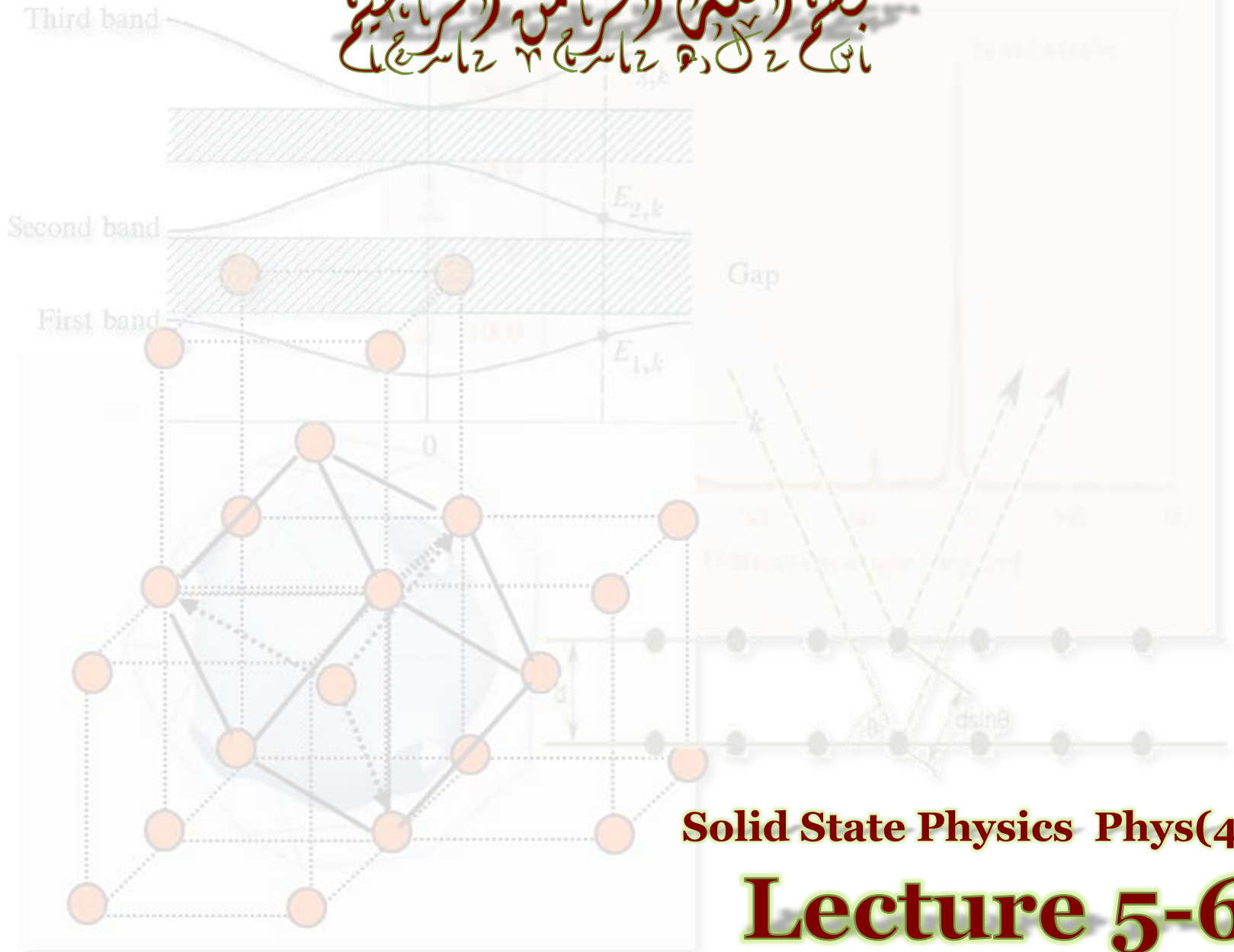
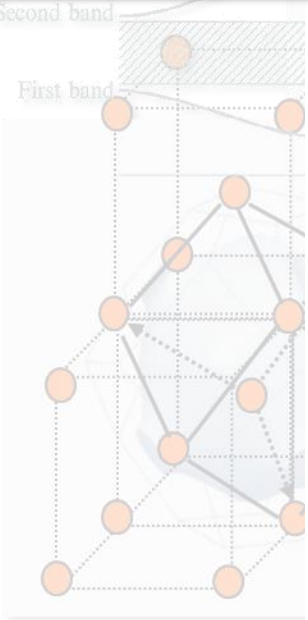
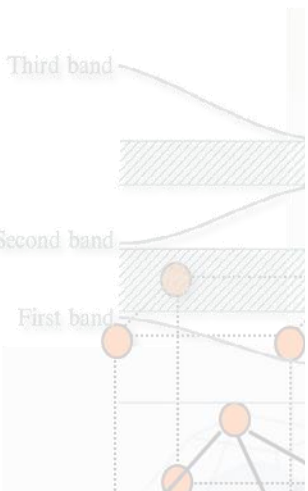


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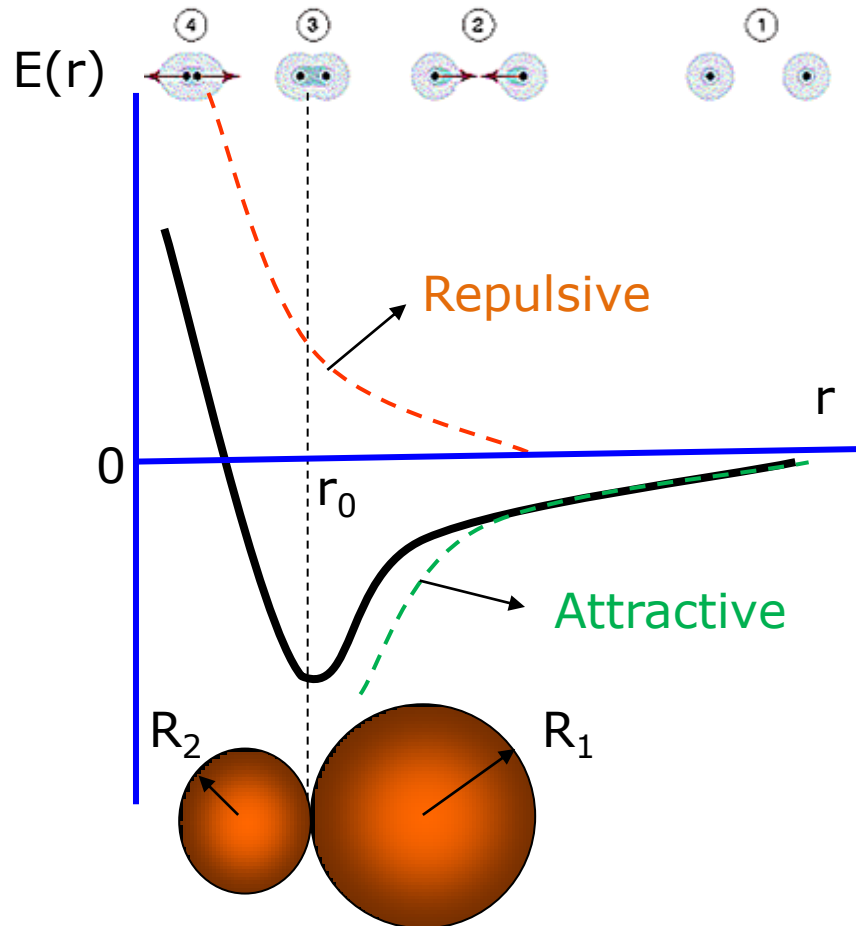
INTERATOMIC FORCES

It has been shown earlier that the atoms in crystalline solids are arranged in neat ordered structures. Now we will describe the nature of the **forces which hold those atoms together**.

- 
- 
- All of the mechanisms which cause bonding between the atoms derive from **electrostatic interaction** between nuclei and electrons.
 - The existence of a stable bonding arrangement implies that the **spatial** configuration of the two atoms has **less total energy** than any other configuration (including infinite separation).
 - The energy of the crystal is lower than that of the free atoms by an amount equal to the energy required to pull the crystal apart into a set of free atoms. This is called the **binding (cohesive) energy** of the crystal.

INTERATOMIC FORCES

Consider, first, two identical atoms in their ground states being brought together from an infinite separation.



➤ Initially, the energy of their interaction is zero.

➤ As the atoms approach, the **attractive forces** increase, and hence the **potential energy** increases, **in a negative sense**.

➤ At a separation of a few atomic radii, **repulsive forces** begin to increase exponentially.

➤ The atoms reach an equilibrium separation r_0 at which the **repulsive and attractive forces are equal** and **the mutual potential energy is a minimum**.

INTERATOMIC FORCES

➤ **The attraction energy** is **negative** since the atoms do the work (+ve work), while the **energy of repulsion** is **positive** as work has to be done on the atoms (-ve work).

➤ Recall:
$$F = -\frac{dE}{dr}$$

➤ Then,

$$E(r) = -E_{\text{att}} + E_{\text{rep}}$$

where $E_{\text{att}} = -\frac{A}{r^n}$ and

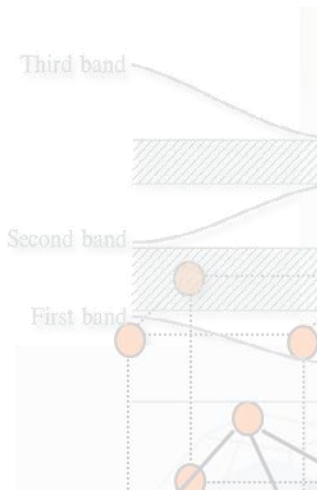
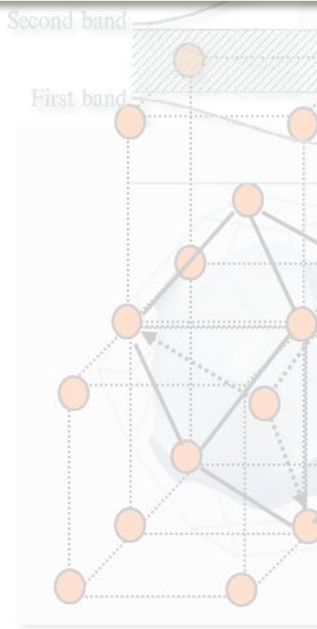
$$E_{\text{rep}} = \frac{B}{r^m} \quad \text{or} \quad = B \exp\left(\frac{-r}{\rho}\right)$$

E(r): the net potential energy of interaction as function of r

r: the distance between atoms, ions, or molecules

A, B: proportionality constant of *attraction* and *repulsion*, respectively

n, m: constants where **n**~2-3 and **m**~9-11



INTERATOMOMIC FORCES

Notes:

➤ It is conventional to classify the bonds between atoms into different types as:

Ionic, Covalent, Metallic, Hydrogen and Van der Waals.

➤ Different bonds give rise to different physical properties in solids.

➤ Most real bonds are intermediate between the 'extreme' types classified below.

➤ **The cohesive energy** ranges in value from **0.1 eV/atom** for the weak **van der Waals** to **7eV/atom** or more in some **covalent** and **ionic compounds** and some metals.

TYPES OF BONDS

1. THE IONIC BOND

Ionic bonding is the electrostatic force of attraction between positively and negatively charged ions (between non-metals and metals).

Typical Example: NaCl whose melting point is 801°C

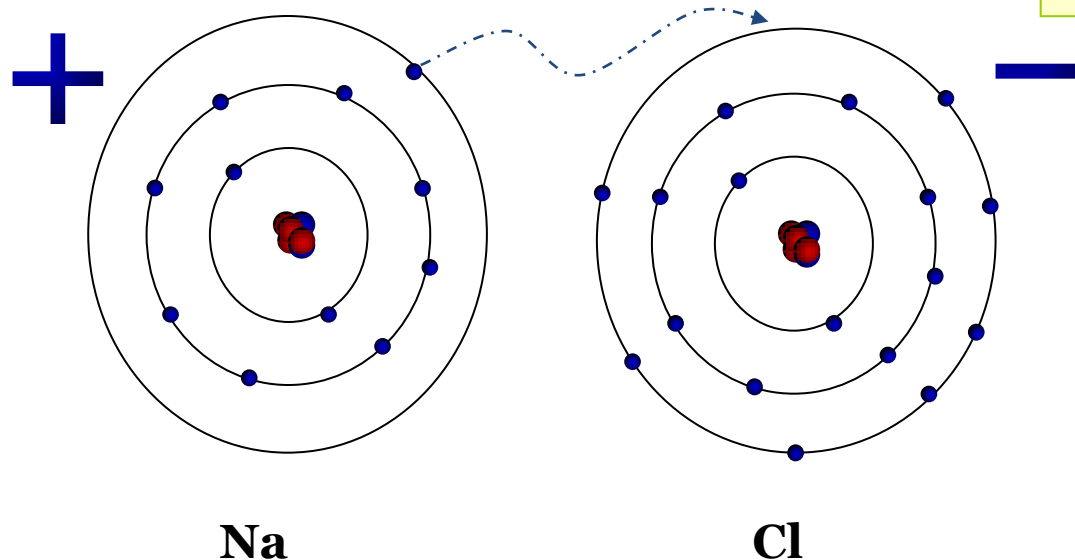
Strength: strong (~5 eV per bond)

Origin: **Transfer** of electrons between two positively and negatively charged ions

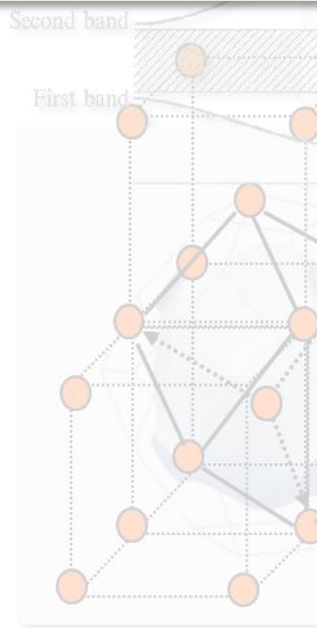
⇒ Formation of (+ve) & (-ve) ions

⇒ Existing of Coulomb force

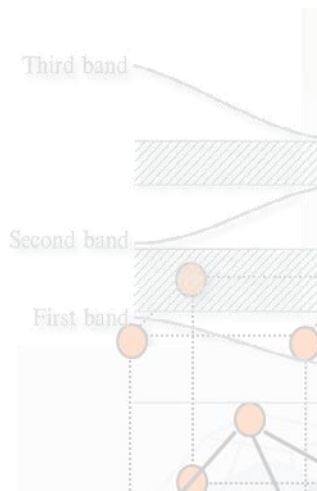
$$\frac{e^2}{4\pi\epsilon_0 R^2}$$



TYPES OF BONDS



Property	Explanation
Melting point and boiling point	The melting and boiling points of ionic compounds are high because a large amount of thermal energy is required to separate the ions which are bound by strong electrical forces.
Electrical conductivity	Solid ionic compounds do not conduct electricity when a potential is applied because there are no free electrons and hence nothing can carry charges.
Hardness	Most ionic compounds are hard; the surfaces of their crystals are not easily scratches. This is because the ions are bound strongly to the lattice and aren't easily displaced.
Brittleness	Most ionic compounds are brittle; a crystal will shatter if we try to distort it. This happens because distortion cause ions of like charges to come close together then sharply repel.



TYPES OF BONDS

2. THE COVALENT BOND

Covalent bonding takes place between atoms with small differences in electronegativity which are close to each other in periodic table (*between non-metals and non-metals*).

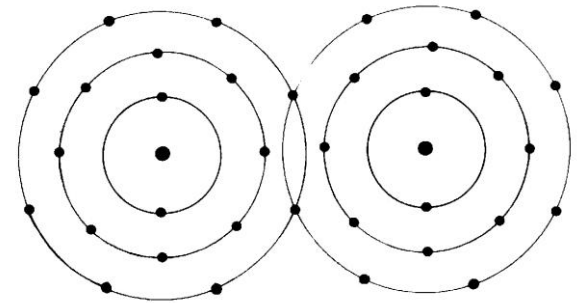
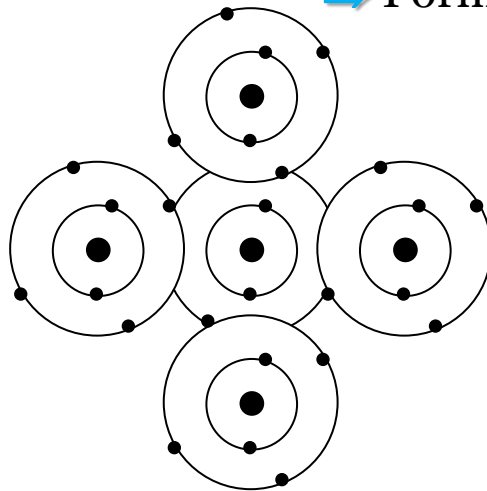
Typical Example: Diamond whose melting point is very high $>3000^{\circ}\text{C}$

Strength: strong (~few eV per bond)

Origin: Existing of 4 (or 2) atoms with 4 (or 7) valence electrons

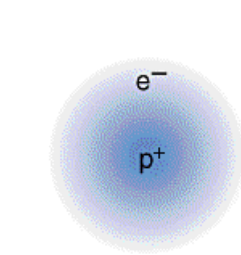
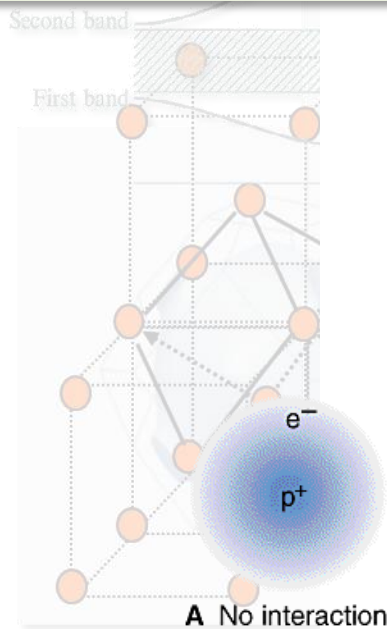
⇒ Each atom contributes by one electron

⇒ Formation of a **double-electron bond**

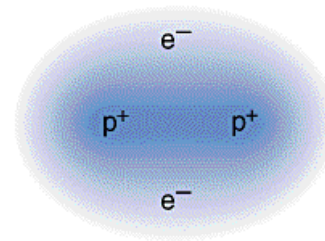


TYPES OF BONDS

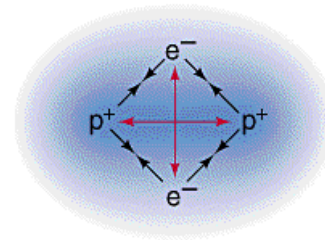
attraction can be visualized as shown in the following figure representing the nuclei and electrons in a **hydrogen molecule**.



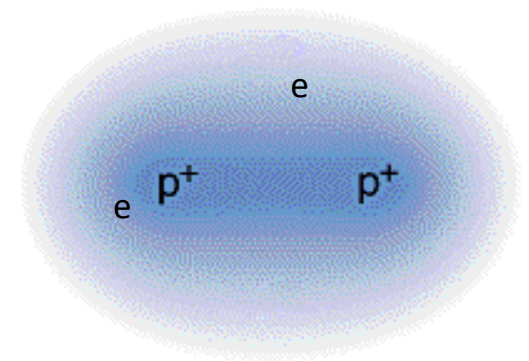
B Attraction begins



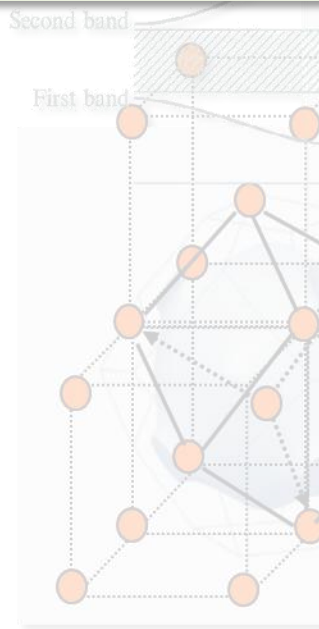
C Covalent bond



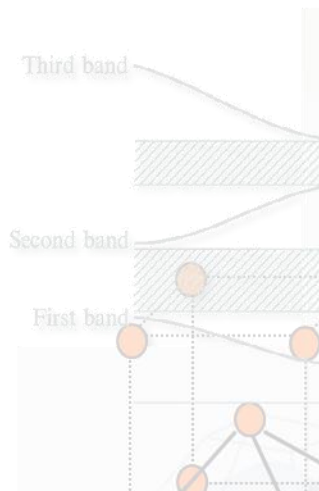
D Combination of forces



TYPES OF BONDS



Property	Explanation
Melting point and boiling point	Very high melting points because many covalent bonds must be broken if the solid is to be melted and hence a large amount of thermal energy is required for this.
Electrical conductivity	Poor conductors because electrons are held either on the atoms or within covalent bonds. They cannot move through the lattice.
Hardness	They are hard because the atoms are strongly bound in the lattice, and are not easily displaced.
Brittleness	Covalent substances are brittle. If sufficient force is applied to a crystal, covalent bonds are broken as the lattice is distorted. Shattering occurs rather than deformation of a shape.



TYPES OF BONDS

3. THE METALLIC BOND

Metallic bonding is an electrostatic force of attraction between positively charged ions and delocalized outer electrons

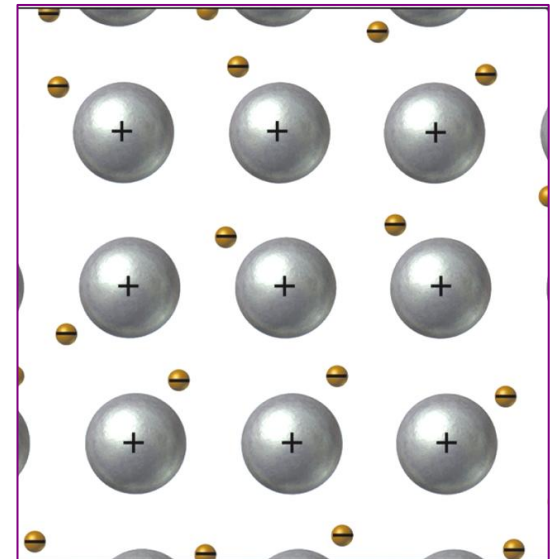
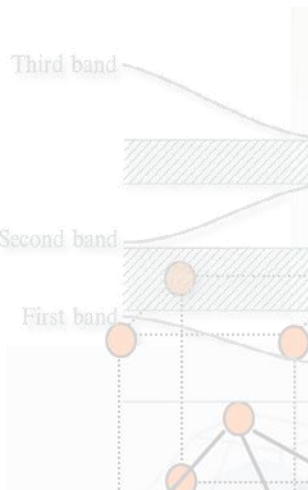
Typical Example: Na whose melting point is 97.8°C

Strength: Somewhat weaker but not negligible

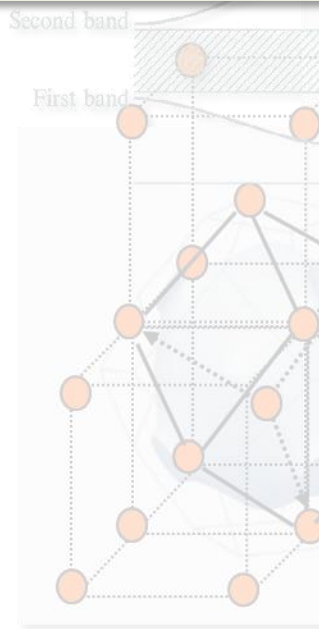
Origin: Existing of atoms with **one or two loosely bound** valence electrons

⇒ As atoms become closer, those electrons become free

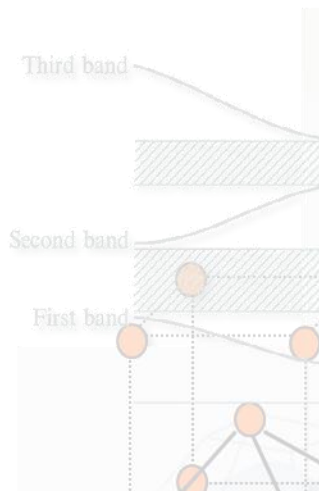
⇒ Formation of cores of (+ve) ions dispersed in a sea of electrons



TYPES OF BONDS



Property	Explanation
Melting point and boiling point	This depends on number of valence electrons in a metal, the more electrons, the stronger the attraction hence higher melting and boiling points.
Electrical conductivity	Metallic compounds are good conductor because valance electrons are relatively bound to the nucleus and therefore they move freely through the metal and they are easily spread out among the atoms .
Hardness	Most metallic compounds are hard; This is because the positively charged cores are held (glued) together by these negatively charged electrons.
Brittleness	metals have high ductility - the “bonds” do not “break” when atoms are rearranged – metals can experience a significant degree of plastic deformation.



TYPES OF BONDS

4. THE HYDROGEN BOND

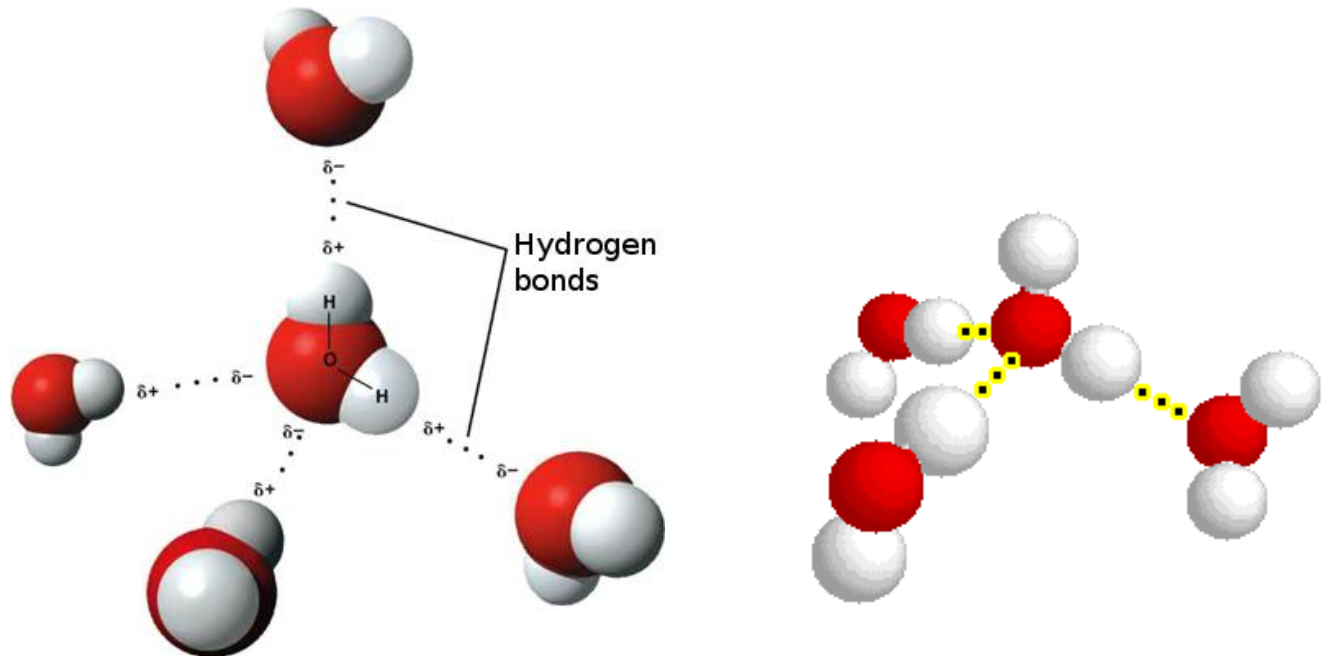
Typical Example: Ice (H_2O) whose melting point is just 0°C

Strength: weak

Origin: Electrons pulled more strongly toward one atom of a molecule

⇒ Formation of an *electric dipole*

⇒ Molecules which are attracted to each



TYPES OF BONDS

5. THE VAN DER WAALS BOND

It is caused by temporary dipoles produced in the electron density of molecules .

Typical Example: Inert- Gas elements (e.g. He) whose melting point is very low -272.2°C

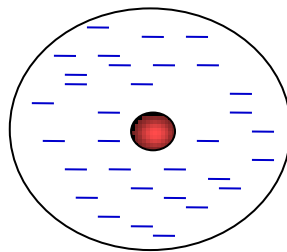
Strength: very weak

Origin: Existing of atoms have a **completely full outer shell**.

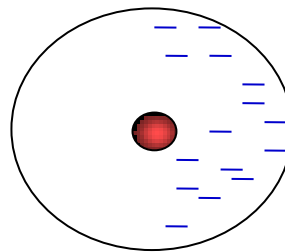
⇒ No exchange or sharing of electrons

⇒ Fluctuations of electrons symmetric distribution around the nucleus

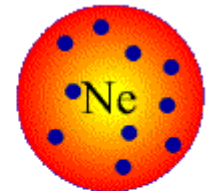
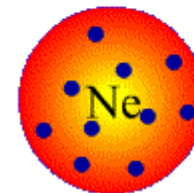
⇒ Formation of a **fluctuating electric dipole** on each atom.



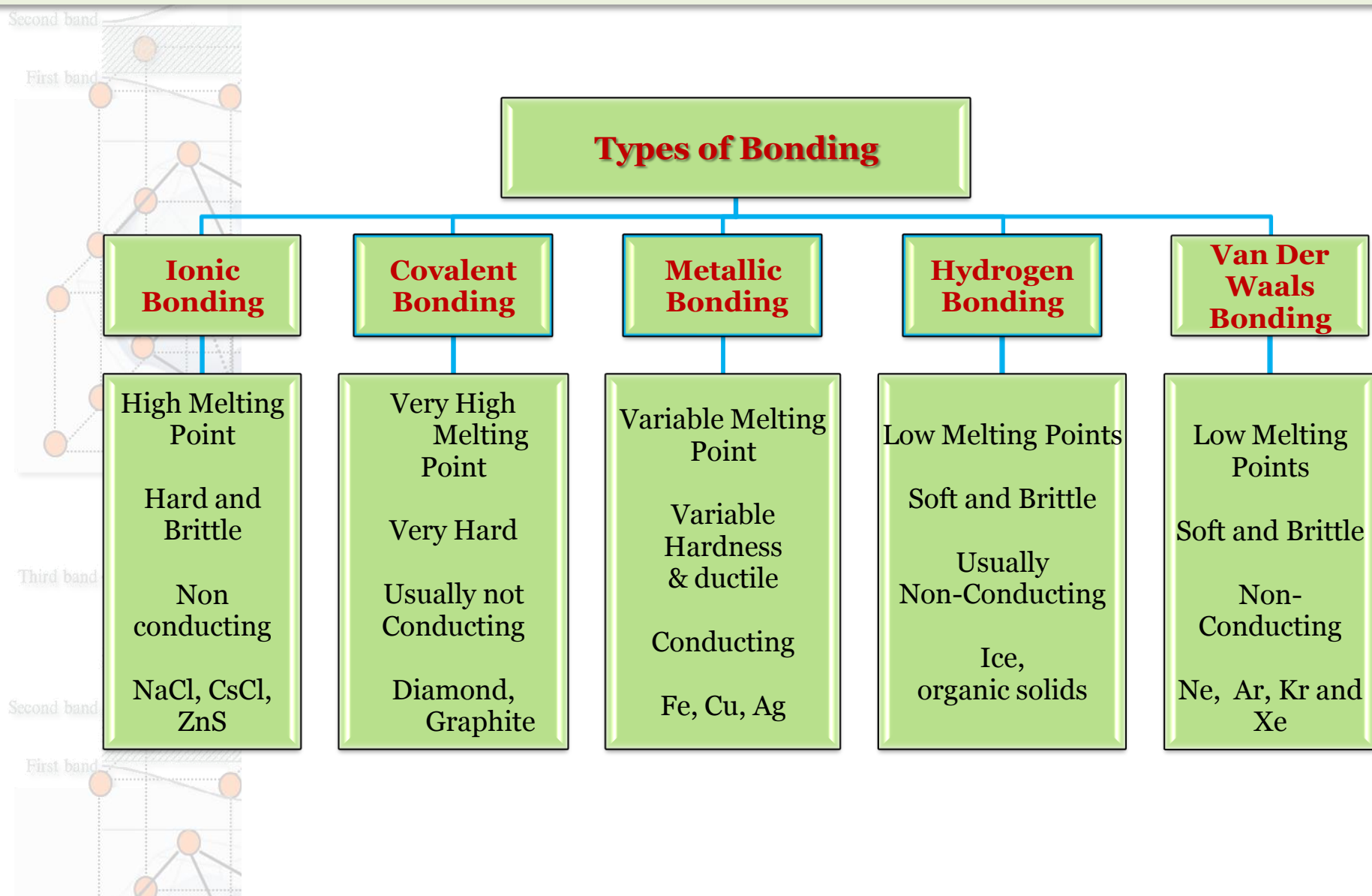
symmetric



asymmetric

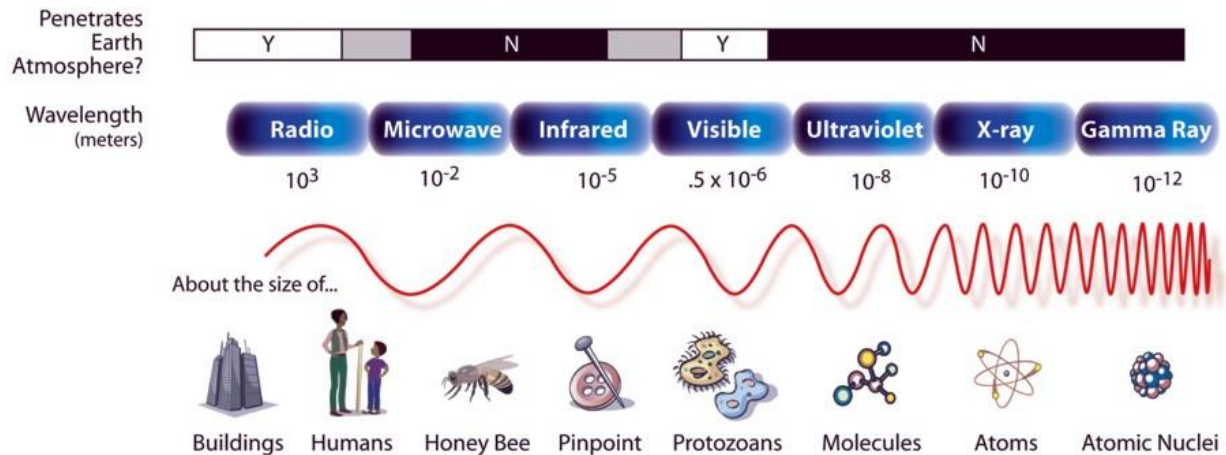


TYPES OF BONDS



X-Ray Diffraction

X-Ray (Nature & Generation)



➤ **X-rays** is **electromagnetic radiation** with wavelengths between roughly **0.1Å** and **100Å**, typically similar to the interatomic distances in a crystal. This is convenient as it allows crystal structures to diffract X-rays.

➤ **X-ray** diffraction is an important tool used to;

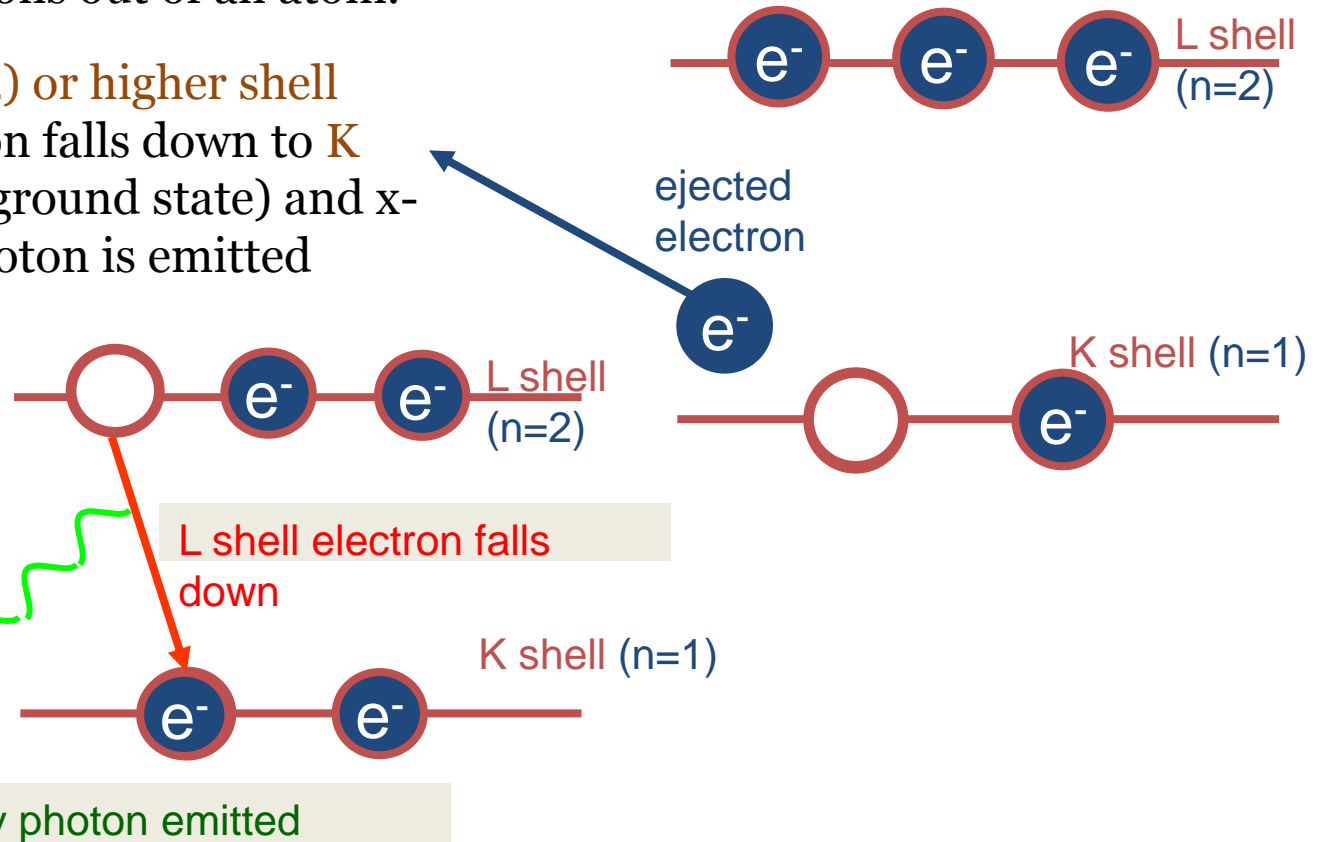
- identify phases by comparison with data from known structures
- determine changes in the cell parameters, orientation, crystallite size and other structural parameters.

X-Ray Diffraction

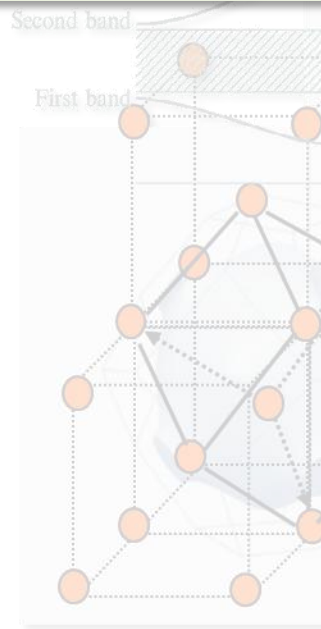
X-Ray (Nature & Generation)

When high kinetic energy electrons hit a metallic target, an incident electron knocks one of the two **K shell** (ground state) electrons out of an atom.

L (n=2) or higher shell electron falls down to **K shell** (ground state) and x-ray photon is emitted



X-Ray Diffraction



Since,

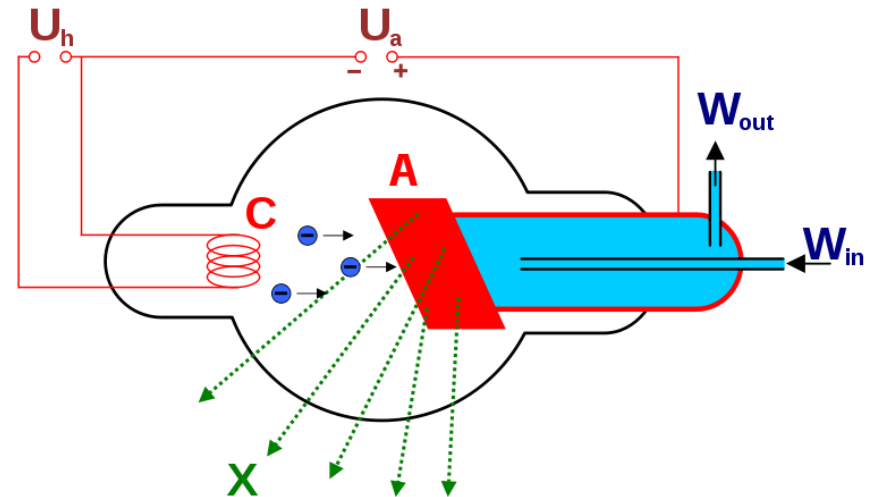
Max. energy a photon can get = K.E of the incident electron

$$h\nu_{\max} = eV$$

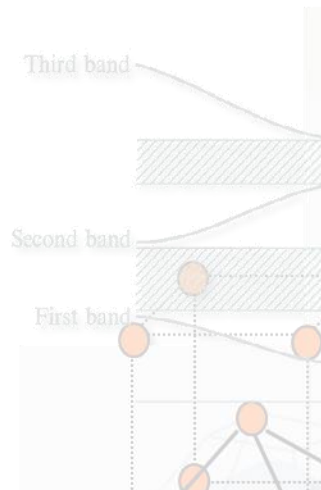
So, The min. wavelength can be obtained is

$$\lambda_{\min} = c/\nu_{\max} = 12.398/E(\text{KeV}) \quad (\text{\AA})$$

The target has to be **metallic** (so that it conducts electrons) and has to have a reasonably **high melting point**, this limits the choice of anode few commonly used materials :



	Chromium	iron	cobalt	copper	molybdenum	Silver
Anode	Cr	Fe	Co	Cu	Mo	Ag
$K\alpha$ (Å)	2.29	1.94	1.79	1.54	0.71	0.56

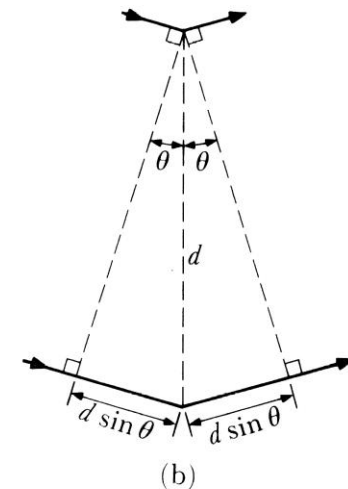
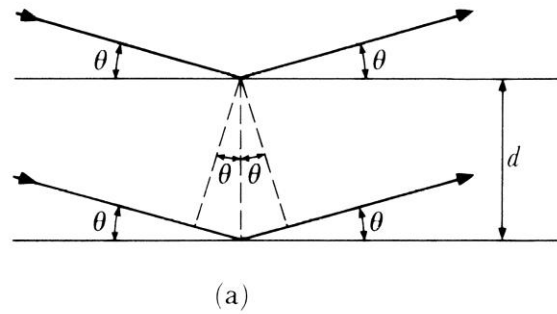
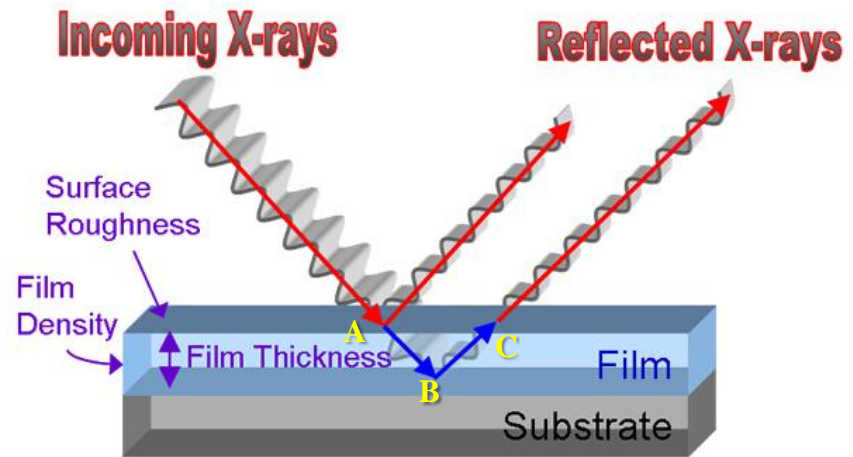


X-Ray Diffraction

Bragg's Law:

Consider an incident beam being reflected by two parallel lattice planes as shown.

Bragg's Law can be derived using this simple geometry. The X-ray hitting the lower plane travels an extra distance $AB + BC$.



Where d is the spacing between planes.

X-Ray Diffraction

To remain in phase with the first X-ray, this distance must be a multiple of the wavelength, thus:

$$\text{Path difference} = n \lambda$$

Or;

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

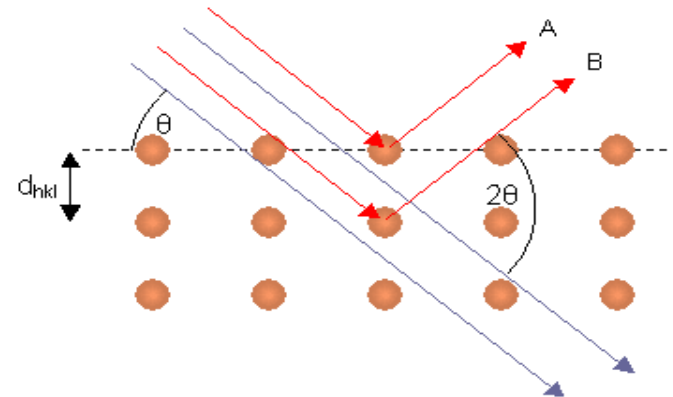
Bragg's Law

Remarks:

1- Bragg's law implies that diffraction **can not** be occurred **unless** the incident wavelength is $\lambda < 2d$

2- The diffraction angle is generally labeled 2θ because of the geometric relationship shown on the left.

3- d and $\sin(\theta)$ are inversely proportional (reciprocal). This means that smaller values of d diffract at higher angles – this is the importance of “**high angle**” data!



X-Ray Diffraction



Interplaner distance (d_{hkl}):

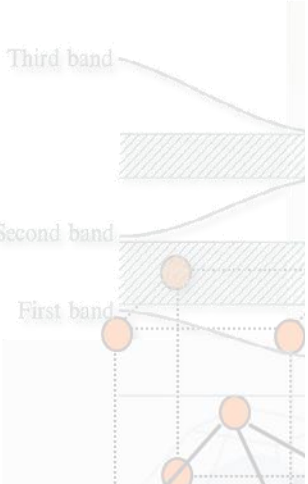
The value of d , the distance between two adjacent planes in the set (hkl) of **a cubic system** is given by,

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where a is the length of the cube side.

In order to consider the general case of hkl planes, **Bragg's Law** can be rewritten as:


$$n\lambda = 2 d_{hkl} \sin \theta_{hkl}$$

X-Ray Diffraction

The Diffraction Pattern:

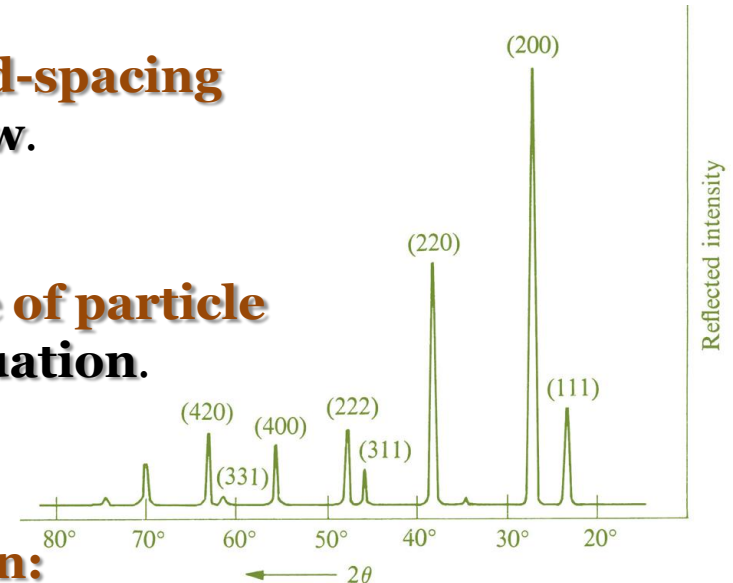
The diffraction pattern consists of a number of sharp peaks with different intensities and various widths. These variations are of fundamental importance in X-ray diffraction and are a signature of the material properties.

position of a peak \longrightarrow **d-spacing**
using **Bragg's Law**.

width of a peak \longrightarrow **size of particle**
using **Scherrer equation**.

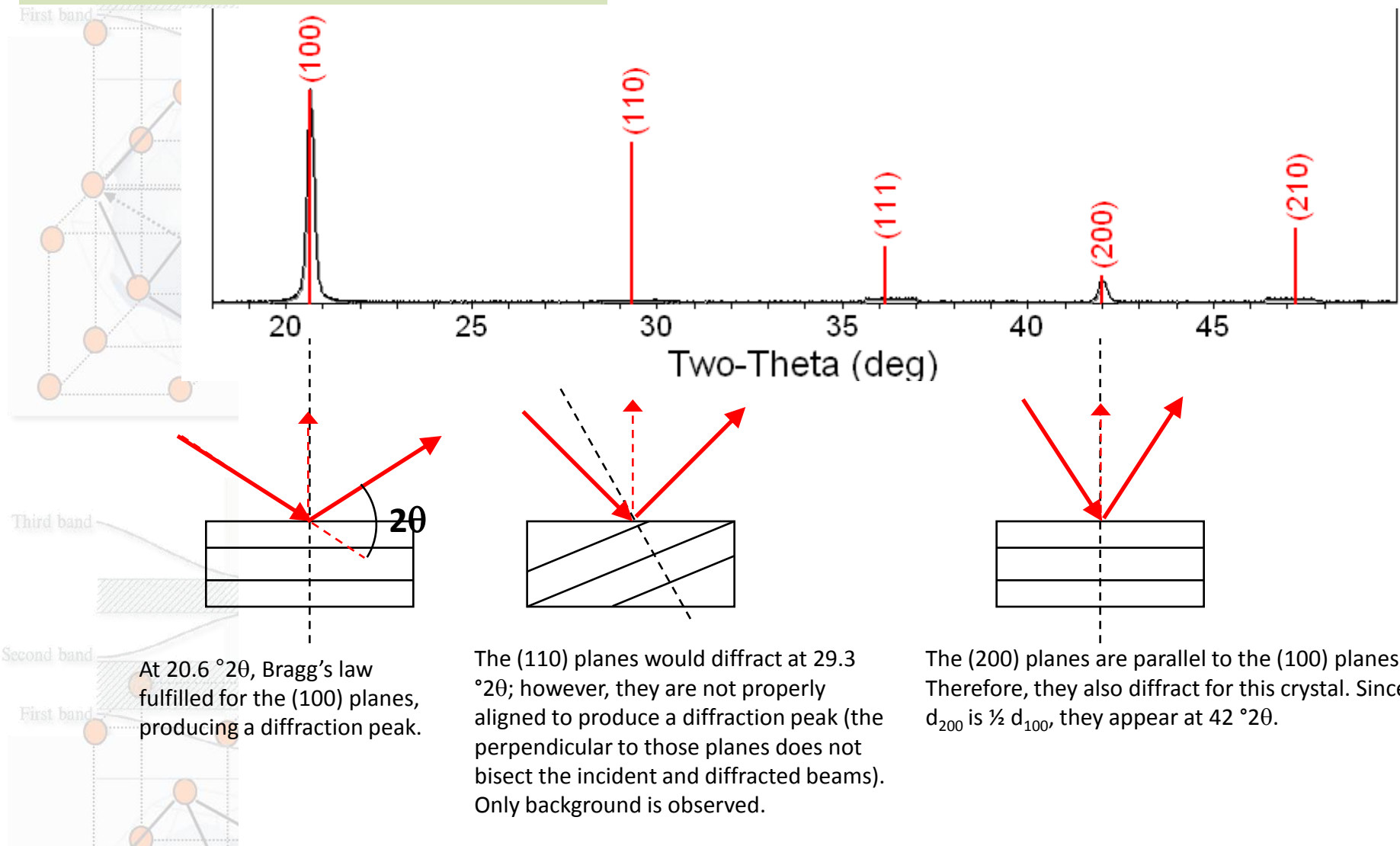
Intensity of a peak depends on:

- No. of electrons in each atom.
- Density of atoms in the plane.
- The incident angle θ .
- The order number n .



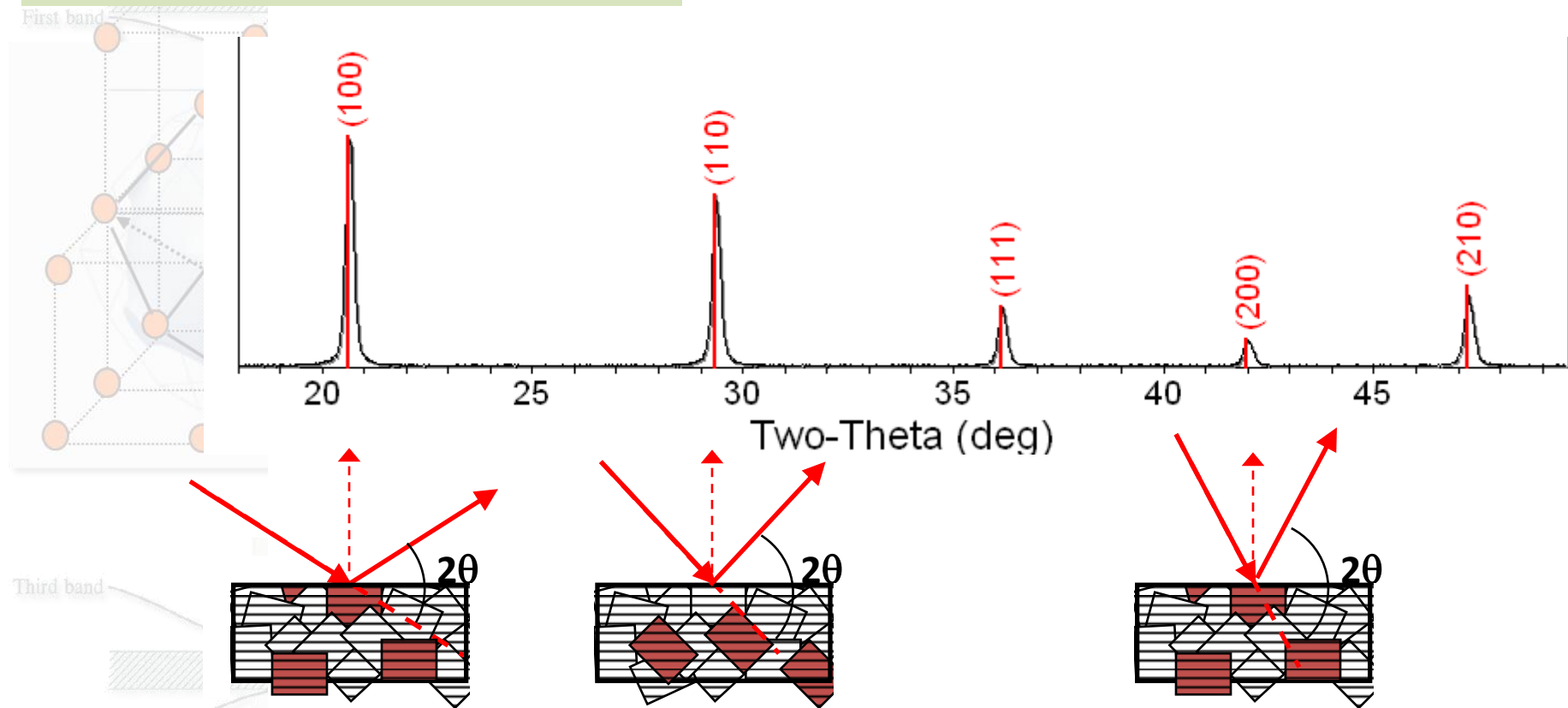
X-Ray Diffraction

The Diffraction Pattern:



X-Ray Diffraction

The Diffraction Pattern:



A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed.