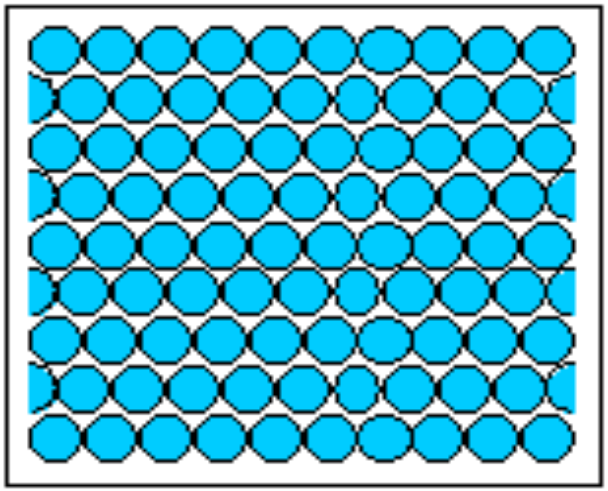
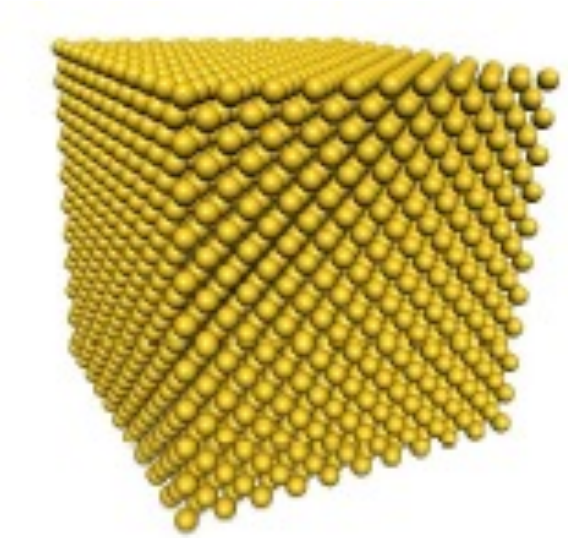
# Crystal Symmetries and Bindings

- **Elementary Crystallography**
  - Solid materials (crystalline, polycrystalline, amorphous)
  - Crystallography
  - Crystal Lattice
  - Crystal Structure
  - Types of Lattices
  - Unit Cell
- **Typical Crystal Structures**
  - 14 Bravais Lattices and the Seven Crystal Systems
- **Crystal Bindings**

# Single Crystals

- **Single crystals** have a periodic atomic structure across its whole volume.
- At long range length scales, each atom is related to every other equivalent atom in the structure by translational or rotational symmetry

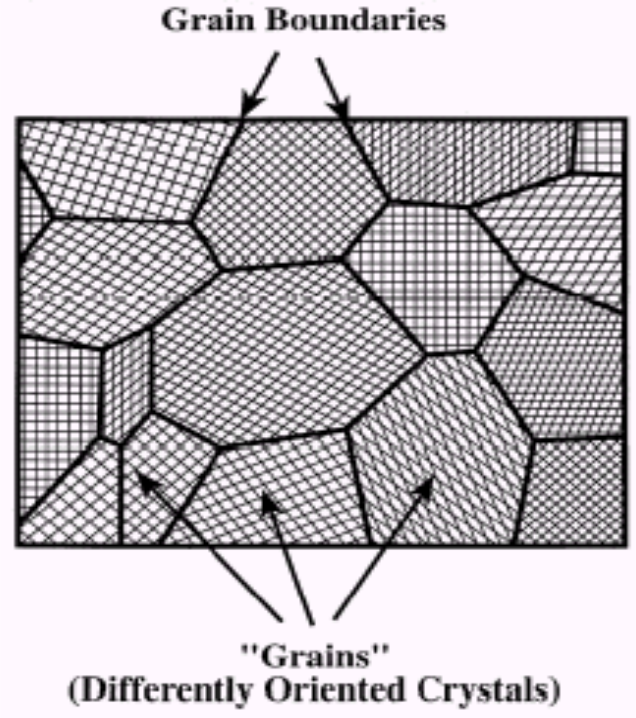




**Single Crystal**

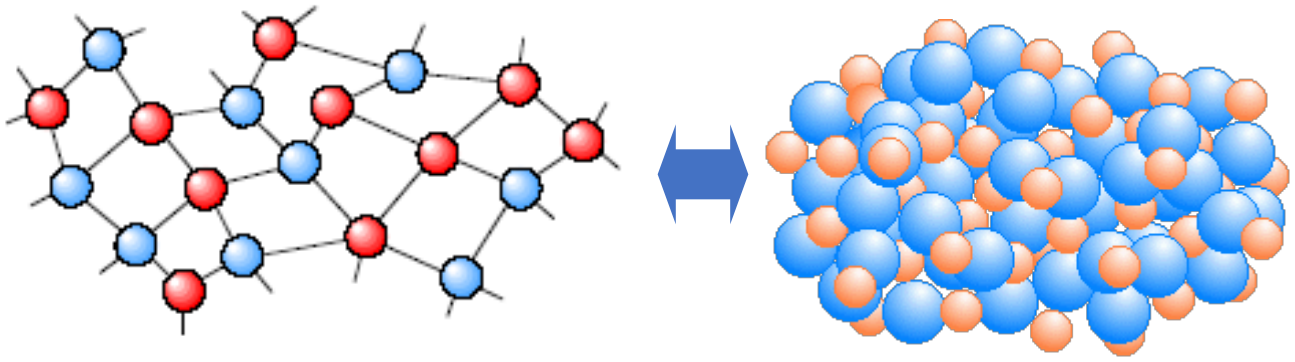
# Polycrystalline Solids

- **Polycrystalline materials** are made up of an aggregate of **many small single crystals** (also called crystallites or grains).
- **Polycrystalline materials** have a high degree of order over many atomic or molecular dimensions.
- **Grains (domains)** are separated by **grain boundaries.** The atomic order can vary from one domain to the next**.**
- The grains are usually **100 nm - 100 microns in diameter**.
- Crystal grains less than 10 nm in diameter are **nanocrystalline**



# Amorphous Solids

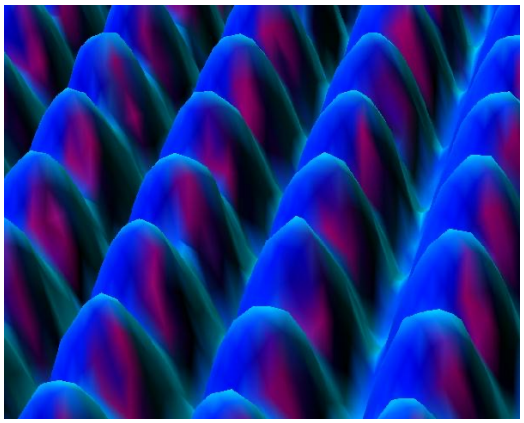
- **Amorphous (Non-crystalline) Solids** are made up of randomly orientated atoms , ions, or molecules that do not form defined patterns or lattice structures.
- Amorphous materials have order only within a few atomic or molecular dimensions.
- Amorphous materials do not have any long-range order, but they have varying degrees of short-range order.
- Examples to amorphous materials include amorphous silicon, plastics, and glasses.
- Amorphous silicons having higher energy bandgaps can be used in solar cells and thin film transistors.



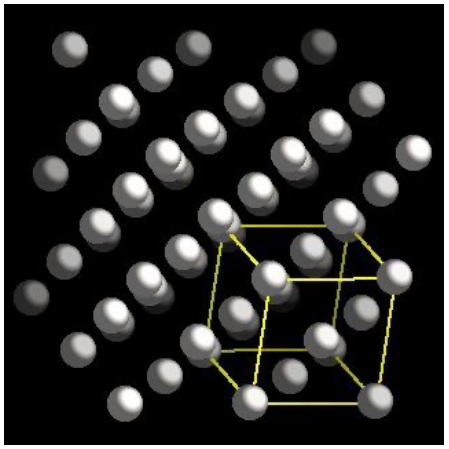
# What is a Crystal Lattice

In crystallography, only the geometrical properties of the crystal are of interest, therefore one replaces each atom by a geometrical point located at the equilibrium position of that atom.

Platinum



Platinum surface
**(scanning tunneling microscope)**



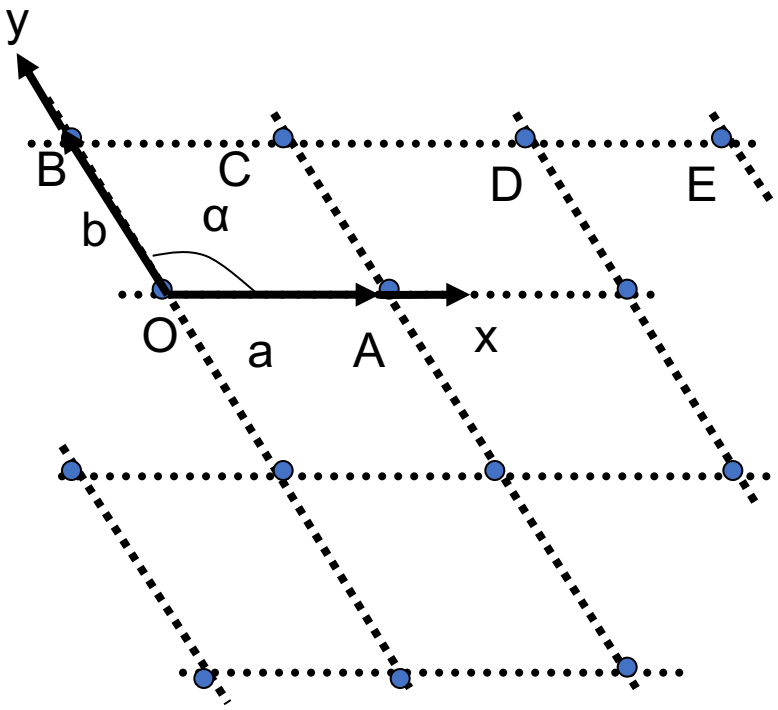
Crystal lattice and structure of Platinum

# Crystal Lattice

**The set of r' defined below for all $u_1$, $u_2$, and $u_3$ defines a lattice.**

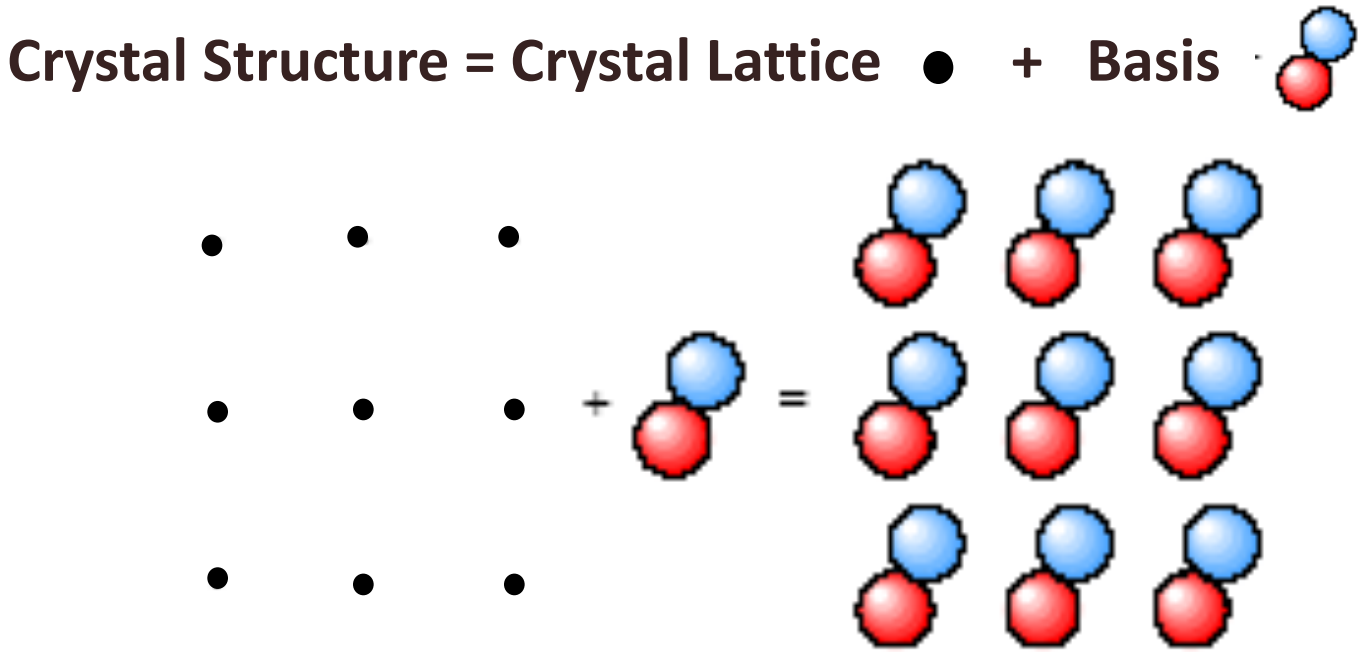
$$\mathbf{r}' = \mathbf{r} + u_1\,\mathbf{a} + u_2\,\mathbf{b} + u_3\,\mathbf{c}$$

- An infinite array of points in space.
- Each point has identical surroundings to all others.
- Arrays are arranged in a periodic manner.



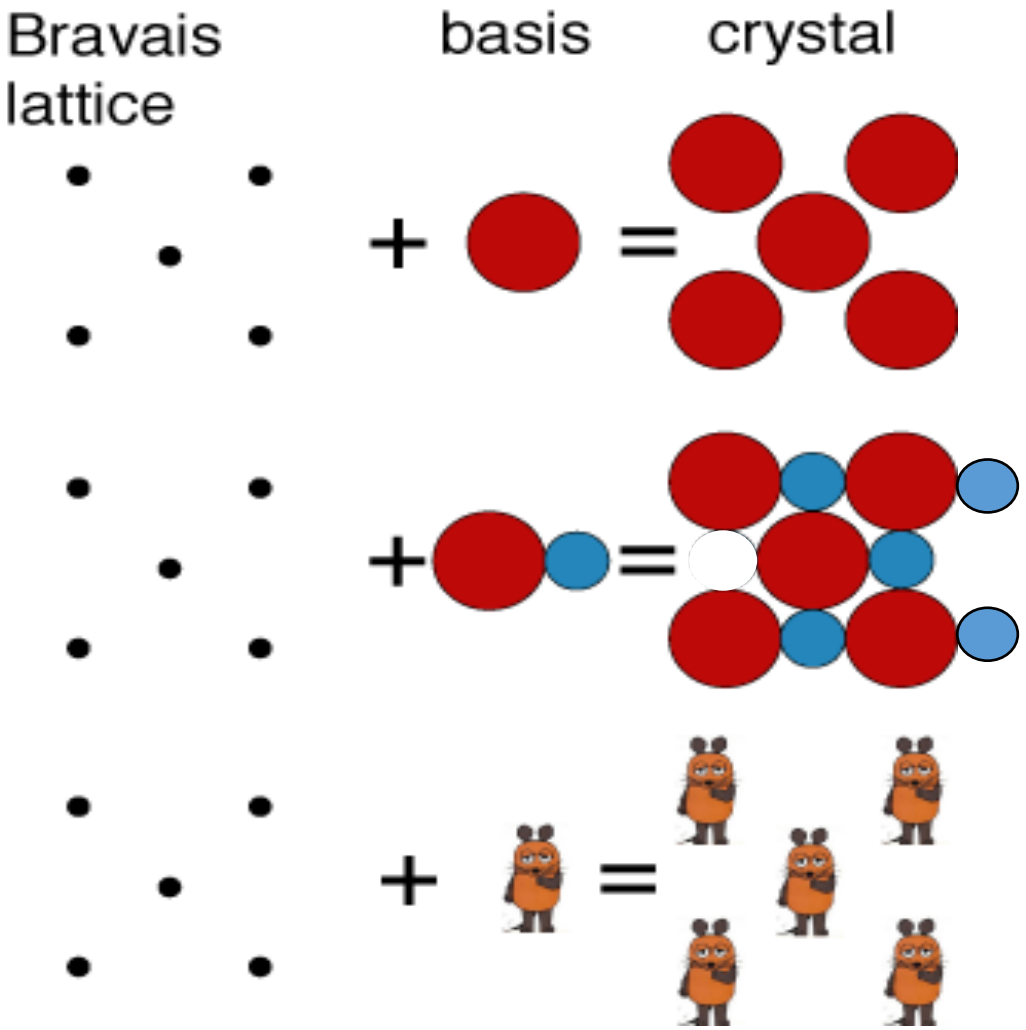
# Crystal Structure

Crystal structures can be obtained by attaching atoms, groups of atoms or molecules which are called basis (motif) to the lattice sides of the lattice point.



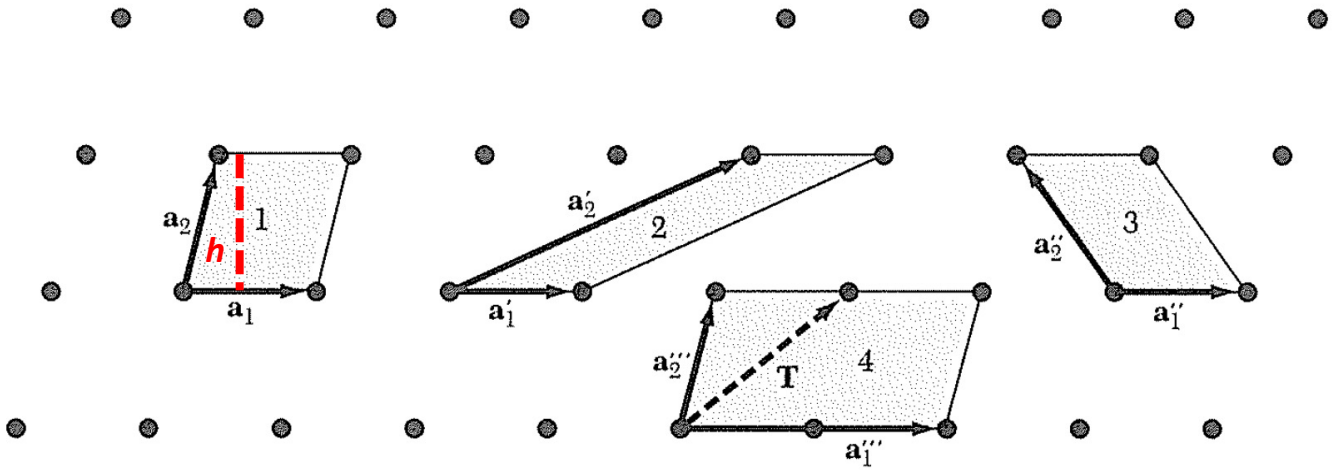

Basis composed of atoms at the positions $\mathbf{r}_j = x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3$, with $j$ = 1,2,...,$s$. Here $x$, $y$, $z$ may be selected to have values between 0 and 1.

# A two-dimensional Bravais lattice with different choices for the basis



# Primitive Cell in 2D

The smallest component of the crystal (group of atoms, ions or molecules), which when stacked together with pure translational repetition reproduces the whole crystal.

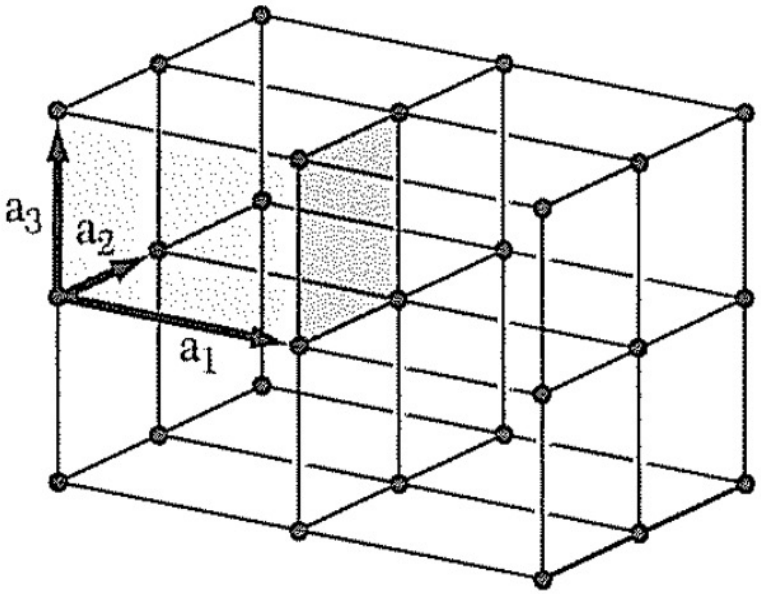


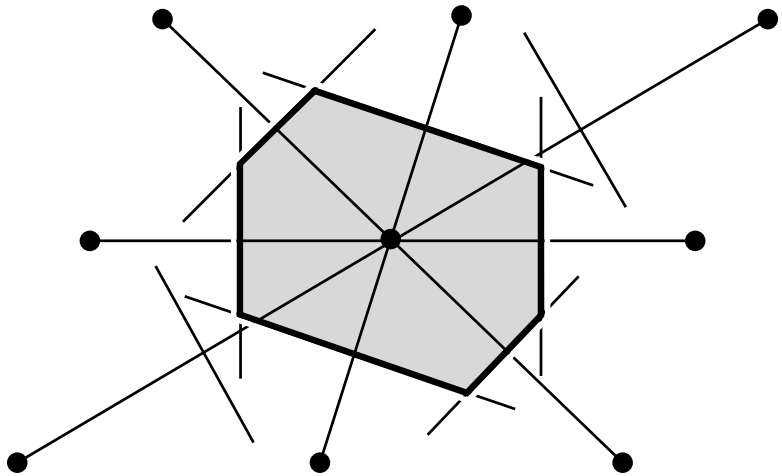

The parallelograms 1, 2, and 3 are primitive cells equal in area but the parallelogram 4 is not.

# Primitive Cell in 3D

A primitive cell contains only one lattice point and the volume of the parallelepiped is

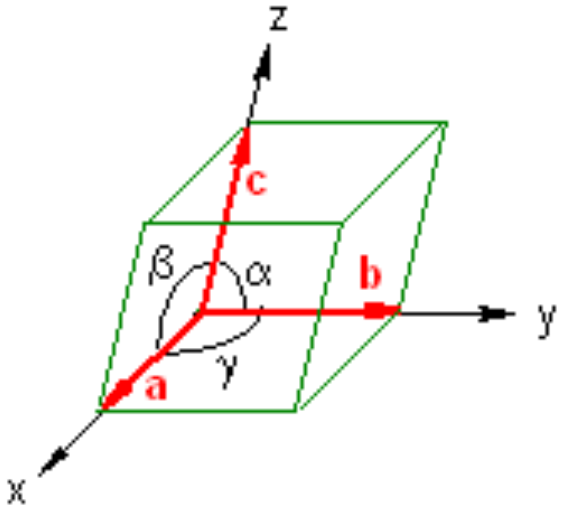
$$V_c = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|$$



Wigner-Seitz primitive cell

# Primitive Cell

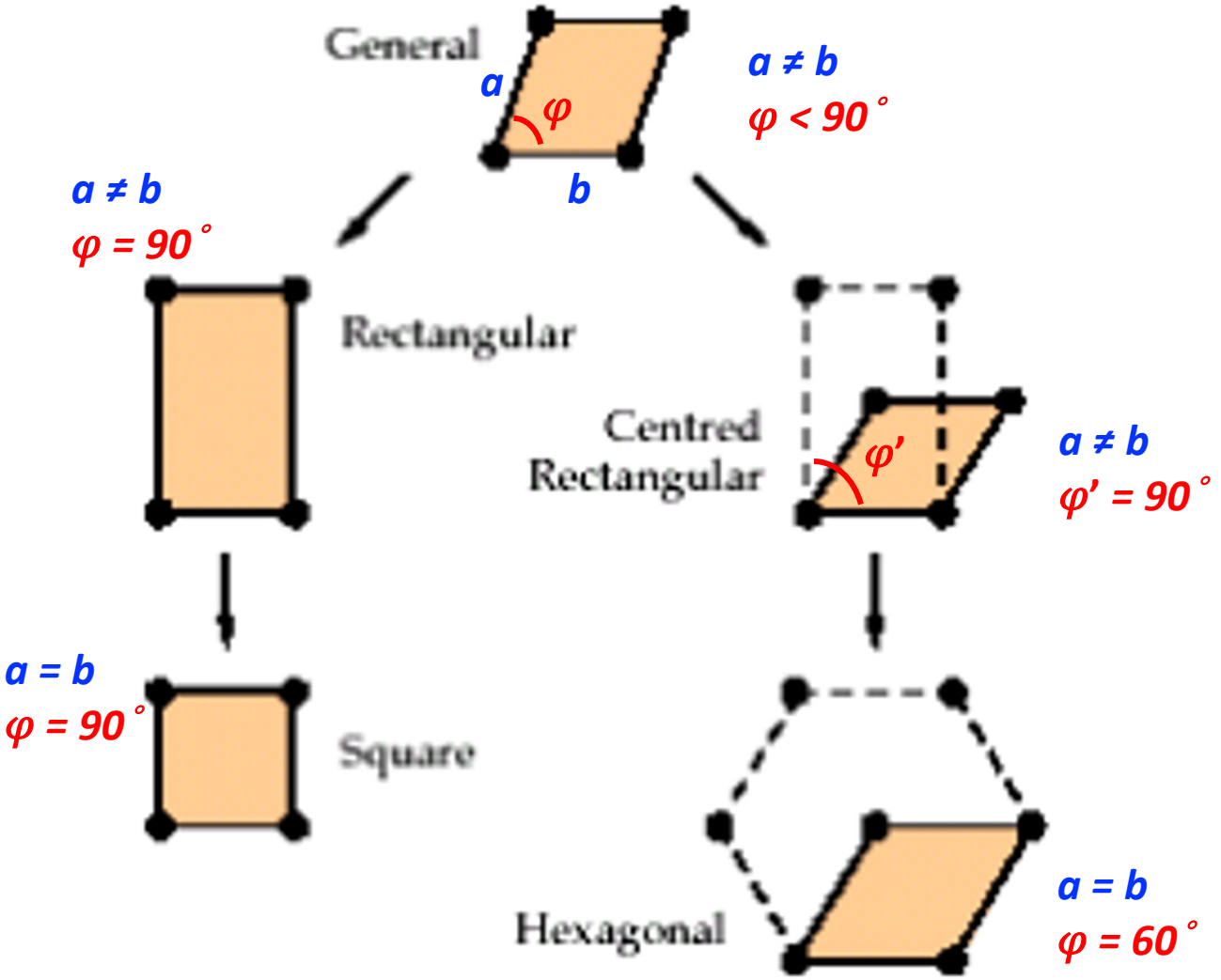



- The primitive cell and, consequently, the entire lattice, is *uniquely* determined by the six lattice constants: a, b, c, α, β and γ.

- Only 1/8 of each lattice point in a unit cell can actually be assigned to that cell.
- Each primitive cell in the figure can be associated with 8 x 1/8 = 1 lattice point.

# Five Bravais Lattices in 2D

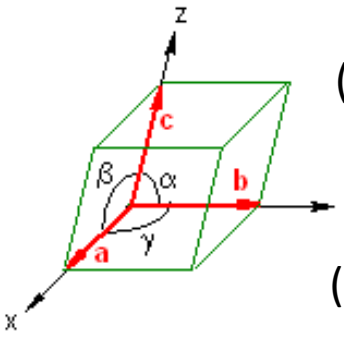
A Bravais lattice is a specific geometric arrangement of points in space where each point is identical and repeated in a regular, periodic manner, giving the crystal its overall translational symmetry.



# Typical Crystal Structures

## 3D – 14 BRAVAIS LATTICES AND SEVEN CRYSTAL TYPES

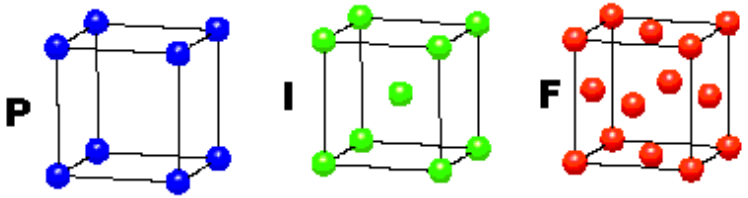
- Cubic Crystal System (SC, BCC,FCC)
- Hexagonal Crystal System (S)
- Triclinic Crystal System (S)
- Monoclinic Crystal System (S, Base-C)
- Orthorhombic Crystal System (S, Base-C, BC, FC)
- Tetragonal Crystal System (S, BC)
- Trigonal (Rhombohedral) Crystal System (S)




(3) **CUBIC**

$a = b = c$

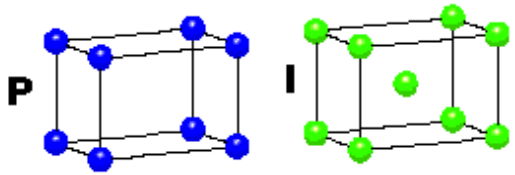
$\alpha = \beta = \gamma = 90°$




(2) **TETRAGONAL**

$a = b \neq c$

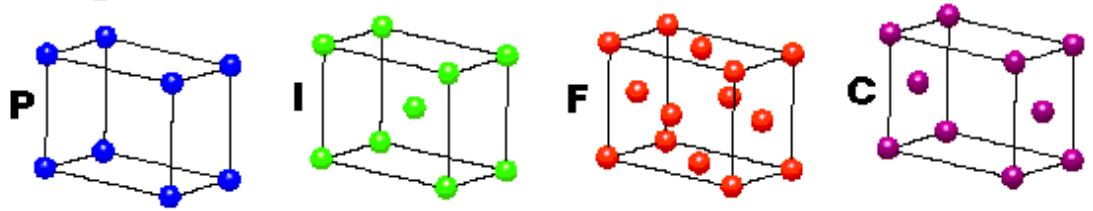
$\alpha = \beta = \gamma = 90°$




(4) **ORTHORHOMBIC**

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

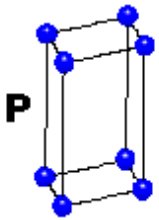



(1) **HEXAGONAL**

$a = b \neq c$

$\alpha = \beta = 90°$

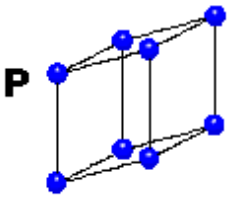
$\gamma = 120°$




(1) **TRIGONAL**

$a = b = c$

$\alpha = \beta = \gamma \neq 90°$

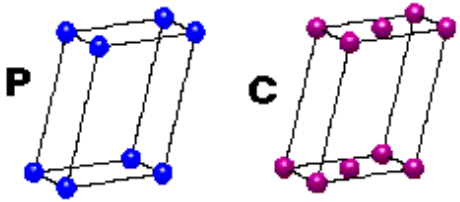



(2) **MONOCLINIC**

$a \neq b \neq c$

$\alpha = \gamma = 90°$

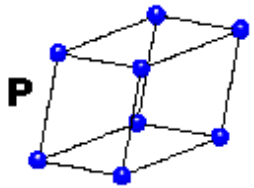
$\beta \neq 120°$




(1) **TRICLINIC**

$a \neq b \neq c$

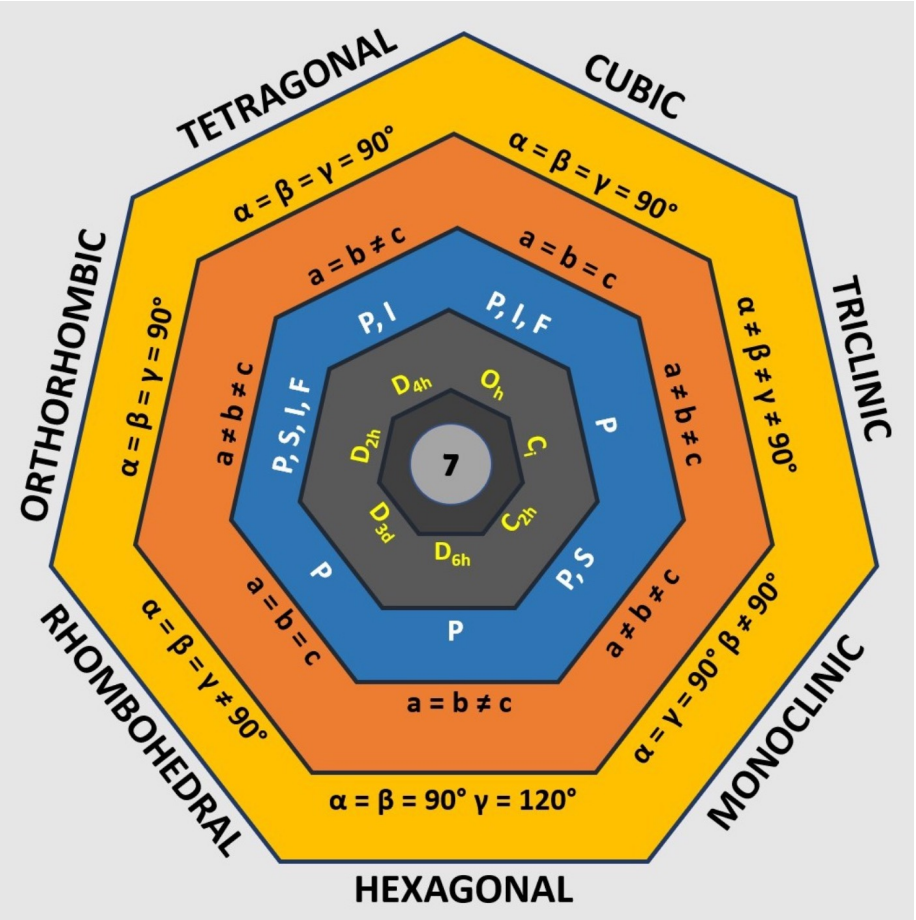
$\alpha \neq \beta \neq \gamma \neq 90°$



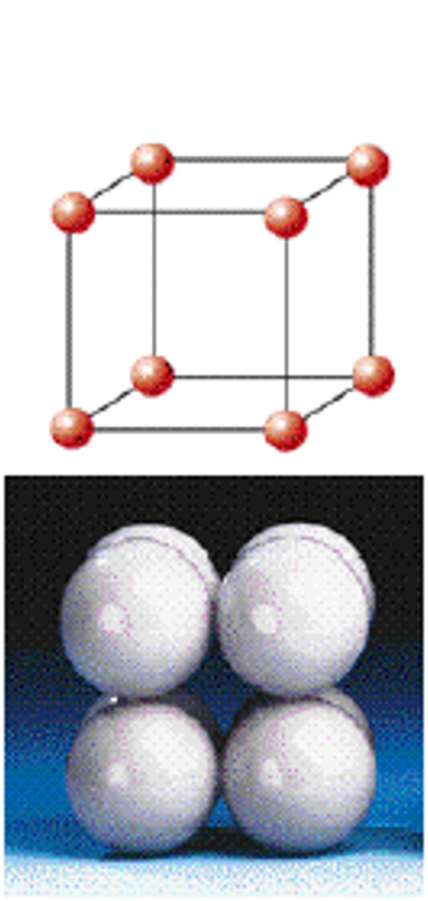

**4 Types of Unit Cell**
**P** = Primitive
**I** = Body-Centred
**F** = Face-Centred
**C** = Side-Centred
+
**7 Crystal Classes**
→ **14 Bravais Lattices**

# Symmetry Elements for Different Lattices

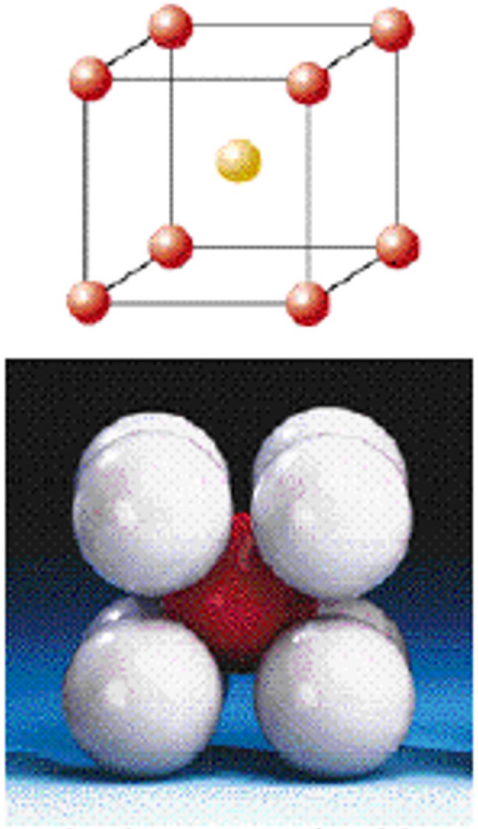
| Crystal System | Bravais Lattices | Symmetry | Axis System |
|---|---|---|---|
| Cubic | P, I, F | m3m | a=b=c, α=β=γ=90 |
| Tetragonal | P, I | 4/mmm | a=b≠c, α=β=γ=90 |
| Hexagonal | P, R | 6/mmm | a=b≠c, α=β=90 γ=120 |
| Rhombohedral* | R | 3m | a=b=c, α=β=γ≠90 |
| Orthorhombic | P, C, I, F | mmm | a≠b≠c, α=β=γ=90 |
| Monoclinic | P, C | 2/m | a≠b≠c, α=γ=90 β≠90 |
| Triclinic | P | 1 | a≠b≠c, α≠β≠γ≠90 |



# Three 3D Conventional Cells

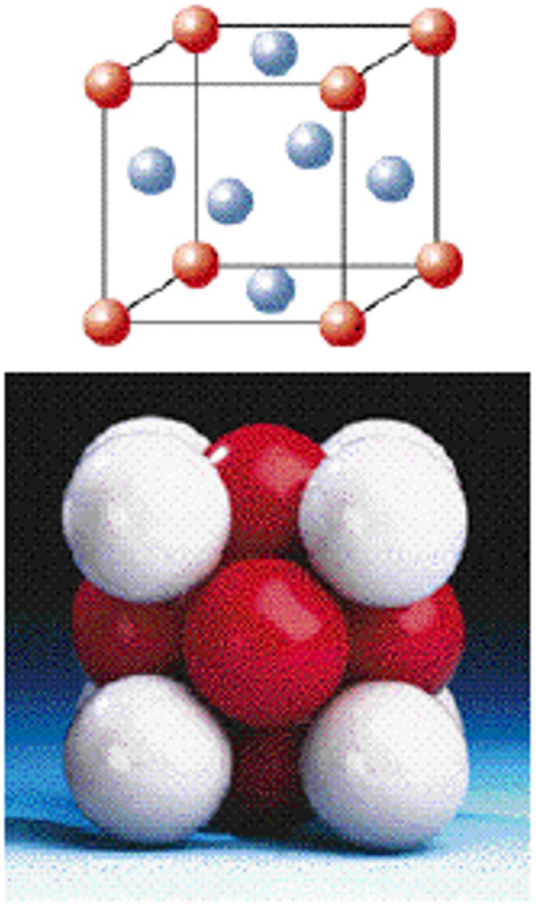


simple cubic



body-centered cubic

$$\mathbf{a}_1 = \tfrac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \;;$$
$$\mathbf{a}_2 = \tfrac{1}{2}a(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \;;$$
$$\mathbf{a}_3 = \tfrac{1}{2}a(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}})$$



face-centered cubic

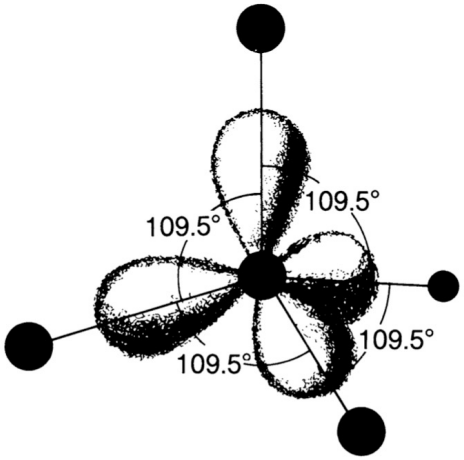
$$\mathbf{a}_1 = \tfrac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}}) \;; \quad \mathbf{a}_2 = \tfrac{1}{2}a(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \;;$$
$$\mathbf{a}_3 = \tfrac{1}{2}a(\hat{\mathbf{z}} + \hat{\mathbf{x}})$$

# Characteristics of cubic lattices[a]

| | Simple | Body-centered | Face-centered |
|---|---|---|---|
| Volume, conventional cell | $a^3$ | $a^3$ | $a^3$ |
| Lattice points per cell | 1 | 2 | 4 |
| Volume, primitive cell | $a^3$ | $\frac{1}{2}a^3$ | $\frac{1}{4}a^3$ |
| Lattice points per unit volume | $1/a^3$ | $2/a^3$ | $4/a^3$ |
| Number of nearest neighbors | 6 | 8 | 12 |
| Nearest-neighbor distance | $a$ | $3^{1/2}\,a/2 = 0.866a$ | $a/2^{1/2} = 0.707a$ |
| Number of second neighbors | 12 | 6 | 6 |
| Second neighbor distance | $2^{1/2}a$ | $a$ | $a$ |
| Packing fraction[a] | $\frac{1}{6}\pi$ $=0.524$ | $\frac{1}{8}\pi\sqrt{3}$ $=0.680$ | $\frac{1}{6}\pi\sqrt{2}$ $=0.740$ |

[a] The packing fraction is the maximum proportion of the available volume that can be filled with hard spheres.

# Diamond Structure



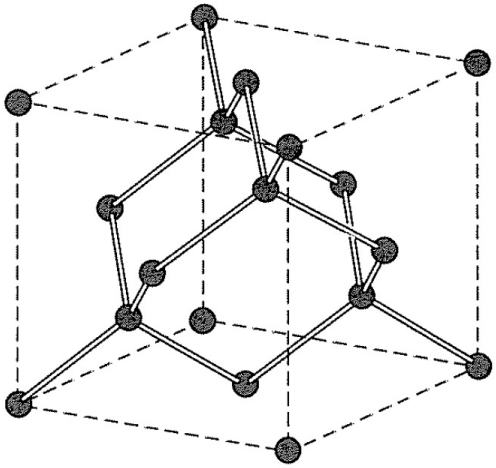
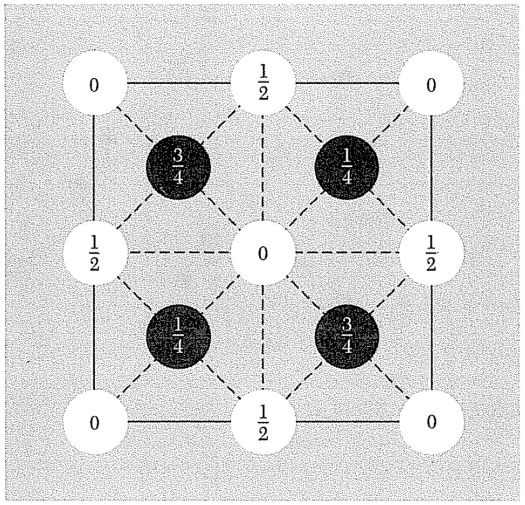



**Figure 23** Crystal structure of diamond, showing the tetrahedral bond arrangement.




- The diamond structure is an example of the directional covalent bonding found in the group IV elements, such as C, Si, Ge.
- The structure is of the fcc lattice, consisting of the basis of two identical elements (000) and (1/4, 1/4, 1/4).
- Each atom has four nearest neighbours and 12 next nearest neighbours.

# Index System for Crystal Planes

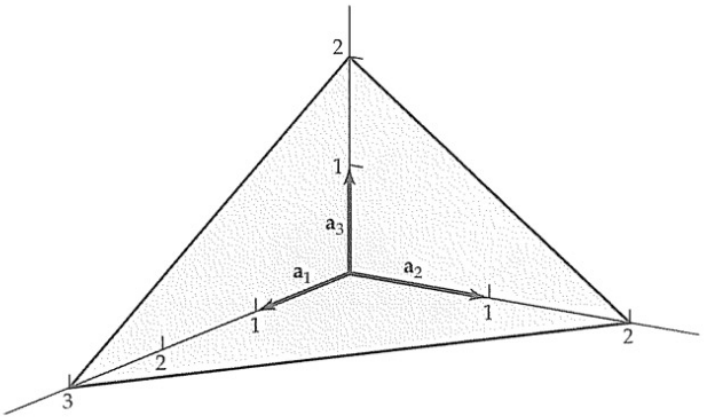



**Figure 13** This plane intercepts the $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ axes at $3\mathbf{a}_1$, $2\mathbf{a}_2$, $2\mathbf{a}_3$. The reciprocals of these numbers are $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).

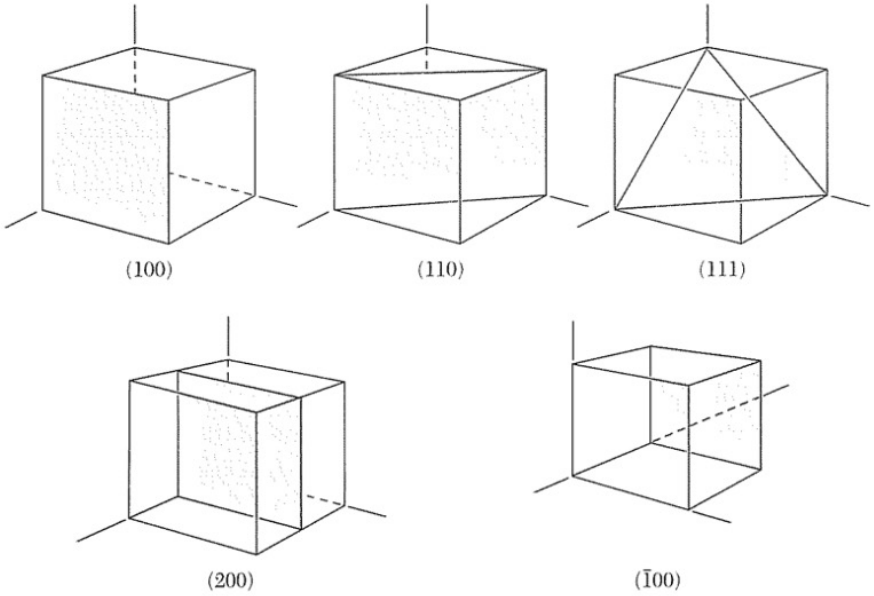



**Figure 14** Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to (100)

- Find the intercepts on the axes in terms of the lattice constants $a_1$, $a_2$, $a_3$. The axes may be those of a primitive or nonprimitive cell.
- Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest three integers. The result, enclosed in parentheses (hkl), is called the index of the plane.

# Lattice Point Group

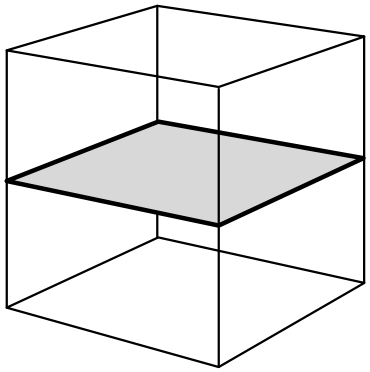
By lattice point group (including rotation, reflection and inversion) we mean the collection of symmetry operations which, applied about a lattice point, carry the lattice into itself.

Crystal lattices can be carried or mapped into themselves by the lattice translations **T** and by various other symmetry operations. A typical symmetry operation is that of rotation about an axis that passes through a lattice point.

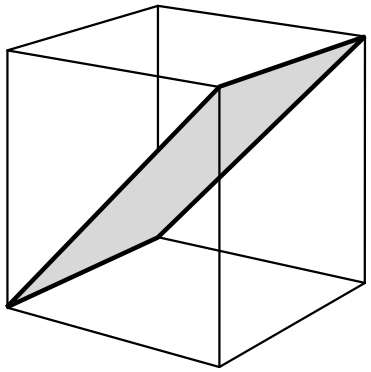
Lattices can be found with rotational symmetry corresponding to rotations by $2\pi$, $2\pi/2$, $2\pi/3$, $2\pi/4$, and $2\pi/6$ radians and by integral multiples of these rotations. The rotation axes are denoted by the symbols 1, 2, 3, 4, and 6.

We can have mirror reflections *m* about a plane through a lattice point. The inversion operation is composed of a rotation of $\pi$ followed by reflection in a plane normal to the rotation axis; the total effect is to replace **r** by -**r**.

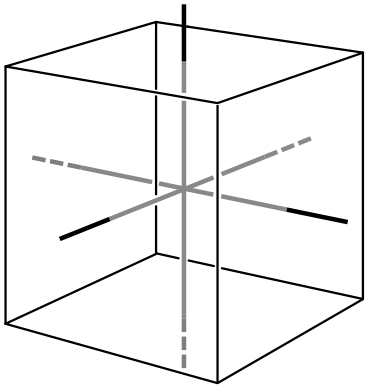
# Symmetry Planes and Axes



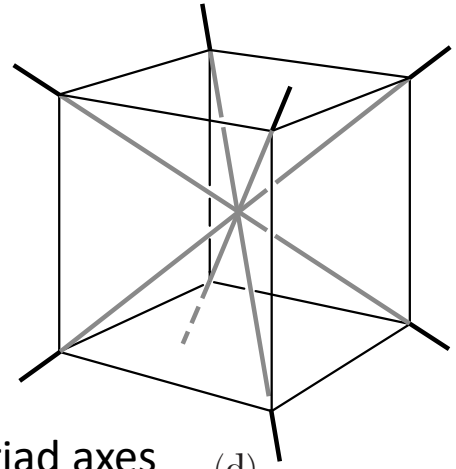
(a)



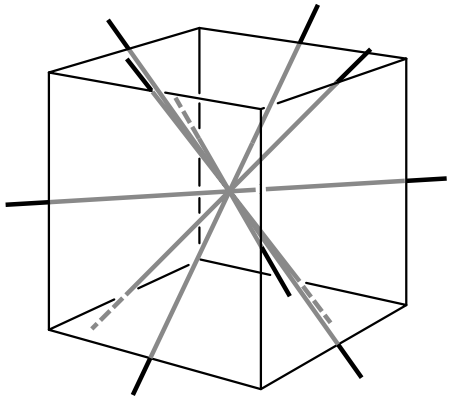
(b)



Tetrad axes (c)



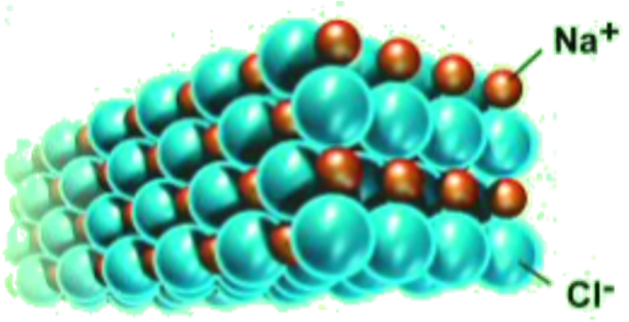
Triad axes (d)

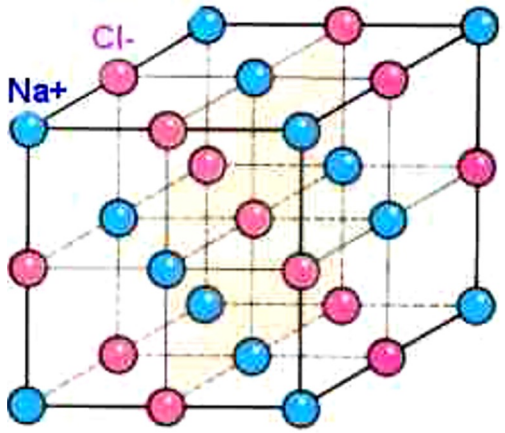


Diad axes (e)

# Sodium Chloride Structure

- Sodium chloride also crystallizes in a cubic lattice, but with a different unit cell.
- Sodium chloride structure consists of equal numbers of sodium and chlorine ions placed at alternate points of a fcc cubic lattice.
- Each ion has six of the other kind of ions as its nearest neighbours.




| | | | | |
|---|---|---|---|---|
| Cl: | $000$ ; | $\frac{1}{2}\frac{1}{2}0$ ; | $\frac{1}{2}0\frac{1}{2}$ ; | $0\frac{1}{2}\frac{1}{2}$ . |
| Na: | $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ; | $00\frac{1}{2}$ ; | $0\frac{1}{2}0$ ; | $\frac{1}{2}00$ . |

Metallic elements have only up to the valence electrons in their outer shell.

When losing their electrons they become positive ions.

Electronegative elements tend to acquire additional electrons to become negative ions or anions.

When the $Na^+$ and $Cl^-$ ions approach each other closely enough so that the orbits of the electron in the ions begin to overlap with each other, then the electron begins to repel each other by virtue of the repulsive electrostatic coulomb force. Of course the closer together the ions are, the greater the repulsive force.

Pauli exclusion principle has an important role in repulsive force. To prevent a violation of the exclusion principle, the potential energy of the system increases very rapidly.

# Cesium Chloride Structure

- Cesium chloride also crystallizes in a cubic lattice, but with a different unit cell.
- Cesium chloride structure consists of equal numbers of cesium and chlorine ions placed at alternate points of a simple cubic lattice with $Cs^+$ ion at (000) and $Cl^-$ at (½, ½, ½).
- Each ion has eight of the other kind of ions as its nearest neighbours.

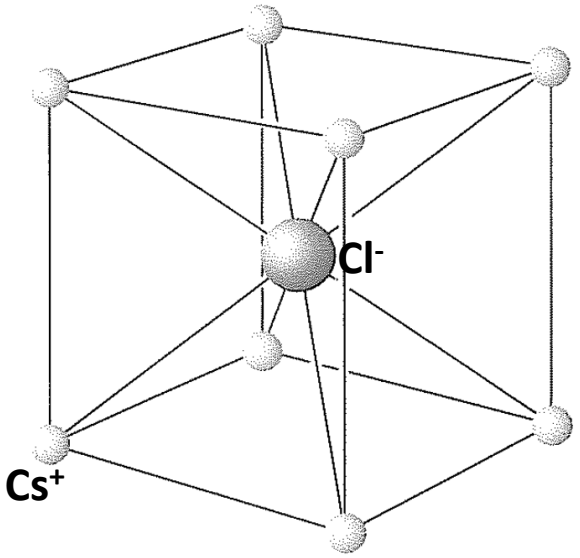
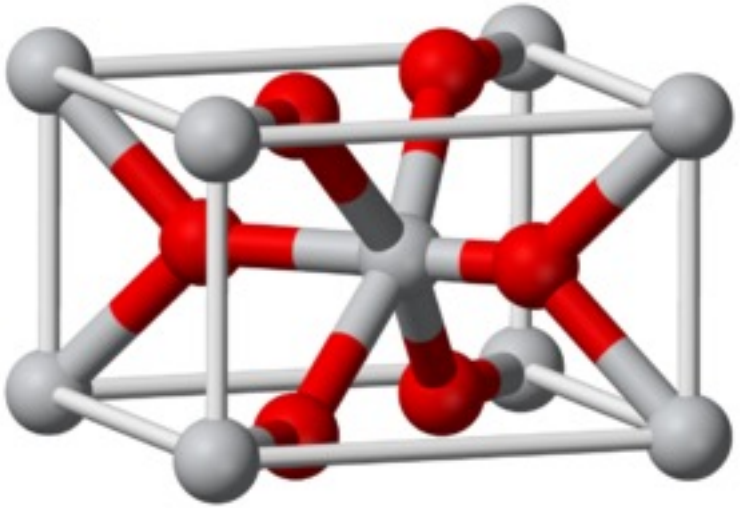
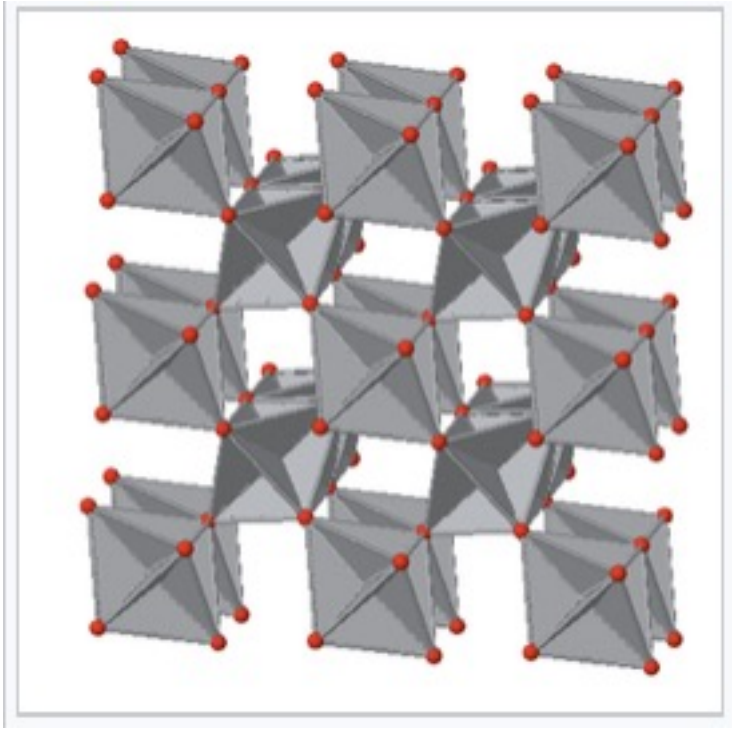



**Figure 18** The cesium chloride crystal structure. The space lattice is simple cubic, and the basis has one $Cs^+$ ion at 000 and one $Cl^-$ ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

# Rutile Structure

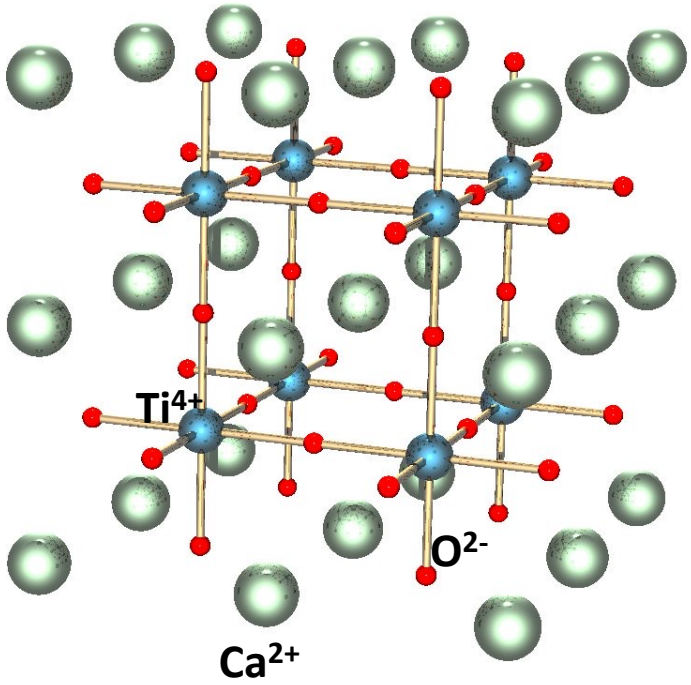
**The rutile structure is an important $MX_2$ (X = O, F) structure. It is a 6:3 structure, in which the cations are octahedrally coordinated by anions, and as such is intermediate in polarity between the $CaF_2$ (8:4) and $SiO_2$ (4:2) structures. The mineral rutile is one of the polymorphs of $TiO_2$, the others (anatase and brookite) also being 6:3 structures.**





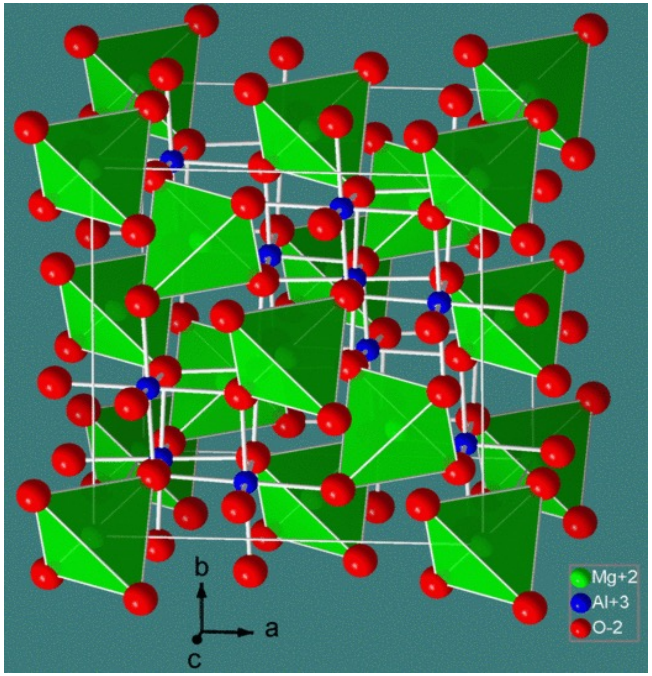
# Perovskite Structure

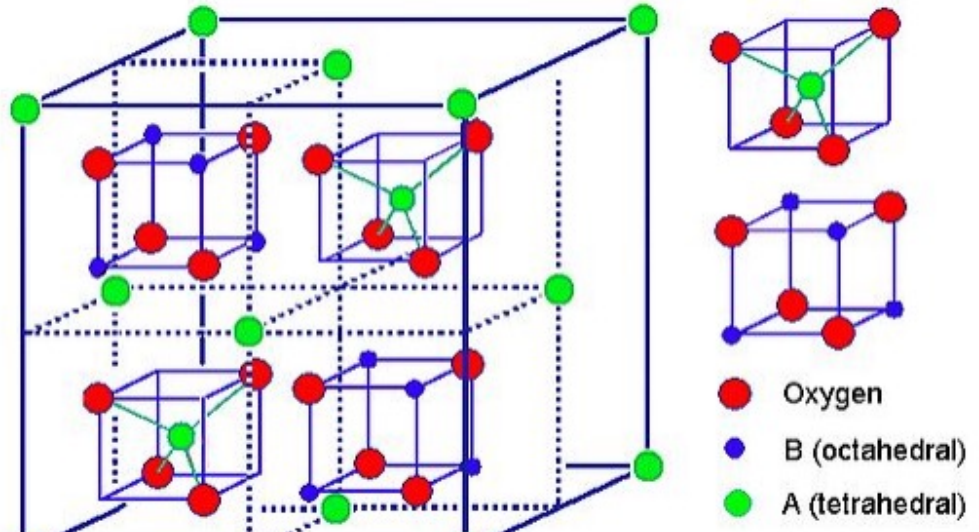
- A perovskite is any material with a crystal structure following the formula $ABX_3$, which was first discovered as the mineral called perovskite, which consists of calcium titanium oxide ($CaTiO_3$).
- Structure of a perovskite with general chemical formula $ABX_3$. The red spheres are X atoms (usually oxygens), the blue spheres are B atoms (a smaller metal cation, such as $Ti^{4+}$), and the green spheres are the A atoms (a larger metal cation, such as $Ca^{2+}$).



# Spinel Structure

**The spinel structure is formulated $MM'_2X_4$, where M and M' are tetrahedrally and octahedrally coordinated cations, respectively, and X is an anion (typically O or F). The structure is named after the mineral $MgAl_2O_4$, and oxide spinels have the general formula $AB_2O_4$.**



# Crystal Bindings

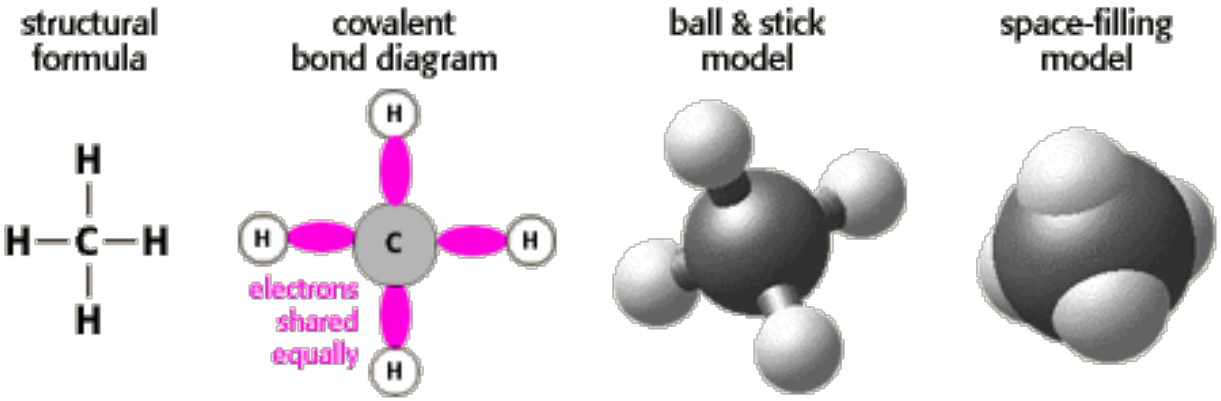
**Forces hold the atoms together in a solid**

- **Covalent bonding**
- **Ionic bonding**
- **Metallic bonding**
- **Van der waals bonding**
- **Hydrogen bonding**

**All bonding is a consequence of the electrostatic interaction between the nuclei and electrons.**

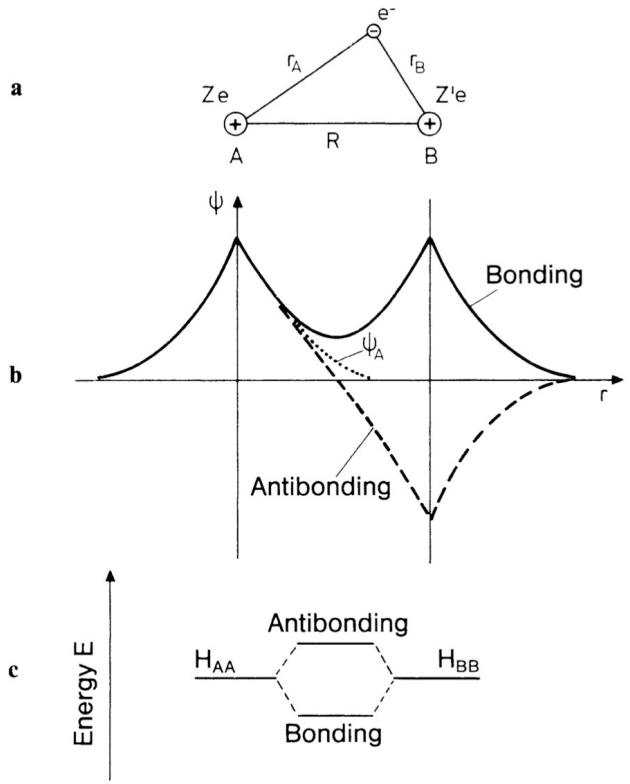
# Covalent Bonding

- Covalent bonding takes place between atoms with small differences in electronegativity which are close to each other in the periodic table (*between non-metals and non-metals*).
- The covalent bonding is formed when the atoms share the outer shell electrons (i.e., s and p electrons) rather than by electron transfer.
- Noble gas electron configuration can be attained.

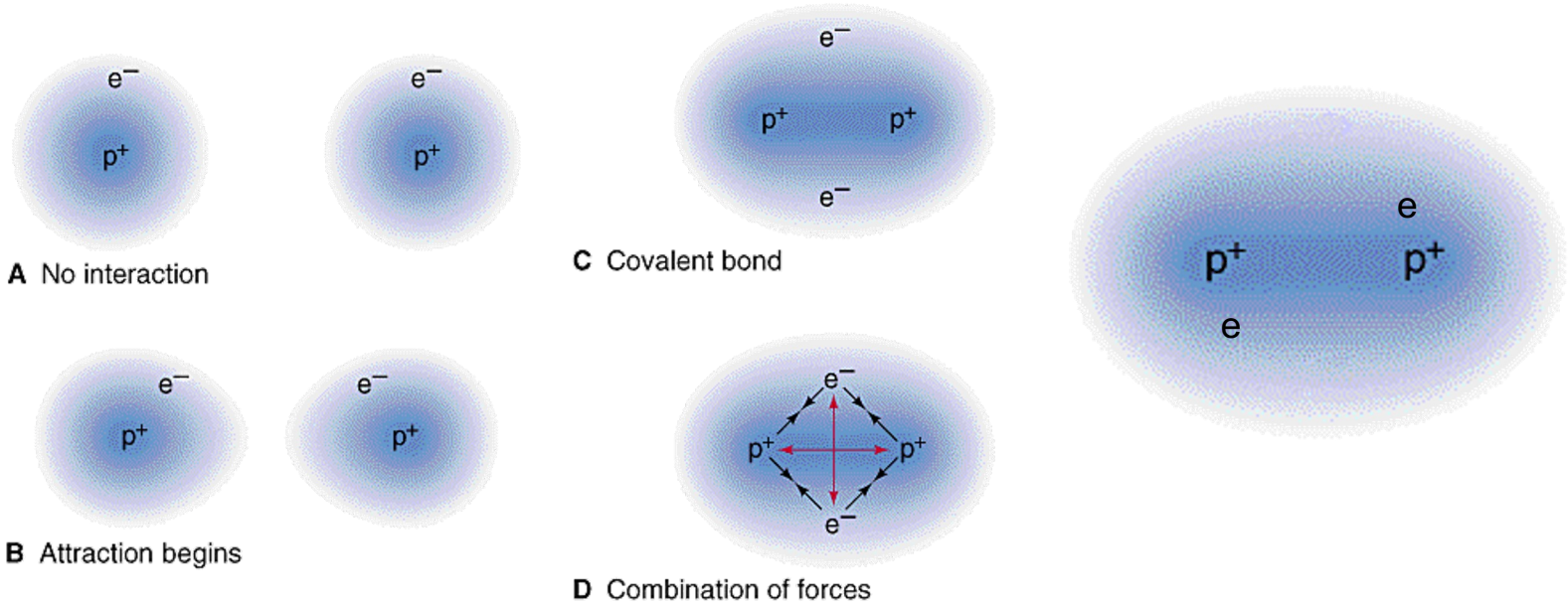


# $H_2^+$ ion

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1}+\frac{1}{\mathbf{r_2}}\right)\right]\psi_{H_{2+}} = \mathbf{E}\,\psi_{H_{2+}}$$

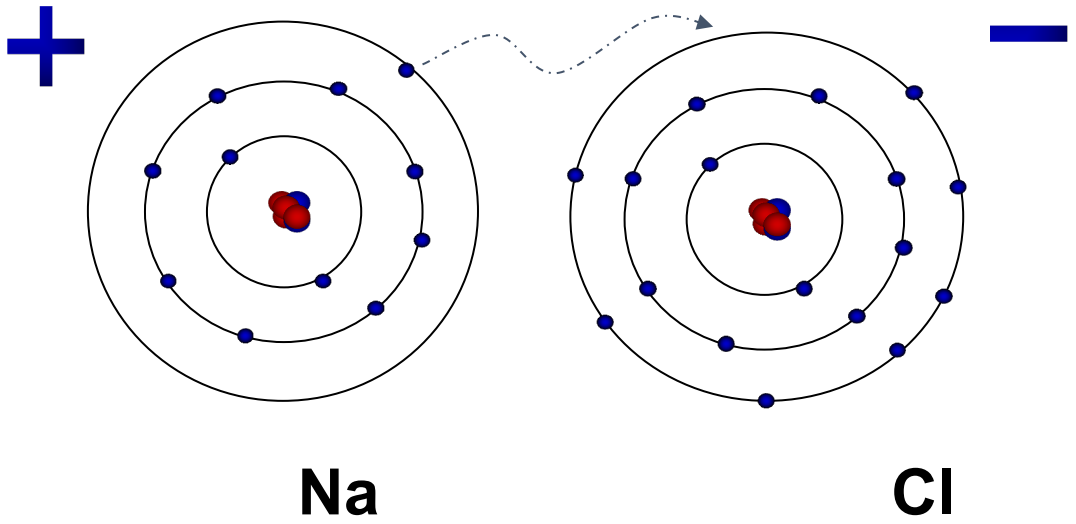


Each electron in a shared pair is attracted to both nuclei involved in the bond. The approach, electron overlap, and attraction can be visualized as shown in the following figure representing the nuclei and electrons in a hydrogen molecule.



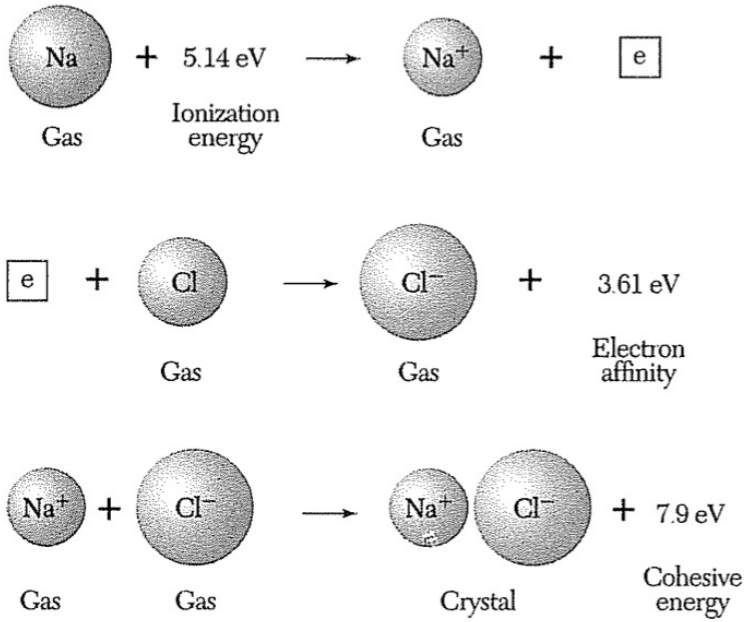
# Ionic Bonding

- Ionic bonding is the electrostatic force of attraction between positively and negatively charged ions (between non-metals and metals).
- All ionic compounds are crystalline solids at room temperature.
- NaCl is a typical example of ionic bonding.



# Energies of Interactions Between Atoms

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.



# Madelung Energy

The main contribution to the binding energy of ionic crystals is electrostatic and is called the **Madelung energy**.

If $U_{ij}$ is the interaction energy between ions *i* and *j*, we define a sum $U_i$ which includes all interactions involving the ion *i*:

$$U_i = \sum_j{}' U_{ij} \ , \qquad U_{ij} = \lambda \, \exp(-r_{ij}/\rho) \pm q^2/r_{ij}$$

If we let $r_{ij} \equiv p_{ij} R$, where *R* is the nearest-neighbor separation in the crystal, then

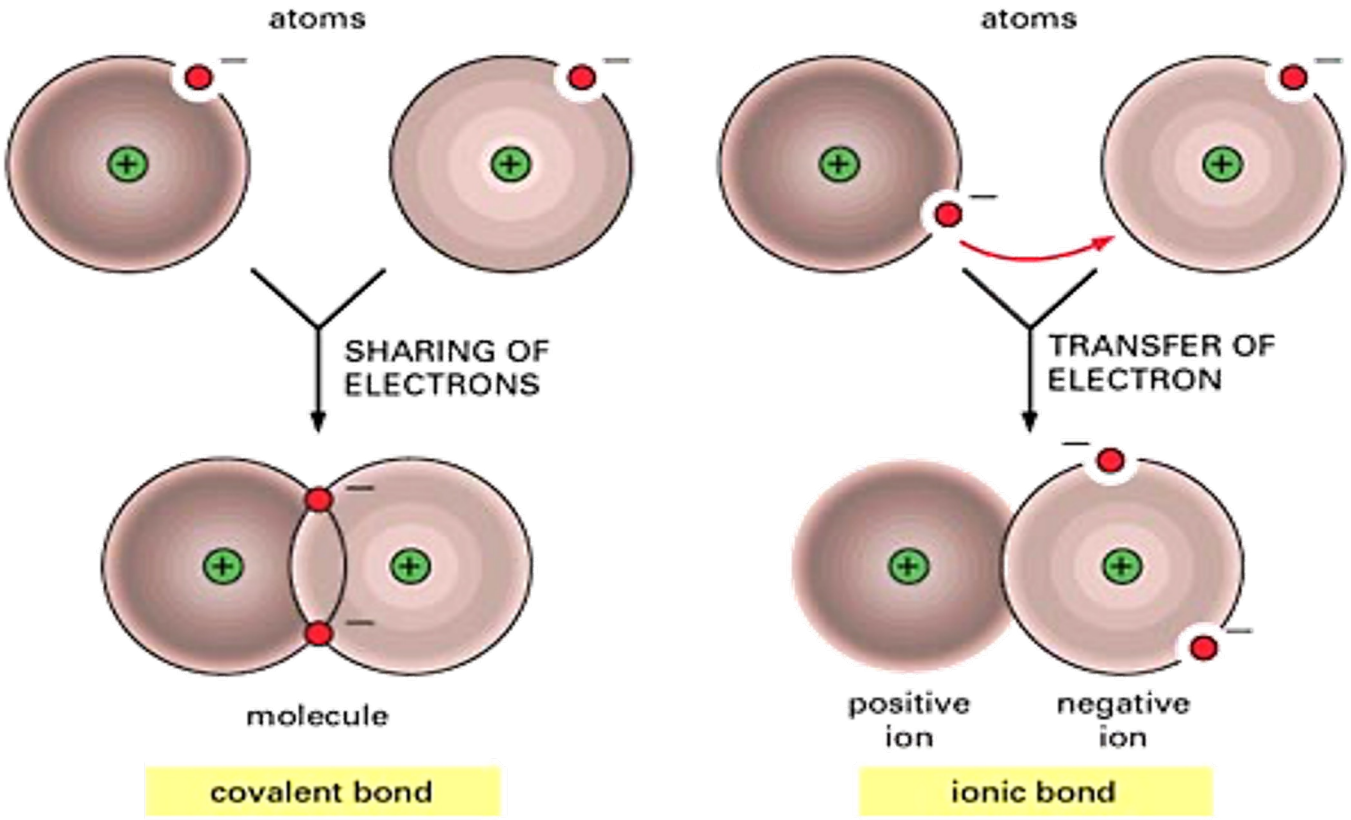
$$U_{ij} = \begin{cases} \lambda \, \exp(-R/p) - \dfrac{q^2}{R} & \text{(nearest neighbors)} \\ \pm \dfrac{1}{p_{ij}} \dfrac{q^2}{R} & \text{(otherwise).} \end{cases}$$

$$U_{\text{tot}} = N U_i = N\left( z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R} \right) \ ,$$

where *z* is the number of nearest neighbors of any ion and

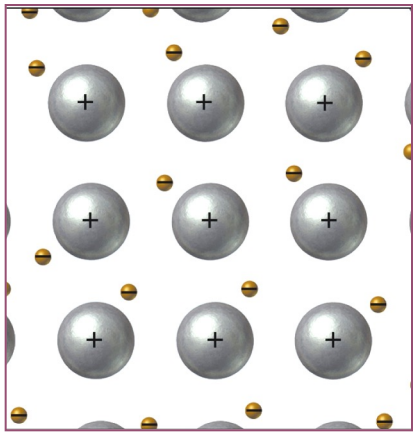
$$\alpha \equiv \sum_j{}' \frac{(\pm)}{p_{ij}} \equiv \textbf{Madelung constant}$$

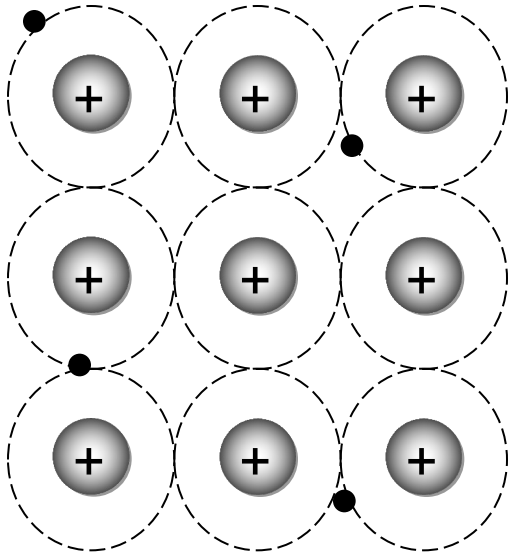
# Comparison of Ionic and Covalent Bonding



# Metallic Bonding

- Metallic bonding is found in metal elements. This is the electrostatic force of attraction between positively charged ions and delocalized outer electrons.
- The metallic bond is weaker than the ionic and the covalent bonds.
- A metal may be described as a low-density cloud of free electrons.
- Therefore, metals have high electrical and thermal conductivity.

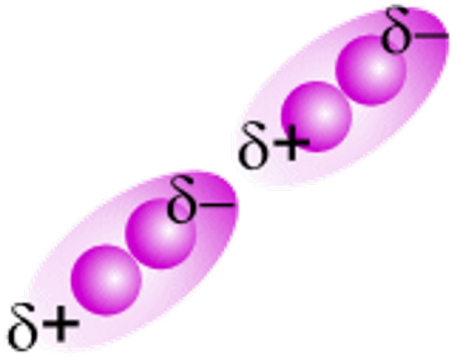




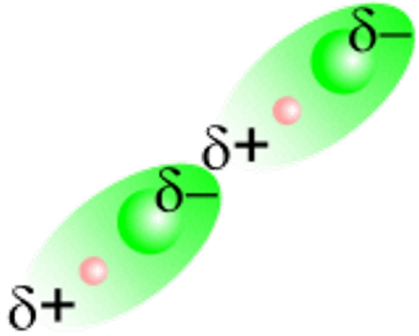
# Van der Waals Bonding

- These are weak bonds with a typical strength of 0.2 eV/atom.
- Van Der Waals bonds occur between neutral atoms and molecules.
- Weak forces of attraction result from the natural fluctuations in the electron density of all molecules that cause small temporary dipoles to appear within the molecules.
- It is these temporary dipoles that attract one molecule to another. They are called van der Waals' forces.

- The **shape** of a molecule influences its ability to form temporary dipoles. Long thin molecules can pack closer to each other than molecules that are more spherical. The bigger the 'surface area' of a molecule, the greater the van der Waal's forces will be and the higher the melting and boiling points of the compound will be.
- Van der Waal's forces are of the order of 1% of the strength of a covalent bond.




Homonuclear molecules, such as iodine, develop temporary dipoles due to natural fluctuations of electron density within the molecule

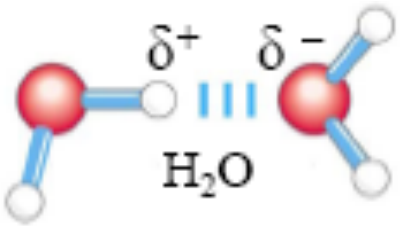



Heteronuclear molecules, such as H-Cl have permanent dipoles that attract the opposite pole in other molecules.

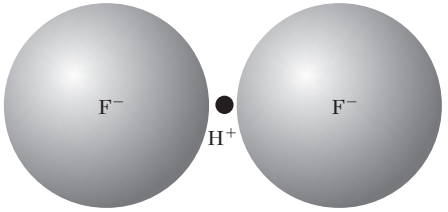
# Hydrogen Bonding

- A hydrogen atom, having one electron, can be covalently bonded to only one atom. However, the hydrogen atom can involve itself in an additional electrostatic bond with a second atom of highly electronegative character such as fluorine or oxygen. This second bond permits a ***hydrogen bond*** between two atoms or strucures.
- The strength of hydrogen bonding varies from 0.1 to 0.5 ev/atom.

Hydrogen bonds connect water molecules in ordinary ice. Hydrogen bonding is also very important in proteins and nucleic acids and therefore in life processes.




In the extreme ionic form of the hydrogen bond, the hydrogen atom loses its electron to another atom in the molecule; the bare proton forms the hydrogen bond.




$HF_2^-$

# Properties of Different Bonding

| Types of Bonding | Ionic | Covalent | Metallic | Van der Waals | Hydrogen |
|---|---|---|---|---|---|
| Melting Point | High | Very High | Variable | Low | Low |
| Hardness | Hard and Brittle | Very hard | Variable | Soft and Brittle | Soft and Brittle |
| Conductivity | Low | Low | High | Non-conducting | Non-conducting |
| Examples | NaCl, ZnS | Diamond, Graphite | Au, Cu, Fe | Ne, Ar, Kr | Ice, Organic solids |

# Exercises

1. Draw the primitive unit cell of the fcc lattice and determine the lengths of the primitive lattice vectors a', b', c' (in units of the conventional lattice constant a) and also the angles a', b', c' between the primitive lattice vectors. (Hint: Express the primitive lattice vectors as a linear combination of the lattice vectors a, b, c of the body-centered cubic lattice and use elementary vector algebra.) What distinguishes this unit cell from that of the rhombic Bravais lattice?
2. Supposing the atoms to be rigid spheres, what fraction of space is filled by atoms in the primitive cubic, fcc, hcp, bcc, and diamond lattices?
3. Take the CsCl structure and assume that the cation radius becomes smaller while the anion radius remains constant. What happens to the binding energy? Show that for small cations the NaCl lattice becomes the preferred structure. For an even smaller cation radius the ZnS lattice has the largest binding energy (Madelung constant A=1.638).