Section 3: Crystal Binding

Interatomic forces

Solids are stable structures, and therefore there exist interactions holding atoms in a crystal together. For example a crystal of sodium chloride is more stable than a collection of free Na and Cl atoms. This implies that the Na and Cl atoms attract each other, i.e. there exist an attractive interatomic force, which holds the atoms together. This also implies that the energy of the crystal is lower than the energy of the free atoms. The amount of energy which is required to pull the crystal apart into a set of free atoms is called the *cohesive energy* of the crystal.

Cohesive energy = energy of free atoms – crystal energy

Magnitude of the cohesive energy varies for different solids from 1 to 10 eV/atom, except inert gases in which the cohesive energy is of the order of 0.1eV/atom (see table 1 in Kittel). The cohesive energy controls the melting temperature (compare table 1 and table 2 in Kittel).
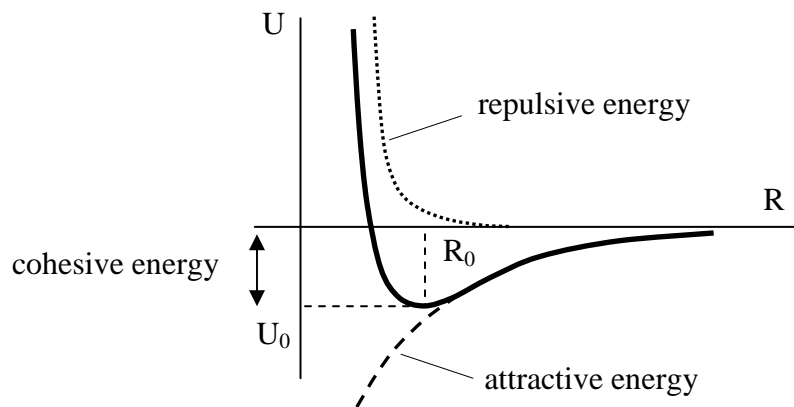

Fig.1

A typical curve for the potential energy (binding energy) representing the interaction between two atoms is shown in Fig.1. It has a minimum at some distance $R=R_0$. For $R>R_0$ the potential increases gradually, approaching 0 as $R\rightarrow\infty$, while for $R<R_0$ the potential increases very rapidly, tending to infinity at $R=0$. Since the system tends to have the lowest possible energy, it is most stable at $R=R_0$, which is *the equilibrium interatomic distance.* The corresponding energy U_0 is the cohesive energy.

A typical value of the equilibrium distance is of the order of a few angstroms (e.g. 2-3Å), so that the forces under consideration are short range.

The interatomic force is determined by the gradient of the potential energy, so that

$$F(R) = -\frac{\partial U}{\partial R} \ .$$
(3.1)

If we apply this to the curve in Fig.1, we see that $F(R)<0$ for $R>R_0$. This means that for large separations the force is *attractive*, tending to pull the atoms together. On the other, hand $F(R)>0$ for $R<R_0$, i.e. the force becomes *repulsive* at small separations of the atoms, and tends to push the atoms apart. The repulsive and attractive forces cancel each other exactly at the point R_0, which is the point of equilibrium.

The attractive interatomic forces reflect the presence of *bonds* between atoms in solids, which are responsible for the stability of the crystal. There are several types of *bonding*, depending on the physical origin and nature of the bonding force involved. The four main types are: *Van der Waals* (or *molecular*) bonding, *ionic* bonding, *covalent* bonding and *metallic* bonding.

Although the nature of the *attractive energy* is different in different solids, the origin of the *repulsive energy* is similar in all solids. The origin of the repulsive force is mainly due to the *Pauli exclusion principle*. The elementary statement of this principle is that two electrons cannot occupy the same orbital. As ions approach each other close enough, the orbits of the electrons begin to overlap, i.e. some electrons attempt to occupy orbits already occupied by others. This is, however, forbidden by the Pauli exclusion principle. As a result, electrons are exited to unoccupied higher energy states of the atoms. Thus, the electron overlap increases the total energy of the system and gives repulsive contribution to the interaction. The repulsive interaction is not easy to treat analytically from first-principles. In order to make some quantitative estimates it is often assumed that this interaction can be described by a central field repulsive potential of the form $\lambda \exp(-r/\rho)$, where λ and ρ are some constants or of the form A/R^n, where n is sufficiently large and B is some constant.

Van der Waals (molecular) bonding

First, we consider crystals of inert gases, which are characterized by *van der Waals (or molecular)* bonding. The electron distribution in such crystals is very close to that in free atoms. The noble gases such as neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe) are characterized by filled electron shells and a spherical distribution of electronic clouds in the free atoms. In the crystal the inert gas atoms pack together within the cubic fcc structure.

What holds atoms in an inert gas crystal together? Consider two inert gas atoms (1 and 2) separated by distance R. The average charge distribution in a single atom is spherically symmetric, which implies that the average dipole moment of atom 1 is zero: $\langle \mathbf{d}_1 \rangle = 0$. Here the brackets denote the time average of the dipole moment. However, at any moment of time there may be a non-zero dipole moment caused by fluctuations of the electronic charge distribution. We denote this dipole moment by $\mathbf{d}_1$. According to electrostatics this dipole moment produces an electric field, which induces a dipole moment on atom 2. This dipole moment is proportional to the electric field which is in its turn proportional to the d_1/R^3 so that

$$d_2 \sim E \sim \frac{d_1}{R^3}.$$

(3.2)

The dipole moments of the two atoms interact with each other. The energy is therefore reduced due to this interaction. The energy of the interaction is proportional to the product of the dipole moments and inversely proportional to the cube of the distance between the atoms, so that

$$-\frac{d_1 d_2}{R^3} \sim -\frac{d_1^2}{R^6}.$$

(3.3)

So we see that the coupling between the two dipoles, one caused by a fluctuation, and the other induced by the electric field produced by the first one, results in the attractive force, which is called the *van der Waals force*. The time averaged potential is determined by the average value of $\langle d_1^2 \rangle$ which is not vanish, even though $\langle \mathbf{d}_1 \rangle$ is zero.

$$U \sim -\frac{\langle d_1^2 \rangle}{R^6} = -\frac{A}{R^6}. \tag{3.4}$$

The respective potential decreases as R^6 with the separation between the atoms.

Van der Waals bonding is relatively weak; the respective cohesive energy is of the order of 0.1eV/atom.
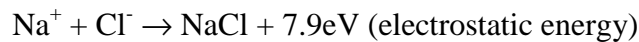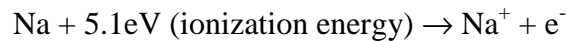
This attractive interaction described by Eq.(3.4) holds only for a relatively large separation between atoms. At small separations a very strong repulsive forces cause by the overlap of the inner electronic shells start to dominate. It appears that for inert gases this repulsive interaction can be fitted quite well by the potential of the form B/R^{12}, where B is a positive constant. Combining this with Eq.(3.4) we obtain the total potential energy of two atoms at separation R which can be represented as

$$U = 4\varepsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^{6} \right], \tag{3.5}$$
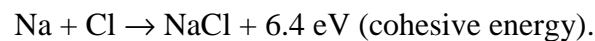
where $4\varepsilon\sigma^6 \equiv A$ and $4\varepsilon\sigma^{12} \equiv B$. This potential is known as Lennard-Jones potential.

Ionic bonding

The ionic bond results from the electrostatic interaction of oppositely charged ions. Let us take sodium chloride as an example. In the crystalline state, each Na atom loses its single valence electron to a neighboring Cl atom, producing Na^+ and Cl^- ions which have filled electronic shells. As a result an ionic crystal is formed containing positive and negative ions coupled by a strong electrostatic interaction.

$$Na + 5.1eV \text{ (ionization energy)} \rightarrow Na^+ + e^-$$

$$e^- + Cl \rightarrow Cl^- + 3.6eV \text{ (electron affinity)}$$

$$Na^+ + Cl^- \rightarrow NaCl + 7.9eV \text{ (electrostatic energy)}$$

The cohesive energy with respect to neutral atoms can be calculated as 7.9eV - 5.1eV + 3.6eV, i.e.

$$Na + Cl \rightarrow NaCl + 6.4 \text{ eV (cohesive energy)}.$$

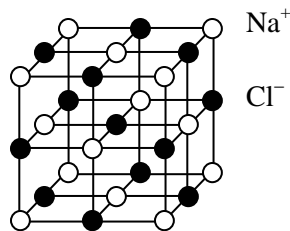The structure of NaCl is two interpenetrating fcc lattices of Na^+ and Cl^- ions as shown in Fig.2.

Na^+

Cl^-

Fig.2

Thus each Na^+ ion is surrounded by 6 Cl^- ions and vice versa. This structure suggests that there is a strong attractive Coulomb interaction between nearest-neighbors ions, which is responsible for the ionic bonding.

To calculate binding energy we need to include Coulomb interactions with all atoms in the solid. Also we need to take into account the repulsive energy, which we assume to be exponential. Thus the interaction between two atoms i and j in a lattice is given by

$$U_{ij} = \lambda\, \mathrm{e}^{-r_{ij}/\rho} \pm q^2 / r_{ij}. \tag{3.6}$$

Here r_{ij} is the distance between the two atoms, q is the electric charge on the atom, the (+) sign is taken for the like charges and the (–) sign for the unlike charges.

The total energy of the crystal is the sum over i and j so that

$$U = \frac{1}{2}\sum_{i,j} U_{ij} = N\sum_{j}\left(\lambda\, \mathrm{e}^{-r_{ij}/\rho} \pm q^2 / r_{ij}\right). \tag{3.7}$$

In this formula ½ is due to the fact that each pair of interactions should be counted only once. The second equality results from the fact in the NaCl structure the sum over j does not depend on whether the reference ion i is positive or negative, which gives the total number of atoms. The latter divided by two gives the number of molecules N, composed of a positive and a negative ion. We assume for simplicity that the repulsive interaction is non-zero only for the nearest neighbors (because it drops down very quickly with the distance between atoms). In this case we obtain

$$U = N\left(z\lambda\, \mathrm{e}^{-R/\rho} - \alpha q^2 / R\right). \tag{3.8}$$

Here R is the distance between the nearest neighbors, z is the number of the nearest neighbors, and α is the *Madelung constant*:

$$\alpha = \sum_{j\neq i} \frac{(\pm 1)}{p_{ij}}, \tag{3.9}$$

where p_{ij} is defined by $r_{ij} \equiv p_{ij}R$. The value of the Madelung constant plays an important role in the theory of ionic crystals. In general it is not possible to compute the Madelung constant analytically. A powerful method for calculation of lattice sums was developed by Ewald, which is called *Ewald summation*. This method is described in the appendix B in the text and can be used for the numerical evaluation of the Madelung constants in solids.

Example- a one-dimensional lattice of ions of alternating sign as shown in Fig.3.

Fig.3

In this case

$$\alpha = 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} + \ldots\right] = 2\ln 2, \tag{3.10}$$

where we took into account the logarithm expansion into series $\ln(1+x) = \sum_{n=1}^{\infty} (-1)^{n-1} \frac{x^n}{n}$.

In three dimensions calculation of the series is much more difficult and cannot be performed so easy. The values of the Madelung constants for various solids are calculated, tabulated and can be found in literature.

Now we calculate the equilibrium distance between the nearest neighbors for the NaCl type lattice using Eq.(3.8). At the equilibrium the derivative dU/dR=0, so that

$$-\frac{z\lambda}{\rho}e^{-R_0/\rho}+\frac{\alpha q^2}{R_0^2}=0$$ (3.11)

and therefore

$$R_0^2\,e^{-R_0/\rho}=\frac{\alpha\rho q^2}{z\lambda}\ .$$ (3.12)

This relationship determines the equilibrium separation R_0 is terms of the parameters ρ and λ of the repulsive potential. Using Eq.(3.8) and Eq.(3.12) the cohesive energy per atom of the ionic solid can be written as follows:

$$U_0=\frac{\alpha N\rho q^2}{R_0^2}-\frac{\alpha Nq^2}{R_0}=-\frac{\alpha Nq^2}{R_0}\left(1-\frac{\rho}{R_0}\right)\ .$$ (3.13)

Let us estimate the magnitude of the cohesive energy in NaCl. The Madelung constant is α=1.75. The interatomic distance is $R_0=a/2\approx2.8$Å. The charge $q=e$. The repulsive interaction of has a very short range of the order of $\rho=0.1R_0$. As follows from Eq.(3.13)

$$\frac{U_0}{N}\approx-\frac{\alpha}{(R_0/a_0)}\frac{e^2}{a_0}\left(1-\frac{0.1R_0}{R_0}\right)\approx-\frac{1.8}{6}27\cdot0.9eV\approx-8eV$$ (3.14)

We see that the typical value of the binding energy per pair of atoms is about 8eV. This implies that ionic bond is very strong. Experimentally, this strength is characterized by the relatively high melting temperatures. For example, the melting temperature of NaCl is about 1100°, while the melting temperatures for the Na metal is about 400°.

Covalent bonding

The covalent bond is another important type of bond which exits in many solids. The covalent bond between two atoms is usually formed by two electrons, one from each atom participating in the bond. The electrons forming the bond tend to be partly localized in the region between the two atoms joined by the bond. Normally the covalent bond is strong: for example, it is the bond, which couples carbon atoms in diamond. The covalent bond is also responsible for the binding of silicon and germanium crystals.

Let me illustrate the appearance of the covalent bond by considering two atoms (e.g., hydrogen atoms), which are described by orbitals ψ_1 and ψ_2. The molecular orbital of the two atoms is a linear combination of the two orbitals. There are only two possibilities,

$$\psi_b=\psi_1+\psi_2$$ (3.15)
or

$$\psi_a = \psi_1 - \psi_2, \tag{3.16}$$

because symmetry considerations preclude any other linear combinations, since the distribution of electron charge must be symmetric with respect to the two atoms.
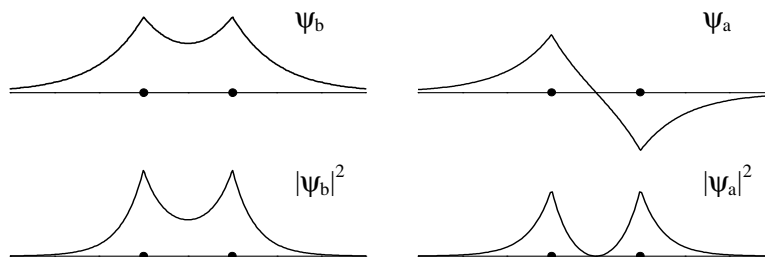

Fig.4

The molecular orbitals are sketched in Fig.4. This figure also shows the charge distribution given by $|\psi_b|^2$ and $|\psi_a|^2$. It can be seen that there is a sizable contribution to the charge density in the region between the nuclei for the symmetric orbital, while there is a zero density between the nuclei for the antisymmetric orbital.

The two orbitals have different energies as is illustrated in Fig.5, which shows the energy as a function of the interatomic distance.
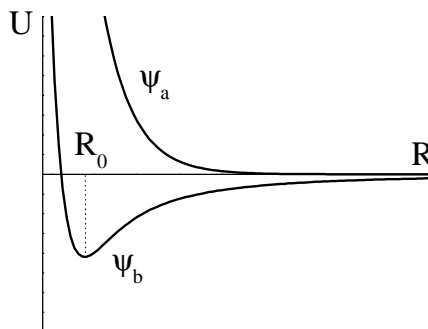

Fig.5

We see that the symmetric orbital has a minimum of energy at certain distance and has a lower energy than antisymmetric orbital. Thus, this is a *bonding* orbital which leads to a stable state of the molecule. The other orbital is called *antibonding* orbital, which has a minimum of energy at infinite separation of the atoms. This is a simple example of the covalent bonding between two atoms.

Note that spins of the two electrons which participate in bonding are antiparallel. This is a consequence of the Pauli exclusion principle which requires the total wave function of the system of electrons to be antisymmeteric with respect to any interchange of the coordinates of two electrons. In the case of the bonding state the orbital wavefunction is symmetric and therefore the spin contribution has to be asymmetric which means that the spins are antiparallel. On the other hand, the spins are parallel for the antibonding orbital. We see that The Pauli principle modifies the distribution of charge depending on the spin orientation of electrons. This spin-dependent contribution to the Coulomb energy is called *exchange interaction*. The simplest example of the covalent bond is a hydrogen molecule.

The covalent bond in solids has a strong directional properties. For example, carbon has four valence electrons $1s^2 2s^2 2p^2$ and form tetrahedral bonds with nearest neighbors, resulting in the diamond type structure. The carbon atom is positioned in the center of tetrahedron, the neighboring carbon atoms being at the vertices of the tetrahedron (Fig.6). Since there are four bonds joining the central atom to its neighbors, each C atom surrounds itself by eight valence electrons, which is a stable structure because the second shell is now completely full. Such tetrahedral coordination is also occurred for the Si and Ge – those elements, which can be found in the fourth column of the periodic table.
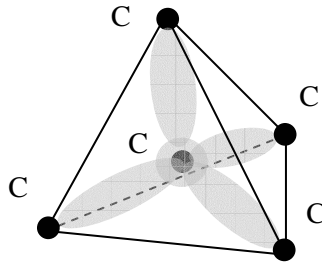

Fig.6

To explain the tetrahedron arrangement in diamond, we note that each C atom has four electrons in the second shell: two 2s electrons and two 2p electrons ($2s^2 2p^2$). The s states are spherically symmetric, whereas the p states represent charge distributions lying along x, y, and z coordinates. The energy difference between these states is not very big. It appears that it energetically favorable to excite one of the s electrons to p states so that the electronic configuration becomes $2s2p^3$. We can now construct the linear combinations of atomic orbitals:

$$\begin{aligned}
\psi_1 &= 1/2\left(s + p_x + p_y + p_z\right) \\
\psi_2 &= 1/2\left(s + p_x + p_y - p_z\right) \\
\psi_3 &= 1/2\left(s + p_x - p_y - p_z\right) \\
\psi_4 &= 1/2\left(s - p_x - p_y - p_z\right)
\end{aligned} \tag{3.17}$$

The densities corresponding to these orbitals are oriented along the tetrahedral directions (Fig.7). These orbitals is therefore a better representation of the electrons states that older s, p_x, p_y, p_z orbitals. The mixing of the s and p states in Eq.(3.17) is referred to as the sp-hybridization. The particular type of hybridization in diamond is known as sp^3 hybridization. The sp^3 hybridization occurs also in Si and Ge. In Si one 3s and three 3p states hybridized to form tetrahedral bonds. In Ge the sp^3 hybridization involves one 4s and three 4p electrons.

Concluding the discussion about ionic and covalent bonds, we note that that there is a continuous range of crystals between the ionic and covalent limits. In many cases it is important to estimate the extent a given bond is ionic or covalent. There are modern theoretical approaches that allow us to quantify the degree on ionicity and covalence in many solids.

Metallic bonding

Metals are characterized by a high electrical conductivity, which implies that a large number of electrons in a metal are free to move. The electrons capable to move throughout the crystal are called the *conductions electrons*. Normally the valence electrons in atoms become the conduction electrons in

solids. The main feature of the metallic bond is the lowering of the energy of the valence electrons in metal as compared to the free atoms. Below, some qualitative arguments are given to explain this fact.

According to the Heisenberg uncertainty principle the indefiniteness in coordinate and in the momentum are related to each other so that $\Delta x \Delta p \sim \hbar$. In a free atom the valence electrons are restricted by a relatively small volume. Therefore, Δp is relatively large which makes the kinetic energy of the valence electrons in a free atom large. On the other hand in the crystalline state the electrons are free to move throughout the whole crystal, the volume of which is large. Therefore the kinetic energy of the electrons is greatly reduced, which leads to diminishing the total energy of the system in the solid. This mechanism is the source of the metallic bonding. Figuratively speaking, the negatively charged free electrons in a metal serve as glue that holds positively charged ions together.

The metallic bond is somewhat weaker than the ionic and covalent bond. For instance the melting temperature of metallic sodium is about 400° which is smaller than 1100° in NaCl and about 4000° in diamond. Nevertheless, this type of bond should be regarded as strong.

In transition metals like Fe, Ni, Ti, Co the mechanism of metallic bonding is more complex. This is due to the fact that in addition to s electrons which behave like free electrons we have 3d electrons which are more localized. Hence the d electrons tend to create covalent bonds with nearest neighbors. The d electrons are normally strongly hybridized with s electrons making the picture of bonding much more complicated.