2. STRUCTURE AND BAND THEORY OF SOLIDS

Objectives:
Gain knowledge about structure of solids and crystal lattices of semiconductors.
Studies of band models of metals, semiconductors and insulators.

Content of the topic:
1. Types of bonds in solids.
2. Crystal lattices.
3. Imperfections of crystal structures.
5. Electron’s effective mass.
6. Band models of metals, semiconductors and insulators.
Interaction of atoms in solids

Many important properties of solids and existence of crystals are predetermined by forces between atoms.
Attractive forces and bonds between atoms arise in solids. Attractive forces have electrostatic nature.

Four types of bonds (ionic, covalent, metallic and molecular) can exist in solids.

In covalent binding the atoms share one or more pairs of electrons. The shared electrons circulate around the nuclei. They spent more time between the nuclei than they do on the outside. The result is an effective negative charge between the positive nuclei. This charge attracts the nuclei.

Carbon, silicon and germanium atoms can form covalent crystals, having diamond type crystal lattices.
In the diamond type crystal lattice each atom shares electron pairs with the four other atoms adjacent to it.
Interaction of atoms in solids

Because attractive force is electrostatic force, it increases, if the distance between acting charges decreases:

\[ F_{\text{atr}} = -\frac{q^2}{4\pi \varepsilon r^2} \]

… with a small distance between atoms, the repulsion force arises and increases rapidly, if the distance between atoms decreases. The repulsive force is due to crowding of electrons into too small volume.

At some distance \( r_0 \) between interacting atoms the sum of the attractive and repulsive forces becomes zero. So, atoms of a solid tend to take positions in which the distance between them is \( r_0 \). It is possible if the atoms of solids are in a regular array.

Three types of solids exist: amorphous, crystalline and polycrystalline solids. Further we will concentrate our attention on the crystalline solids or crystals.
Crystal lattices

The essential characteristic of crystal structures of solids is regularity in arrangement of atoms. According to this real crystals are modelled by crystal lattices. In a crystal lattice every atom has identical surroundings in three dimensional space.

Crystal lattices consist of unit cells.

If atoms are dislocated only in the lattice nodes or points, we have a simple (primitive) lattice. The simple cubic lattice has nodes lying only at the intersections of the network of axes.

The body-centred (volume-centred) cubic lattice has additional nodes at the cube centres. The base-centred cubic lattice has additional nodes at the centres of bases. Lastly, the face-centred cubic lattice has additional nodes at the centres of the cube faces.

... centred cubic lattices are at the same time primitive lattices.
Crystal lattices

... there are lattices that can be arranged only by translation of groups of atoms. Such a group of atoms is called a crystal lattice basis (base). The translation of the basis gives a lattice consisting of interpenetrating sublattices. One of them is displaced from the other.

The simple semiconductors (silicon and germanium) have the diamond type crystal lattice.

The basis of a diamond lattice consists of two atoms.

The crystal lattice of a simple semiconductor may be represented as two face-centred cubic lattices; one is put into another and shifted by 1/4 of the space diagonal of the unit cell.

Each atom of a simple semiconductor is surrounded by four others that occupy the corners of a regular tetrahedron.
Crystal lattices

A three-dimensional model of the silicon structure is too cumbersome for most discussions.
It may be replaced by a two-dimensional representation.

The compound semiconductors have *zinc blend* or *sphalerite* lattice.
Each atom of the compound semiconductor is surrounded by four atoms of another element.
Structure of crystals. Crystallographic indices

The disposition of nodes and the crystal properties along different directions are different. Therefore it is necessary to find a convenient way to specify the orientation of crystal planes and directions. We can describe the disposition of a node by three coordinates $x = ma$, $y = nb$, and $z = pc$. But, if the lattice constants $a$, $b$, $c$ are known, it is enough to specify integers $m$, $n$, $p$. The set of the integers in double square brackets $[[m n p]]$ is the crystallographic index of the node.

The direction in the crystal can be specified by the vector, going from the origin of the coordinate system.

The direction is determined by the first node in the direction of the vector and is indicated by the bracketed index of the node: $[m n p]$. 
Structure of crystals. Crystallographic indices

The crystallographic indices of the plane are obtained using the following procedure:

- Determine the intercepts of the plane on the three crystal axes.
- Measure the distances of the intercepts from the origin in multiples of the lattice constants.
- Take the reciprocals of the intercepts.
- Reduce the reciprocals to the smallest integers that are in the same ratio.

The calculation is based on the basic equations (intercept and normal forms) of a plane:

\[
\frac{x}{m} + \frac{y}{n} + \frac{z}{p} = 1; \\
hx + ky + lz = D;
\]

Here \( D \) is the common denominator.

In the cubic system the direction is always perpendicular to the plane having the same indices.
Imperfections in crystal structures

Real crystals differ from ideal crystals. Imperfections or defects exist in real crystals. Lattice vibrations cause dynamic defects of the crystal lattice. The energy of lattice vibrations is given by

\[ W_k = \sum_i \hbar \omega_i \left(n_i + \frac{1}{2}\right) \]

... the energies of thermal vibrations of a crystal have a quantum character. The vibratory wave-particle entities are called phonons.

Point defects, line defects and surface defects are the main kinds of static defects of crystal lattices.

There are two types of the line defects: edge dislocations and screw dislocations.
Structure of solids. Problems

1. The diamond lattice constant is \( a \). Find the distance between the nearest atoms and the atomic radius.

2. Find coordinates of intersections of planes (213) ir (210) with coordinate axes \( x, y \) and \( z \).

3. Atomic mass \( A \), the constant of cubic lattice \( a \) and number of atoms \( N \) in a unit cell of a crystal are known. Derive the formula for calculation of material density.

4. Density of silicon is \( 2.33 \cdot 10^3 \) kg/m\(^3\), its atomic mass is 28. Number of atoms in a unit cell is 8. Find the lattice constant.
Energies of electrons in solids

Let us now examine what changes in the energies of electrons occur when atoms come together to form a solid.

Let us use simplified models for analysis. Let us begin with the strong bonding of two sodium atoms.

A sodium atom has 11 electrons. The electronic structure of a sodium atom is 1s^2 2s^2 2p^6 3s^1. If the distance between the atoms is relatively great, electrons of one atom are separated from another atom by high and wide potential barriers.

... Electrons of the atom cannot interact with electrons of the other one.
... The height of the potential barriers for electrons depends on the potential level.
Energies of electrons in solids

... If atoms approach, widths and heights of the barriers decrease.

At \( d = a \) the conditions for electrons in the lower states are essentially unchanged. But the state \( 3s \) belongs to both atoms. Electrons in the state \( 3s \) can move from one atom to another. They are free (unlocalized) in the system.

![Diagram showing energies of electrons in solids](image)

If the system consists of \( N \) atoms, \( N \) valence electrons exist.

... According to the Pauli’s exclusion principle only two electrons with different spin quantum numbers can occupy the state \( 3s \).

Way out of this situation is found assuming that the outer electrons of each atom in the crystal are affected by the neighbouring atoms.

The result is that the energy levels of each atom are disturbed slightly and the discrete energy states split in the crystal to form a band of allowed energy states.
Energies of electrons in solids

The split energy levels in solids form *allowed energy bands* in which the energy of electrons can change almost continuously. The allowed energy bands are separated by the forbidden regions, *forbidden energy bands* or forbidden energy gaps in which electrons cannot exist.

Thus, the energy spectrum of electrons in solids has the band structure.

The allowed energy bands in the crystal correspond to the allowed energy levels in the isolated atoms.

Similar results may be obtained mathematically solving the Schrödinger equation.
Energies of electrons in solids

Simplified mathematical model of a solid was proposed by Kronig and Penney. It consists of a regular one-dimensional array of square-well potentials.

According to the model the periodic field of atoms in a crystal is modelled by the periodic function.

If the height of the barriers is zero, the electron is free. In this case

\[ W_k = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m \lambda^2} = \frac{p^2}{2m} \]

Energy spectrum of a free electron is continuous.
Energies of electrons in solids

If the periodic barriers exist, the solution of the Schrodinger equation in the form of the $W-k$ or $W-p$ diagram becomes more complicate.

The curve $W_k(k)$ is not continuous.

According to the diagram, the allowed and forbidden energy bands exist for an electron in a solid.
Electron’s effective mass

Let us consider an electron moving in the crystal under the influence of an externally applied electric field.

\[
dW = F \, dx = F v_g \, dt \quad v_g = \frac{d\omega}{dk} \quad \omega = \frac{W}{\hbar} \quad dW = \frac{1}{\hbar} F \frac{dW}{dk} \, dt
\]

\[
\frac{dk}{dt} = \frac{F}{\hbar} \quad a = \frac{d^2 W}{dt^2} = \frac{d^2 W}{dk^2} \, \frac{d^2 W}{dt \, dk} = \frac{1}{\hbar} \frac{d^2 W}{dk^2} \quad \frac{d^2 W}{d\omega \, dk} = \frac{1}{\hbar} \frac{d^2 W}{dk^2}
\]

\[
a = \frac{1}{\hbar^2} \frac{d^2 W}{dk^2} \quad F = \frac{F}{m_n}
\]

\[
m_n = \frac{\hbar^2}{d^2 W / dk^2}
\]

If the electron is free:

\[
W_k = \frac{\hbar^2}{2m} \quad k^2 = \frac{h^2}{2m \lambda^2} = \frac{p^2}{2m} \quad d^2 W / dk^2 = \hbar^2 / m
\]

\[
m_n = m \quad \text{... the effective mass of the free electron is the same as its mass } m.
\]
Electron’s effective mass

\[ W_k \]
\[ \frac{dW_k}{dk} \]
\[ \frac{d^2W_k}{dk^2} \]
\[ m_n \]

... In the allowed band the **effective mass of an electron in a crystal is not constant**. It can vary over a range from a few per cents of the electronic rest mass \( m \) to much greater than \( m \).

**Using the effective mass concept it is possible to treat an electron in a solid as a classical particle.** The electron-lattice interaction is included in the effective-mass term.

... We must notice that the effective mass of an electron in a crystal becomes negative at the top of the allowed band. Having a negative effective mass, the electron is accelerated in the direction of the electric field. So, it acts as a positive charge and is called a **hole**. We will see later that holes correspond to the unoccupied electron states at the top of the allowed band.
Band models of solids

Let us begin with lithium. A lithium atom has 3 electrons. Its electronic structure is given by $1s^22s^1$.

If the distance between the lithium atoms decreases, the energy levels split, and the allowed energy bands, corresponding to allowed energy levels, appear.

Two electrons may be in the state $2s$ in an atom. So the energy band $2s$ is only partially occupied by electrons. There are unoccupied levels over the occupied levels in the band $2s$. 
Band models of metals

Beryllium electronic structure is given by $1s^22s^2$. So the state $2s$ in a beryllium atom is completely occupied by electrons. But we must have in mind and estimate that the allowed level exists over the level $2s$. It is unoccupied (empty) in isolated atoms. When atoms become closer to form a crystal, energy bands $2s$ and $2s$ overlap. As a result, the hybrid allowed energy band appears. It is only partially occupied by electrons.

Both materials (lithium and beryllium) are conductors. So partially filled energy band is a characteristic feature of the band structure of conductors.

... Energy levels are filled in the band up to some level $W_F$, above which there are many empty states.

... Because properties of conductors are defined by the processes that take place only in the surroundings of the energy level $W_F$, usually we use the simplified energy diagram of conductors.
Band models of semiconductors and insulators

Now let us take such materials as carbon C (having a diamond lattice), silicon Si and germanium Ge. Electronic structures of atoms of these materials are given by:

C: 1s²2s²2p²  
Si: 1s²2s²2p⁶3s²3p²  
Ge: 1s²2s²2p⁶3s²3p⁶3d¹⁰4s²4p²

Eight electrons can occupy the levels s and p in an isolated C, Si and Ge atom. So there are 4 unoccupied states in each atom.

When the atoms form crystals, valence electrons go into covalent bonds. Two common electrons for each two neighbour atoms appear. As a result each atom in a diamond crystal is linked with 8 electrons and all states in the allowed valence band are occupied by electrons.
Diamond is insulator. Silicon and germanium are semiconductors. According to the analysis the completely full valence band is the characteristic feature of the band structure of insulators and semiconductors. A forbidden energy band and an empty band, the conduction band, exist over the valence band.

... The band structure of semiconductors is similar to that of insulators. These band structures differ in the width of the forbidden band. The width of the forbidden gap of semiconductors is much smaller than for insulators. It is of the order of 1 eV.

If the temperature increases, the vibration of the crystal lattice also increases. At room temperature there are electrons in the valence band that can have energy to jump to the conduction band. When electrons appear in the conduction band, we have a situation similar to that in conductors. There are energy levels occupied by electrons and empty states over them. So electrons in the conduction band can carry charge in a crystal and current flow becomes possible.

It is not necessary to show the full band diagram of a semiconductor. The properties of a semiconductor are defined by the processes between the top of the valence band and the bottom of the conduction band.

\[ \Delta W = W_c - W_v \]
Electrons in solids. Problems

1. What changes in the energies of electrons occur when atoms come together to form a solid?
   • Draw and explain the energy level diagrams for a conductor.
   • Draw and explain the energy level diagrams for semiconductor and insulator.
   • The lattice constant of silicon is 0.542 nm. A unit cell contains 8 atoms. Find the number of valence electrons in a unit volume.