

3. CRYSTAL BINDING (K p. 49-73).

Aim: To understand the various types of crystal binding occurring in solid materials. To answer the question: "What holds a crystal together?"

In order for a crystal to hold together there must exist attractive interactions. This is common for all solids; it is an electrostatic attraction between positive and negative charges. As the atoms come close together their closed electron shells will start to overlap. The Pauli principle says that each electron state can be occupied by only one electron. In order to have overlap of closed shells, electrons have to be excited to higher states. This costs energy and leads to a repulsive interaction between the atoms. The repulsive interaction dominates for short distances between atoms, while the attractive interaction dominates at large distances. The actual atomic spacing in a crystal is defined by the equilibrium where the potential energy exhibits a minimum.

The **cohesive energy** is the energy that must be added to the crystal to separate it to neutral free atoms at rest, at infinite separation. For ionic crystals the term **lattice energy** is used instead; the definition is similar except that the energy is defined relative free ions at rest at infinite separation.

Depending on the distribution of the outer electrons with respect to the ions, different binding types can occur. We will treat four types, using simple models that give a good approximation to atomic distances and cohesive energies.

A. van der Waals interaction (K p. 53-60).

This type of binding is exhibited by solid noble gas crystals. The outermost electron shell is completely filled and the electron distribution is spherically symmetric. Each atom is neutral and has no permanent dipole moment.

The attractive force between the atoms arises from fluctuations in the electron distribution. These give an instantaneous fluctuating dipole moment in the atom. Its interaction with induced dipole moments in the neighbouring atom leads to a weak interaction.

Kittel gives a complicated quantum mechanical derivation, but the simple classical model below gives the same result. Here R is the distance between the atoms.

The dipole moment in atom 1 (p_1) gives rise to the electric field $E = 2p_1 / (4\pi\epsilon_0 R^3)$

The induced dipole moment of atom 2 becomes $p_2 = \alpha E$, where α is the polarisability.

From electrostatics we know the interaction energy between two dipoles. Assuming they are parallel we obtain $U(R) = -2p_1 p_2 / (4\pi\epsilon_0 R^3) = -A/R^6$, the constant A does not depend on R .

For the repulsive term a direct calculation is very complicated and one usually resorts to empirical formulae such as $U(R) = B/R^{12}$. When this is summed with the attractive term above, we obtain the **Lennard-Jones potential** (K p. 58). This is the potential for an atom pair.

Now we can calculate the cohesive energy of the crystal of N atoms. This is done by summing the Lennard-Jones potential over all atom pairs in the crystal (K p. 58-59). It is illustrative to do it in two steps:

1. Sum up the interactions between atom i and all other atoms j.
2. By taking each atom as the reference atom i, we obtain N/2 identical terms. The factor 1/2 occurs so that we will not count each atom pair twice.

The sums over the lattice sites arising in step (1) can be carried out numerically. The equilibrium distance between two atoms can be calculated by putting the derivative of $U_{\text{tot}}(R)$ equal to zero. This distance corresponds to a minimum in $U_{\text{tot}}(R)$ at $R=R_0$. The cohesive energy can then be evaluated as $U(R_0)$. Using gas-phase data for the constants in the potential gives very good agreement with experiment for the equilibrium interatomic distance and the right order of magnitude for the cohesive energies. They are of the order of 0.02 - 0.2 eV/atom.

B. Metallic binding (K p. 69-70).

In metals the outer electrons can move freely within the solid and are called conduction electrons. One may say that the electrons are shared between all the atoms.

We treat a simple model of a free electron gas surrounding the positive ion cores. Assume a spherical electron distribution within a radius R (the "radius" of the Wigner-Seitz cell). The potential at distance r from the ion can be written as

$$\Phi(r) = q(r)/4\pi\epsilon_0 r, \text{ where } q(r) = e - e(r/R)^3 \text{ is the charge within } r.$$

The potential energy of a thin spherical shell at distance r from the ion is

$$dU_A = \Phi(r) dq = \Phi(r) 4\pi r^2 \rho dr. \text{ Here } \rho \text{ is the charge density and } dq \text{ is the charge in the shell } dr.$$

Inserting $\Phi(r)$ into this expression and integrating it from 0 to R we obtain:

$$U_A(R) = - 9e^2 / 40\pi\epsilon_0 R.$$

This is the potential energy due to the net attraction between the ions and the conduction electrons. It takes into account both ion-electron and electron-electron interactions. We need also the repulsive term which is due to quantum mechanical effects. It can be approximated by the kinetic energy of the electron gas. As shown later in the course it is given by (m is the electron mass):

$$U_R(R) = 3(h/2\pi)^2 (9\pi/4)^{2/3} / (10 m R^2).$$

We can now compute the interatomic distance and cohesive energy just as for the v.d. Waals solid. R_0 turns out to be the same for all metals. This is of course due to the simplifications of the model, but the value, 2.6 Å, is very close to the interatomic distances of free electron like metals such as Au and Cu. The computed cohesive energy, about 5 eV/atom is of the right order, but a little too high (Cu: 3.5 eV; Au 3.8 eV). A more accurate computation must start from a detailed knowledge of the electronic structure of metals.

Most metals have close-packed structures: fcc, hcp but also bcc.

C. Ion binding (K p. 60-65).

Ion binding is treated in detail in Kittel so here we give only some brief remarks. The ions have closed electron shells and a spherically symmetric charge distribution. The origin of the lattice energy is the electrostatic attraction between the positive and negative ions. The attraction is given by a Coulomb potential, while the repulsive term often is modelled by an empirical exponential expression. We sum over the lattice in the same way as before for the v.d. Waals case. Instead of the lattice sums, the Madelung constant now enters into the final expression.

The computed lattice energy is of the order of 6 eV per ion pair. It is a strong interaction.

The structures of ionic compounds are determined to maximize the attractive interactions and minimize the repulsive ones. Negative ions are often larger than the positive ones. Hence the negative ions can occupy lattice positions in the close-packed structures, while the positive ones enter interstitial sites. In many cases the lattice is expanded so that the negative ions do not touch each other.

Ex: NaCl structure. fcc with basis of Cl^- at (000) and Na^+ in $(1/2, 1/2, 1/2)$. The positive ions occupy interstitial octahedral positions.

The figures below depict common crystal structures of ionic compounds.

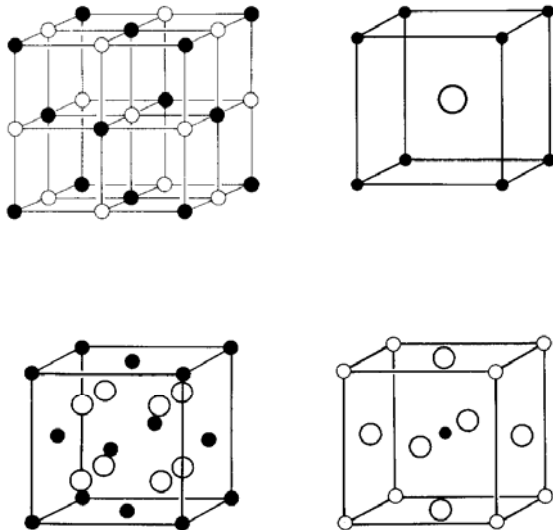


Fig. 1: Some common crystal structures of compounds:
Upper left: NaCl structure. Upper right: CsCl structure.
Lower left: Fluorite structure (ex. CaF_2).
Lower right: Perovskite structure (ex. BaTiO_3).

D. Covalent binding (K p. 67-69).

This is a strong binding, almost comparable to the ionic one. A pair of electrons with different spin directions is localized between the atoms and make up the bond. It is hence strongly directional in character.

In a two-atomic molecule (one electron per atom) the energy levels are split into a binding and an antibinding one. The two electrons are shared between the two atoms and fill the lowest, binding, molecular orbital. In a solid the energy levels are no longer discrete but the binding and antibinding levels become broad **energy bands**.

The structure of covalent crystals is determined by the direction of the bonds, they have often fewer nearest neighbour atoms (lower coordination number). See for example the diamond structure (C, Si, Ge), where the origin is the tetrahedrally oriented bonds of these substances (K p. 16-17). The analogous structure for compounds is the so called ZnS-structure (K p.17-18).

Compounds where the atoms have different number of valence electrons exhibit a mixture of ionic and covalent binding. Ex: GaAs. Ga has 3 valence electrons and As has 5. On the average we have 4 electrons per atom which can be shared in tetrahedral bonds with neighbouring atoms. However if the bonds are to be symmetrical the Ga will be negatively charged and As positively charged. Hence partial ionic binding can not be avoided in this and similar cases.