

Structures of solids

LATTICE \equiv An infinite array of points in space, in which each point has identical surroundings to all others.

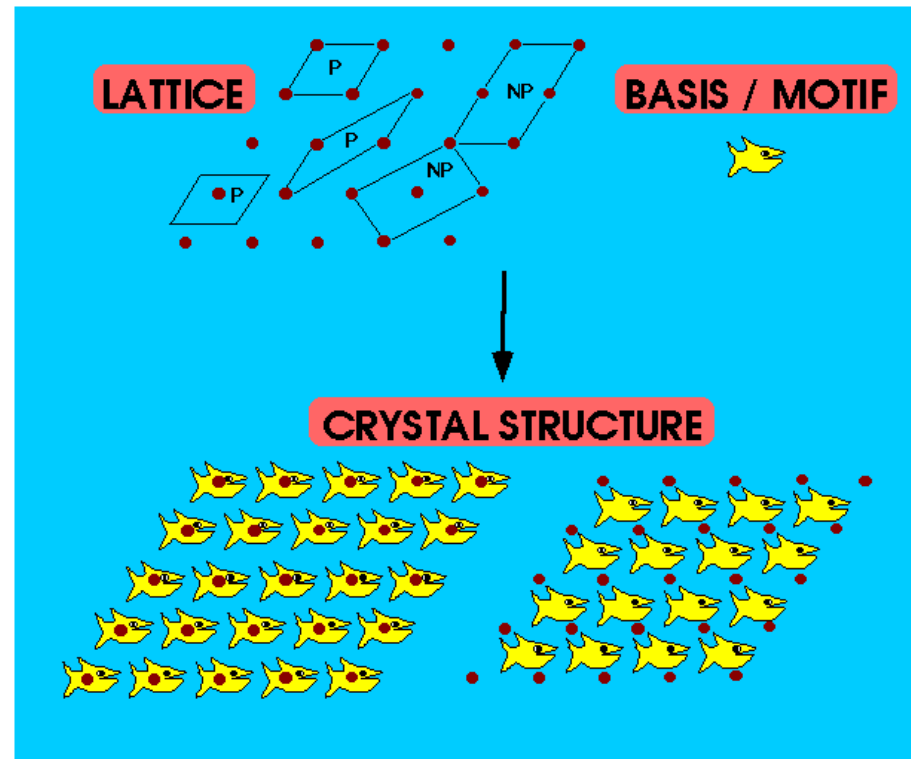
CRYSTAL STRUCTURE \equiv The periodic arrangement of atoms in the crystal. It can be described by associating with each lattice point a group of atoms called the **basis (motif)**.

Lattice + Basis = Crystal Structure

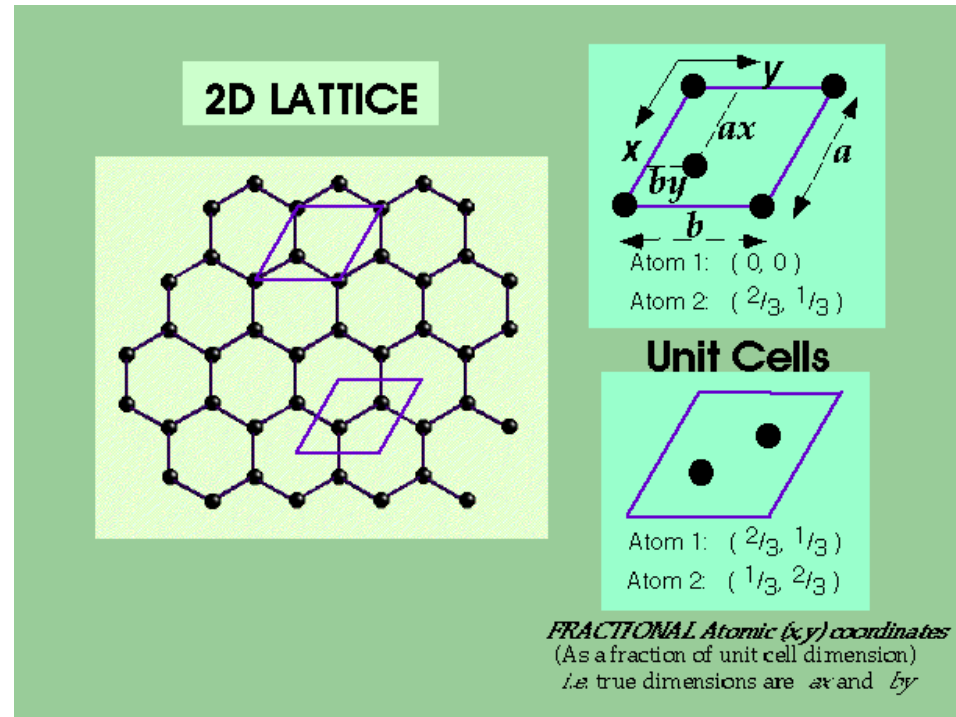
- Don't mix up atoms with lattice points
- Lattice points are infinitesimal points in space
- Atoms are physical objects
- Lattice Points do not necessarily lie at the centre of atoms

UNIT CELL \equiv The smallest component of the crystal, which when stacked together with pure translational repetition reproduces the whole crystal.

Primitive (P) unit cells contain only a *single lattice point*



Hexagonal pattern of a **single layer of GRAPHITE**



Counting Lattice Points/Atoms in 2D Lattices

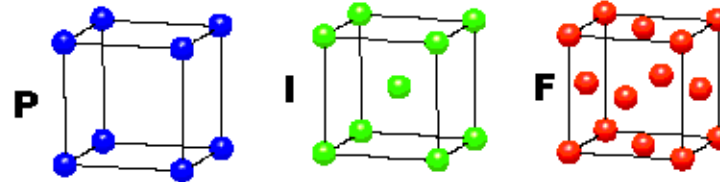
- Unit cell is **Primitive (1 lattice point)** but contains **TWO atoms** in the **basis**
- Atoms at the **corner** of the 2D unit cell contribute only $\frac{1}{4}$ to unit cell count
- Atoms at the **edge** of the 2D unit cell contribute only $\frac{1}{2}$ to unit cell count
- Atoms **within** the 2D unit cell contribute **1** (i.e. uniquely) to that unit cell

The 14 possible BRAVAIS LATTICES

CUBIC

$$a = b = c$$

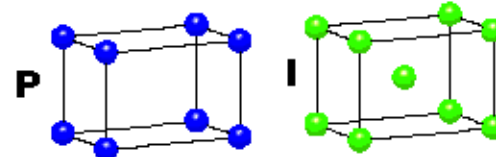
$$\alpha = \beta = \gamma = 90^\circ$$



TETRAGONAL

$$a = b \neq c$$

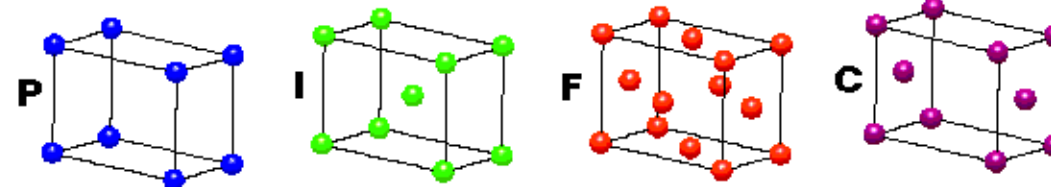
$$\alpha = \beta = \gamma = 90^\circ$$



ORTHORHOMBIC

$$a \neq b \neq c$$

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

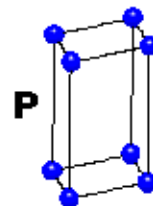


HEXAGONAL

$$a = b \neq c$$

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

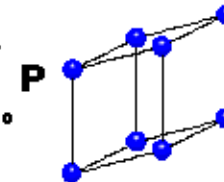
$$\gamma = 120^\circ$$



TRIGONAL

$$a = b = c$$

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

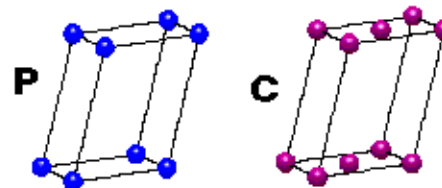


MONOCLINIC

$$a \neq b \neq c$$

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

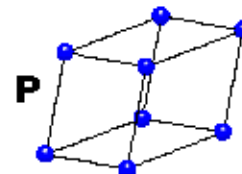
$$\beta \neq 120^\circ$$



TRICLINIC

$$a \neq b \neq c$$

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



4 Types of Unit Cell

P = Primitive

I = Body-Centred

F = Face-Centred

C = Side-Centred

+

7 Crystal Classes

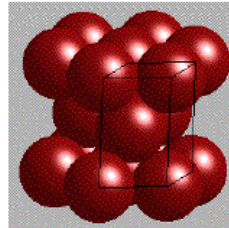
→ 14 Bravais Lattices

Close-Packed Structures

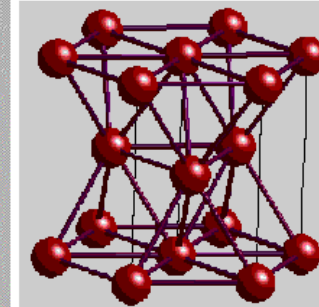
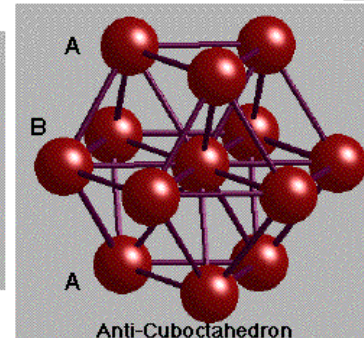
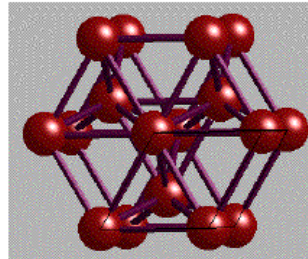
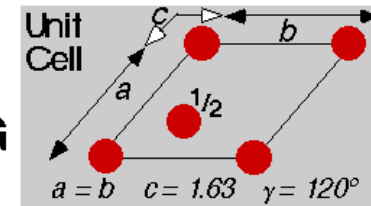
(Coordination Number = 12; 74% of space is occupied)

Hexagonal Close-Packing
(HCP): ABABAB....

2 lattice points in the unit
cell: $(0, 0, 0)$ $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$

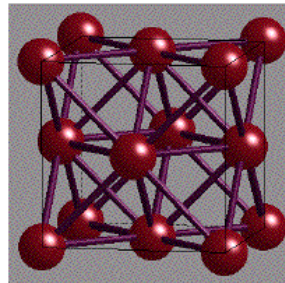


HEXAGONAL
CLOSE-PACKING



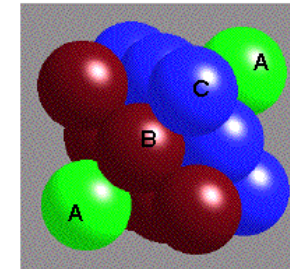
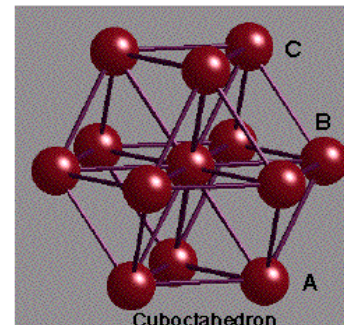
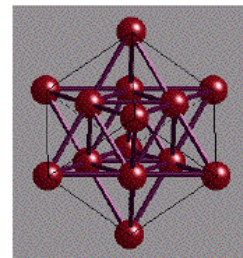
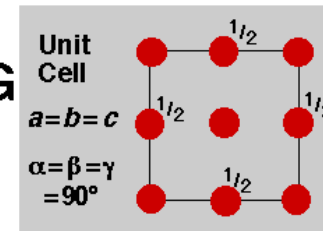
Cubic Close-Packing
(CCP): ABCABC....

4 lattice points in the unit
cell: $(0, 0, 0)$ $(0, \frac{1}{2}, \frac{1}{2})$
 $(\frac{1}{2}, 0, \frac{1}{2})$ $(\frac{1}{2}, \frac{1}{2}, 0)$

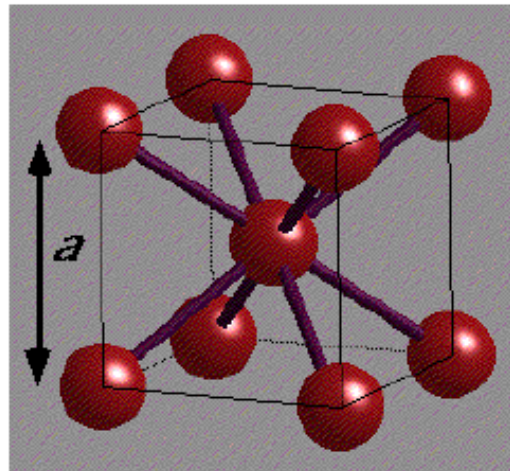


CUBIC
CLOSE-PACKING

Face-Centred Cubic
(FCC) Unit Cell

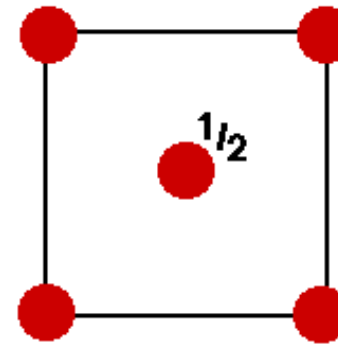


A non-closed-packed structure adopted by some metals

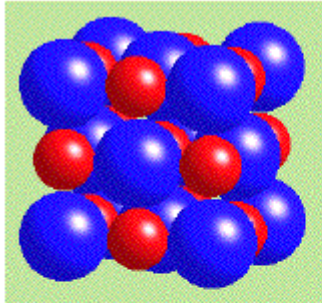


Body-Centred Cubic

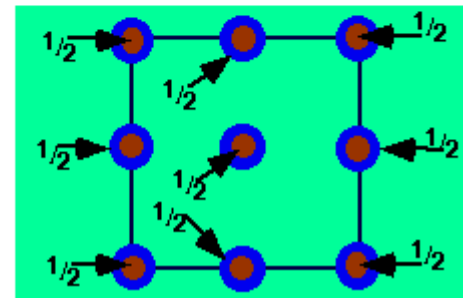
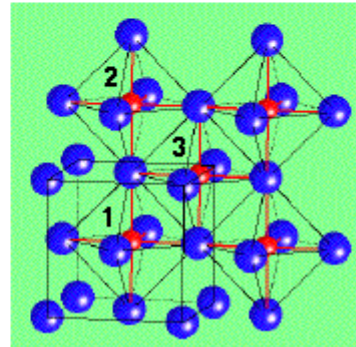
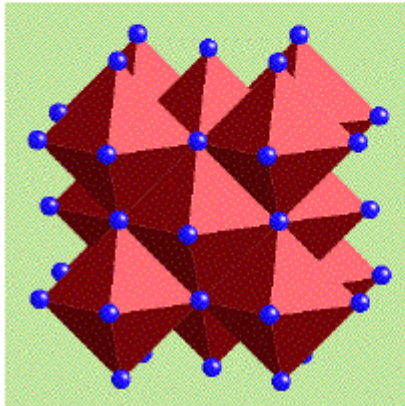
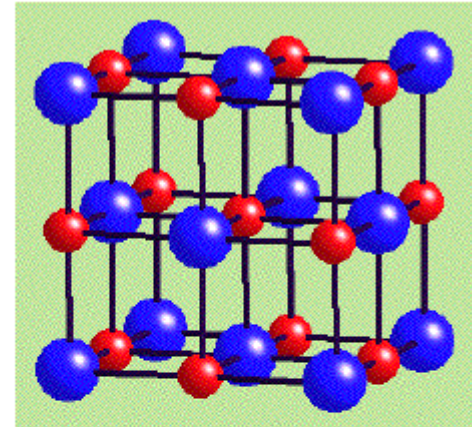
BCC



- Two lattice points in the unit cell
- 68% of space is occupied
- 8 Nearest Neighbours at $0.87a$
- 6 Next-Nearest Neighbours at $1a$

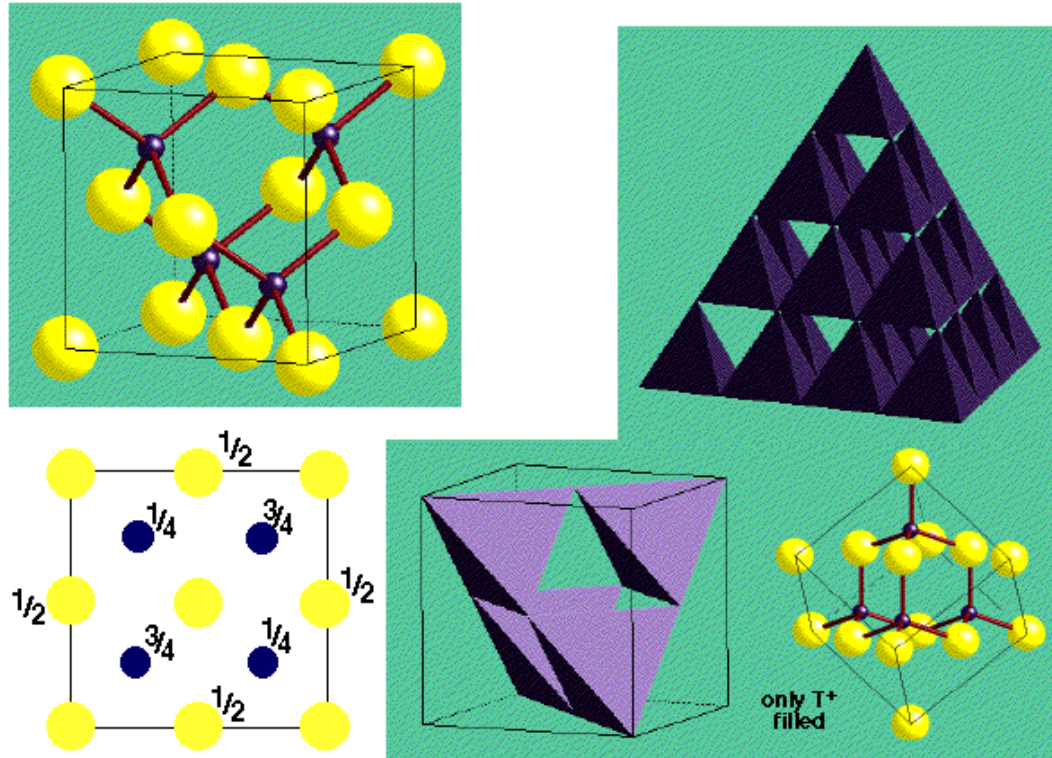


NaCl
Rock Salt
(*Halite*)



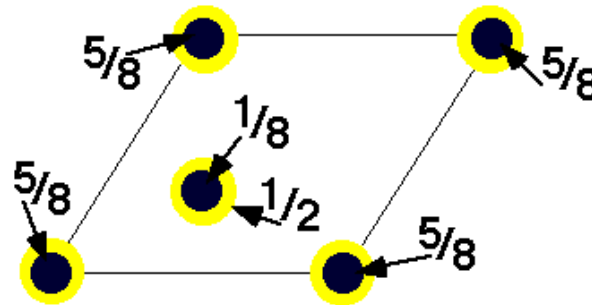
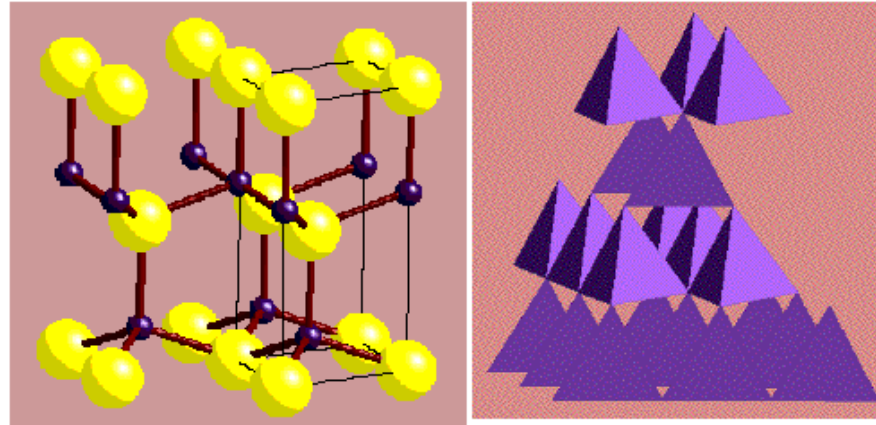
- CCP Cl^- with Na^+ in all Octahedral holes
- *Lattice*: fcc
- *Basis*: Cl at (0,0,0); Na at ($1/2$,0,0)
- 4 NaCl in unit cell
- *Coordination*: 6:6 (octahedral)
- Cation and anion sites are topologically identical

ZnS Zinc Blende (Sphalerite)



- CCP S²⁻ with Zn²⁺ in half Tetrahedral holes (only T⁺ {or T⁻} filled)
- *Lattice*: fcc
- 4 ZnS in unit cell
- *Basis*: S at (0,0,0); Zn at ($1/4, 1/4, 1/4$)
- *Coordination*: 4:4 (tetrahedral)
- Cation and anion sites are topologically identical

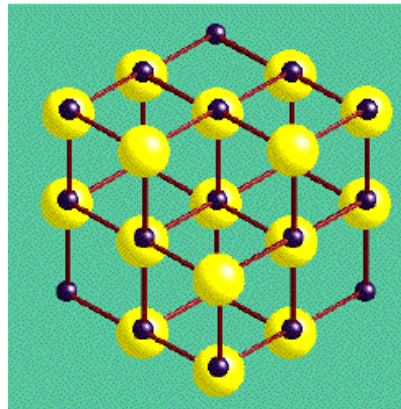
ZnS Wurtzite



- HCP S^{2-} with Zn^{2+} in half Tetrahedral holes (only T^+ {or T^- } filled)
- *Lattice*: Hexagonal - P
- $a = b$, $c = \frac{8}{3}a$
- *Basis*: 2S at $(0,0,0)$ & $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$; 2Zn at $(\frac{2}{3}, \frac{1}{3}, \frac{1}{8})$ & $(0,0, \frac{5}{8})$
- 2 ZnS in unit cell
- *Coordination*: 4:4 (tetrahedral)

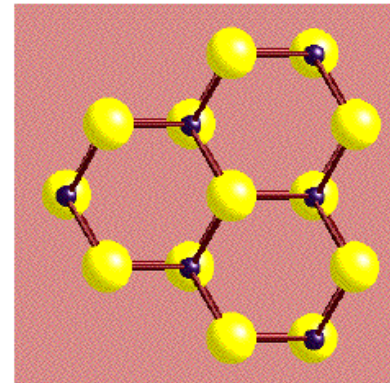
Comparison of Wurtzite and Zinc Blende

PLAN VIEWS



Zinc Blende

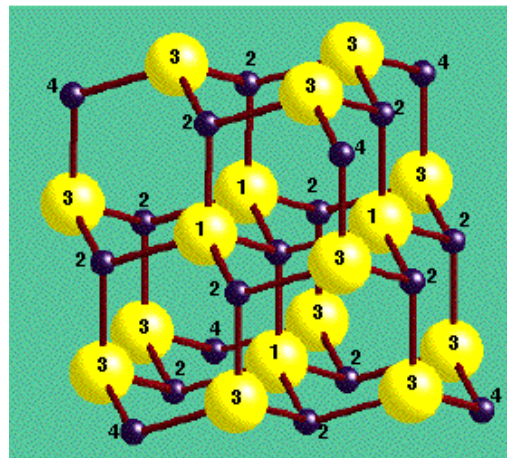
CCP ABC repeat



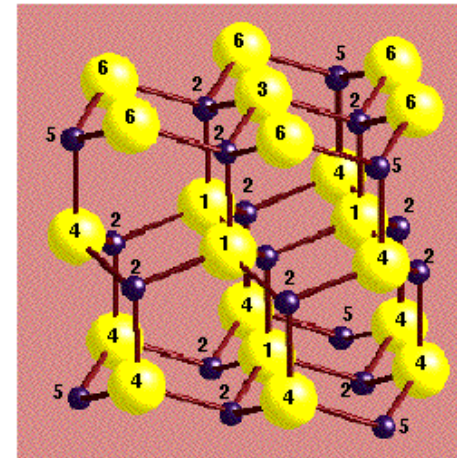
Wurtzite

HCP AB repeat

COORDINATION ENVIRONMENTS



Zinc Blende



Wurtzite

4 Nearest Neighbours (*Tetrahedral*)

12 Next-Nearest Neighbours

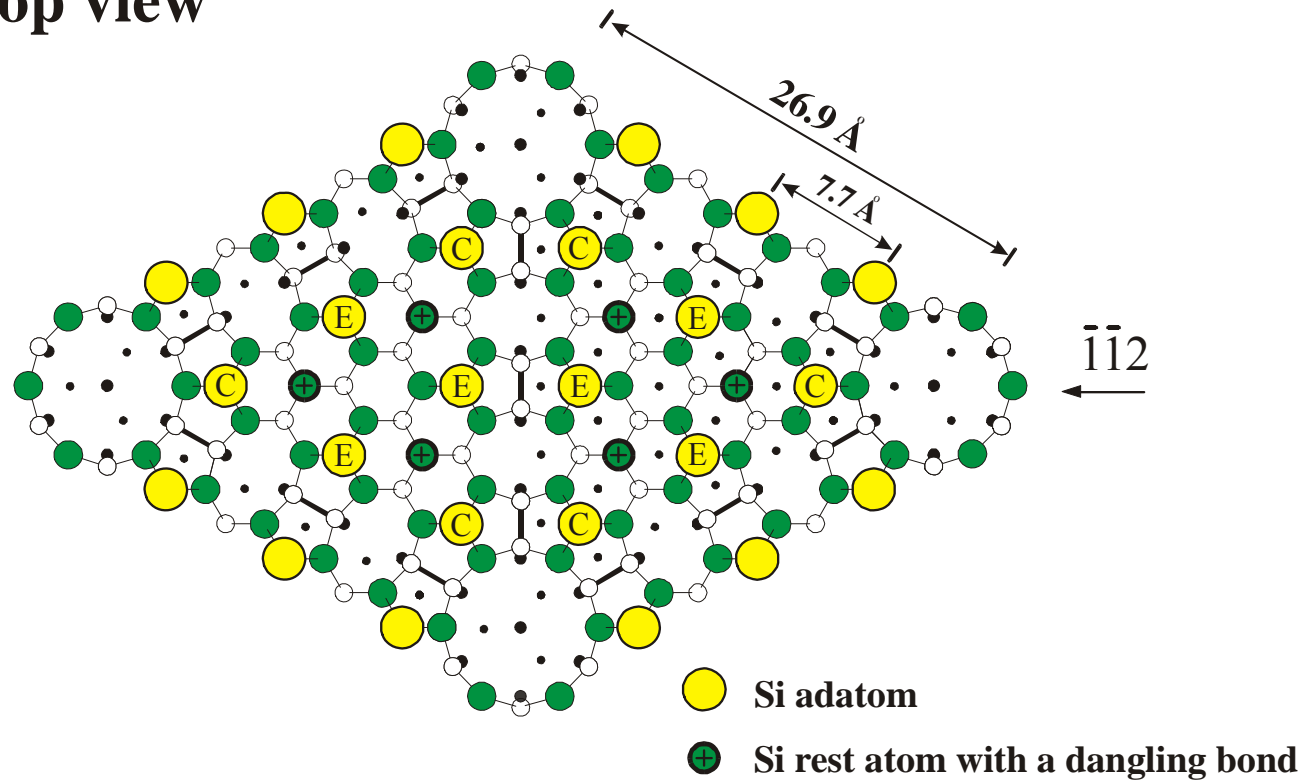
Cuboctahedral

Anti-Cuboctahedral

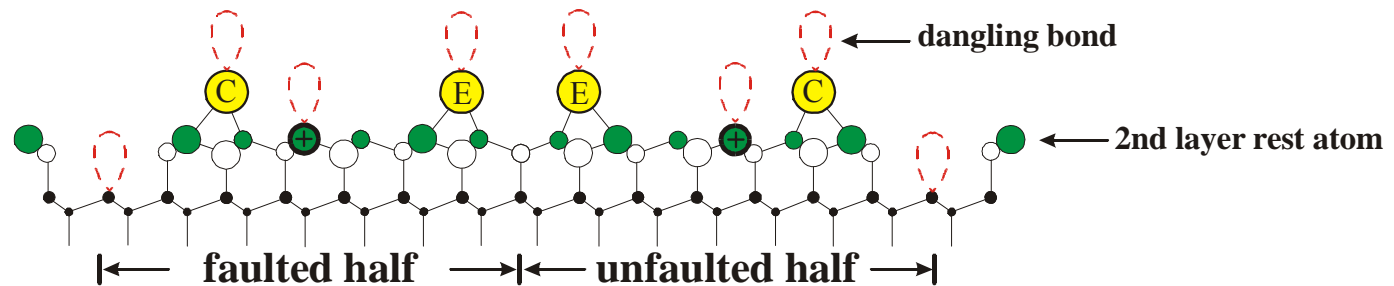
Very different Next, Next-Nearest Neighbour Coordinations & beyond

Atomic Model of Si(111)-(7×7)

Top view

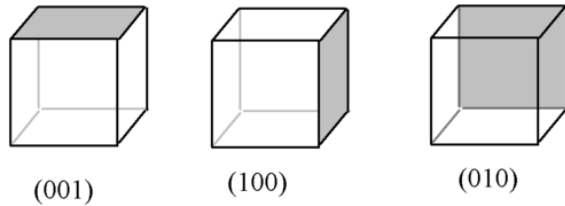


Side view

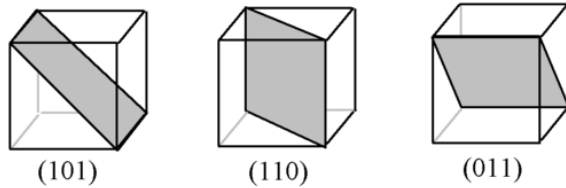


Miller indices

Miller indices are a notation system in crystallography for planes and directions in crystal (Bravais) lattices.

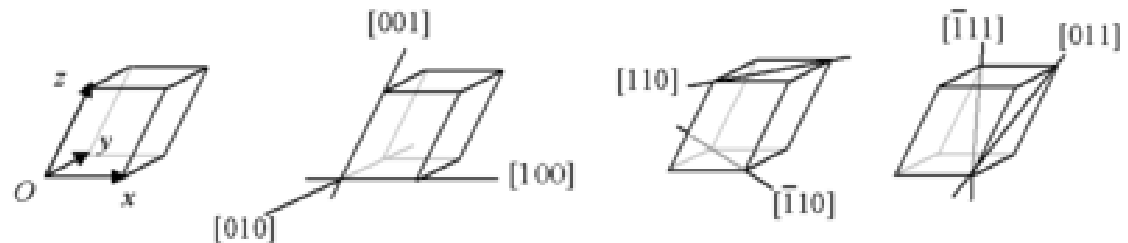
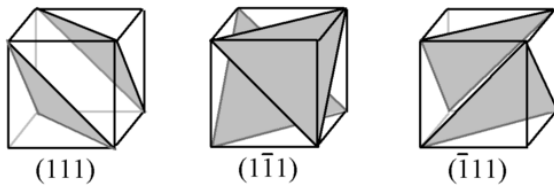


Step 1 : *Identify the intercepts on the x- , y- and z- axes.*



Step 2 : *Take the reciprocals of the intercepts.*

Step 3 : *Reduce to three integers having the same ratio.*

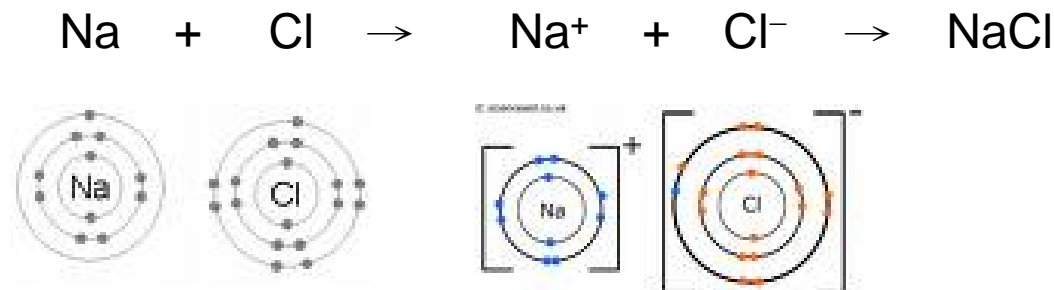


Bonds of solids

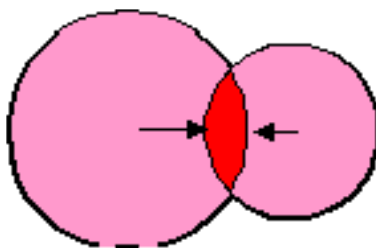
Ionic Bonds

An **ionic bond** is a type of chemical bond that involves a metal and a nonmetal ion through electrostatic attraction. In short, it is a bond formed by the attraction between two oppositely charged ions. The metal donates one or more electrons, forming a positively charged ion or cation with a stable electron configuration. These electrons then enter the non metal, causing it to form a negatively charged ion or anion which also has a stable electron configuration. The electrostatic attraction between the oppositely charged ions causes them to come together and form a bond.

For example:

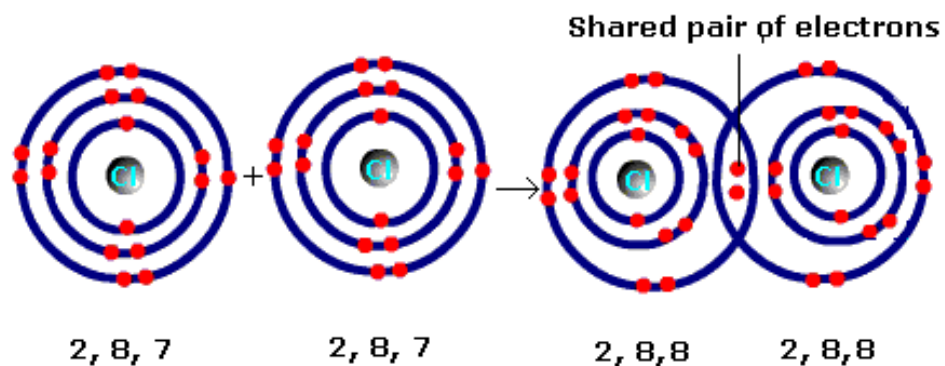


Covalent Bonds



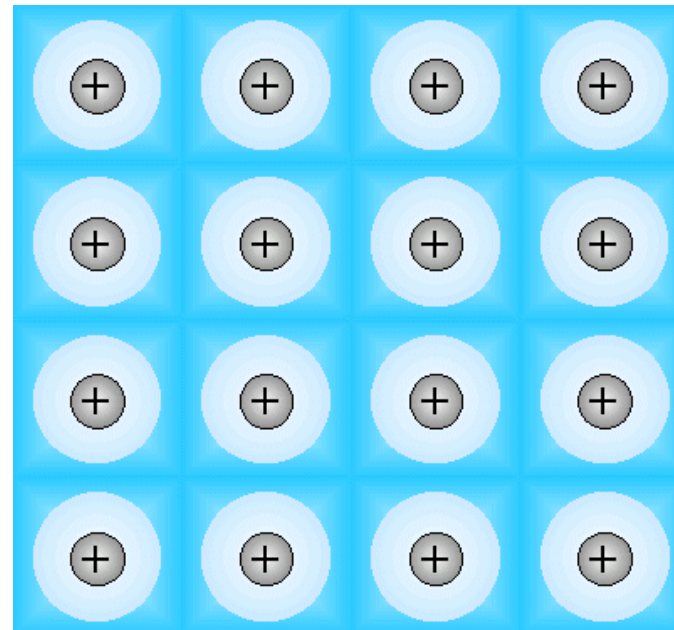
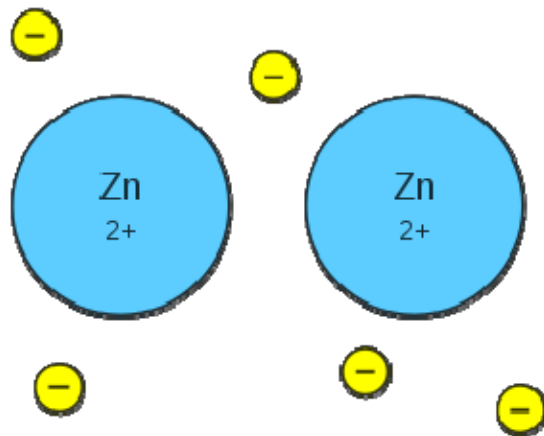
A covalent bond is formed when the electron clouds of two atoms overlap. Where the clouds overlap they are thicker, and their electric charge is stronger.

Both nuclei feel a force of attraction towards this thick electron cloud, and so the two atoms are held together.



Metallic Bonds

Metallic bonding is the electromagnetic interaction between delocalized electrons, called conduction electrons and gathered in an "electron sea", and the metallic nuclei within metals. Understood as the sharing of "free" electrons among a lattice of positively-charged ions (cations; however, this simplistic view holds true for very few metals. In a more quantum-mechanical view, the conduction electrons divide their density equally over all atoms that function as neutral (non-charged) entities. Metallic bonding accounts for many physical properties of metals, such as strength, malleability, thermal and electrical conductivity, opacity, and luster.



Molecular Bonds

Consist of atoms or molecules held together by intermolecular forces (dipole-dipole, dispersion and hydrogen bonds). These forces are weaker than chemical (covalent) bonds. Therefore molecular solids are soft, and have a generally low melting temperature. Most substances that are gasses or liquids at room temperature form molecular solids at low temperature (e.g. H₂O, CO₂)

Comparison of bond energies for different types of bonds

<u>Type of bond</u>	Energy (kJ/mol)
Dispersion (Carbon - carbon van der Waals)	~1.0
Hydrogen bond (strongest dipole-dipole)	~12-16
Ionic	~50-100
Covalent	~100-1000

$$E_{\text{coh}} = E_{\text{solid}} - \sum_A E_A^{\text{isolated}}$$

Madelung constant for ionic crystal

The **Madelung constant** is used in determining the electrostatic potential of a single ion in a crystal by approximating the ions by point charges.

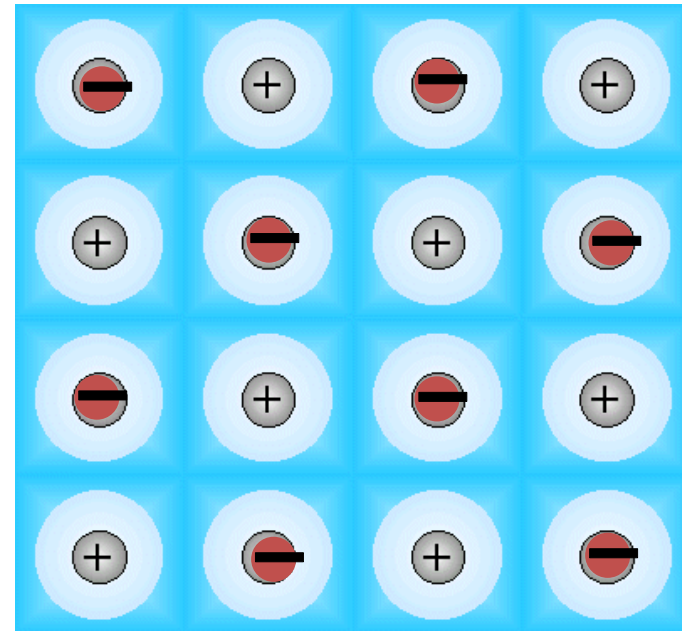
$$V_i = \frac{e}{4\pi\epsilon_0} \sum_{j \neq i} \frac{z_j}{r_{ij}}$$
$$V_i = \frac{e}{4\pi\epsilon_0 r_0} \sum_j \frac{z_j r_0}{r_{ij}} = \frac{e}{4\pi\epsilon_0 r_0} M_i$$

$r_0 \equiv$ the nearest neighbor distance

$M_i \equiv$ the Madelung constant

Examples of Madelung Constants

Structure	M
NaCl	1.7476
CsCl	1.7627
Cubic ZnS	1.6381



Homework#6 (Nov. 30, 2009):

Consider the periodic two-dimensional solid with part of it as shown in the figure below. The white atoms form a closed pack hexagonal structure, and each black atom sits on top of three white ones.

(a) Indicate the unit cell and lattice vectors.

(b) Let the radius of the white atoms be a_0 . What is the size (area) of a unit cell in terms of a_0 ?

(c) How many white atoms are there per unit cell?

