

3 Binding in solid-state materials

3.1 Draw the interaction potential for a metal (n-atoms, with $n = 10^{23}$). Discuss the conclusions, i.e. typical properties of the metals including their crystalline structure. Transform the knowledge to semiconductors and discuss their properties with respect to the metals.

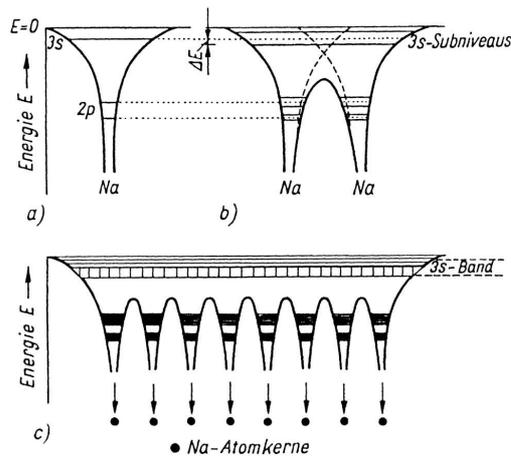


Figure 1: Formation of metals.

Approaching 2 sodium atoms, they form 2 common 3s sublevels. In a crystal built out of n atoms, n 3s sublevels exist, which are, in practice, the 3s band. This band is half filled by electrons termed **electron gas** and **conduction electrons**, respectively. The interaction of the ion cores with the conduction electrons largely contributes to the binding energy. The characteristic, however, is the lower energy of the valence electrons in the crystal with respect to the free atom.

Characteristics of metals: Presence of undirectional bonding leads to dense packing (hcp, fcc, bcc). The freely moving electrons are the reason for the characteristic gleam and colour, and for good heat and electrical conductivity. Because defects are not closely related to charges, moving dislocations, which determine the plastic deformation, are initiated by small amounts of mechanical or thermal energy.

Semiconductors

Semiconductor - is a material with electrical conductivity due to electron flow intermediate in magnitude between that of a conductor and an insulator. In semiconductors, current is often schematized as being carried either by the flow of electrons or by the flow of positively charged "holes" in the electron structure of the material.

If the temperature rise, electrons are excited to a conduction band. Therefore at elevated temperatures, semiconductors behave like conductors.

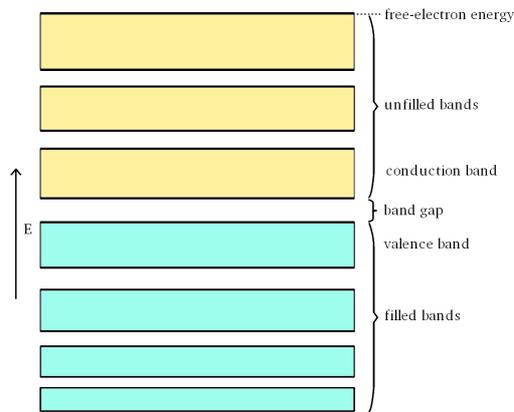


Figure 2: Possible energy bands of semiconductor.

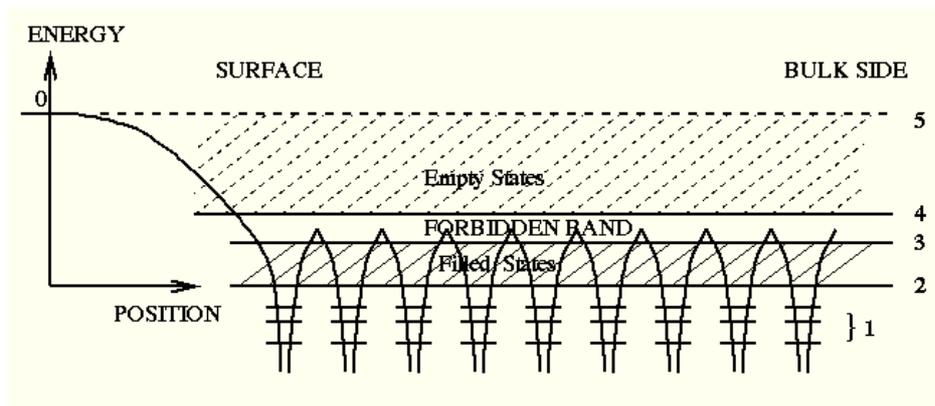


Figure 3: Possible energy bands of semiconductor in ground state.

Alternatively, the band gap explanation.

In insulators the band gap is too big for promotion of valence band electrons to the conduction band.

In semi-conductors the band gap is small enough that electrons from the partially filled valence band can be promoted to the conduction band.

In metals there is a free flow between valence band and conduction.

3.2 Draw the interaction potential for two atoms. What mathematical descriptions do you recognize for the potentials? Please explain the empirical relationship between Young's modulus, melting temperature and thermal expansion of solid state materials using a scheme of a typical inter-atomic potential.

Inter-atomic or inter-molecular forces are described by attractive and repulsive interaction potentials and are present in all kinds of solid states.

$$E = \int (P_a + P_r) dr,$$

$$r((dE/dr) = 0) \equiv r_0,$$

$$P_a = -P_r,$$

$$E(r = r_0) = E_{min}.$$

r_0 - equilibrium inter-atomic distance;

E_{min} - dissociation energy;

P_a - attractive force;

P_r - repulsive force.

The Lennard-Jones potential

The Lennard-Jones potential is a mathematically simple model that approximates the interaction between a pair of neutral atoms or molecules.

$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] = P_a + P_r$$

where ϵ is the depth of the potential well, σ is the finite distance at which the inter-particle potential is zero, r is the distance between the particles. *AB form* of Lennard-Jones potential is a simplified formulation that is used by some simulation software packages:

$$V_{LJ}(r) = \frac{A}{r^{12}} - \frac{B}{r^6},$$

where A, B - material constants.

Exact formula of Lennard-Jones potential for Ti:

$$V_{LJ} = \epsilon \left[\frac{m}{n-m} \left(\frac{r_0}{r} \right)^n - \frac{n}{n-m} \left(\frac{r_0}{r} \right)^m \right]$$

$$\epsilon = 468.61 \text{ kJ/g} * \text{atom}$$

$$r_0 = 2.929 \times 10^{-10} \text{ m}$$

$$m=4.5$$

$$n=8.5$$

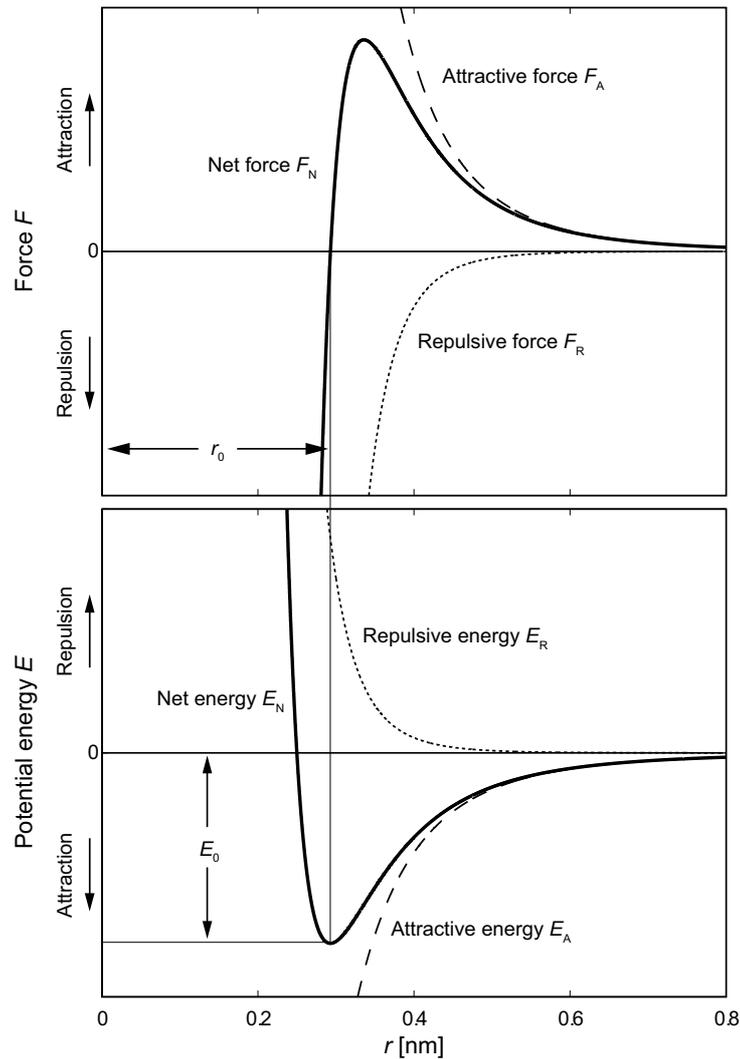


Figure 4: (a) The dependence of repulsive, attractive, and net forces on interatomic separation for two isolated atoms. (b) The dependence of repulsive, attractive, and net potential energies on interatomic separation for two isolated atoms.

There is an empirical relationship between physical properties of solid-state material and inter-atomic potential:

The thermal expansion is represented by the asymmetric potential.

The melting point is related to E_{min} , i.e. the deepest of the potential.

The Young's modulus is represented by the shape at the bottom of the potential.

3.3 What types of inter-atomic bonds are present in solid-state materials? How do these different types of bonding determine the materials properties (mechanical, electrical, thermal)? Detailed view, please.

3.3.1 Ionic bond

- *electrostatic attraction (Coulomb) between oppositely charged ions. In other words, attraction between positively and negatively charged ions.*

This type of bond is always found in compounds that are composed of both metallic and nonmetallic elements. The ionic bond results from the electrostatic interaction of oppositely charged ions. The energy of the molecule within the ionic crystal is lower than the energy of the separated neutral atoms.

It is an example of hetero-polar bonding. The positively and negatively charged ions apply equal and opposite forces on each other. Sometimes this behavior is called non-directional.

Examples of ionic crystals are NaCl and MgO.

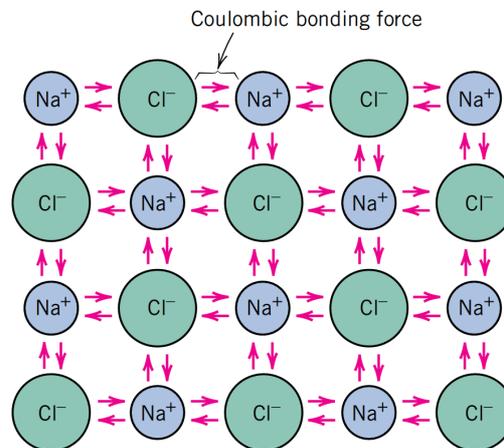


Figure 5: Schematic representation of ionic bonding in sodium chloride (NaCl).

3.3.2 Covalent bond

- *type of bonding when electron sharing provides an attractive force between the atoms.*

The covalent bond is the classical electron pair or homopolar bond of chemistry, particularly of organic chemistry. It is a strong bond: the bond between two carbon atoms in diamond with respect to separated neutral atoms is comparable with the bond strength in ionic crystals. The covalent bond has strong directional properties. The covalent bond is formed by one or more electron pairs, one electron from the valence shell each atom participating in the bond. The electrons forming the bond tend to be localized in the region between the two atoms joined by the bond. The spins of the two electrons in the bond are antiparallel.

The covalent bond can be explained best with the help of the hydrogen molecule H_2 . The two $1s$ orbitals can overlap and form an energetically favorable state. The strongest configuration occurs if the spins are antiparallel. The spin-dependent Coulomb energy is termed the exchange interaction. Covalent bonds are also formed in complex molecules.

Depending on the relative electronegativities of the atoms involved, covalent bonds can be classified as

- "pure" in covalent bonds. (eg. C-H bonds), where the difference in electronegativities is very small (0.35 Pauling units)
- "polar" (eg. C-F bonds), where the difference in electronegativities is very large (1.43 Pauling units in this case)

When the difference in electronegativities becomes very large, the electrons all reside with one atom, a charge separation is formed and the bond is ionic.

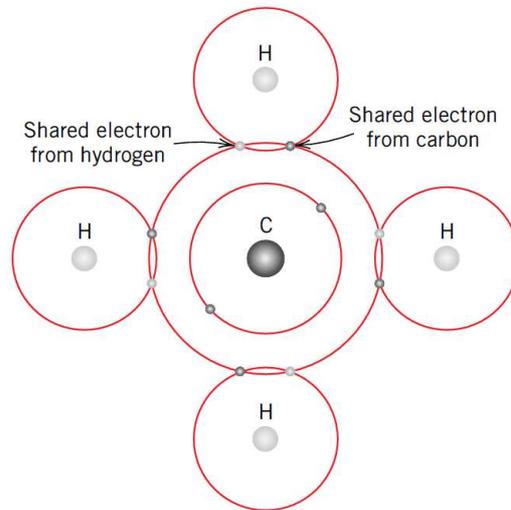


Figure 6: Schematic representation of covalent bonding in a molecule of methane.

Diamond bonding

Due to directional properties of covalent bonds. The ground state of C is $1s^2 2s^2 2p^2$, but in molecules one finds the configuration $1s^2 2s^1 2p^3$ (requires 4 eV). The energy required to promote the orbitals to the sp^3 hybrid orbitals is more than compensated for by the lower energy state of the bonded molecules. The related overlapping is called *hybrid* and results in a modified electron distribution. Such a configuration leads to low filling of space (0.34) compared to the closed-packed structure (0.74). Note that carbon plays a crucial role in biology and silicon in geology and semiconductor technology.

3.3.3 Metallic bonding

Combination of electrostatic attraction between ion cores and conduction electrons and inter-ion repulsion leads to a net attraction. This bonding is less strong than covalent and ionic ones. The characteristic feature of metallic binding is the lowering of the energy of the valence electrons in the metal as compared with the free atom. In the transition metals there is additional binding from inner electron shells.

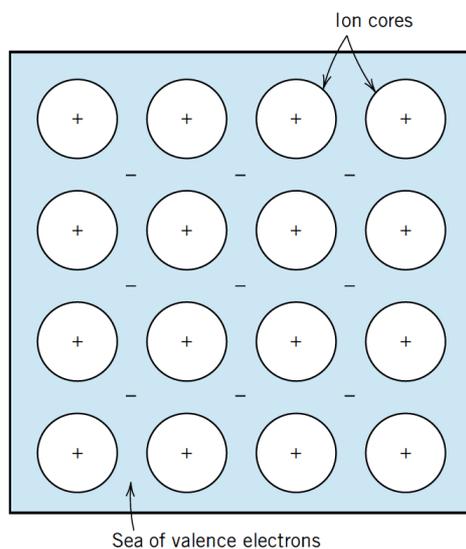


Figure 7: Schematic illustration of metallic bonding.

3.3.4 Van der Waals-London Interaction

- *type of weak bonding when polarised atoms or molecules provide electrostatic attraction.*

This is called the van der Waals interaction, known also as the London interaction or the induced dipole-dipole interaction. Fluctuations in the electron shell surrounding the atomic nucleus lead to transient induced dipole moments. The induced moments cause a transient attractive interaction between the atoms or molecules. It is the principal attractive interaction in crystals of inert gases and also in crystals of many organic molecules.

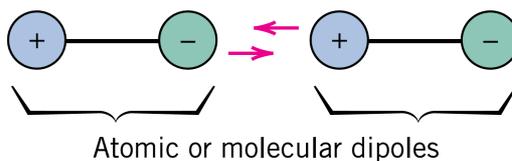


Figure 8: Schematic illustration of van der Waals bonding between two dipoles.

3.3.5 Rest valence bonds

- The strongest rest valence bond is the hydrogen bond between molecules, which may have very different size.

Because neutral hydrogen has only one electron, it should form a covalent bond with only one other atom. It is believed that the hydrogen bond is largely ionic in character. 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. The atoms adjacent to the proton are so close that more than two of them would get in each other's way; thus the hydrogen bond connects only two atoms. The hydrogen bond is an important part of the interaction between H_2O molecules and is responsible together with the electrostatic attraction of the electric dipole moments for the striking physical properties of water and ice. It is important in certain ferroelectric crystals, and is the main force that holds together the two strands of our DNA double helix.

- Weaker bonds are the dispersion forces between multipoles and oriented forces between permanent dipoles. Dispersion forces act between multi-poles exchanging the valence electrons. Permanent dipoles are generated by asynchronous oscillations of positively charged nucleus and valence electrons. Because the dipoles are always oriented anti-polar, one terms such dipole-dipole interactions as oriented forces/bonds. They are strongly temperature dependent, since phonons disturb the resonances.
- Dispersion and oriented forces between permanent dipole and within an ion induced dipole.
- Induced bonds between permanent dipole and induced dipoles within neutral atoms.

However, if a hydrogen is covalently bond to an O, F or N, it has a positive dipole moment because of the strong electronegative nature of O, F and N.

This positive dipole moment can form a strong attractive force with another O, F or N atom, with a bond energy of 0.1 eV.

Type of bond	Electrical properties	Thermal properties	Mechanical properties
Ionic bond	In general, do not contain free electrons: \Rightarrow insulators, electric conductivity is poor, transparent. But solutions are conductive. The conductivity highly depends on electron conductivity and lattice conductivity (lattice oscillations).	Do not contain free electrons \Rightarrow heat conductivity is poor, high temperature stability.	Transparent, large Young's modulus, brittle (but there are some exceptions), difficult to deform, flat cutting edges, relatively low chemical reactivity.
Covalent bond (almost all organic molecules)	In general, insulating properties, diamagnetism. But can be conductive due to defects (ion migration).	Extremely high melting point.	Hardness (diamond is extremely hard), transparency. But depend on lattice orientation.
Metal bond	Freely moving electrons \Rightarrow electrical conductivity.	Freely moving electrons \Rightarrow heat conductivity.	Close-packed structures \Rightarrow easy, plastic deformation.
Weak bonds	Electrical conductivity. For example graphite which can conduct electricity, but only in one direction (direction of weak bonds between layers).	Heat conductivity.	Easy to deform, but also easy to destroy.

- **Ionic bond**

Electrical properties: In general, do not contain free electrons: \Rightarrow insulators, electric conductivity is poor, transparent. But solutions are conductive. Their conductivity highly depends on electron conductivity and lattice conductivity (lattice oscillations).

Thermal properties: Do not contain free electrons \Rightarrow heat conductivity is poor, high temperature stability.

Mechanical properties: Transparent, large Young's modulus, brittle (but there are some exceptions), difficult to deform, flat cutting edges, relatively low chemical reactivity.

- **Covalent bond (almost all organic molecules)**

Electrical properties: In general, insulating properties, diamagnetism. But can be conductive due to defects (ion migration).

Thermal properties: Extremely high melting point.

Mechanical properties: Hardness (diamond is extremely hard), transparency. But depend on lattice orientation.

- **Metal bond**

Electrical properties: Freely moving electrons \Rightarrow electrical conductivity.

Thermal properties: Freely moving electrons \Rightarrow heat conductivity.

Mechanical properties: Close-packed structures \Rightarrow easy, plastic deformation.

- **Weak bonds**

Electrical properties: Electrical conductivity. For example graphite which can conduct electricity, but only in one direction (direction of weak bonds between layers).

Thermal properties: Heat conductivity.

Mechanical properties: Easy to deform, but also easy to destroy.