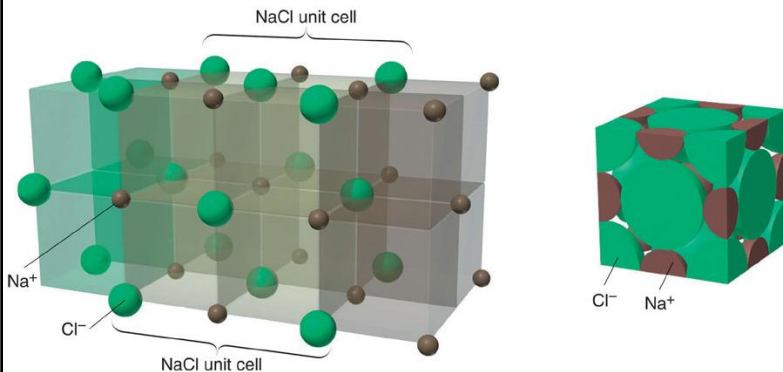


Types of Crystalline Solids

- **Atomic solids** – consist of atoms
 - The atoms are held together by weak dispersion forces (Examples: **Ne, Ar, Kr, Xe, Rn**)
 - Quite soft; very low T_m ; poor electrical and thermal conductors (T_m increases with increasing molar mass)
- **Molecular solids** – consist of molecules
 - Non-polar molecules are held together by dispersion forces (Examples: **O₂, CH₄, CO₂, ...**)
 - Polar molecules are held together by dispersion, dipole-dipole and in some cases H-bonding forces (Examples: **H₂O, SO₂, sugar, ...**)
 - Soft; low T_m ; poor electrical and thermal conductors

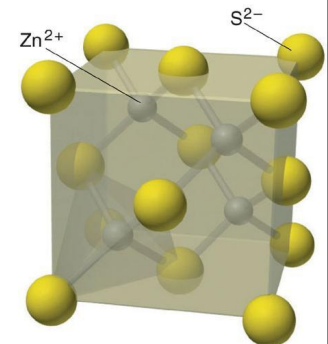
- **Ionic solids** – consist of + and – ions
 - Ions are held together by very strong ion-ion electrostatic attractions (ionic bonds) → Examples: NaCl, MgO, CaF₂, ...
 - Hard and brittle; high T_m ; conduct electricity and heat when molten
 - The unit cell has the same composition (ratio of cations to anions) as the empirical formula
 - Typically the smaller cations fit in the gaps between the larger anions
 - **Radius ratio** → $r_{\text{cat}}/r_{\text{an}}$
 - Depending on the radius ratio and the ion ratio, different structures are possible
- Ionic compounds with 1:1 ion ratio

- **Rock salt structures** – FCC arrangement of the anions; the cations fit in the gaps between the anions and also form FCC structure (NaCl, KBr, MgO, ...)
 - Typical for compounds with radius ratios of **0.4 - 0.7** (small cations large anions)
 - **Coordination #** → **(6,6)** – 6 for cations and 6 for anions



- **Cesium chloride structures** – BCC unit cell with eight ions in the corners and one counter-ion in the body center of the cube (CsCl, CsI, ...)
 - Typical for compounds with radius ratios larger than **0.7** (cations and anions with similar sizes)
 - **Coordination #** → **(8,8)** – 8 for cations and 8 for anions

- **Zinc blende structures** – FCC structure of anions penetrated by FCC structure of cations; each cation is tetrahedrally surrounded by 4 anions and vice versa (ZnS, CdS, AgI, CuCl, ...)
 - **Coordination #** → **(4,4)** – 4 for cations and 4 for anions



→ Ionic compounds with 1:2 or 2:1 ion ratios

➤ **Fluorite structures** – FCC unit cell of cations, penetrated by 8 anions in the gaps between the cations (CaF₂, SrF₂, BaCl₂, ...)

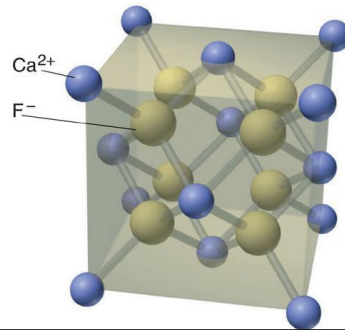
➤ Typical for 1:2 compounds with large radius ratios

Coordination # → **(8,4)** – 8 for cations and 4 for anions

➤ **Antifluorite structures** – FCC unit cell of anions, penetrated by 8 cations in the gaps between the anions (K₂S, ...)

➤ Typical for 2:1 compounds with small radius ratios

➤ **Coordination #** → **(4,8)** – 4 for cations and 8 for anions

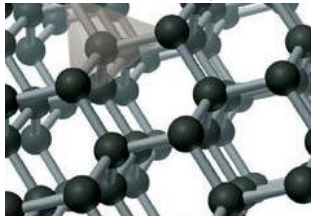


- **Metallic solids** – consist of metal atoms
 - The atoms are held together by strong metallic bonding forces (Examples: **Fe, Cu, Ti, Na, ...**)
 - Wide range of hardness; luster; malleable and ductile; wide range of T_m ; excellent electrical and thermal conductors
- **Network solids** – consist of atoms
 - The atoms are held together by strong covalent bonds [Examples: **C(diamond), SiO₂(quartz), ...**]
 - Most are very hard; very high T_m ; usually poor electrical and thermal conductors
 - Hardness and conductivity vary with the way atoms are bonded together

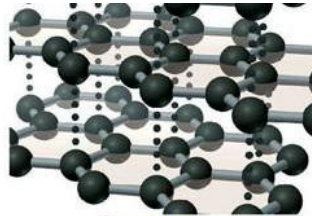
Example: Carbon has two common allotropic forms:

➤ **Diamond** → tetrahedral network of covalently σ -bonded C atoms in sp^3 hybridization → extremely hard; poor conductivity (insulator)

➤ **Graphite** → flat sheets of covalently bonded C atoms in sp^2 hybridization (can be viewed as condensed benzene rings with delocalized π -bonding) → soft and slippery (weak **IFs** between the sheets allow sliding); good conductivity (delocalization of the π -electrons)



Diamond



Graphite

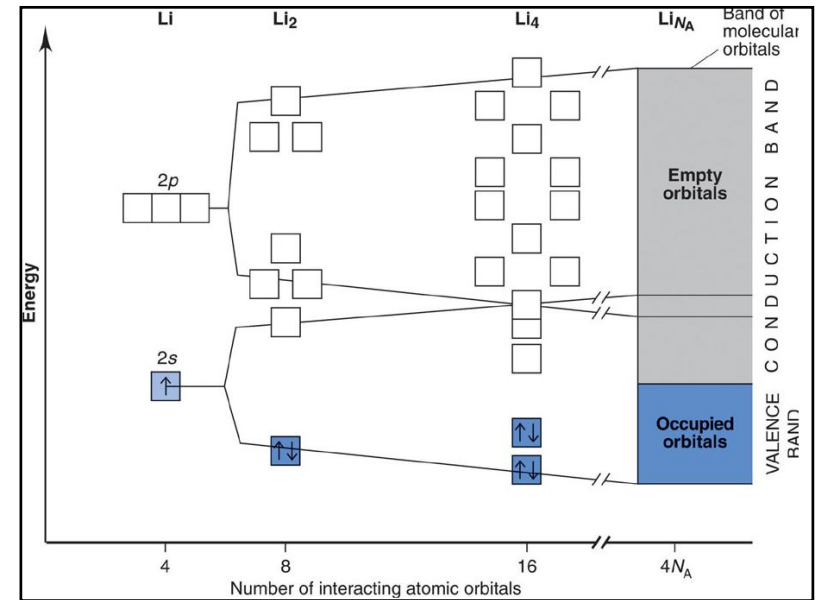
The Band Theory of Solids

- Application of the **MO** theory to solids
 - A metallic crystal can be viewed as one enormous molecule made of many atoms
 - The valence **AOs** of these atoms merge to form delocalized **MOs** (N AOs produce N MOs)
 - The large number of **MOs** form “**bands**” of closely spaced energy levels
 - The different types of **AOs** (s, p, d, ...) form different bands (s-band, p-band, ...)
 - Some bands are separated by **band gaps** where energies are not allowed
 - Bands can be empty, partly filled, or filled with e^-

- The band occupied by the valence electrons is called **valence band**
- The band of empty orbitals directly above the valence band is called **conduction band**
- Electrons from the valence band can be excited to the conduction band and become mobile → provide conductivity

Example:

In **Li**, each atom contributes **1** s-electron to the s-band. N Li atoms contribute N electrons. N Li atoms have N s-orbitals and produce N MOs. N MOs can hold $2N$ electrons ⇒ The s-band is half-full.



- **Metal conductors** – the valence and conduction bands overlap (no band gap) ⇒ the electrons need an extremely small amount of energy to jump in the conduction band
 - Conductivity decreases with increasing T since the random motion of the atoms hinders the directional motion of electrons
- **Semiconductors** – the valence and conduction bands are separated by a small band gap ⇒ the electrons need a fairly small amount of energy to jump in the conduction band
 - Conductivity increases with increasing T since the electrons are thermally excited to the conduction band

- **Insulators** – the valence and conduction bands are separated by a large band gap ⇒ the electrons can not be excited to the conduction band → no conductivity
- **Superconductivity** – conduction with no energy loss (extremely low resistance)
 - Metals can super conduct at very low T ($<4K$)
 - New materials can super conduct at higher T s

