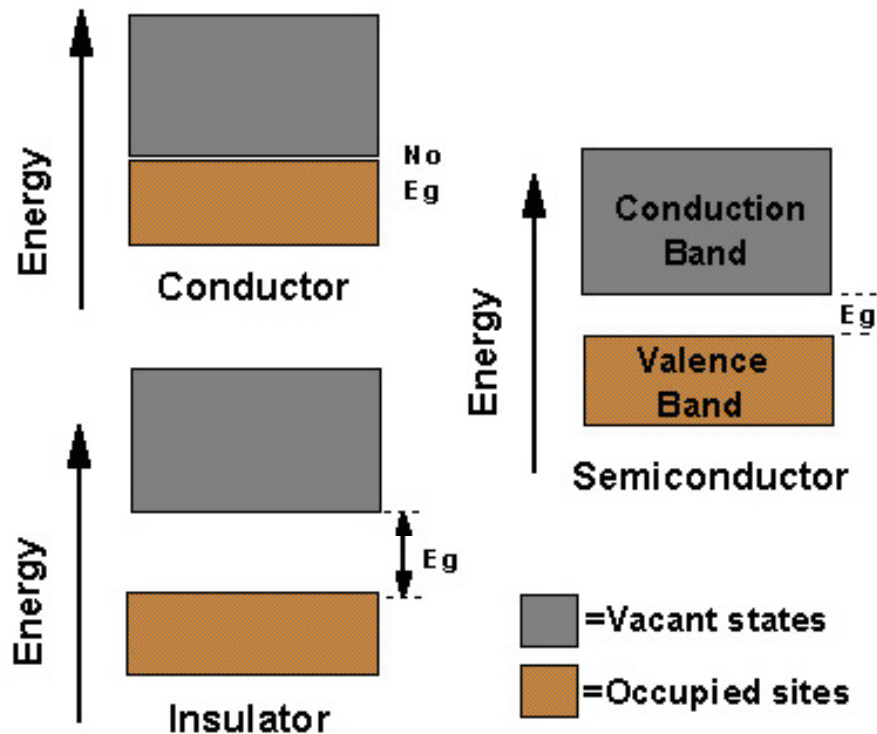
E_g = band gap, which is the amount of energy used to excite the electron to move to excited state or conduction band.

E_g~2 eV or lower → semiconductor
E_g very high → insulator

How does semiconductor work?

Conduction Band

Electrically conductive state

Electron becomes free to move

e-

← →

- electron

Band Gap
(TiO2 3.2 ev)

Excitation by light

+ hole

e- e- e- e- e-
e- e- e- e- e- e-
e- e- e- e- e-

Valence Band

When an electron in the valence band absorb the energy (high enough to jump to conduction band, which is more than the band gap energy; E_g), the electron will then moves to the conduction band leaving the hole in the valence band.

The moving of an electron and hole, causing the conduction, whether a electrical or thermal.

http://www.greeninnovationsgroup.com/titania/mechanism.htm

Semiconductor

1. Intrinsic Semiconductor : pure element that has semiconductive properties

: e.g. Si and Ge

2. Doped Semiconductor : the crystal structure of element is modified by an impurity atoms that intently added into the material in order to increase the semiconductive properties.

: e.g. GaP, GaAs, InSb, CdS and ZnTe

The band gap of some semiconductors are shown in the table below;

Material	Band Gap (eV)
Si	1.11
Ge	2.2
GaAs	1.42
InSb	0.17
ZnTe	2.26

Data taken from G.L.Miessler and D.A.Tarr, "*Inorganic Chemistry*" 3rd Edition, **2004**, Pearson Education International, New Jersey.

Doped Semiconductor is classify into n-type and p-type, depending on the function of the doped element comparing to the host element. This is to reduce the band gap energy to be lower than the undoped one.

1. **n-type semiconductor**
    - the added material (doped) has more electrons in the valence shell comparing to the host material. → P in Si host, As in Si host

2. p-type semiconductor
    - the doped material has less electron in the valence shell than the host. → Ga in Si host, B in Si host
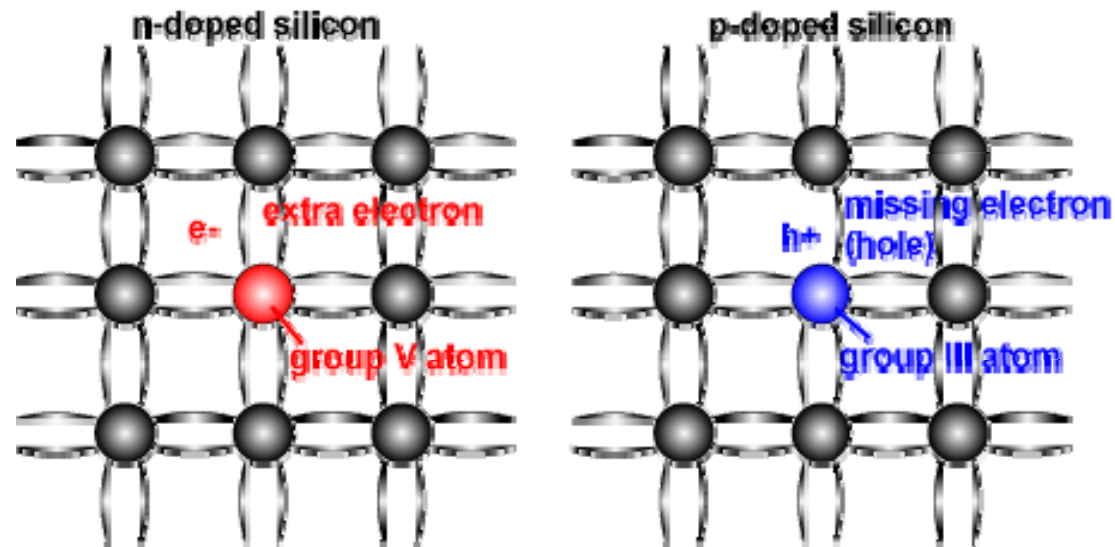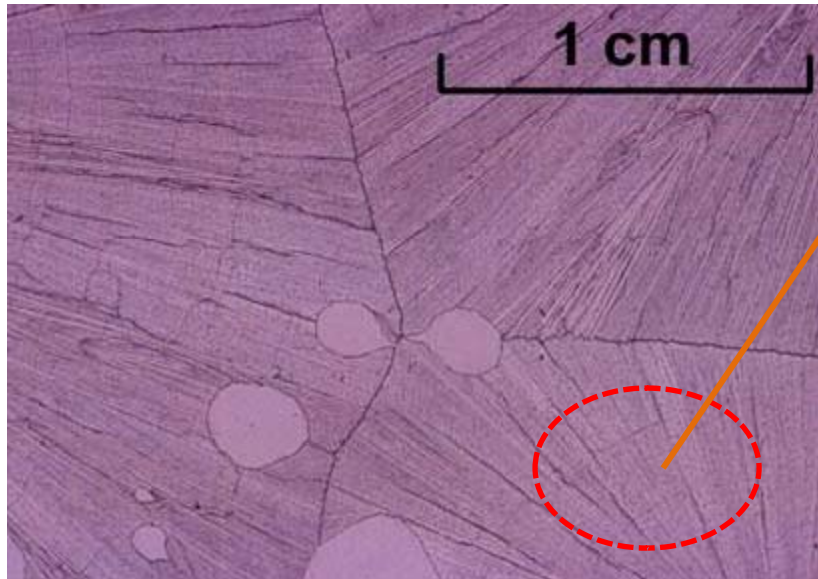
3. Imperfections in Solids

Solid in this case means the substance or compound or element that composes of many crystalline phases, so called **"polycrystalline solids"**. Assuming that the solids are slowly cooled leading the crystallisation of the crystalline phases in the solids as shows in the picture below;

http://www.rsc.org/education/teachers/resources/jesei/cooling/home.htm
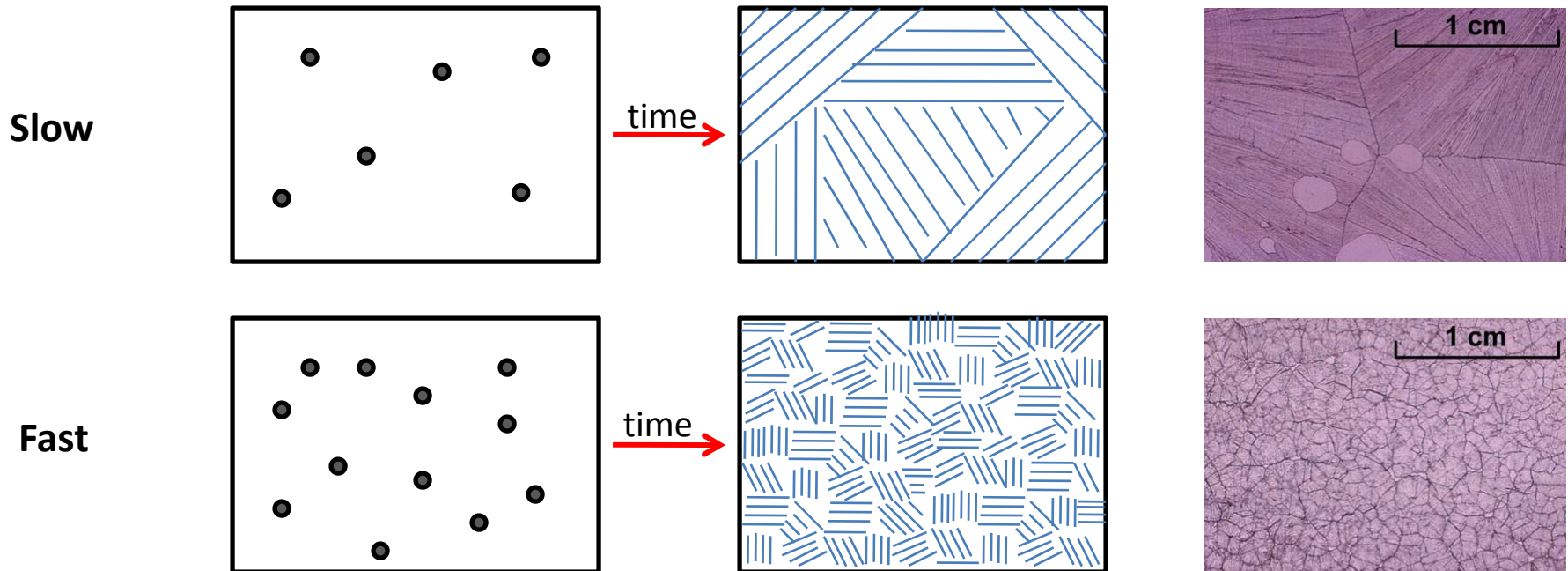
3. Imperfections in Solids

Imperfections occur inside phase grain, i.e. in the crystal structure, even if the solid is slow cooled.

All possible imperfections or defects are

1. Vacancy

2. Self-interstitial   Point defect

3. Substitution

4. Dislocation

5. etc. → plane defect, bulk defect

Point defect

i.e. Vacancy, self-interstitial, and substitution

Vacancy

- missing of atom(s)
- usually occurs at high temperature as atom will possess the higher energy causing the vibration of atom or releasing of atom leaving a hole, so called "VACANCY".

Self-interstitial and interstitial impurity atom

- Extra atom(s)

Substitutions

- May be common = like in metal alloy
- large effects on properties of solids e.g. mechanical properties and electrical properties.

Self Interstitial Atom

Vacancy

Interstitial Impurity Atom

Substitution Impurity Atom

Line defects - Dislocations

- Two types : edge dislocations and screw dislocations
- undesirable in crystals
- Dislocation leads to the mechanically failure or causing the reducing in some electrical properties

https://courses.eas.ualberta.ca/eas421/lecturepages/microstructurediags.html