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**DEPARTMENT OF METAL TECHNOLOGY AND MATERIALS
SCIENCE NAMED AFTER O. M. PETRYCHENKO**



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SOLID STATE CHEMISTRY

Lecture Notes

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INTRODUCTION

Solid state chemistry is a fundamental discipline that shapes scientific understanding of the nature of the chemical bond, the electronic structure of solids, and their relationship with physicochemical properties. The course covers research methods, as well as the thermodynamics and kinetics of phase transformations.

In developing and modifying modern materials, specialists constantly encounter complex chemical reactions and physicochemical processes. Most materials are studied at many levels: from the crystal structure and defect structure to the electronic, magnetic and nanoscale structure. For example, the different crystalline forms of carbon (diamond, graphite, graphene) have the same chemical composition but radically different properties, which is explained by the different symmetry of their bonds and electron shells. Knowledge of solid state chemistry and physics is therefore an essential foundation for the training of future materials engineers.

LECTURE 1

SYMMETRY OF SOLIDS

1.1 CRYSTAL SYMMETRY

In crystalline solids, the constituent particles (atoms, molecules, ions) are arranged regularly in three-dimensional space. In single crystals this regularity extends throughout the entire volume of the solid, whereas polycrystalline specimens contain regular regions – grains – whose dimensions considerably exceed the distances between the microparticles. At the boundaries between these regions, the orientation of the regular structure changes abruptly.

The differences in the geometric shapes of the crystals of various substances are associated with the symmetry features of their crystal lattices. The most important symmetry elements are axes, planes and the centre of symmetry.

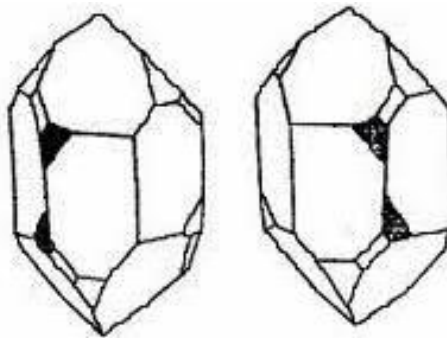


Figure 1.1

The regular arrangement of the microparticles forming a crystal is represented as a crystal lattice, i.e. a network of points regularly repeated in space, which are called lattice sites (nodes). The centres of the particles (hereinafter, atoms) forming the crystal are located at these sites.

If the crystal lattice coincides with itself upon rotation through a certain angle about an imaginary axis, this indicates that the crystal possesses an axis of symmetry. An n -fold axis of symmetry is an imaginary straight line about which a rotation through the angle $\alpha = 360^\circ/n$ brings all parts of the crystal into coincidence with their initial position. If a crystalline solid has several axes of symmetry, the one with the largest n is called the principal axis of symmetry.

The absence of five-fold, seven-fold and higher-order symmetry axes in crystals is a consequence of the requirement that the crystal be filled completely (i.e. without voids).

If we consider a plane perpendicular to the possible symmetry axes, it can be completely filled with squares (rotation about the axis through 90°), equilateral triangles (rotation through 120°), parallelograms (rotation through 180°) or hexagons

(rotation through 60°). A rotation through 360° returns any figure to its initial position. Rotations through any other angles do not fill space completely. Symmetry of this kind is observed in quasicrystals, which include solid metallic alloys and other bodies with long-range order whose diffraction peaks are arranged with non-crystallographic symmetry.

If one or several planes can be drawn through a crystal in such a way that one part of the crystal lattice is the mirror image of the other, the crystal possesses planes of symmetry.

The reflection operation is denoted by δ . Sometimes δ is given a subscript indicating the position of the plane relative to the principal axis: δ_h for a horizontal plane and δ_v for a vertical plane. If the reflection plane passes through a diagonal axis, it is denoted δ_d (diagonal). All these planes are shown, as an example, for the principal axis C_4 in Fig. 1.2.

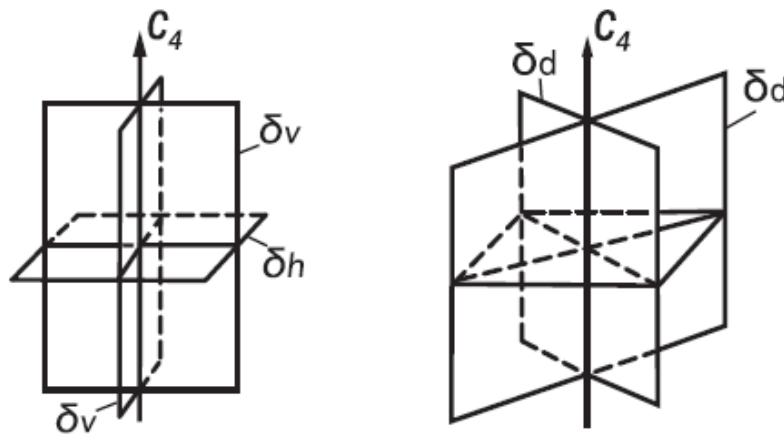


Figure 1.2

A centre of symmetry is a point inside a body at which all straight lines connecting points on opposite bounding surfaces of the body intersect and are bisected. A simple figure with a centre of symmetry (point O) is shown in Fig. 1.3. The segments OA_1 and OA_2 are equal for any position of the straight line A_1OA_2 .

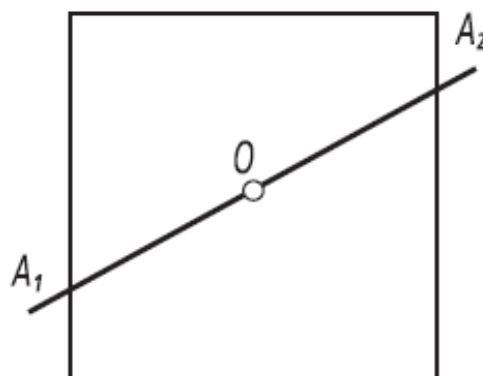


Figure 1.3 – Figure with a centre of symmetry

The fundamental property of a crystal structure and of the space lattice characterising it is infinite periodicity: any two lattice sites can be brought into coincidence by a translation, i.e. a parallel displacement through a certain definite distance, which is called the translation period.

The combination of translations with planes and axes of symmetry gives rise to screw axes of symmetry.

A screw axis of symmetry is the combination of an axis of symmetry and a translation parallel to it acting together. Screw axes may be two-, three-, four- and six-fold. The order of the axis is equal to $360^\circ/\alpha$, where α is the minimum rotation angle in the symmetry operation. Right-handed and left-handed screw axes are distinguished. For a right-handed screw axis, displacement along the axis is associated with clockwise rotation, and for a left-handed axis, with counter-clockwise rotation.

Thus, crystalline solids simultaneously possess many symmetry elements. In 1890, E. S. Fedorov calculated all possible combinations of the symmetry elements of crystal lattices and established that the number of stable combinations is 230.

In his opinion, this number exhaustively characterised the entire diversity of possible crystal structures. However, the discovery of quasicrystals refuted the validity of this view.

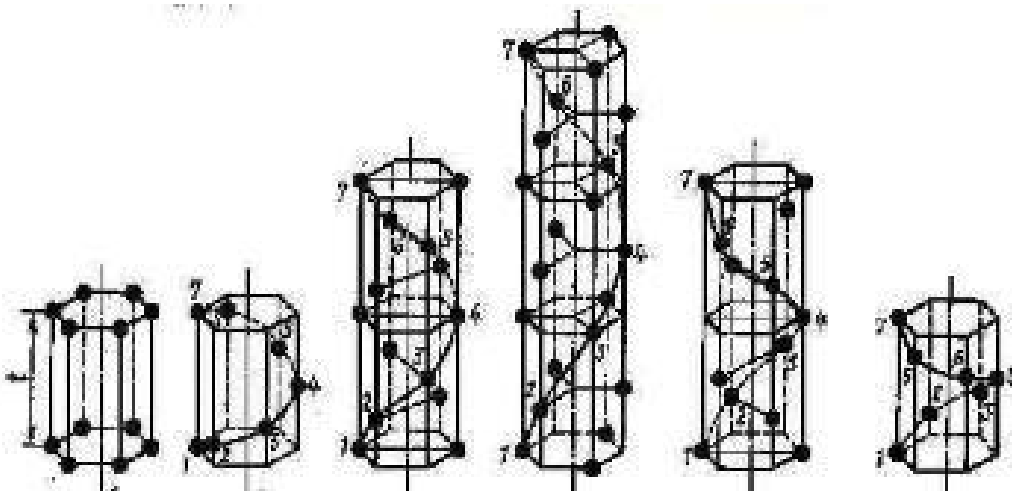


Figure 1.4

1.2 TYPES OF UNIT CELLS

When the spatial structure of a crystal is being determined, a simple structural unit – the unit cell – is mentally singled out. The most important parameters of a crystal are the shape and dimensions of its unit cell.

The lengths of the edges of the unit cell are defined as the equilibrium distances, along the characteristic axes, between the centres of the particles

occupying adjacent lattice sites; they are called the lattice constants or lattice parameters.

The unit cells of crystals are built on three vectors a , b , c , which are also called translations. For a complete description of a space lattice as a geometric three-dimensional body, it is necessary to specify the ratio of a , b , c and the angles α , β , γ between the corresponding edges of the unit cell. Depending on the relationship between the translation lengths a , b , c and the angles α , β , γ between them, seven crystal systems or six syngonies are distinguished.

The division into crystal systems is made according to the set of symmetry elements describing the crystal, whereas syngonies classify crystals according to the shape of their unit cell. Thus, since the trigonal and hexagonal crystal systems have a unit cell of the same shape, they are assigned to a single syngony, namely the hexagonal one. However, in the specialised literature the terms syngony and crystal system are often used as synonyms.

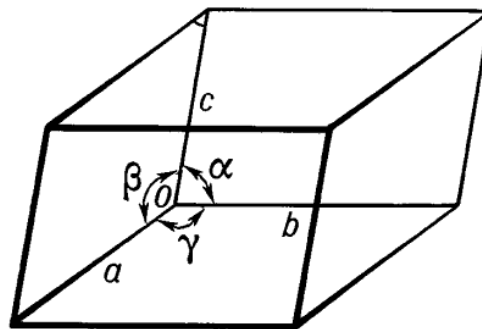


Figure 1.5

Proceeding from the idea of a periodic arrangement of the centres of gravity of spherical material particles in a crystalline substance, A. Bravais in 1848 described the entire diversity of crystal structures known to him by means of 14 types of lattices, which differ in the shape of their unit cells and are subdivided into crystal systems, or syngonies. These lattices were named Bravais lattices.

Three conditions are used to select a Bravais cell: the syngony of the chosen parallelepiped of repetition must correspond to the syngony of the entire lattice; the unit cell must contain the maximum possible number of right angles and equal edges; and the unit cell must have the minimum volume.

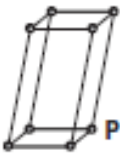
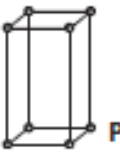
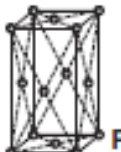
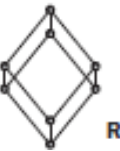
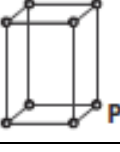
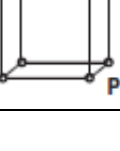
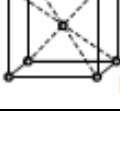
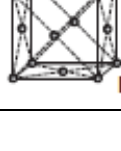
The types of Bravais lattices and their symbols are given in Table 1.1.

In the simplest case, atoms occupy positions at the vertices of the chosen parallelepiped. These are the so-called corner (nodal) atoms. If a unit cell contains only such atoms, it is called primitive.

In other cells, atoms may be located, in addition to the vertices, in the volume of the parallelepiped or on its faces. Such cells are classified as complex (non-primitive).

The lowest category (all translations unequal) includes: the triclinic system ($a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$); the monoclinic system ($a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$); and the rhombic, or orthorhombic, system ($a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$). The intermediate category (two of the three translations equal) includes: the tetragonal system ($a = b \neq c, \alpha = \beta = \gamma = 90^\circ$); the trigonal system ($a = b \neq c, \alpha = \beta = \gamma \neq 90^\circ$); and the hexagonal system ($a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$). The highest category (all translations equal) includes the cubic system ($a = b = c, \alpha = \beta = \gamma = 90^\circ$).

Table 1.1

Crystal system	Lattice type, symbol			
	primitive	base-centred	body-centred	face-centred
Triclinic				
Monoclinic				
Orthorhombic				
Trigonal (rhombohedral)				
Tetragonal				
Hexagonal				
Cubic				

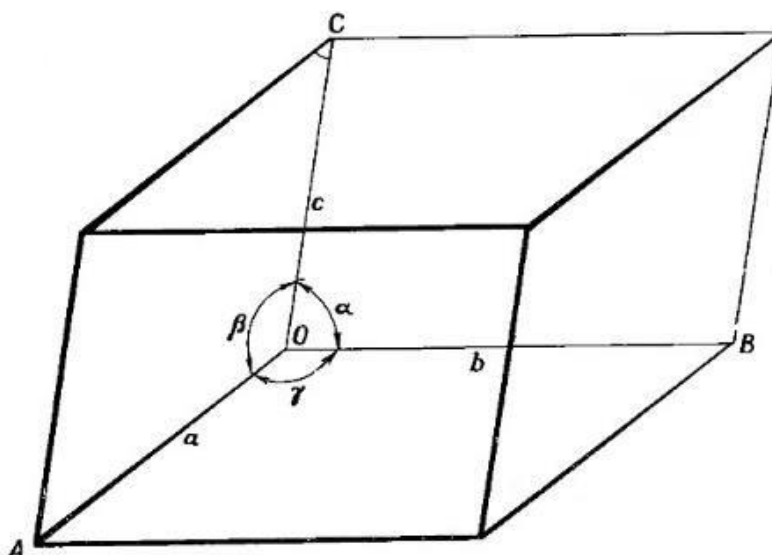


Figure 1.6

1.3 SYMMETRY IN QUASICRYSTALS

Quasicrystals are solids characterised by long-range order but with a symmetry that is forbidden in classical crystallography. Quasicrystals include solid metallic alloys and other bodies with long-range order whose diffraction peaks are arranged with non-crystallographic symmetry.

In 1984, D. Shechtman presented an electron diffraction pattern of a metallic phase with long-range orientational order but without translational symmetry in a rapidly quenched Al_6Mn alloy. This alloy was named shechtmanite. Subsequently, such structures came to be called quasicrystalline.

Hundreds of quasicrystalline systems based on Mn, Cu, Cd, Ni, Ti and other elements are known to date. Among the most popular and widely studied systems in which quasicrystalline structures form are aluminium-dominated compositions, namely Al–M alloys, where M denotes the transition metals Ni, Co, Fe and Cu.

Unlike the symmetry of the crystal lattices of periodically ordered crystals, which is based on the possibility of translating unit cells along the basis vectors so as to fill all space without gaps, quasicrystals lack translational symmetry. The translational symmetry of classical crystals imposes restrictions on the possible orders of their rotational symmetry, forbidding rotations about five-fold axes and axes of any order higher than six. Quasicrystals, by contrast, may possess symmetry axes of the orders forbidden in classical crystallography, i.e. non-crystallographic symmetry.

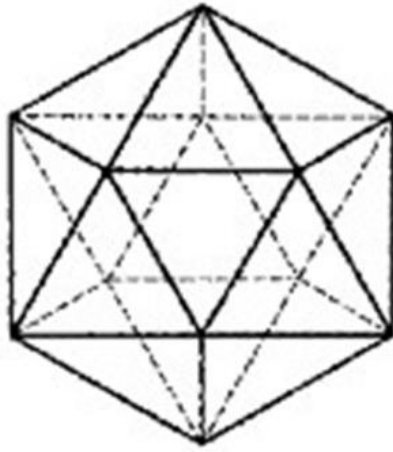


Figure 1.7

Icosahedral symmetry is characteristic of many quasicrystals. An icosahedron is a regular convex polyhedron. Each of its 20 faces is an equilateral triangle; it has 30 edges and 12 vertices.

Self-assessment questions

1. Explain the concept of a crystal lattice.
2. What are the principal axis of symmetry and the plane of symmetry of a crystal?
3. Describe the features of screw symmetry and right- and left-handed screw axes.
4. Describe the types of Bravais lattices.
5. What is the difference between the structure of a primitive and a complex crystal cell?
6. Name the distinguishing features of the three categories of crystal systems.
7. Describe the characteristic features of symmetry in quasicrystals and the features of their icosahedral symmetry.

LECTURE 2

CHEMICAL BONDS IN SOLIDS

The physicochemical and many other properties of solids are determined by the type of chemical bond between their constituent particles. According to the type of chemical bond, molecular, metallic, covalent, ionic and mixed crystals are distinguished.

The structural units of molecular crystals are molecules held together by electrostatic van der Waals forces.

Typical examples of such crystals are solid methane CH_4 , solid carbon dioxide CO_2 , and the noble gases argon Ar, neon Ne and others.

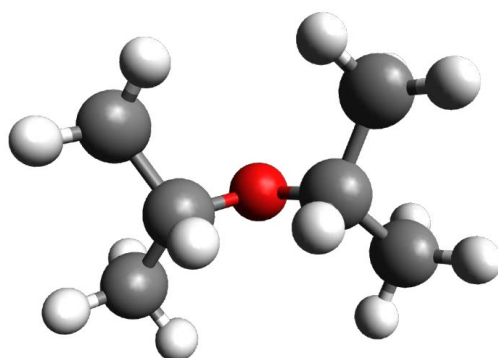


Figure 2.1

The main type of van der Waals forces responsible for molecular bonding is the dispersion forces, which arise from the instantaneous induction of electric dipole moments in atoms by the electric field of the dipole moments of neighbouring atoms, in which these moments are generated by changes in the instantaneous positions of the electrons.

The bond energy in molecular crystals is 0.08–0.11 eV. A special kind of molecular bond, the hydrogen bond, is stronger, amounting to 0.2–0.68 eV.

Under certain conditions, a hydrogen atom can be bonded fairly strongly to two other atoms. Having only one stable orbital, a hydrogen atom is able to form only one covalent bond, but also one hydrogen bond.

For example, in an ice crystal each water molecule is tetrahedrally bonded by hydrogen bonds to its four nearest molecules. A hydrogen bond is longer than a covalent bond; therefore, the structure of ice is not dense. The hydrogen bonds formed by the molecules are responsible for the density maximum of water (at 3.98 °C), its expansion on freezing and other properties of water.

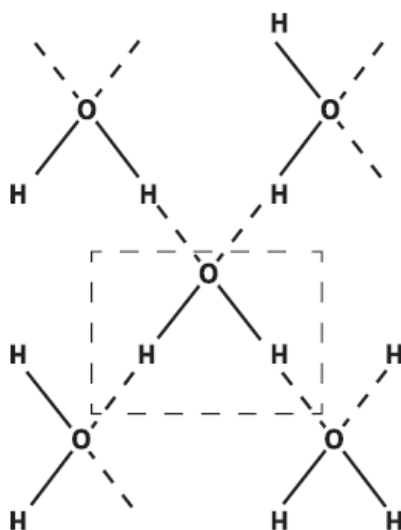


Figure 2.2

Metallic crystals. In the solid state, 98 known chemical elements exhibit metallic properties. These include all s-elements except hydrogen and helium, all d- and f-elements, and some of the p-elements:

- 6 in the group of alkali metals;
- 6 in the group of alkaline-earth metals;
- 38 in the group of transition metals;
- 11 in the group of light metals;
- 7 in the group of semimetals;
- 14 in the group of lanthanides + lanthanum;
- 14 in the group of actinides + actinium;
- beryllium and magnesium, outside any particular group.

Numerous alloys of these elements, including most known quasicrystals, also exhibit metallic properties. Positive metal ions are located at all sites of the crystal lattice of metallic crystals. Between them move the valence electrons detached from the outer electron shells of the atoms (called valence shells) during ion formation. The electrons act as a "cement", holding the positive ions together. At the same time, the electrons are held by the ions within the crystal lattice and cannot leave it. The chemical bond in metals is characterised by delocalisation, unsaturability and non-directionality. The energy of the metallic bond is 1.08–4.35 eV.

The density of most metals is high, which indicates a very close-packed structure of metallic crystals. Their high malleability and toughness indicate the absence of rigidity in the metallic structure.

Typical metallic properties are exhibited by elements that have a small number of valence electrons and, conversely, a large number of unoccupied orbitals in the outer quantum shell of their atoms. On crystallisation, the atoms of the substance are packed with the maximum possible density so that their unoccupied orbitals are filled

as completely as possible by the small number of available valence electrons of neighbouring atoms.

Covalent crystals. The structural units in crystal lattices of this type are atoms of one or of different elements, the bond between which is covalent and acts along all three characteristic axes. The covalent bond is characterised by localisation, directionality and saturability. Covalent crystals are comparatively few in number. Examples of crystals of this type are diamond, silicon, germanium, grey tin, and crystals of compounds such as quartz, silicon carbide, zinc sulphide and aluminium nitride.

The strength of the covalent bond is high, 1.5–12.5 eV.

Ionic crystals. The dominant mechanism of chemical bond formation in ionic crystals is the electrostatic Coulomb interaction – attraction between oppositely charged ions and repulsion between like-charged ions. The crystal lattices of ionic crystals consist of alternating positively and negatively charged ions, between which electrostatic forces of attraction act.

It is correct to regard an entire ionic crystal as a single giant molecule in which each ion experiences a significant influence from all the other ions. Ionic crystals are formed by the interaction of atoms with a large difference in electronegativity.

Ideally ionic compounds practically do not exist. In many ionic crystals, covalent and van der Waals forces act together with the electrostatic bonding forces.

The contribution of the latter can be neglected; however, the presence of covalency in an ionic crystal causes certain deviations in its physicochemical properties that cannot be explained by the electrostatic model.

The smallest influence of covalency is observed in the alkali metal halides.

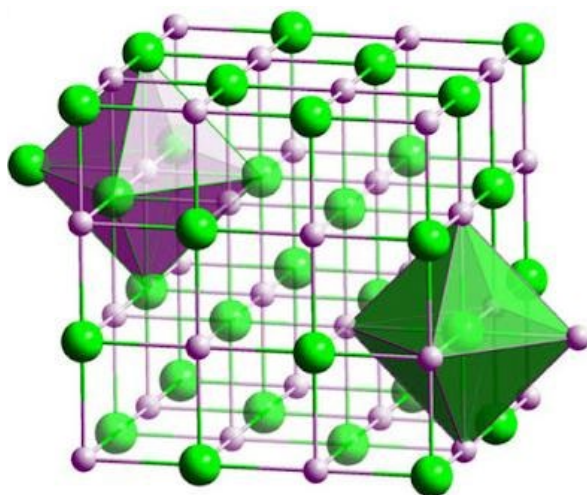


Figure 2.3

Examples of crystals in which the ionic type of bond predominates are NaCl, CaF₂, KF, etc. However, even in the alkali metal halides the degree of ionicity of the bond is 70–90 %. In most real compounds the bonds are ionic-covalent.

Ionic compounds may also contain complex ions, for example NO_3^- and SO_4^{2-} . In substances of ionic nature with polyatomic ions, the geometric shape of the ions distorts the spatial structure of the crystal.

Figure 2.4 shows the structures of the ionic crystals NaCl and CaCO_3 ; comparing them makes it possible to assess the degree of distortion of the crystal structure caused by the trigonal symmetry of the carbonate ion.

The ionic bond is very strong. The bond energy is 7.8–10.5 eV.

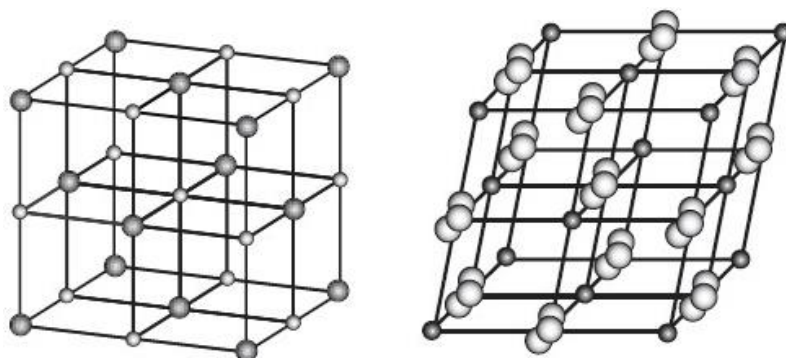


Figure 2.4 – Structures of the ionic crystals NaCl and CaCO_3

The bonding in real crystals never fully corresponds to one of the types described. An ionic bond always contains an element of covalent bonding, and in complex substances the bonds between different atoms may be of different types. Thus, in molecular crystals of the H_2O and HCl type, hydrogen bonding acts together with van der Waals forces.

In the graphite structure, the carbon atoms are bonded to one another by covalent bonds so as to form flat two-dimensional layers, whereas the bonding between the two-dimensional layers of graphite is provided by weak van der Waals forces. Thus, graphite is a molecular crystal in one direction and a covalent crystal in the other.

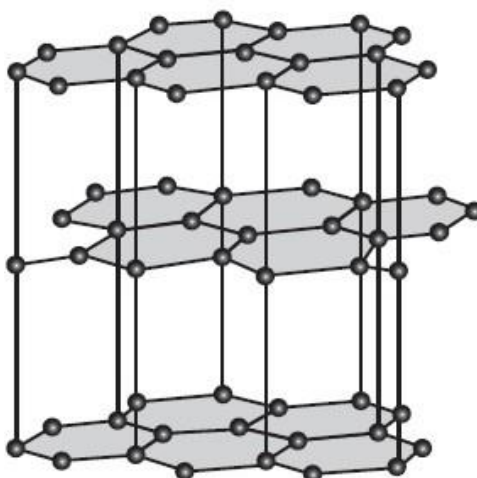


Figure 2.5

The distance between the graphite layers is fairly large, so other atoms or molecules can penetrate between them. This produces compounds called intercalation compounds, layered compounds or clathrates. Examples of such compounds are the graphite fluorides, in which fluorine atoms are inserted between the layers of the graphite lattice.

Crystal structures in which predominantly forces of one type act between all the atoms are called homodesmic, and those in which bonds of different types act are called heterodesmic.

Homodesmic structures are coordination structures in which the atoms are distributed uniformly throughout the crystal space. Examples of coordination structures are the structure of NaCl with ionic bonding, of diamond with covalent bonding, of crystals of the noble-gas elements with van der Waals bonding, and the structures of Cu, Mg and Fe with metallic bonding.

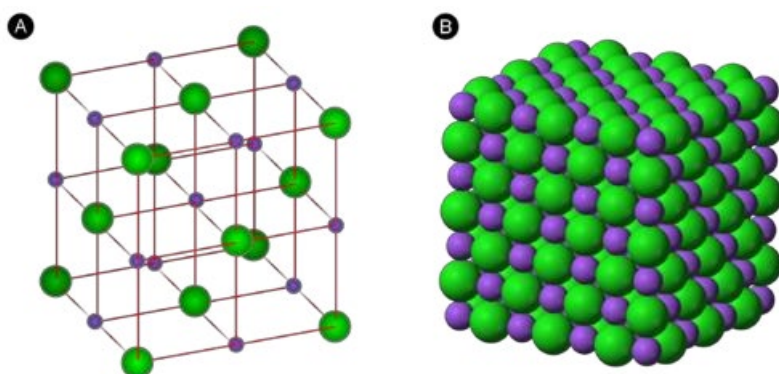


Figure 2.6

The types of heterodesmic structures are island, chain and layered structures.

Island structures consist of separate finite groupings (often molecules), within which one type of bond is realised and between which another type acts. For example, in calcite CaCO_3 the bond within the carbonate group CO_3^{2-} is covalent, whereas the bond between the anion CO_3^{2-} and the cation Ca^{2+} is predominantly ionic.

An example of a chain structure is the structure of selenium, in which covalent bonding is realised between Se atoms incorporated in chains, while the bonds between atoms of different chains are close to van der Waals bonds.

The structure of graphite is layered: covalent bonds (with an admixture of metallic bonding) are realised within a layer, and van der Waals bonds act between the layers.

Amorphous bodies, in particular those in the vitreous state (glasses), are solid-state systems of atoms and atomic groups predominantly with covalent bonds between them.

Self-assessment questions

1. List and explain the types of chemical bonds in solids.
2. What are the structural features of covalent crystals? Give examples.
3. What are the structural features of metallic crystals?
4. How do covalent crystals differ from ionic crystals?
5. Explain what causes the structural distortion of some ionic crystals.
6. Give examples of crystals with mixed chemical bonds. How does this affect the crystal structure?
7. What is the difference between homodesmic and heterodesmic crystal structures?
8. Describe the varieties of molecular bonding.

LECTURE 3

ELEMENTS OF CRYSTAL CHEMISTRY

3.1 GENERAL PRINCIPLES

Crystal chemistry studies the relationship between the chemical composition of crystalline solids and their structure, the spatial arrangement and chemical bonding of the microparticles in crystals, and the dependence of the properties of crystalline bodies of different chemical composition on their structure.

Crystal chemistry, like crystallography, considers ideal models that do not reflect the presence of structural defects, impurities and other structural features of real solids.

In the traditional description of crystal structures using the concept of the unit cell, account is taken of the type and dimensions of the unit cell, the arrangement of atoms in it, and the fact that the atoms forming the cell belong to it only in part, as shown in Fig. 3.1.

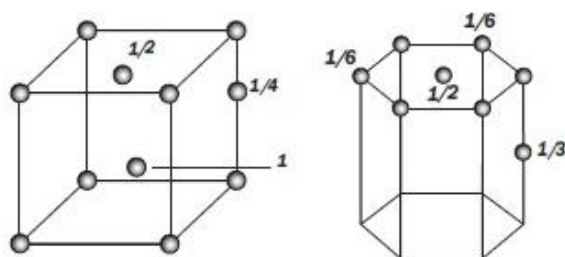


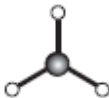
Figure 3.1

Information on the unit cell and the coordinates of the particles forming a crystal is not always sufficient to visualise the spatial structure of a solid. Therefore, a larger region of the crystal is considered, i.e. a certain number of unit cells is included, and the mutual arrangement of the atoms, their coordination numbers, interatomic distances, bond types, etc., are analysed. This approach makes it possible to compare different structural types of crystalline bodies.

The coordination number (CN) of a given atom (ion) is the number of nearest surrounding atoms (ions) of the same kind in the crystal lattice. If the centres of the nearest atoms are joined by straight lines, a coordination polyhedron (CP) is obtained. The atom or ion for which the coordination number is calculated is located at the centre of the coordination polyhedron. Clearly, the coordination polyhedron is in no way related to the external shape of the crystal and does not correspond to it.

Table 3.1

Type	Image	CN
Dumbbell		2

Type	Image	CN
Triangle		3
Tetrahedron		4
Octahedron		6
Hexahedron (cube)		8
Cuboctahedron		12

Each coordination number corresponds to its own coordination polyhedron, as shown in Table 3.1. The crystals of many substances have a similar spatial structure. If, in addition, their chemical nature is also similar, such substances are called isomorphous. If they are substances of different chemical nature, they are called isostructural.

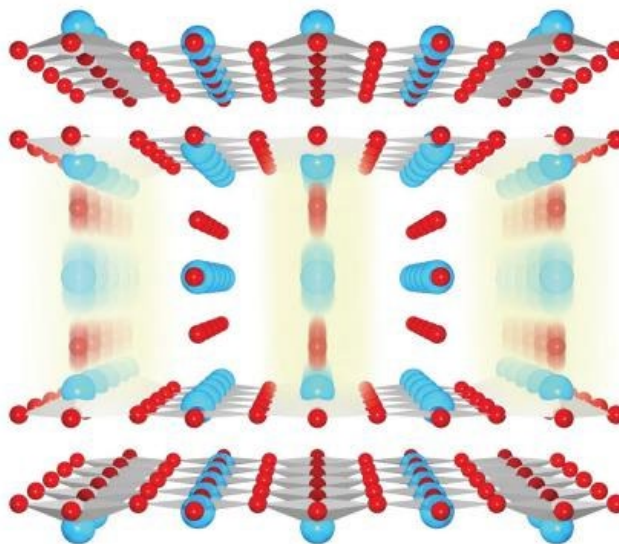


Figure 3.2

Some metals exhibit polymorphism, i.e. the ability to form structures of different types. Iron, for example, depending on temperature, can exist in the face-centred cubic (fcc) or body-centred cubic (bcc) modification; cobalt, in addition to

the fcc and hexagonal modifications, also forms other forms with a more complex alternation of close-packed layers.

In this case, a special kind of polymorphism is observed – polytypism, in which the structural differences between individual modifications (polytypes) appear in one direction only.

3.2 CLOSEST-PACKED STRUCTURES

Particles are arranged in space lattices so as to ensure the maximum bond energy possible for the given type of crystal, as well as the energetic homogeneity of the crystal as a whole.

Among the most informative approaches in crystal chemistry are descriptions of the structure of substances in the approximation of closest packing of spherical particles.

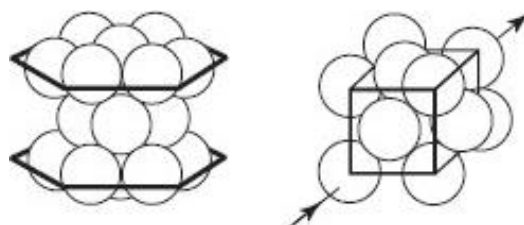


Figure 3.3

For spherical particles, the most favourable arrangement is often one in which each sphere is in contact with the largest number of nearest neighbours. Such spatial formations are called closest-packed structures.

In structures formed by spherical particles of the same size, closest packing can be realised in the form of two energetically equivalent modifications: hexagonal close-packed (hcp) and face-centred cubic (fcc, or, equivalently, cubic close-packed). The coordination number in each of these structures is 12, and the spheres themselves occupy 74 % of the crystal volume, which is the maximum possible for structures built of spheres of equal diameter.

Such structures are characteristic of most metals and alloys.

The structures of ionic, covalent and molecular crystals can also be described on the basis of the concept of closest packing. In structures without close packing, the packing fraction is less than 0.74.

Table 3.2

Lattice	Simple cubic	bcc	fcc	hcp	Diamond
Coordination number (CN)	6	8	12	12	4
Number of atoms	1	2	4	2	8
Packing density, %	52.4	68.0	74.0	74.0	34.0

If the particles forming a crystal are not spherical or differ in size, their closest packing is distorted. The coordination number then becomes less than 12, and the fraction of unoccupied volume in the crystal increases.

The close packing of spheres of equal size in a layer is shown in Fig. 3.4: each sphere, for example A, is in contact with the six spheres surrounding it.

Regular repetition of this motif produces infinite close-packed layers. In a close-packed layer, three close-packing directions (XX' , YY' and ZZ') are distinguished, along which rows of touching spheres are located; sphere A belongs simultaneously to all three rows.

The most efficient way of packing spheres in three dimensions is to stack close-packed layers one on top of another. Let us denote these layers A, B, C, etc. The simplest and at the same time most important stacking sequences are ABABAB and ABCABCABC. They correspond to the hexagonal close-packed (hcp) and the cubic close-packed (fcc) structures.

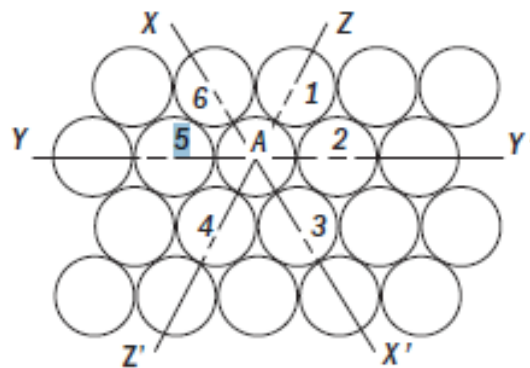


Figure 3.4

Six nearest "neighbours" lie in the same plane as the central sphere. The other six are located in the layers above and below this layer – three spheres in each layer. The hcp and fcc structures differ only in the relative orientation of these triads of spheres in the nearest environment of the central sphere.

In closest-packed metals, the structure of all atomic layers is the same, and the structural differences are associated only with the manner in which the layers are stacked. By analogy with pure metals, many alloys can be regarded as close-packed structures. For example, the copper–gold alloy crystallises in the fcc structure.

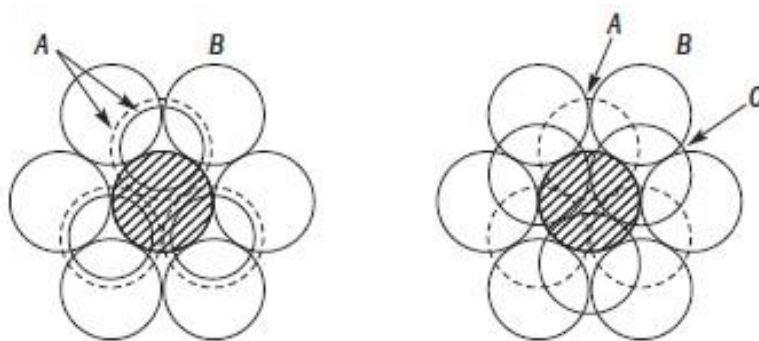


Figure 3.5

Ionic compounds, unlike metals, whose closest-packed structures are built of atoms of one kind with nearest neighbours touching one another, consist of oppositely charged ions. Their structure can be regarded as the result of a balance between electrical forces of repulsion and attraction.

Since such compounds A_aB_b contain at least two types of ions, the structure is influenced by the ratio of the ionic radii of the cations r_k and the anions r_a . For ionic structures there is a certain range of radius ratios from $(r_{k+}/r_{a-})_{\min}$ to $(r_{k+}/r_{a-})_{\max}$ that is permissible without a change in coordination numbers (Pauling's first rule).

The ionic structures of substances such as NaCl, Al_2O_3 , Na_2O and ZnO (in which the anions are larger than the cations) can be regarded as built of close-packed layers of anions whose interstices are occupied by cations. If the cations are too large to enter the corresponding interstices freely, they can enter the structure only if the anion sublattice expands. As a result, the anions do not touch one another. Such structures are called eutactic.

In structures with close packing of anions, two types of interstices are formed – tetrahedral and octahedral (Fig. 3.6). In tetrahedral interstices, the three anions forming the base of the tetrahedron belong to one close-packed layer, while the anion forming the apex of the tetrahedron belongs to the layer adjacent to the base layer from above or below (Fig. 3.6, a and b).

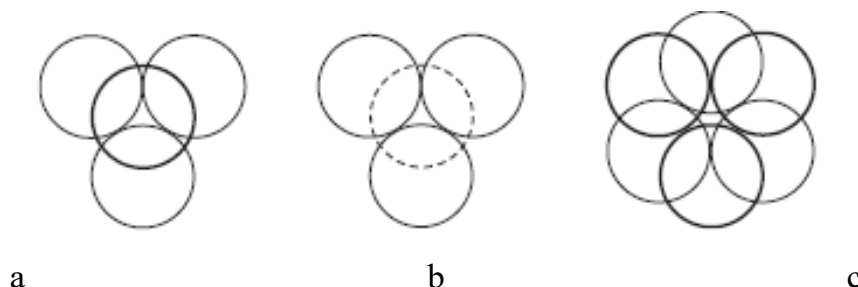


Figure 3.6

Accordingly, two types of tetrahedra are formed, T^+ and T^- , with their apices pointing up or down, respectively. Octahedral interstices (O) are formed by two triads of ions lying in adjacent layers.

Some (relatively few) structures can be represented as formed by close-packed layers of cations with anions located between them. A typical example of such structures is fluorite CaF_2 .

The concept of close packing also extends to structures in which the close-packed layers contain large cations and anions, while the interstices are filled with smaller cations.

Complete filling of interstices of all types in close-packed structures is extremely rare. Much more often, interstices of one type are filled completely or partially, while the positions of the other two types remain empty.

Most covalent structures are similar to the structures of ionic compounds. Thus, diamond can be represented as a structure in which half of the carbon atoms form a cubic close-packed lattice and the other half occupy the tetrahedral interstices T^+ in this lattice.

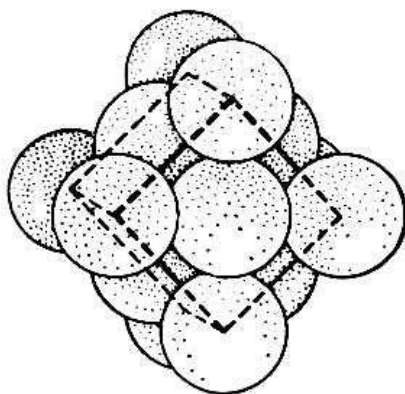


Figure 3.7

Many molecular compounds also form close-packed structures, even though only weak van der Waals forces act between neighbouring molecules in them.

3.3 DESCRIPTION OF THE STRUCTURAL TYPES OF CRYSTALLINE SOLIDS

Figure 3.8 shows the lattices of the structural types of copper (Cu), magnesium (Mg), tungsten (W) and diamond.

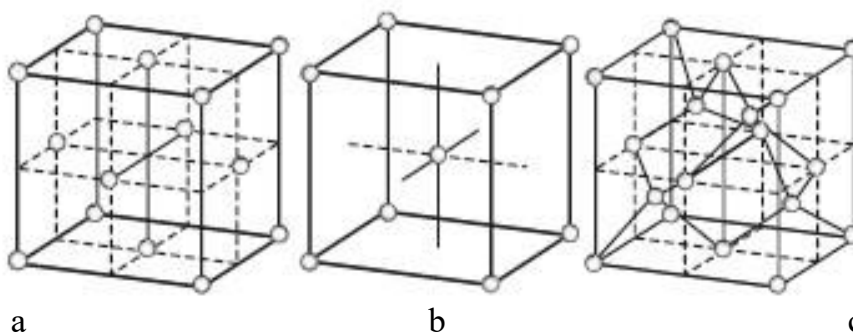


Figure 3.8

The unit cell of the Cu type is face-centred cubic (fcc). This structure is found in the metals Pt, Au, Ag, Ni, Pb, etc. The unit cell of the Mg type is hexagonal close-packed (hcp), characteristic of the metals Be, Zn, Cd, Ce, Ti, Ni, Cr, Co, etc.

The unit cell of the W type is body-centred cubic (bcc), characteristic of the metals Cs, Rb, Ba, Mo, V and α -Fe, as well as of the ionic compound CsCl. The diamond structure is adopted by the semiconductors Ge, Si and α -Sn.

Structure of copper, Cu. The unit cell of copper (Fig. 3.8, a) is an F-cell. There are 4 atoms per unit cell. Each atom is surrounded by 12 nearest atoms, i.e. the coordination number is 12, and the coordination polyhedron is a cuboctahedron.

Structure of magnesium, Mg. The unit cell of magnesium is a hexagonal primitive cell P. The hexagonal prism consists of three elementary rhombic prisms. A magnesium atom is located at the centre of one of them, while the other contains no such atom. These prisms alternate with one another.

There are 12 magnesium atoms at the top and the base of the prism. Each of them belongs by 1/2 to the cell located above and by 1/2 to the cell located below the given hexagonal prism. The hexagonal prism has a lateral environment.

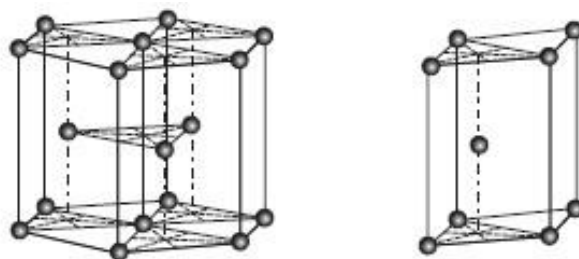


Figure 3.9

Each atom belongs to it only by 1/3, and by 2/3 to the neighbouring hexagonal prisms.

Directly in the given prism, an atom of the upper or lower base belongs to it only by $1/2 \cdot 1/3 = 1/6$, i.e. the 12 atoms in the upper and lower bases contribute $1/6 \cdot 12 = 2$ atoms to the unit cell. Two atoms are located at the centres of the upper and lower bases of the prism; each of them belongs to the hexagonal cell by 1/2 and together they contribute $1/2 \cdot 2 = 1$ atom to the hexagonal cell. The three atoms inside the cell belong to it entirely. Thus, the hexagonal cell of magnesium contains $2 + 1 + 3 = 6$ atoms.

A similar calculation can be made for the rhombic prism, which is a component of the hexagonal cell. Since the hexagonal primitive cell is formed by three rhombic prisms, there are only two magnesium atoms per prism.

Figure 3.10 shows the coordination environment of the central atom (a) and the coordination polyhedron (b) in the magnesium lattice.

The central atom is surrounded by six atoms in the same layer, three in the adjacent layer above and three in the adjacent layer below, i.e. the coordination number is 12. The coordination polyhedron is a hexagonal cuboctahedron.

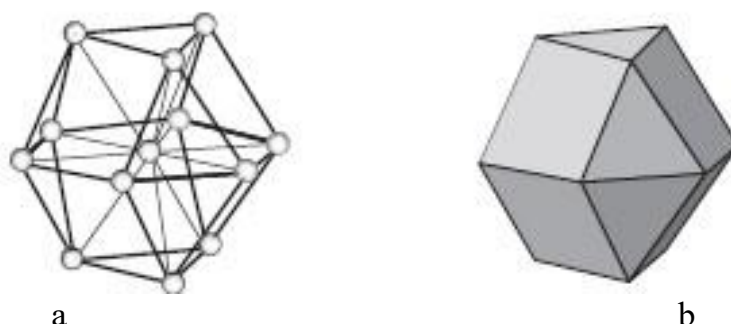


Figure 3.10 – Coordination environment of the central atom (a) and the coordination polyhedron (b) in the magnesium lattice

Structure of diamond. The unit cell type is fcc. Carbon atoms occupy all the sites of the face-centred cell, as well as the centres of 4 of the 8 octants into which the cube can be divided. Filled and empty octants alternate in a chessboard pattern.

Table 3.3 gives the characteristics of the types of compounds with AB stoichiometry, where A denotes ions of one kind and B ions of another.

Table 3.3 – Characteristics of the types of compounds with AB stoichiometry

Type	Description	Compounds
NaCl	fcc packing of B; A fills all octahedral voids	NaCl, KBr, LiF, ZrO, MgO, BaS, PbS, UC
CsCl	Simple cubic packing of B; A fills all voids	CsCl, CsBr, CsI, RbCl, AlCo, AgZn, BeCu, RuAl
Sphalerite	fcc packing of B; A fills 1/2 of the tetrahedral voids	ZnS (sphalerite), AgI, AlP, BeS, CdSe, CuF, GaAs, β -SiC
Wurtzite	hcp packing of B; A fills 1/2 of the tetrahedral voids	ZnS (wurtzite), ZnO, SiC, AlN, CdSe
NiAs	hcp packing of B; A fills the octahedral voids	NiAs, CoTe, CrSe, FeS, NiSn, PtBi, VP, ZrTe

The lattices of the structural types of the binary compounds sodium chloride NaCl, sphalerite ZnS, wurtzite ZnS and caesium chloride CsCl, as well as fluorite CaF₂, are shown in Fig. 3.11.

Structural type NaCl. The unit cell is fcc (an F-cell). Each sodium ion is surrounded by six chloride ions and each chloride ion by six sodium ions, i.e. the coordination number of sodium with respect to chlorine is equal to the coordination number of chlorine with respect to sodium and equals six.

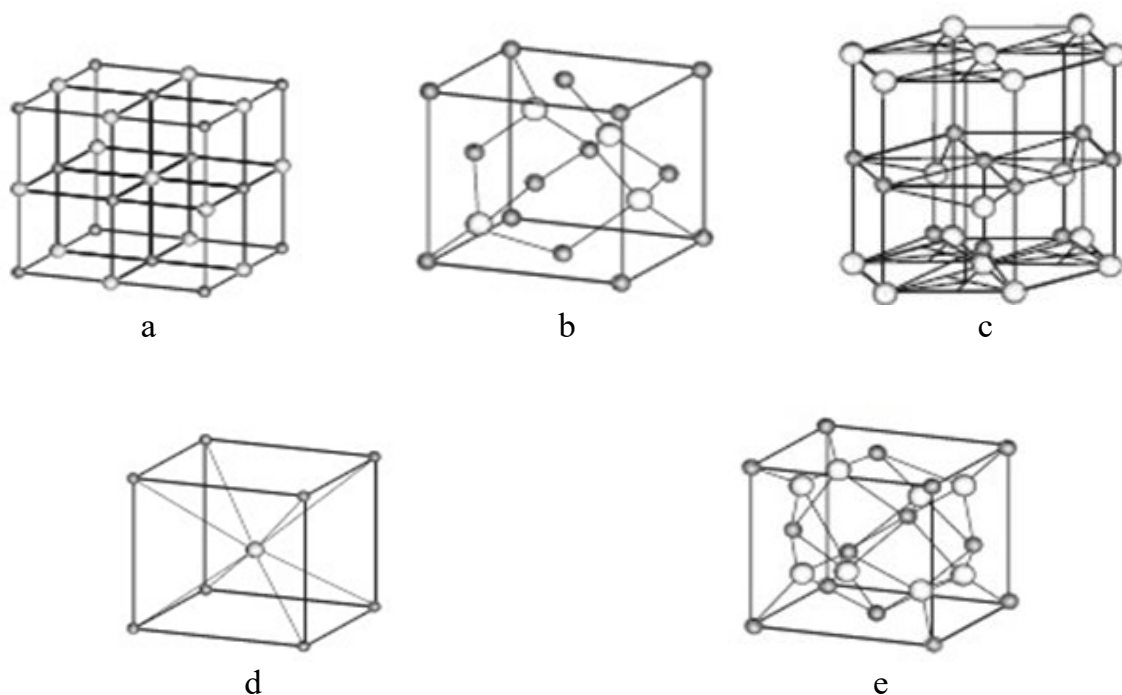


Figure 3.11 – Lattices of the structural types of binary compounds: a – NaCl structural type, b – sphalerite ZnS structural type, c – wurtzite ZnS structural type, d – CsCl structural type, e – fluorite CaF_2 structural type

Many halides and hydrides of the alkali metals, silver and ammonium, and numerous chalcogenides (including oxides) of divalent metals, among them alkaline-earth and transition metals, belong to this structural type. Many of these compounds are ionic, while others, for example TiO , are metallic in character.

Sphalerite structural type. Zinc sulphide crystallises in the form of cubic sphalerite (zinc blende) or hexagonal wurtzite. The sphalerite structure is regarded as cubic closest packing of sulphur in which zinc ions occupy half of the tetrahedral voids. The coordination number of zinc with respect to sulphur is equal to that of sulphur with respect to zinc and equals 4.

Table 3.4 gives the unit cell parameters of compounds with AB stoichiometry that crystallise in the sphalerite structure. The bonding in these compounds is less ionic than in the corresponding AB compounds with the rock-salt structure.

Wurtzite structural type. The unit cell of wurtzite is hexagonal close-packed. The S^{2-} ions occupy the sites of the cell, and the Zn^{2+} ions occupy half of the octahedral voids.

Table 3.4 – Unit cell parameters of compounds with AB stoichiometry

Compound	a , Å	Compound	a , Å	Compound	a , Å	Compound	a , Å	Compound	a , Å
CuF	4.255	BeS	4.842	β -CdS	5.818	BN	3.616	GaP	5.448
CuCl	5.416	BeSe	5.070	CdSe	6.077	BP	4.538	GaAs	5.653
γ -CuBr	5.691	BeTe	5.540	CdTe	6.481	BAs	4.777	GaSb	6.095
γ -CuI	6.051	β -ZnS	5.406	HgS	5.852	AlP	5.451	InP	5.869

Compound	a , Å	Compound	a , Å	Compound	a , Å	Compound	a , Å	Compound	a , Å
γ -AgI	6.495	ZnSe	5.667	HgSe	6.085	AlAs	5.662	InAs	6.058
β -MnS (red)	5.600	ZnTe	6.103	HgTe	6.453	AlSb	6.135	InSb	6.478
β -MnSe	5.880	β -SiC	4.358						

Table 3.5

Compound	a , Å	c , Å	u	c/a	Compound	a , Å	c , Å	u	c/a
ZnO	3.2495	5.2069	0.345	1.602	MnSe	4.12	6.72		1.631
ZnS	3.811	6.234		1.636	AgI	4.58	7.494		1.636
ZnSe	3.98	6.53		1.641	AlN	3.111	4.978	0.385	1.600
ZnTe	4.27	6.99		1.637	GaN	3.18	5.166		1.625
BeO	2.698	4.380	0.378	1.623	InN	3.533	5.693		1.611
CdS	4.1348	6.749		1.632	TaN	3.05	4.94		1.620
CdSe	4.30	7.02		1.633	NH ₄ F	4.39	7.02	0.365	1.600
MnS	3.976	6.432		1.618	SiC	3.076	5.048		1.641

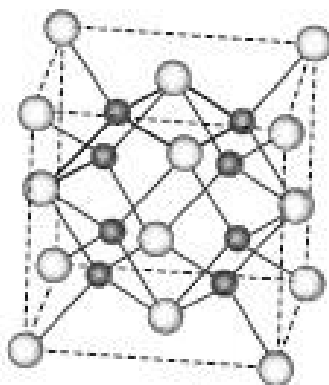


Figure 3.12

Fluorite structural type, CaF_2 . Compounds of divalent cations with monovalent anions (SrF_2 , BaF_2 , etc.), as well as compounds of monovalent cations with divalent anions (Li_2O , Na_2S , K_2O , etc.), crystallise in the fluorite structural type. The unit cell of fluorite is F. The Ca^{2+} ions occupy the sites of the face-centred cell and form cubic closest packing, while the F^- ions occupy the centres of the eight octants.

Perovskite structural type. The compounds BaTiO_3 , FeTiO_3 , CaZrO_3 , PbTiO_3 , etc., crystallise in the perovskite structural type. In the perovskite unit cell, titanium ions occupy the vertices of the cube, oxygen ions are located at the midpoints of the edges, and the calcium ion is inside the cell.

Although there is an ion at the centre of the cell, the lattice is not body-centred but primitive. A body-centred lattice requires the ions or atoms located at the vertices

of the cube and at its centre to be of the same kind. In the perovskite lattice, however, titanium ions are located at the vertices of the cube and a calcium ion at the centre.



Figure 3.13

The calcium ion belongs to the cell entirely. The titanium ions at the vertices of the cube belong to the cell by $1/8$ each and together contribute 1 ion to the cell. The oxygen ions located on the edges of the cell belong to it by $1/4$ each and contribute 3 ions to the cell.

The coordination number of calcium with respect to oxygen is 12 (the coordination polyhedron is a cuboctahedron), and that of titanium with respect to oxygen is 6.

Spinel structure. MgAl_2O_4 is noble spinel. The basis of the spinel structure MgAl_2O_4 can be pictured as a three-layer closest packing of oxygen atoms. The unit cell consists of eight small face-centred cubes, i.e. F-cubes, which is due to the filling of half of the octahedral and one eighth of the tetrahedral voids of the cubic closest packing of O atoms by Al and Mg atoms.

The spinel structure is characteristic of compounds of the type $\text{Me}^{2+}\text{Me}_2^{3+}\text{O}_4^{2-}$, where Me^{2+} and Me^{3+} are divalent and trivalent metals, at least one of which belongs to the group of transition elements. The divalent metal cations are represented by Mg^{2+} , Mn^{2+} , Fe^{2+} , Ni^{2+} and Zn^{2+} , and the trivalent metal cations by Al^{3+} , Cr^{3+} , Fe^{3+} and Mn^{3+} . The anion O^{2-} is oxygen. Chemical compounds with the spinel structure are also known in which the anion is F^- , Cl^- , CN^- , S^{2-} , Se^{2-} or Te^{2-} instead of oxygen.

3.4 CALCULATION OF ATOMIC (IONIC) RADII AND INTERATOMIC DISTANCES

It is often necessary to find the bond length or some other interatomic distance in crystal structures. For crystals with orthogonal unit cells ($\alpha = \beta = \gamma = 90^\circ$), this can be done on the basis of geometric considerations using the formulae given in Table 3.6 and data on the unit cell parameters.

The radii of the atoms or ions making up a crystal are not constant quantities. They vary depending on the compound in which they occur.

For example, the radius of the Na ion in NaCl is 1.02 Å, whereas in a crystal of metallic sodium it is 1.66 Å. This is due to the non-uniform distribution of electron density in the interatomic space around the same ion when it is located in different chemical compounds.

Table 3.6

Structure	Interatomic distance	Number of neighbours at this distance	Formula for calculating the distance from the lattice parameters
Rock salt (cubic)	Na – Cl	6	$a/2 = 0.5a$
	Cl – Cl	12	$a/\sqrt{2} = 0.707a$
	Na – Na	12	$a/\sqrt{2} = 0.707a$
Sphalerite (cubic)	Zn – S	4	$a\sqrt{3}/4 = 0.433a$
	Zn – Zn	12	$a/\sqrt{2} = 0.707a$
	S – S	12	$a/\sqrt{2} = 0.707a$
Fluorite (cubic)	Ca – F	4 or 8	$a\sqrt{3}/4 = 0.433a$
	Ca – Ca	12	$a/\sqrt{2} = 0.707a$
	F – F	6	$a/2 = 0.5a$
Wurtzite* (hexagonal)	Zn – S	4	$a\sqrt{3}/8 = 0.612a = 3c/8 = 0.375c$
	Zn – Zn	12	$a = 0.612c$
	S – S	12	$a = 0.612c$
Nickel arsenide* (hexagonal)	Ni – As	6	$a/\sqrt{2} = 0.707a = 0.433a$
	As – As	12	$a = 0.612c$
	Ni – Ni	2	$c/2 = 0.5c = 0.816a$
	Ni – Ni	6	$a = 0.612c$

Therefore, crystal chemistry uses effective radii, which are defined as the minimum distances to which the spheres of atoms can approach the surfaces of the spheres of neighbouring atoms. The distance between touching spheres is assumed to be equal to the sum of their radii.

3.5 DETERMINATION OF METALLIC AND IONIC RADII

The figure shows how the metallic radius of copper, which crystallises in the fcc lattice, is determined. With $a = 3.61$ Å, found by X-ray diffraction analysis, the radius of the copper atom is

$$r_{\text{Cu}} = a\sqrt{2} / 4 = 1.25 \text{ Å}.$$

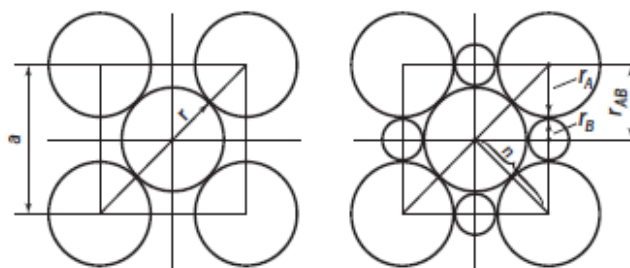


Figure 3.14

The same scheme is used to find ionic radii.

Although an AB lattice consists of ions of different charges and sizes, the additivity rule $r_{AB} = r_A + r_B$ is still used. First, one of the radii, r_A or r_B , is found and then subtracted from the interatomic distance r_{AB} .

For large anions and small cations, if it can be assumed that the latter are located in the voids between the anions and the anions are in direct contact with one another, the radii of the large ions r_A can be calculated by halving the distance n found by X-ray diffraction analysis, and then r_B is calculated by the formula $r_B = r_{AB}\sqrt{2} - r_A$.

Self-assessment questions

1. What is the coordination number of an atom in a crystal lattice?
2. What is polymorphism in some crystalline substances?
3. Which spatial formations are called closest-packed structures?
4. Explain the structural features of the unit cells of copper and magnesium.
5. Explain the crystal structure of diamond.
6. What crystal structure do chalcogenides have?
7. Explain the structure of ternary compounds – perovskite and spinels. Give examples.
8. Why are the radii of the atoms or ions in crystals not constant quantities?
9. Explain the concept of the effective radius of an atom or ion.
10. What is the algorithm for determining metallic and ionic radii?

LECTURE 4

BAND STRUCTURE AND ELECTRICAL CONDUCTIVITY OF SOLIDS

A characteristic property of metals is their high electrical conductivity, due to the directed transport of their electrons in an electric field. A number of solids with molecular, ionic or covalent bonds are dielectrics. Their electrical conductivity is 20–30 orders of magnitude lower than that of metals. A large number of solids occupy an intermediate position between metals and dielectrics in terms of electrical conductivity.

Quantum-mechanical concepts of the nature of the energy spectrum of electrons have been applied successfully to explain the differences in the electrical conductivity of solids. In the late 1930s, F. Bloch and R. Peierls introduced the concept of band structure and proposed the foundations of the band theory of solids. The terms band structure and band theory reflect the nature of the energy spectrum of electrons in solids.

The band model of a solid follows from the solution of the Schrödinger equation for electrons in a system consisting of many atomic nuclei and electrons. Band theory is based on the one-electron approach, in which the extremely complicated many-electron problem is reduced to the problem of the motion of each electron in the averaged field of the nuclei and all the other electrons.

The formation of a crystalline solid can be pictured as the result of bringing many separate atoms together.

Band theory adopts approximations that make it possible to solve the Schrödinger equation while retaining the essential features that distinguish a crystal from an individual isolated atom.

The solid is an ideal periodic crystal consisting of ions and valence electrons, i.e. conduction electrons.

It is assumed that all the electrons of an atom, except the valence electrons, together with the nuclei form positively charged ions. These ions form the core (framework) of the crystal. The Schrödinger equation considers the motion of the valence electrons in the potential field of the fixed ions.

Because the ratio of the electron mass to the ion mass is negligible, the equilibrium positions of the lattice sites are fixed, i.e. the nuclei are considered to be stationary. This is the adiabatic approximation. The effect of all the other electrons on a valence electron is described by an effective averaged external field in which each electron moves independently. This is the essence of the one-electron approximation.

As atoms approach one another in a crystal, the outer shells of different atoms may overlap. The electrons of the outer shells, called valence electrons, belong to all

the atoms of the crystal lattice simultaneously, and the energy spectra of the electrons of the individual atoms are transformed into the energy spectrum of the electrons in the solid. The energy levels of electrons in crystals split and form energy bands of allowed and forbidden energies.

Entire ranges of energy values that electrons in the crystal may have arise on the energy scale. Thus, whereas certain energy values are forbidden for individual electrons in an isolated atom, entire forbidden bands arise in crystals, and the energy spectrum acquires a band structure.

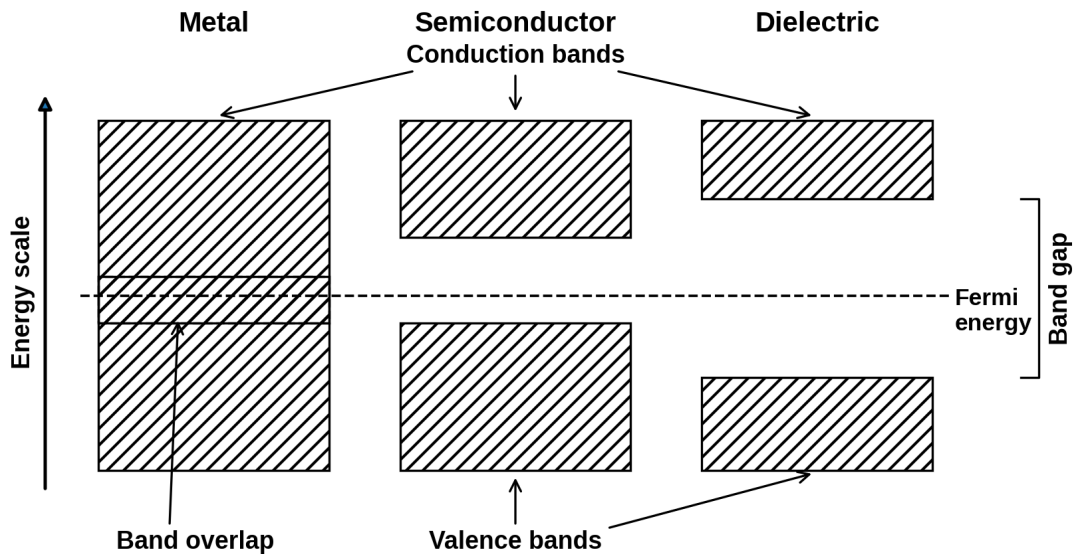


Figure 4.1

The differences in the properties of various crystalline solids are associated with the different structure of the electron energy spectrum, i.e. with the different widths of the allowed and forbidden energy bands and with the way they are filled with electrons.

At absolute zero, all the electrons of a crystal occupy the lowest one-electron energy levels. The energy below which all electron states can be occupied at absolute zero, and above which all states are empty, is called the Fermi energy. The values of the Fermi energy in solids of various kinds are of the order of a few eV.

The isoenergetic surface inside the crystal lattice corresponding to the Fermi energy is called the Fermi surface. The vast majority of the properties of crystalline solids depend on the interaction of external forces with those electrons whose energy levels correspond to the Fermi surface.

In metallic crystals at 0 K the valence band may be partially or completely filled with electrons. The alkali metals belong to the type of metals with a valence band partially filled with electrons at 0 K. Crystals consisting of divalent atoms may serve as examples of the other type.

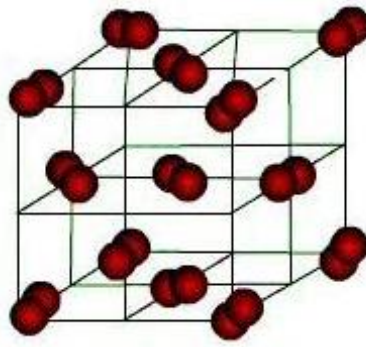


Figure 4.2

Under the influence of an applied external electric field, electrons move to higher energy levels. A conduction band with a practically continuous energy distribution is thereby formed in the crystal.

When the valence band is partially filled with electrons, the conduction band overlaps it. When the valence band is completely filled at 0 K, its upper energy level is also the lower energy level of the conduction band, i.e. the bands do not overlap.

All metals are good conductors. Semimetals (As, Sb, Bi) are distinguished as a separate type of solid, since they are characterised by a small band overlap. The latter results in an electrical conductivity lower than that of metals.

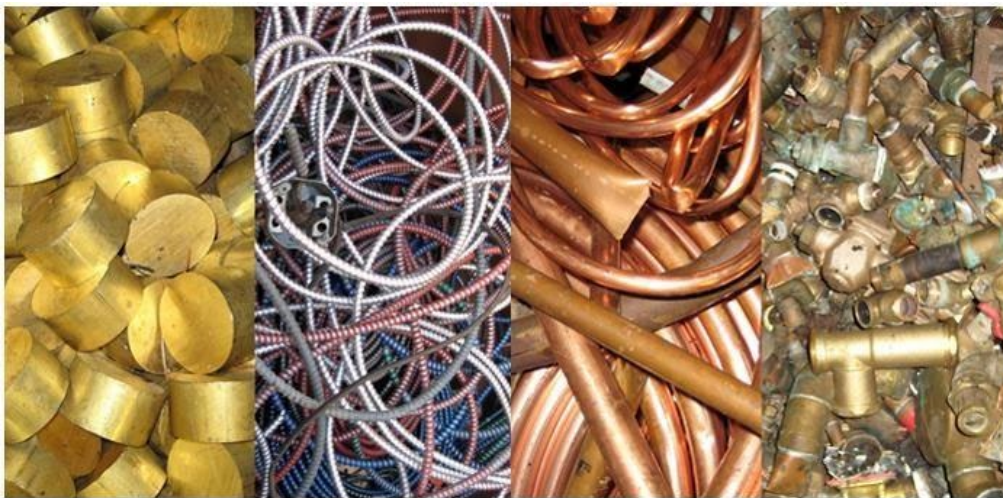


Figure 4.3

Dielectrics are solids in which the valence band and the conduction band do not overlap: at 0 K their valence band is completely filled, above it lie the forbidden band and the conduction band (which are empty), and the forbidden band is wide – up to 10 eV.

Thus, in the dielectric diamond the band gap is 6–7 eV. Under the condition of minimum energy at 0 K, all the valence electrons of the carbon atoms completely fill the valence band, while the conduction band is empty. To pass into this band, the electrons must be given an energy of about 7 eV. However, the required energy exceeds the bond energy in the diamond crystal and cannot be supplied. Even at room

temperature, diamond is a good insulator, since thermal energy is insufficient to transfer electrons from the valence band to the conduction band.

Semiconductors are solids in which the conduction band and the valence band also do not overlap in the ground state, but the distance between them on the energy scale is less than 3.5 eV (according to some sources, less than 2.0 eV). Thus, semiconductors differ from dielectrics in having a narrower band gap (in eV), for example Ge – 0.74; Si – 1.12; GaAs – 1.5. All these crystals in the pure state are insulators at absolute zero, but acquire electrical conductivity as the temperature rises.

If the band gap is relatively small, then when a certain amount of energy is supplied to the solid (for example, when the temperature is raised), some of its electrons can be transferred from the completely filled valence band to the conduction band and take part in current transport; such substances are called intrinsic semiconductors.

Intrinsic semiconductors are distinguished in which the completely filled valence band touches the conduction band without a band gap and without overlap. These are the so-called gapless semiconductors, for example $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$, $\text{Pb}_{1-x}\text{Sn}_x\text{Sb}$ ($x < 0.16$), HgTe, HgSe, etc.

A feature of intrinsic semiconductors is that, when some of the electrons pass into the conduction band, an equivalent number of so-called holes appear in the valence band; these carry a positive charge and also take part in current transport.

A positively charged hole can be identified with an unsaturated bond. This state can be passed on, relay-fashion, to neighbouring atoms by the filling of the vacancy with electrons of neighbouring atoms. This relay-type movement of electrons is interpreted as the movement of holes with a positive charge equal in magnitude to the electron charge.

Intrinsic semiconductors have electron–hole conductivity and conduct current weakly.

Extrinsic (impurity) semiconductors have become widespread. In them, the majority of the charge carriers – electrons and holes – arise from introduced impurities whose energy levels lie between the valence and conduction bands of the host crystal.

The energy levels of donor impurities lie in the band gap below the conduction band and supply electrons to it. The corresponding crystals are called electronic, or n-type (from the word *negative*), semiconductors.

The energy levels of acceptor impurities lie in the band gap above the valence band of the host crystal and capture electrons from it, thus giving rise to holes and hole conductivity. Semiconductors with such impurities are called p-type (from the

word *positive*) semiconductors. Figure 4.4 shows a diagram of the arrangement of the energy levels of impurities of different kinds in the band gap of semiconductors.

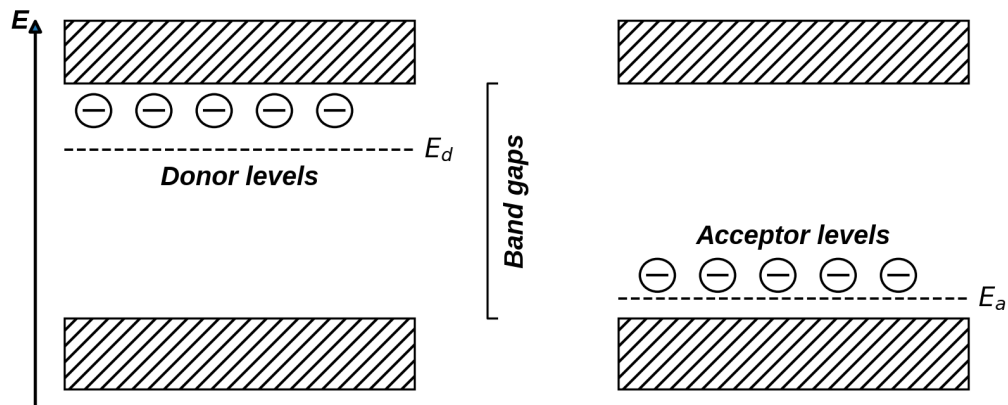


Figure 4.4

For example, when donor impurities (phosphorus, arsenic, antimony) are introduced into a germanium crystal, their electrons pass into its conduction band, sharply increasing the number of electrons in it; n-type conductivity results.

When acceptor impurities (boron, aluminium, indium) are added to germanium, electrons from its valence band pass to the free energy levels of these impurities. This is accompanied by the formation of holes in its valence band, which move deeper into this band. p-Type conductivity results.

The number of solids with semiconducting properties is very large. According to their crystal structure and chemical nature, they are divided into a number of types:

- semiconductors with a diamond-like lattice: silicon, germanium, α -tin, indium antimonide, gallium arsenide;
- semiconductors with a molecular lattice: selenium, tellurium;
- chalcogenides with a sphalerite-type crystal lattice: sulphides, selenides and tellurides of zinc, cadmium, mercury and lead;
- ionic crystals (NaCl type): silver and copper(I) chlorides and bromides;
- oxides: Cu_2O , NiO (NaCl type), ZnO (wurtzite type);
- ternary semiconductor compounds: CuFeS_2 , ZnGeAs_2 , SbSI ;
- amorphous and vitreous semiconductors, and others.

Thus, according to the mutual arrangement and structure of their energy bands, solids are divided into:

- conductors – the conduction band and the valence band form a single band called the conduction band; electrons can move freely after receiving any arbitrarily small energy; all metals are conductors;

– dielectrics – the bands do not overlap and the band gap exceeds 3.5 eV; a considerable energy is required to transfer an electron from the valence band to the conduction band, so dielectrics practically do not conduct current;

– semiconductors – the bands do not overlap and the band gap is less than 3.5 eV; less energy is required to transfer an electron from the valence band to the conduction band than in a dielectric.

Semiconductors and dielectrics also differ from metals in the following respects. In metals the charge carriers are electrons only, whereas in semiconductors they are electrons and holes, as well as cations and anions (in ionic semiconductors).

In semiconductors and dielectrics, the concentration of charge carriers is many orders of magnitude lower than in metals, where their number is comparable to the number of lattice sites and amounts to 10^{22} – 10^{23} per cm^3 .

The most important difference is that the electrical conductivity of semiconductors and dielectrics increases with rising temperature, whereas that of metals decreases. The latter is because the concentration of charge carriers, i.e. conduction electrons, in metals is high and independent of temperature. However, as the temperature rises, the intensity of collisions between the moving electrons and their scattering at the lattice sites increase. This reduces their mobility (the unit of mobility is $\text{m}^2/(\text{V}\cdot\text{s})$).

A feature of most semiconductors compared with metals is their ability to change their electrical properties sharply when small amounts of electrically active impurities are introduced (the sensitivity limit for impurities capable of affecting the resistance of a semiconductor is estimated at an impurity concentration of 10^{-10} at. %), their extreme sensitivity to structural defects of crystals, and their high sensitivity to light and various ionising radiations.

Self-assessment questions

1. What approximations are adopted in band theory?
2. Define the concept of the Fermi energy.
3. Which solids are dielectrics?
4. How do the concepts of the valence band and the conduction band differ?
5. Which solids are semiconductors? How do they differ from dielectrics?
6. Give a comparative description of n-type and p-type semiconductors.
7. Compare electron, electron–hole and hole conductivity in solids.

LECTURE 5

DEFECTS IN CRYSTALS

Real crystals always contain a considerable number of disturbances of the crystal lattice or of the energy state of the structural units (hereinafter, atoms). Both kinds of disturbance are called defects.

A number of important properties of solids – reactivity, strength, electrical conductivity, thermal conductivity, optical and magnetic properties, and catalytic activity – depend on the extent to which their crystal structures deviate from the ideal. Crystal defects sometimes impart very valuable properties to solids, and for this reason they are created artificially.

Defects are of different nature and origin. Their appearance changes the energy state of crystals and may also affect the way in which the lattice sites are occupied.

Defects in crystals arise for various reasons. One of the main reasons is the thermal motion of the particles forming the crystal. As the temperature of the solid rises, the energy of this motion increases, and so does the probability of forming defects, which are called intrinsic or thermal defects.

Another kind of defect is associated with the presence of various impurities. When the impurities present significantly change the properties of the solid, one speaks of defects of chemical composition of the crystal, or impurity defects. Defects in crystals may also arise as a result of external mechanical loading. Thus, irreversible stretching of a crystal results in its plastic deformation, in which slip planes with the greatest shear arise in the material. Mechanical loads may also give rise to cracks and other macrodefects in the crystal.

Defects of a particular type affect the properties of a solid depending on their position in the crystal lattice and on the number of such disturbances per unit volume of the crystal.

One usually speaks of the concentration of defects, referring their number either to unit volume or to one mole of the substance.

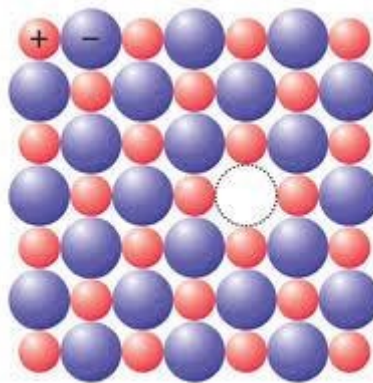


Figure 5.1

Various approaches have been proposed for the classification of defects. Macro- and microdefects are distinguished. Examples of macrodefects are pores, cracks and cavities in metal castings, foreign inclusions of impurity clusters, and the visible boundaries of individual crystals, i.e. the grains of polycrystals. Microdefects, or defects considered at the atomic level, are those in which at least one of the three dimensions (x, y, z) is comparable to the lattice period $a = 0.2\text{--}0.5\text{ nm}$.

5.1 DIMENSIONAL CLASSIFICATION OF DEFECTS

This is a classification according to the geometry and extent of the disturbance of the crystal field.

A distinction is made between point (zero-dimensional) defects, for which $x < a$, $y < a$ and $z < a$; line (one-dimensional) defects, which are small in two directions and arbitrarily extended in the third; planar (two-dimensional) defects, which are small in one direction; and volume (three-dimensional) defects, which in practice already belong to macrodefects.

This dimensional classification also includes associated defects, which are associations of several identical or different defects, for example divacancies, ion pairs of impurity atoms, or even more complex formations consisting of many impurity atoms.

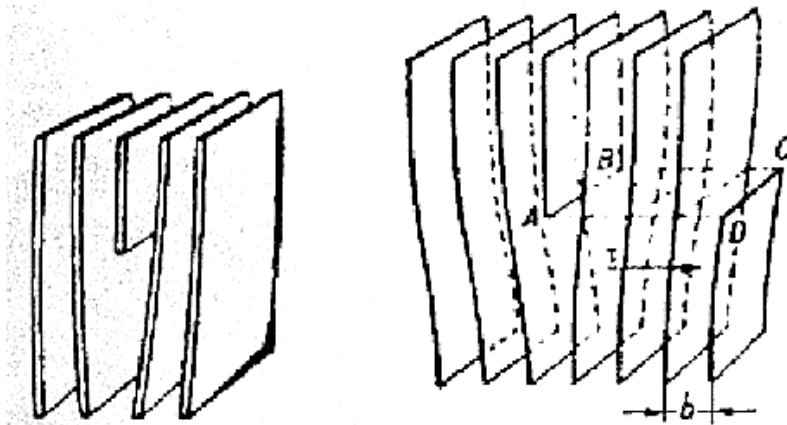


Figure 5.2

5.2 POINT DEFECTS

Zero-dimensional (point) defects include all defects associated with the displacement or replacement of a small group of atoms (intrinsic point defects), as well as with impurities. They arise on heating, alloying, during crystal growth, as a result of radiation exposure, etc. In addition to an increase in temperature, the formation of point defects in crystals is favoured by large distances between lattice sites and by small particle sizes.

The concepts of "classical" point defects were presented in the works of Schottky, Frenkel, Wagner and others in the 1930s.

Point defects arise when an individual isolated atom, molecule or ion leaves its lattice site and moves either into an interstice or to the surface of the crystal, leaving an unoccupied site in the lattice, called a vacancy.

The most studied types of intrinsic point defects are:

- vacancy – a free, unoccupied site of the crystal lattice;
- self-interstitial atom – an atom of the host element located in an interstitial position of the unit cell;
- substitutional impurity atom – an atom of one type replacing an atom of another type at a lattice site. Atoms that differ relatively little from the host atoms in size and electronic properties can occupy substitutional positions;
- interstitial impurity atom – an impurity atom located in the interstices of the crystal lattice. In metals, interstitial impurities are usually hydrogen, carbon, nitrogen and oxygen. In semiconductors, these are impurities that create deep energy levels in the band gap, for example copper and gold in silicon.

The mechanism of formation of intrinsic point defects is shown in Fig. 5.3.

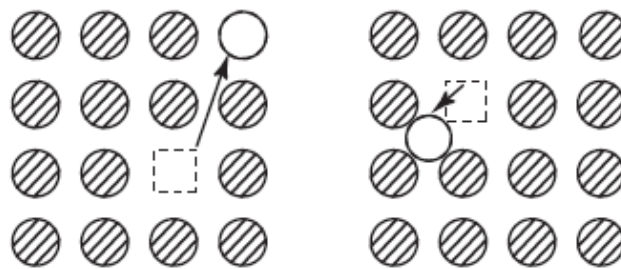


Figure 5.3 – Mechanism of formation of intrinsic point defects

When point impurity defects are formed, impurity particles (molecules, atoms or ions) are located either at the sites of the space lattice of the crystal, displacing the particles of the host substance from them, or occupy interstitial positions. Impurity defects in crystals may exist in either a neutral or a charged state.

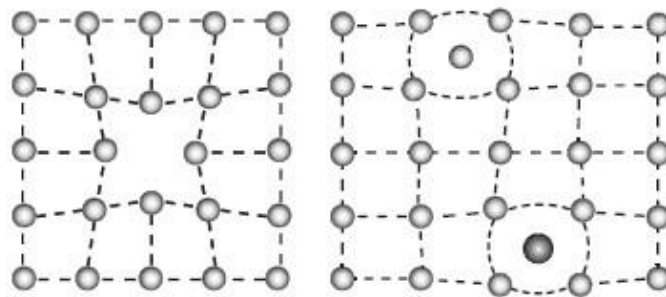


Figure 5.4

Under certain conditions, impurity atoms may become ionised, significantly changing the properties of the crystal. Although point defects are considered to consist of a single atom or a defect position – a vacancy or an interstice – in reality the immediate atomic environment of such a defect is also distorted to some extent.

5.3 VACANCIES IN METALS AND METALLIC ALLOYS

The physical nature of vacancy formation is associated with the thermal vibrations of atoms in crystals. Among the atoms there are some whose kinetic energy exceeds the average energy of most atoms at the given temperature. Such high-energy atoms are able to leave their equilibrium positions and move into the interstices of the lattice.

After an atom has moved from a site to an interstice, the reverse transition – recombination, i.e. the return of the atom to the vacant site – is possible. However, there is another possibility: diffusion of the atom from the interstice nearest to the vacancy to more distant ones. In this case, "vacancy – interstitial atom" pairs, called Frenkel pairs, are formed. The vacancies of this type are called Frenkel vacancies.

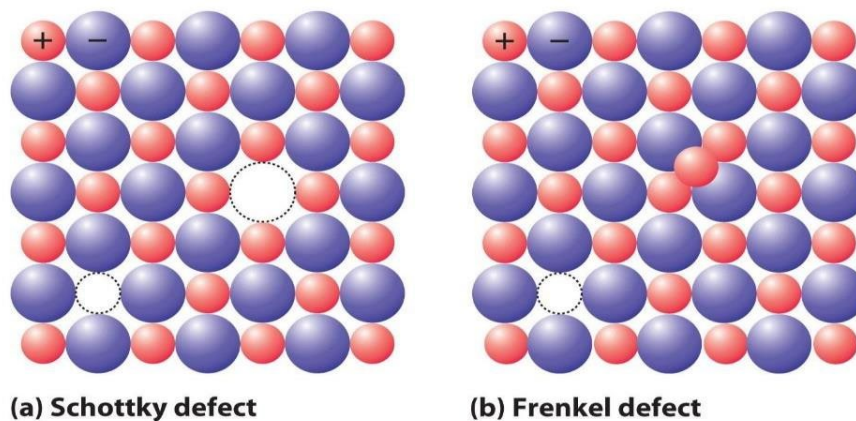


Figure 5.5

The numbers of Frenkel vacancies and interstitial atoms formed in this process are equal. A true vacancy is created in this process if the interstitial atom moves a considerable distance away from it. From the moment a Frenkel pair is formed, both the interstitial atoms and the vacancies can migrate through the crystal simultaneously, the latter by replacing neighbouring lattice atoms. The formation of wandering vacancies and interstitial atoms will continue until an interstitial atom and a vacancy meet again at neighbouring positions, where they recombine and both disappear, or until one of them reaches the surface.

If a vacancy diffusing through the crystal reaches the surface, an atom from a deeper atomic layer can jump into its place. An atom from the next layer will move into the vacancy thus released, and as a result the crystal will contain vacancies without interstitial atoms – Schottky vacancies.

A similar situation arises when an interstitial atom moves from the interior to the surface. The atom that has emerged in this case builds onto the surface, i.e. the volume of the crystal increases somewhat.

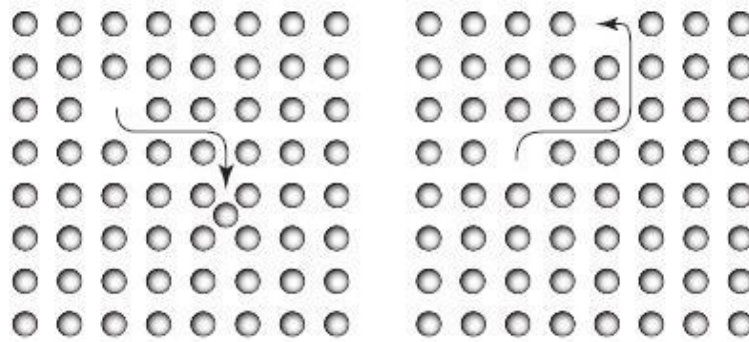


Figure 5.6

In metallic crystals, especially those with close-packed lattices, the interstices are small, and the accommodation of crystal atoms in them and diffusion through the interstices are hindered. Therefore, the formation of Schottky vacancies is more probable in metals.

The concentration of vacancies of both types depends primarily on temperature. Their formation is caused by thermal excitation of atoms, so the number of vacancies should increase with temperature. In a real crystal, the vacancy concentration is also determined, in addition to temperature, by the previous heat treatment or, as is often said, by the history of the crystal.

5.4 VACANCIES IN CRYSTALS WITH IONIC CHEMICAL BONDING

The main distinguishing feature of ionic solids is the equal number of cations and anions in their crystal lattice. Therefore, if a vacancy is formed at one of the sites, the balance of positive and negative charges is disturbed. Yet the crystal as a whole must be electrically neutral.

The requirement of electroneutrality necessarily leads to the appearance of a charge of the opposite sign that compensates the charge arising from the formation of a vacancy in the ionic crystal lattice. Various situations are possible:

- equal numbers of cation and anion vacancies may be formed (this situation corresponds to Schottky defects);
- the ionic vacancies are matched by an equal number of ions of the same sign in interstices, i.e. an ionic Frenkel pair is formed;
- the charges of the removed ions are compensated by the addition or removal of electrons, in particular by external influences.

The formation of Schottky defects in ionic crystals reduces the density, since cations and anions move to the surface and increase the volume of the crystals while

their total mass remains unchanged. Frenkel defects do not increase the volume of the crystal and therefore do not change its density.

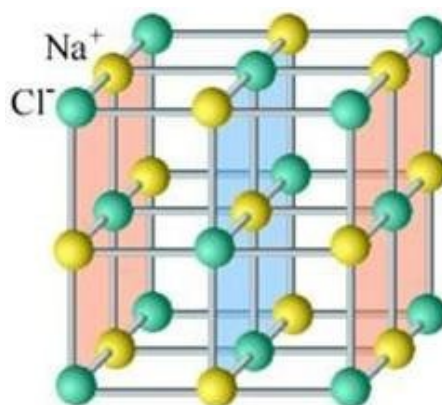


Figure 5.7

Substitutional alloys are solid solutions in which a certain number of the sites of the host crystal are replaced by atoms of another substance.

Interstitial alloys are alloys in which the atoms of the solute are located in the interstices of the solvent lattice.

5.5 VACANCIES IN COVALENT CRYSTALS

In covalent crystals, the formation of vacancies, like a change in their concentration, is accompanied by a change in the electron concentration; however, unlike in metals, these changes occur against the background of an extremely small number of free intrinsic electrons.

Typical representatives of covalent crystals are diamond and the diamond-like semiconductors germanium and silicon. The crystal structure of these solids is relatively loose, with fairly large tetrahedral interstices.

Thus, the sizes of the interstices in germanium (0.110 nm) and silicon (0.105 nm) are close to the sizes of the atoms at the lattice sites of these crystals: 0.122 nm and 0.117 nm, respectively. Therefore, according to geometric considerations, Frenkel defects might be expected to predominate in covalent crystals. However, there is also the opposite point of view, that Schottky defects predominate in crystals with the diamond structure.

5.6 STOICHIOMETRIC AND NON-STOICHIOMETRIC DEFECTS

Schottky defects, i.e. pairs formed by anion and cation vacancies, are stoichiometric defects of ionic crystals. To preserve electroneutrality, the numbers of anion and cation vacancies both in the bulk and at the surface of the crystal must be equal. Schottky defects are the main type of defect in the alkali metal halides. It is

Schottky defects that determine the optical and electrical properties of NaCl. The figure schematically shows a Schottky defect in NaCl.

Frenkel defects are also stoichiometric. Thus, in silver chloride, which has the NaCl-type structure, defects of this type, i.e. silver ions located in interstices, predominate.

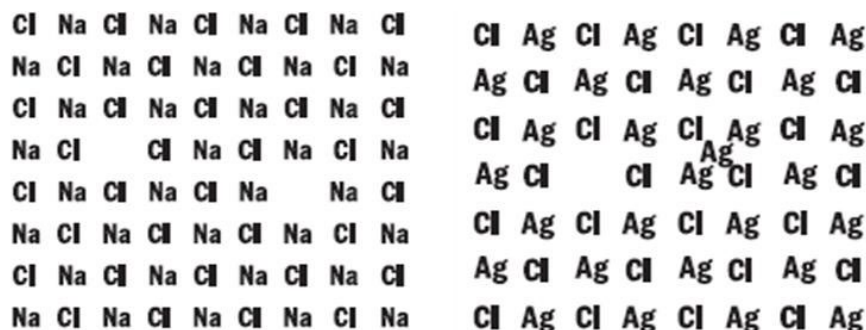


Figure 5.8

Frenkel pairs and Schottky pairs, being electrically neutral, are dipoles. Owing to this, they can attract one another, forming large aggregates – clusters or complexes.

The presence of point defects explains the existence in nature of a large number of non-stoichiometric compounds (compounds of variable composition), i.e. substances whose composition in the solid state deviates from their molecular composition.

For example, titanium oxide crystals may have a variable composition from $\text{TiO}_{0.6}$ to $\text{TiO}_{1.35}$, depending on the oxygen pressure in the environment. With an excess of titanium atoms the crystal contains a corresponding concentration of oxygen vacancies, and with an excess of oxygen atoms titanium vacancies appear. In ZnO crystals, the excess content of zinc atoms is explained by their location in the interstices of the space lattice.

Defects of non-stoichiometric crystals may result from doping a pure crystal with heterovalent impurities, i.e. impurities containing atoms in oxidation states different from those of the matrix atoms.

5.7 INTRINSIC DISORDER DEFECTS

The most important examples of intrinsic disorder are electronic defects – free electrons in metals, conduction electrons and holes in semiconductors – and atomic defects – vacancies at lattice sites and interstitial atoms. Atoms are direct participants in various transformations in solids – diffusion, decomposition of solid solutions, etc.

Intrinsic defects also include:

- phonons – carriers of quanta of the vibrational energy of the crystal lattice;

- polarons – electrons moving slowly in a polar crystal and interacting with phonons;
- motion defects – groups of atoms rotating out of phase with the bulk of the atomic groups of the crystal;
- orientation defects.

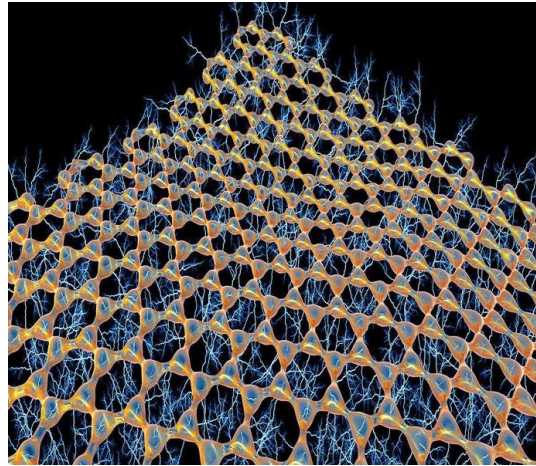


Figure 5.9

The latter appear, for example, in NH_4Cl crystals as the temperature rises, whereas at low temperatures all the ammonium groups rotate synchronously.

Similar defects may also occur when the magnetic moments of atoms in a crystal become disoriented: at low temperatures in a magnetic field they are all oriented in the same way, whereas as the temperature rises some of them become disoriented.

More complex intrinsic disorder defects are associated defects, including impurity-related ones. These include:

- excitons (an electron and a hole held together as a single neutral centre);
- electron–hole pairs (they differ from excitons in that the electrons and holes forming the pair are in the ground rather than excited energy states);
- divacancies – the product of the binding of two vacancies. The formation energy of a divacancy is always less than the formation energy of the two monovacancies that make it up, so the formation of divacancies is energetically more favourable than that of separate vacancies in the crystal. However, divacancies form only when the migration rates of monovacancies in the crystal are sufficiently high.

5.8 ASSOCIATED IMPURITY DEFECTS

These include ion pairs and impurity associates. Ion pairs are the product of the interaction of two oppositely charged impurity ions. The most important forces in ion pairing are Coulomb interaction forces. In some cases, the formation of a stable chemical bond plays an essential role.

Ion pairs as defects play an important role in semiconductors. This is because the energy levels of each of the ions forming the pair change, approaching the edges of the allowed energy bands. The level of the positively charged donor rises, and the attachment of an electron to the donor becomes more difficult. Likewise, the hindered attachment of a hole to an acceptor leads to a lowering of its level in the band gap.

Since the ions forming the pair are located at short distances from each other, a Coulomb interaction arises between them, and a direct interaction of the electron and the hole takes place, with the disappearance of the latter. This process is called charge-carrier recombination, or inter-impurity recombination.

Impurity associates are formed when impurity atoms can exist in the crystal simultaneously in several forms, and not only as a substitutional solution in which they are completely ionised. This effect is called polytropy (multiplicity of impurity forms). It is sometimes also called polygeny. Various causes leading to the polytropy of impurities are known. The main ones are ordinary inclusions of a foreign phase with the formation of impurity associates.

5.9 COLOUR CENTRES

In ionic crystals, associated defects that colour the crystal – the so-called colour centres – can form. A-centres are the product of the interaction of a dissolved oxygen atom with a vacancy. On heating to higher temperatures, A-centres migrate through the crystal as a whole, i.e. as a kind of quasi-molecule. As a result of prolonged annealing, A-centres meet and combine into larger oxygen-containing associates.

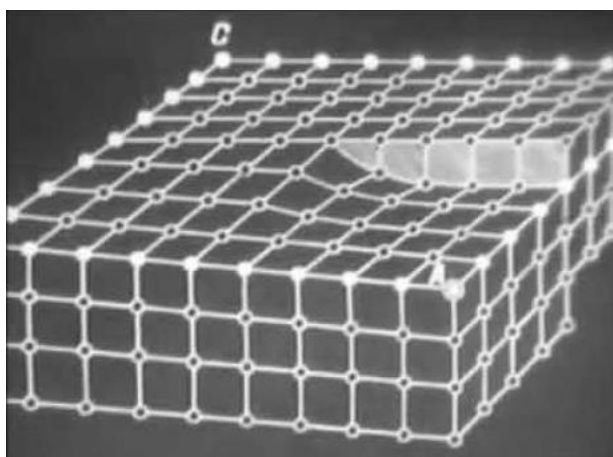


Figure 5.10

F-centres in ionic crystals consist of an anion vacancy of the crystalline compound that has captured an electron. The formation of F-centres is characteristic

of alkali metal halides with an excess of metal. Owing to the presence of F-centres, alkali metal halides become coloured in various colours.

There are also other, more complex associated centres that colour ionic crystals: F'-, M- and R-centres.

An F'-centre is formed from two F-centres under the action of light.

An M-centre consists of two adjacent anion vacancies, each of which has captured an electron, resulting in a bound state of two electrons.

An R-centre consists of three adjacent anion vacancies, each of which has also captured one electron.

In addition to colour centres associated with vacancies, associates not related to vacancies have also been found in ionic crystals:

V_K-centre – two adjacent negative ions, for example chloride ions, bound by a positive hole.

H-centre – consists of an interstitial chloride ion, a chloride ion at a lattice site and a hole binding them.

5.10 LINE DEFECTS

Line defects are a complex type of disturbance of the crystal structure. Their occurrence is due to the displacement of a whole group of particles located along an imaginary line in the crystal. Line defects include dislocations – edge and screw dislocations. A dislocation is the boundary of a region of incomplete slip in a crystal.

A dislocation, or dislocation line, is understood as the line separating the slipped region of the crystal from the unslipped one. The magnitude and direction of the displacement of atoms in the crystal lattice are determined by the Burgers vector $\mathbf{b}$. This can be understood with the aid of the so-called Burgers circuit, constructed by going around the dislocation line in a plane perpendicular to this line. Such a dislocation is called an edge dislocation.

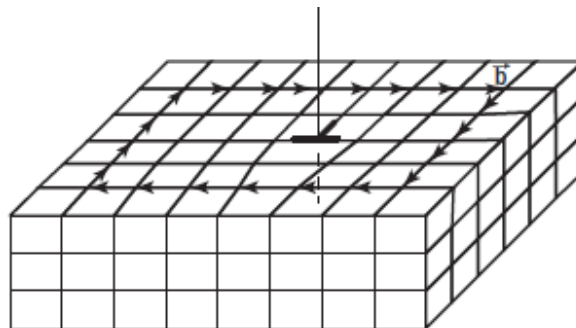


Figure 5.11

When the Burgers circuit is traversed clockwise in steps equal to the interatomic distance, it can be seen that on one side of the dislocation plane the lattice consists of n atomic rows, and on the opposite side of $n + 1$ atomic rows.

The formation of dislocations requires a large amount of energy, so their number depends little on the temperature of the crystal and is usually of the order of 10^6 – 10^7 per 1 cm^3 . As a rule, dislocations are formed during crystal growth or during mechanical or thermal treatment.

The dislocation defectiveness of real solids is characterised by the dislocation density, i.e. the total length of dislocation lines in a volume of 1 cm^3 (unit cm^{-2}). The dislocation density varies within very wide limits. For example, under special technological conditions it is possible to grow semiconductor single crystals entirely free of dislocations. At the same time, as a result of the mechanical working of metals (forging, riveting, grinding, twisting, etc.), the dislocation density can reach 10^{12} cm^{-2} .

Dislocations are characterised not only by the slip vector (the Burgers vector $\vec{b}$) but also by the angle φ between it and the dislocation line. At $\varphi = 90^\circ$ the dislocation is called an edge dislocation, at $\varphi = 0^\circ$ a screw dislocation, and at other angles a mixed dislocation, which can then be resolved into screw and edge components. The distribution of dislocations and their behaviour under external actions determine the most important mechanical properties, in particular strength, ductility, etc.

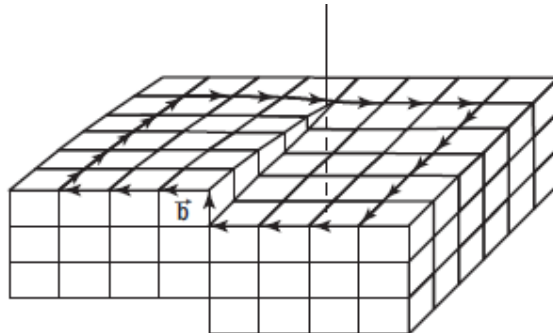


Figure 5.12

5.11 PLANAR DEFECTS

An even more complex type of crystal distortion is two-dimensional, i.e. planar, defects. Their presence means that polycrystalline substances consist of a certain set of grains or blocks joined together and oriented arbitrarily. The regions at the boundaries between grains have a distorted crystal structure.

Two-dimensional defects are typical of materials with a layered structure, especially those exhibiting polytypism. For example, cobalt can exist in two main forms (polytypes) that differ in the manner of packing of the metal atoms: cubic closest packing corresponds to the layer sequence ABCABC, and hexagonal closest packing to the sequence ABABAB.

Graphite also exhibits polytypism: it usually forms hexagonal closest packing and, less often, cubic closest packing. Stacking faults arising from the intermixing of these two polytypes are characteristic of graphite.

5.12 EFFECT OF DEFECTS ON THE PROPERTIES OF CRYSTALLINE SOLIDS

It is sometimes considered that point, line and planar defects should be studied by different branches of solid state science. In this view, vacancies, interstitial atoms and stacking faults are regarded as "chemical" defects inherent in the given structure. They are assigned an important role in chemical reactions and mass transfer. Dislocations and other defects of non-zero dimensionality are regarded rather as "physical defects" and are considered mainly responsible for the mechanical properties of materials. However, at the present level of understanding of defect behaviour, there is no doubt that point, line and planar defects are closely interrelated and that all of them influence the properties of solids.

Point defects, both intrinsic and impurity, significantly affect practically all the properties of solids. One of these is electrical conductivity. In their motion through the crystal, charge carriers collide with point defects. Such collisions are most effective when they occur with vacancies, interstitials and impurity ions.

The presence of two-dimensional defects leads to a decrease in the mobility of charge carriers. In metals, in which the concentration of free electrons can be considered constant, the electrical conductivity depends only on the electron mobility.

The main role of point defects in semiconductors is the formation of donor and acceptor energy levels in the band gap.

In ionic dielectric crystals, the dielectric properties are determined mainly by the characteristics of the bulk structure, and the role of defects in them is insignificant. The conductivity of such crystals cannot result from electron jumps from the valence band to the conduction band because of the very large band gap (up to 10 eV). Therefore, in such crystals conductivity is not electronic but ionic, caused by the movement of ions. The ability of ions to carry current increases markedly in the presence of vacancies. In turn, impurities play a significant role in the formation of vacancies in ionic crystals.

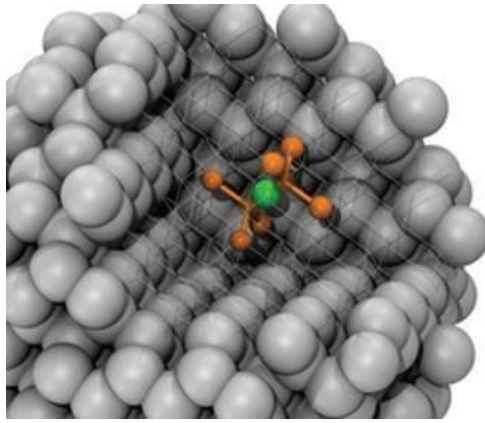


Figure 5.13

As a rule, interstitial impurity defects impede the motion of dislocations, making the mechanical working of metals more difficult.

The features of the block structure of a substance significantly affect the optical and electrical characteristics of a solid, as well as its chemical activity. Usually, the substance at grain and block boundaries has an increased reactivity and may even differ in chemical composition from the rest of the grain volume.

Self-assessment questions

1. Name the types of defects found in crystals.
2. Describe the types of point defects.
3. Describe the mechanism of formation of Frenkel vacancies.
4. Describe the mechanism of formation of Schottky vacancies.
5. Describe the features of the mechanism of vacancy formation in crystals with ionic chemical bonding.
6. Discuss stoichiometric and non-stoichiometric defects in covalent crystals.
7. Explain the concept of the "polytropy effect".
8. What are colour centres? What are the mechanisms of coloration?
9. Describe the features of line defects and defects of other dimensionalities.
10. How do defects affect the properties of solids?

LECTURE 6

DIFFUSION IN CRYSTALS

Diffusion in a crystal is the transport of atoms (ions) caused by their random thermal motion, which may become directed under the action of a concentration or temperature gradient. In other words, two kinds of particle motion may coexist simultaneously in a crystalline system: random thermal motion and directed drift. The driving force of directed motion may also be an electric field gradient.

According to Ya. Frenkel's theory, the thermal motion of atoms or ions is represented by the following set of processes:

- atoms may vibrate about a regular equilibrium position at the lattice sites;
- an atom or ion having sufficient energy may move from its lattice site into an interstice; Ya. Frenkel called this process the "dissociation of bound atoms";
- a dissociated atom may move to a free lattice site (a "hole"); Ya. Frenkel called this phenomenon the "association of dissociated atoms";
- a dissociated atom may vibrate about its interstitial position until it jumps over the potential barrier to another free site.

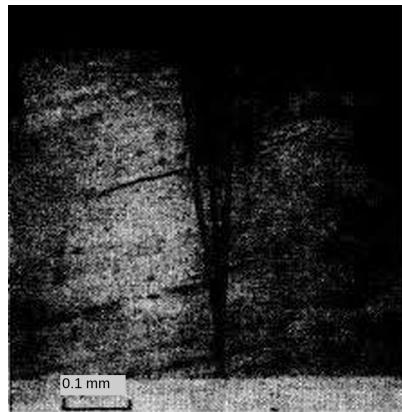


Figure 6.1

The intrinsic atoms (ions) of the crystal lattice can diffuse. This is self-diffusion, or homodiffusion. Self-diffusion takes place at constant concentration.

Ya. Frenkel called the process of atoms jumping from one regular equilibrium position to another the "diffusion of holes in the lattice". Thus, diffusion proceeds through the movement of holes and the motion of atoms (or ions) in the interatomic space.

As can be seen from Fig. 6.2, the mechanisms by which atoms move through a crystal may be: direct exchange of atoms – a; ring exchange – b; movement through interstices – c; relay (interstitialcy) diffusion – d; movement via vacancies – e; dissociative movement – f; movement along dislocations, stacking faults and grain

boundaries. Direct exchange consists in two neighbouring atoms exchanging places in the crystal lattice in a single jump.

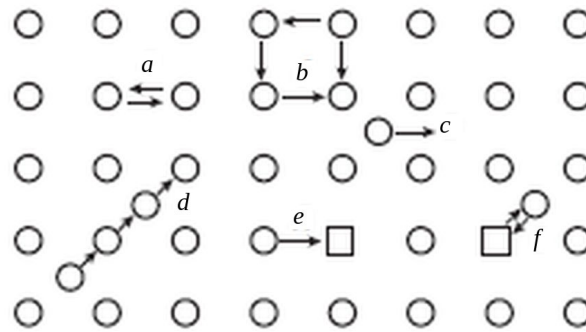


Figure 6.2 – Mechanisms of atom movement through a crystal

The interstitial mechanism of diffusion consists in the transfer of matter between the atoms occupying lattice sites. Diffusion by this mechanism is intensive. If for some reason the crystal contains a large number of interstitial atoms, they move easily through the lattice.

The vacancy mechanism of diffusion consists in the migration of atoms through the crystal lattice by means of vacancies. The atoms around a vacancy vibrate and, having acquired a certain energy, one of them may jump into the vacancy and take its place in the lattice, leaving a vacancy behind it in turn. In this way atoms and vacancies move through the lattice, and hence mass transfer occurs.

In any diffusion process in crystalline solids, as a rule, all the listed mechanisms of atomic motion take place.

In the same crystal, under different conditions and for different atoms, diffusion may proceed by different mechanisms with different activation energies. However, the probabilities of these processes in the crystal differ. Thus, direct exchange of atoms requires a very large local distortion of the lattice and the associated concentration of energy in a small region. Therefore, this process is unlikely. Ring exchange is also of little significance.

In addition to bulk diffusion, surface diffusion and diffusion along grain and block boundaries, pores and dislocations are observed in crystals. In a polycrystalline substance, grain-boundary diffusion may be the main type of diffusion.

The energy required to move a vacancy or an atom through the lattice is called the activation energy. In solids under normal conditions, diffusion processes are slow, and an increase in temperature always accelerates diffusion. Diffusion may be a complex multistage process in which each stage has its own temperature dependence.

Pressure has a complex effect on diffusion, which depends on the diffusion mechanism. If diffusion proceeds by the vacancy mechanism, an increase in pressure reduces the vacancy content.

This is because an increase in vacancy content increases the volume of the crystal, whereas pressure tends to decrease its volume and therefore lowers the vacancy content, correspondingly reducing the diffusion rate. If diffusion proceeds by the interstitial mechanism, then, on the one hand, an increase in pressure raises the content of interstitial atoms, and, on the other hand, the atoms in the crystal come closer together, and movement between the sites becomes more difficult. Other mechanisms are also distinguished (Fig. 6.3):

- displacement (interstitialcy) mechanism 5 – an atom first enters an interstice and then pushes the nearest neighbouring atom out of its site and takes its place; the atom displaced into the interstice pushes out the next "neighbour", and so on;

- crowdion mechanism 6 – small displacements of each atom along a row in a certain direction, as a result of which a crowdion is formed, i.e. a group of atoms compressed owing to the presence of an extra atom in their row.

Atoms of other chemical elements dissolved in the matrix phase can also diffuse. This is impurity diffusion, or heterodiffusion. Heterodiffusion under a non-uniform concentration distribution of chemical species in the crystal lattice of another substance is called chemical diffusion.

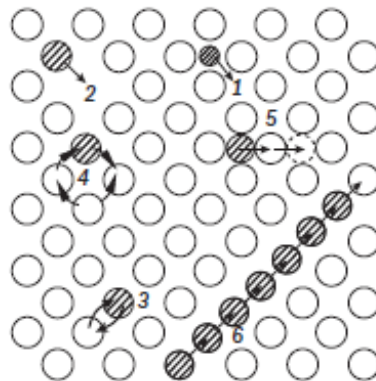


Figure 6.3

Directed movement of the atoms of one substance in the lattice of another may also be caused both by its concentration gradient and by inhomogeneities of temperature, of the elastic stress field, or of the concentrations of other substances.

When an external electric field is applied to crystals, in addition to the ordinary diffusion flux, directed transport of charged vacancies and interstitial atoms also arises, i.e. ionic conduction takes place. Defect diffusion in ionic crystals can be significantly influenced by an external electric field, since the intrinsic point defects in them are charged. In a number of cases, defects with charges of different signs are present in ionic crystals.

At the initial stage of the study of diffusion processes, it was assumed that the only driving force of the process was the concentration gradient of the diffusing atoms.

The electric current density arising from ionic conduction in this case has two components describing the transport of both positively (+) and negatively (–) charged defects. The fraction t_i contributed by a particular defect to the total ionic conductivity is called the transport number.

Table 6.1 – Transport numbers of ionic crystals

Crystal	t , °C	t_+	t_-	Crystal	t , °C	t_+	t_-
NaF	550	1.00	0.00	KI	610	0.90	0.16
NaF	625	0.86	0.14	AgBr	20–300	1.00	0.00
NaCl	500	0.98	0.02	AgCl	20–300	1.00	0.00
NaCl	600	0.95	0.05	BaF ₂	500	0.00	1.00
NaBr	710	0.12	0.88	BaCl ₂	350–450	0.00	1.00
NaBr	435	0.96	0.04	PbF ₂	200	0.00	1.00
NaBr	600	0.83	0.17	PbCl ₂	200–425	0.00	1.00
KCl	525	0.88	0.12	PbBr ₂	200–365	0.00	1.00
KCl	600	0.88	0.12	PbI ₂	255	0.39	0.61
KBr	605	0.59	0.50	CuCl	300	0.98	0.00

If it is assumed that the flux per unit time through a unit area of cross-section perpendicular to the direction of the flux, i.e. the flux density, is proportional to the concentration gradient of component i , one can write:

$$J_i = -D_i \partial c_i / \partial x,$$

where J_i is the flux of component i along the x axis;

D_i is the diffusion coefficient of component i ;

c_i is the concentration of component i .

This formula expresses Fick's first law.

The change in concentration per unit time τ at a given point of the cross-section, numerically equal to $\partial c / \partial \tau$, can be expressed by the equation of Fick's second law:

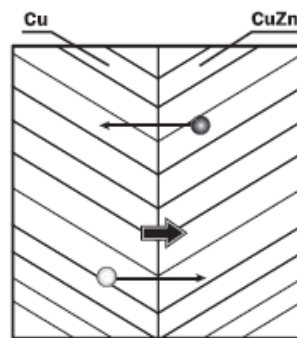
$$\partial c_i / \partial \tau = D_i \partial^2 c_i / \partial x^2.$$

These equations are valid for a system of diffusing particles that do not interact with one another and are in random motion, when all parts of the system are characterised by the same physical conditions (no temperature gradient, no elastic stress, etc.) but by different concentrations of the diffusing substance.

The driving force of diffusion in these equations is the concentration gradient. The diffusion flux is then directed from regions of high concentration of the diffusing

substance to regions of low concentration. In other words, so-called levelling diffusion takes place.

In practice, the phenomenon of uphill diffusion has also been found in multicomponent crystalline systems, when a flux of a certain kind is directed from a region of lower concentration to a region of higher concentration of the diffusing particles. Thus, in multicomponent crystalline systems (for example, in alloys with carbon), cross-effects of the interdiffusion of components occur. Cross-effects in interdiffusion can be very significant. The flux of any of the components is then determined by the concentration gradients of all the components.



- – Zn atoms; ○ – vacancies; – direction of motion of the Cu/CuZn interface

Figure 6.4

The sum of the fluxes of all the components relative to the crystal lattice is non-zero owing to the different mobilities of the components (i.e. the different frequencies of exchange of atoms of different kinds with vacancies).

Thus, the cross-effect may lead to uphill diffusion, i.e. diffusion of a component against its own concentration gradient.

At the phase boundary of a two-component crystalline system, on heating, the crystal lattice moves as a whole from the side of the slow component towards the fast one. Through this motion, the system equalises the fluxes of the components.

If inert markers are introduced into the crystal, they will record the motion of the interface, which manifests itself as the Kirkendall effect.

For example, if inert markers (molybdenum wires) are placed at the interface between two phases – copper and α -brass CuZn – as shown in Fig. 6.5, these markers move closer together. This happens because the main type of diffusion is the diffusion of zinc from the brass into the copper by the vacancy mechanism. The counter-flux of vacancies from the copper into the brass causes the markers to approach each other.

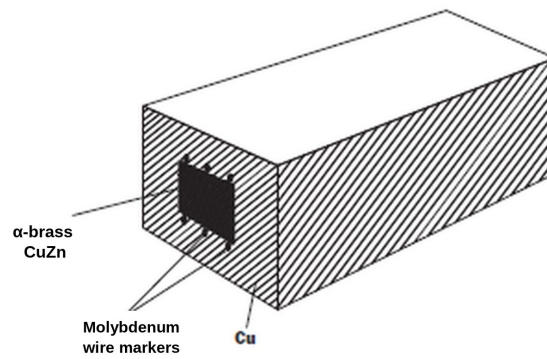


Figure 6.5

The standard interpretation of the Kirkendall effect is that the difference in partial fluxes generates a flux of vacancies towards the more mobile component of the diffusion couple (Zn). On the side of the slower component (Cu), new lattice grows.

The interface then moves towards the fast-diffusing component, as a result of which the phase based on the slow-diffusing component (Cu) grows in volume, while the phase based on the fast component (α -brass) decreases in volume.

Diffusion processes have a very significant effect on the mechanisms and rates of chemical reactions involving crystalline solids.

Self-assessment questions

1. Name the features of diffusion processes in crystals.
2. Explain the Kirkendall effect.
3. Name the possible mechanisms of self-diffusion of atoms in crystals.
4. Explain the interstitial mechanism of diffusion.
5. Explain the vacancy mechanism of diffusion.
6. What are transport numbers in ionic crystals?
7. Name the common and distinguishing features of levelling and uphill diffusion.
8. State and explain Fick's first and second laws.

LECTURE 7

STRUCTURAL FEATURES AND PROPERTIES OF THE SURFACE OF SOLIDS

7.1 MODELS OF THE CRYSTAL SURFACE

The concept of an ideal crystalline body does not include the surface, since changes in structure and properties compared with atoms in the bulk are observed at the surface of real crystals, in particular a break in translational symmetry, a change in the coordination numbers of surface atoms and a number of others.

Although crystal surfaces resemble the bulk in their structural properties and reactivity, there are also significant differences:

- in the arrangement of atoms and ions;
 - in the number, nature and arrangement of point defects and dislocations;
 - in the mobility of particles at the surface;
 - in the presence of groups of different chemical composition;
 - in the ability of surfaces to concentrate substances from the adjacent phases,
- etc.

The surface is regarded as a special state of a crystalline body. In the microscopic sense, the surface of a crystal is an abrupt transition from its bulk to an ideal vacuum.

Ideally clean and smooth surfaces, like an ideal vacuum, do not exist. Therefore, the concepts of an atomically clean and atomically smooth surface are introduced, in which the characteristic scale of irregularities is one atomic diameter.

To preserve such a surface for a long time, an ultra-high vacuum with a residual pressure of 10^{-9} – 10^{-10} Pa is maintained.

Several models are used to describe the surface of solids.

The surface of solids is often described using the dangling-bond model. For example, in the elemental covalent semiconductor silicon, the reduced coordination number of the surface atoms means that, among the four tetrahedrally arranged orbitals of each atom capable of participating in chemical bonding, at least one orbital must be directed away from the surface. This is a broken (dangling, unsaturated) bond.

The saturated character of the bonds of surface atoms can be restored either by adsorption of atoms or molecules from the environment or by a change in the surface structure.

Under ultra-high vacuum conditions, the bond strength of the atoms of the first layer can be restored without excessive weakening of the bonds of the atoms of subsequent layers, in particular by creating previously absent bonds between surface

atoms, and also by strengthening their bonding with one another or with atoms of the second layer.

A distinction is made between relaxation and reconstruction of the surface. Relaxation means a displacement of the surface plane along the normal to the surface. Relaxation of a clean surface always occurs towards the bulk of the crystal, and the interaction of the surface atoms with the atoms of the substrate is thereby strengthened.

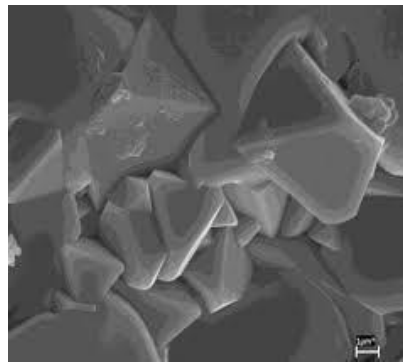


Figure 7.1

In surface reconstruction, a change in the lattice constants is observed. The rearrangement of the surface structure of a solid accompanies the processes of chemisorption and desorption (Fig. 7.2).

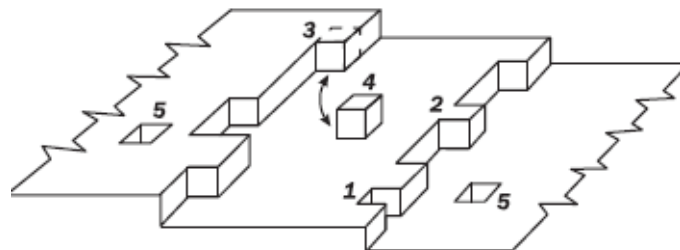


Figure 7.2 – Structure of a crystal surface: 1, 2 – kinks; 3, 4 – exchange of atoms between kinks and the adsorbed layer; 5 – surface vacancies

During chemisorption the surface structure changes in one direction, and during desorption in the other.

The statistical model is based on the chemical approach. The surface is described in terms of surface centres, i.e. atoms or groups of atoms belonging to the surface. Surface centres may be surface atoms of the host lattice with a "broken" (free) bond; centres associated with defects of an inhomogeneous surface at crystallographic steps and at dislocation outcrops; and impurities on the surface. A surface centre is always localised on the real surface of the solid and has a certain chemical activity.

The band model is based on the electronic, or energy, approach. In this model, the surface is described in terms of surface states, to which surface electron energy

levels correspond. In the band model, surface states are understood as electronic states that are spatially localised at the interface between a solid (semiconductor) and some medium (vacuum, gas, etc.), have an energy position within the band gap of the semiconductor and change their charge state depending on the position of the Fermi level at the surface.

Surface centres are of two types – donor and acceptor. Donor-type states are positively charged if they lie above the Fermi level and neutral if they lie below it. Acceptor-type states are neutral if they lie above the Fermi level and negatively charged if they lie below it. The geometric model is based on consideration of the geometric characteristics of the surface.

7.2 ADSORPTION ON THE SURFACE OF SOLIDS

A solid on which the uptake of gases and vapours takes place is called an adsorbent, and the adsorbed substance is called the adsorbate. The process reverse to adsorption is called desorption.

Most often, the amount of adsorption, i.e. the quantity of adsorbed gas (or vapour), is expressed in moles of adsorbed substance per 1 g of adsorbent. The amount of adsorption of a given substance is the higher, the more accessible the adsorbent surface is to this substance. Therefore, the specific surface area, i.e. the surface area of 1 g of adsorbent, is given as a characteristic of solids.

Molecules can be adsorbed on a surface in two ways, i.e. physical and chemical adsorption may take place. In physical adsorption, the interaction between the surface and the adsorbed molecule is due to intermolecular interaction, which does not lead to the breaking or formation of new chemical bonds. The adsorbed molecule then interacts not with a single centre on the adsorbent surface but with many neighbouring centres.



Figure 7.3

In chemical adsorption (chemisorption), molecules are held on the surface as a result of the formation of a chemical (quasi-chemical), usually covalent, bond. The

amount of energy released in chemisorption is, as a rule, greater than in physical adsorption and is often equal to the energy of a chemical bond.

When considering the interaction of adsorbates with the surface of solids, it is necessary to take into account both attractive forces and repulsive forces, which increase rapidly as the distance decreases. The attractive forces are determined by interactions of the following types:

- dispersion interaction, associated with the correlated motion of electrons in approaching molecules;
- orientation interaction, observed in the adsorption of polar molecules on charged surfaces;
- induction interaction, associated with the appearance of induced dipole moments in the adsorbed molecules or in the adsorbent.

The chemisorption of oxygen on metals leads to the formation of an oxide film. The products of O_2 chemisorption, however, differ from the corresponding oxides. For example, WO_3 is reduced by hydrogen, whereas the compound formed by the adsorption of oxygen on tungsten does not react with hydrogen even at 1600 °C. In chemisorption, electron transfer between the solid and the adsorbate and electron sharing are also observed.

On most clean metals, a chemisorbed oxygen layer forms even at temperatures below room temperature. Transition metals show the greatest activity in chemisorption, owing to the participation of d-orbitals in the formation of adsorption bonds.

Chemisorption on semiconductors and dielectrics may lead to the saturation of dangling bonds through the formation of a local chemical bond at the surface. Adsorption on the surface of ionic solids having acidic or basic centres is of the same type. An acid–base covalent bond is formed with the corresponding base or with species from the gas phase.

7.3 FEATURES OF ADSORPTION ON THE SURFACE OF SOLIDS

Solid surfaces are used as adsorbents for the adsorption of gases or liquids, and the adsorption processes then take place at the solid–gas (S/G) and solid–liquid (S/L) interfaces. The surface of solids is geometrically and energetically inhomogeneous. Adsorption processes are always associated with the structural features of the solid surface.

Solid adsorbents may contain pores. Therefore, the nature of the adsorbent surface and the size and shape of its pores influence adsorption, changing its quantitative and qualitative characteristics, i.e. the adsorption mechanism.

Depending on their porosity, solid adsorbents are divided into two groups: non-porous and porous. The porosity Π is equal to the ratio of the total pore volume V_p to the total volume of the adsorbent V_{tot} , i.e.

$$\Pi = V_p / V_{\text{tot}}.$$

Table 7.1 – Characteristics of adsorbents

Adsorbents	Pore diameter, nm	Specific surface area, m ² /kg
Non-porous	–	1–500
Macroporous	> 4.0	$(0.5\text{--}2.0) \cdot 10^3$
Mesoporous	1.2–4.0	$< 4 \cdot 10^5$
Microporous	< 1.2	$> 4 \cdot 10^5$

In non-porous adsorbents, the interface corresponds to the contour of the solid. In porous adsorbents, this surface is considerably larger owing to the pores. Porous adsorbents are often used in the form of powders. Adsorption on powdered adsorbents is determined by their specific surface area.

The specific surface area of porous powdered adsorbents considerably exceeds that of non-porous adsorbents and depends to a greater extent on the pore surface than on the surface defining the particle contour. The characteristics of non-porous and porous powdered adsorbents are given in Table 7.1.

Porosity not only sharply increases the specific surface area of an adsorbent but also affects the adsorption mechanism. The adsorption of gases on micro- and mesoporous adsorbents differs substantially from their adsorption on non-porous and macroporous adsorbents, on which monomolecular and polymolecular adsorption is observed.

Adsorption on microporous adsorbents consists in the volume filling of the pore space, while adsorption on mesoporous adsorbents consists in the capillary condensation of the adsorbate vapour.

The adsorption capacity of micropores is determined not only by their specific surface area but also by the volume of the micropores themselves. For powdered adsorbents, the difference between them is due only to the value of the specific surface area.

Some non-powdered and powdered disperse systems are macroporous adsorbents. These include fabrics, asbestos, etc.

A considerable part of disperse systems and their products can be classed as non-porous adsorbents. These include, in particular, metals and metal articles. In industry, micro- and mesoporous adsorbents based on mineral substances and carbon materials are used.

Siliceous rocks of natural clays, which belong to the group of aluminosilicates ($\text{Al}_2\text{O}_3 + \text{SiO}_2$) of alkali and alkaline-earth metals, are mesoporous adsorbents; they are used in the form of suspensions deposited on a filtering base, usually a fabric.

Microporous mineral powdered adsorbents include zeolites, which are alkali (Na, K) and alkaline-earth (Ca, Mg) aluminosilicates characterised by the general formula $\text{Me}_n\text{Al}_x\text{Si}_y(\text{H}_2\text{O})_z$, where Me is a metal ion.

Zeolites may be natural or synthetic. Zeolites are of greatest importance in the drying of gases and air, as well as in the purification of liquid products.

Carbon adsorbents are widely used in various industries. Microporous carbon adsorbents are obtained by high-temperature treatment, without access of air, of various fossil coals and other carbon-rich substances. After additional treatment with steam or inert gases to clean the pores and to introduce additives that promote adsorption, activated carbon is obtained. Owing to its porosity, its specific surface area exceeds $4 \cdot 10^5 \text{ m}^2/\text{kg}$, and its pore volume exceeds $0.5 \cdot 10^{-2} \text{ m}^3/\text{kg}$.

7.4 SURFACE ENERGY AND SURFACE TENSION OF SOLIDS

The concepts of surface tension and specific free surface energy apply to all condensed systems, including solids.

Any crystalline body has an internal and a surface energy. The work required to divide a crystal into separate parts determines the internal energy, which is proportional to the magnitude, number and nature of the bonds in the bulk of the crystal.

The surface energy of a crystal is proportional to its surface area. Dispersion of a crystal, which leads to an increase in its surface area without a change in its volume, must be accompanied by an increase in surface energy.

The formation of a new surface is conventionally represented as two stages. At the first stage, after the substance has been divided into parts, the molecules near the surface remain in the positions they previously occupied in the bulk. During the second stage, the molecules at the surface rearrange and take up equilibrium positions.

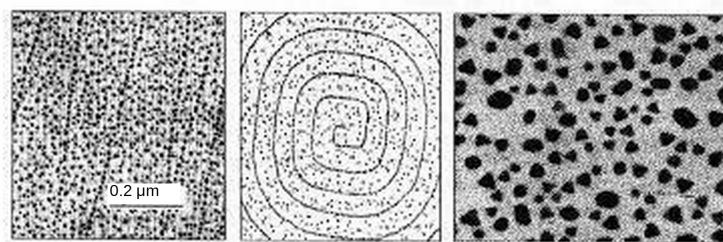


Figure 7.4

In this case, for example, a surface metal atom may have from 3 to 9 nearest neighbours, and its energy increases by an amount proportional to the number of missing bonds. Therefore, the energy of surface atoms is greater than that of atoms in the interior. When estimating the surface energy of metals in the solid state, it is also necessary to take into account the excess energy contributed by lattice defects of the crystals.

To move an internal part of a crystal to its surface, a certain amount of work must be expended, which at the surface is converted into the potential energy of the surface part, or the excess potential energy of the surface layer. This excess energy, referred to unit surface area, is called the surface energy, or also the surface tension.

When the surface of a solid is formed, irregularities associated with the limited mobility of the molecules of these bodies arise at the interface. Therefore, the work expended on the formation of unit surface area, i.e. the specific free surface energy, will differ at different points of the solid surface. The inhomogeneity of the surface of a solid also affects its surface tension.

As a rule, the surface tension and the specific free surface energy of solids are considered to be numerically equal. Indeed, at elevated temperatures the concepts of surface energy and surface tension are equivalent for solids. However, at low temperatures, when the mobility of the atoms of the solid is low, the surface tension and the surface energy will not be quantitatively equal. In this connection, it makes sense to consider the specific free surface energy and the surface tension of solids either at a point or as certain averaged quantities. Therefore, all crystalline bodies are characterised by anisotropy of their properties, including the surface energy, whose value depends not only on the bonding forces between the particles of the crystal but also on the geometric structure of the lattice adjacent to the surface in question.

The surface energy differs for different faces. The total surface energy of a crystal is determined by the sum of the surface energies of all its faces. If the surface energy is regarded as the result of incomplete atomic bonding, it is evident that its minimum value corresponds to the most densely packed crystallographic planes.

It has been established that the surface layer of a pure metal is a nanostructure whose physical properties differ significantly from the bulk properties of the metal, and its thickness does not exceed 10 nm. However, size effects begin to appear at a somewhat greater metal film thickness, so that a transition layer of metal adjoins the bulk phase. It is precisely on this scale that the processes of fracture of a solid take place.

There are a number of methods for determining the surface tension of solids. At present there is no universal method for determining surface tension in the solid phase over a wide temperature range. Each method is practically limited either by temperature or by quantities that are determined experimentally with low accuracy.

In the zero-creep method, a specimen (a long wire or foil) is heated to a sufficiently high temperature that it begins to contract in length under the action of surface tension. An external force is applied to the specimen to keep its shape unchanged. The surface tension is determined from the magnitude of this force. The method is applicable mainly to metals. G. Tammann and co-workers also used this method to determine the surface tension of amorphous bodies.

The crystal fracture (cleavage) method is based on the idea that the work expended on fracturing a crystal is equal to the surface energy of the new surfaces thus formed, provided that the fracture is brittle. The values of surface energy obtained in this way cannot be absolutely reliable, since some hard-to-control part of the work expended is released as heat during partial deformation of the crystals.

Also known are the neutral drop method, the powder dissolution method, the method of growth steps of a crystal from the gas phase and its evaporation, the conical specimen method, the method of determining the critical surface tension at the interface with a solid, the Yurov method, and others.

7.5 NATURE OF SURFACE CENTRES

Lewis acid and base centres and Brønsted centres may exist on the surface of a solid.

A Lewis acid surface centre is a centre on the surface that has a vacant orbital with a high affinity for an electron pair, i.e. it is an electron-pair acceptor. Therefore, when an adsorbed basic molecule (for example, NH_3) shares its electron pair with the centre, a considerable decrease in energy occurs.

A Lewis base surface centre has electron pairs in high-energy orbitals, i.e. it is an electron-pair donor. When an electron pair is shared between the surface centre and an adsorbed acceptor, a considerable decrease in energy also occurs.

Brønsted acid surface centres tend to donate a proton, while Brønsted base centres act as proton acceptors. A solid, for example an oxide, must have two types of centres even in the case of a homogeneous surface. On the surface of an oxide, the unoccupied orbitals of the cations act as acceptor surface states, or Lewis acid centres, while the orbitals of the oxygen ions are donor surface states, or Lewis base centres. As a result of the adsorption of water on the oxide surface, two classes of centres may also arise, but these are now Brønsted centres.

The presence of adsorbed water, as well as of various types of centres on the surface of solids, determines their electrochemical and chemical activity as catalysts, in corrosion processes, and in electrochemical processes, including electron transfer at the surface, in photoelectrochemical and photochemical processes, etc.

Self-assessment questions

1. Explain the concept of an "ideal crystalline body".
2. What do the concepts of an "atomically clean" and an "atomically smooth" surface have in common, and how do they differ?
3. Explain the dangling-bond model of the surface of solids.
4. Explain the statistical model describing the structure of crystal surfaces.
5. How do donor and acceptor centres on crystal surfaces work?
6. Explain the approaches on which the band model of the crystal surface is based.
7. Explain the concept of the surface tension of solids. What are the features of its determination for solids?
8. Describe Lewis acid and base surface centres.
9. Describe Brønsted acid and base surface centres.
10. Describe the mechanism of physical adsorption on the surface of solids.
11. Describe the mechanism of chemical adsorption (chemisorption) on the surface of solids.

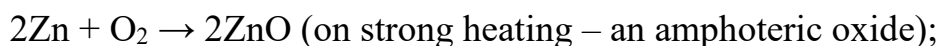
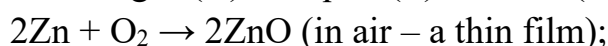
LECTURE 8

SOLID-STATE CHEMICAL REACTIONS

8.1 TYPES OF SOLID-STATE REACTIONS

Chemical reactions involving one or several solids are heterogeneous reactions. They are also called solid-state reactions. Examples of some typical heterogeneous reactions involving solids are given below:

1) oxidation reactions, or reactions of film formation on the surface of solids (S) on their interaction with a gas (G) or liquid (L) – $S_1 + G(L) \rightarrow S_2$:



2) chemical reactions of salt decomposition with the formation of gaseous products: $S_1 \rightarrow S_2 + G$:

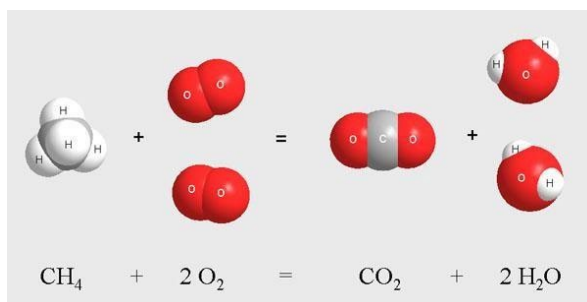
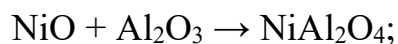
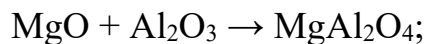
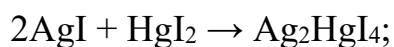


Figure 8.1

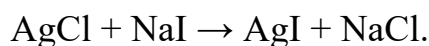
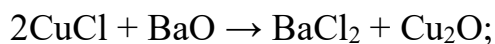
3) chemical reactions of the reduction of metal oxides by carbon: $S_1 + S_2 \rightarrow S_3 + G$:



4) spinel-forming reactions: $S_1 + S_2 \rightarrow S_3$:



5) double decomposition (metathesis) reactions of solids:



8.2 FEATURES OF TOPOCHEMICAL REACTIONS

Solid-state reactions localised in space are called topochemical reactions. Topochemical reactions in the narrow sense of the word are characterised by the presence of solids both among the starting components and among the reaction

products. From the kinetic point of view, topochemical reactions also include reactions in which there is a difference in composition between different parts of the reacting system. These are reactions that proceed locally in certain regions of a solid, where the solid product phase is also localised.

A chemical transformation in heterogeneous systems cannot occur at an arbitrary point in space. Molecular transformations must take place at the contact between phases. In all heterogeneous transformations a reaction zone appears, usually of small thickness, separating two regions of space occupied by substances of different composition with different properties. This is the so-called reaction front. For the reaction to proceed, the reacting particles must enter the reaction zone.

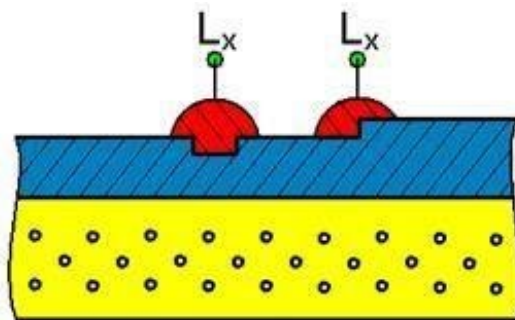


Figure 8.2

Therefore, heterogeneous processes are accompanied by diffusion processes, which are necessary for transporting the particles of the reactants into the reaction zone and removing the reaction products.

The appearance of a reaction front is due to various causes, which can be divided into two groups. In some cases, the existence of a reaction front is caused by the relative slowness of diffusion: the slower the diffusion, the thinner the reaction zone and the more slowly it moves.

In other cases, the formation of a reaction front is due to chemical causes, namely the high reactivity of the atoms or molecules located at the surface of the solid or at the interface. If the reaction front is caused by a chemical process, one can speak of the existence of a reaction interface. This term implies the existence of an interface between two different phases at which the chemical reaction takes place.

In real crystalline systems, the surface separating two phases with different chemical and physical properties has a very small thickness, for example close to the size of a single molecule. The surface of a phase has properties completely different from the bulk properties of the material. Therefore, the surface is regarded as a transition zone in which a significant rearrangement of the crystal packing takes place, the stress between the two lattices decreases, the chemical composition changes, and the various rearrangements are accompanied by the movement of atoms and molecules.

The overall rate of a heterogeneous transformation is always a function of the rates of two processes: the chemical reaction and diffusion. In most processes, the rates of the chemical reaction are comparable to the rates of diffusion. It is often possible to accelerate one or the other group of processes if a way of influencing one of them is found. Thus, a change in temperature t has a stronger effect on the rate of the chemical reaction, since its temperature dependence is, as a rule, exponential, while the rate of diffusion is proportional to $t^{1.5}$. For reactions that are limited to a greater or lesser extent by processes occurring at the interface, the limiting effect of the concentration of the reactants can be avoided by special technological techniques: stirring the liquid or gas, grinding or spraying the solid reactant. In this group of processes, the main role is always played by the chemical interaction, since it is this that determines the rate of the whole process, and the nature of the chemical transformation depends on it.

In all topochemical reactions, the processes of the appearance and growth of nuclei, i.e. formations capable of growing, the smallest particles of the new phase, are considered. The rate of topochemical reactions is usually proportional to the surface area of the nuclei at each given moment and depends on the compactness of the reaction products, since it is also determined by the diffusion of the components through their layer. Structural defects have a significant effect on the rate of topochemical reactions. They manifest themselves both in a change in the number of potential reaction centres on the surface and in the conditions for diffusion.

Wagner's theory of the interaction of solids arose from studies of the mobility of ions in crystals and from the fact that a large number of solid phases exist. Deviation from stoichiometry, the presence of impurities in the crystal, or the transition of atoms from regular crystal sites to the surface or into interstices for various reasons is accompanied by the appearance of vacant cation or anion sites. Owing to this disorder, it is possible to explain diffusion in solids, which proceeds, in particular, by jumps of individual ions from lattice sites to the nearest interstices and vacant sites.

In semiconductor crystals, in which cations, anions and electrons can migrate simultaneously, ionic diffusion takes place under the influence of the concentration gradient and the electric field.

8.3 OXIDATION REACTIONS OF METALS AND ALLOYS

The chemical action of gases on metals and alloys (at high temperatures) leads to their oxidation. The most important oxidising agents are oxygen, the oxides CO, CO₂ and SO₂, as well as H₂S and other gases. As a result of the chemical interaction of the metal with these gases, an oxide film forms on its surface. Figure 8.3 shows a

diagram of the formation of an oxide film on a metal during oxidation by atmospheric oxygen.

The main stages of the oxidation of metals are:

- 1 – ionisation of the metal and its passage in the form of ions and electrons into the oxide layer;
- 2 – movement of the metal ions Me^{n+} and electrons in the oxide layer;
- 3 – transfer of oxygen from the gas flow to the oxide surface;
- 4 – adsorption of oxygen on the oxide surface;
- 5 – conversion of the adsorbed oxygen into O^{2-} ions;
- 6 – movement of the oxygen ions O^{2-} in the oxide layer;
- 7 – the oxide formation reaction.

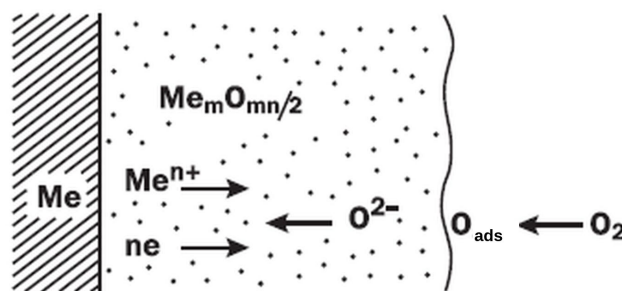


Figure 8.3 – Diagram of the formation of an oxide film on a metal during oxidation by atmospheric oxygen

All stages of the process are interrelated and proceed sequentially. The overall rate of the process is determined by the rate of the slowest step. For example, if stage 3 is slow, the process is limited by external diffusion; if stages 1, 2 or 6 are slow, the process is under internal diffusion control. A metal ion has a smaller radius than the corresponding metal atom. Consequently, mainly metal ions and electrons will move from the metal through the film. Oxygen ions diffuse towards the metal. The ionisation of oxygen then takes place at the outer surface of the oxide film. The radius of metal ions is smaller than that of the oxygen ion. Therefore, metal ions have a high mobility in diffusion, and the film growth zone is shifted towards the outer boundary.

Diffusion in a solid at temperatures below the melting point of the crystals can proceed by one of two mechanisms:

- movement of atoms or ions between the sites of the crystal lattice;
- movement of atoms or ions via vacant lattice sites or along dislocations and grain boundaries.

The first mechanism operates in the formation of oxides whose metal ions are small compared with the lattice parameters. ZnO and Al_2O_3 films form according to this principle. The second mechanism is more probable when oxides with vacant sites in the crystal lattice can form. Cu_2O and FeO form by this mechanism.

To understand the oxidation mechanism for various metal–gas combinations, it is necessary to know the composition and structure of the stable compounds formed in such a combination, and since most oxidation reactions are accompanied by the diffusion of ions, it is necessary to know the nature of the lattice defects that play the main role in the diffusion mechanism.

If a metal has several oxidation states and forms a series of compounds with the gas, these compounds are arranged in layers, the layer richest in gas being located at the oxide–gas interface and the layer richest in metal adjoining the metal base. Thus, at high temperatures, the following oxides may form on the surface of iron: FeO, Fe₃O₄, Fe₂O₃.

Iron(II) oxide FeO (wüstite) has a cubic lattice. The crystallographic cell contains four Fe²⁺ ions and four O²⁻ ions. This oxide contains oxygen in amounts exceeding the stoichiometric ones. The oxygen dissolved in the oxide is ionised, taking electrons from some of the divalent iron ions Fe²⁺, which become trivalent ions Fe³⁺. This creates favourable conditions for the diffusion of Fe²⁺ ions and the movement of electrons via the transition $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e$. The iron oxide Fe₃O₄ (magnetite) has a spinel-type crystal lattice. In the lattice, there are two Fe³⁺ ions for each Fe²⁺ ion in regular crystallographic alternation. Fe₃O₄ has electronic conductivity. This is because the regular alternation of $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ ions in the oxide structure facilitates the transfer of an electron from one cation site to another.

On heating in an oxidising atmosphere to 220 °C, magnetite transforms into γ-Fe₂O₃. In this case, the composition of the oxide changes from Fe₃O₄ to Fe₂O₃ without a change in the crystallographic structure. On heating to 400–500 °C, α-Fe₂O₃ is formed. The iron oxide Fe₂O₃ (haematite) has a rhombohedral lattice structure. Haematite exists over a wide temperature range, but above 1100 °C it partially dissociates.

If two metals of an alloy interact with a gas X, or one metal interacts with two gases X and Y (or with a gas of composition XY), complex reaction products are formed, which may exist on the metal surface as a heterogeneous mixture or as separate layers; the formation of a new double compound is also possible. The compound formed in excess may "impose" its structure on the entire set of reaction products, the secondary components being "built into" the lattice of the main one. At the same time, in a number of systems (Fe₃O₄ – Mn₃O₄, Al₂O₃ – Cr₂O₃, CaO – MnO, etc.), solid solutions with unlimited solubility are formed. In these cases, the periodicity of the lattice is hardly disturbed. However, if the two metals have different valences, the initial lattice becomes less perfect.

8.4 REDUCTION OF IRON FROM ITS OXIDES

Heterogeneous reactions of the same chemical nature may proceed differently and be limited by different factors depending on the process conditions and on the structure of the initial phase and of the reaction products. Typical and at the same time the most complex in this respect are the reactions of the reduction of iron from its oxides.

Iron reduction processes are characterised by a sequence of transformations of higher oxides into lower oxides and then into the metal. At temperatures above 570 °C, reduction proceeds successively through the stages of formation of all the oxides and their corresponding crystal lattices: $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}_{\text{met}}$.

The ordered rearrangement of the lattices is not maintained for long because of the changes in specific volumes accompanying the phase transformations.



Figure 8.4

The stresses that develop disrupt the continuity of the crystalline aggregates and cause them to split along the phase-conjugation zones. An interface appears on which gas adsorption develops. Thus, the reaction surface advances into the solid, driving the zone of phase transformations ahead of it.

In the case of diffusion inhibition of the process, when the rate of supply of the reducing agent and removal of the products exceeds the rate of solid-state diffusion, the reduction of the oxides proceeds zonally. On the surface of a grain, where the concentration of the reducing gas is highest, a reaction zone corresponding to the final stages of reduction develops, while in deeper layers, where its concentration is lower, zones corresponding to the initial stages of reduction develop. Zonal reduction is characteristic of dense (previously annealed or sintered) materials.

When diffusion inside the specimen is not limiting, reduction proceeds stepwise. In stepwise reduction, a reaction zone corresponding to the $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ interface advances into the grain, and only after its disappearance, as a result of the complete conversion of iron(III) oxide into the mixed iron(II,III) oxide, does a second reaction zone, $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$, form on the surface of the grain and develop inwards.



Figure 8.5

After this reaction zone disappears, the last reaction zone, $\text{FeO} \rightarrow \text{Fe}_{\text{met}}$, appears and advances into the specimen. A somewhat different stepwise reduction regime is also possible, which develops throughout the entire volume of the specimen without localisation of the reaction zone. This regime is possible under external diffusion control and provided that the microparticles of the specimen are equally accessible to the reducing gas. This regime can be observed in the reduction of loose, porous specimens, and also of those that swell during reduction.

8.5 SPINEL-FORMING REACTIONS

As a rule, solids do not react with one another at ordinary temperature. Heating is required, often to 1000–1500 °C.

When MgO and Al_2O_3 crystals in close contact along a common plane interact, a layer of spinel MgAl_2O_4 forms at the interface between the crystals as a result of the corresponding heat treatment. A comparison of the structure of MgAl_2O_4 with those of MgO and Al_2O_3 reveals both similarities and differences. Both MgO and spinel have cubic closest packing of oxygen ions, whereas Al_2O_3 has distorted hexagonal closest packing. In both Al_2O_3 and spinel, the Al^{3+} ions occupy octahedral positions, while the Mg^{2+} ions occupy octahedral positions in MgO but tetrahedral positions in MgAl_2O_4 . At the first stage, MgAl_2O_4 nuclei are formed. The

considerable structural differences between the starting substances and the product hinder nucleation, since the structural rearrangement involved requires the breaking of existing bonds and the formation of new ones, as well as the migration of atoms over distances that may be very considerable on the atomic scale. The Mg^{2+} ions in MgO and Al^{3+} ions in Al_2O_3 occupy regular lattice sites, and their movement to an adjacent unoccupied site is very difficult. Only at high temperature do the ions acquire sufficient thermal energy for an ion to leave its normal position in the lattice and begin to diffuse through the crystal. Thus, the formation of MgAl_2O_4 nuclei requires some rearrangement of the oxygen ions at the site of the future nucleus and, simultaneously, a mutual exchange of Mg^{2+} and Al^{3+} ions across the interface between the two crystals.



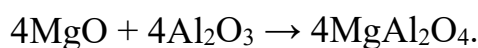
Figure 8.6

For the reaction to proceed further and the thickness of the MgAl_2O_4 layer to increase, counter-diffusion of Mg^{2+} and Al^{3+} ions through the existing spinel layer to the new reaction surfaces is required. Two such surfaces then appear: one separating MgO from MgAl_2O_4 and the other separating MgAl_2O_4 from Al_2O_3 .

The mechanism of the reaction between MgO and Al_2O_3 , which includes the counter-diffusion of Mg^{2+} and Al^{3+} ions through the product layer followed by reaction at the boundaries separating the product and the reactants, is the Wagner mechanism. To maintain electroneutrality, for every three Mg^{2+} ions diffusing to one boundary, two Al^{3+} ions must move to the other boundary. The reactions occurring at the boundaries can be described by the equations:



which, when added together, give the equation of the overall process:



Three times as much product forms at the spinel/ Al_2O_3 boundary as at the MgO /spinel boundary. Consequently, the former boundary must move three times

faster than the left-hand one. In systems where the boundaries can easily be observed, they can serve as convenient natural markers that make it possible to follow the progress of the reaction. Recall that the displacement of a marker during diffusion processes is known as the Kirkendall effect.

8.6 FACTORS DETERMINING THE RATE OF SOLID-STATE REACTIONS

The rate of solid-state reactions depends to a large extent on the following three factors:

- the area of contact between the reacting solid phases and, hence, the surface area of the reactants;
- the rate of nucleation of the new phase;
- the rates of ion diffusion in the phases participating in the reaction, especially in the product phase.

The surface area of the same amount (mass) of a solid can vary within very wide limits depending on whether the substance is in the form of a single crystal or a coarse or fine powder. In other words, the surface area depends on the particle size.

The surface area of the reactants has the strongest effect on the reaction rate, since an increase in the total surface of the interacting particles also increases the total area of the contacting surfaces (the contact area). The actual area of direct contact between the interacting particles is always smaller than the total surface of the particles of the substance. The formation of the product of the interaction of two solids can be divided into two stages – the formation of nuclei and their subsequent growth. Nucleation occurs more easily (faster) when the reaction product is structurally similar to at least one of the reactants, since this reduces the number of structural rearrangements required for nucleus formation. In particular, in the interaction of MgO and Al_2O_3 , the spinel formed has a packing of oxygen ions similar to that in MgO . Therefore, spinel nuclei can form on the surface of MgO , and the oxygen sublattice at the MgO /spinel boundary remains almost continuous. Such similarity (sometimes only partial) between the nucleating phase (spinel) and the substrate phase (MgO) facilitates nucleation.

For solid-state reactions whose nucleation is based on the structural similarity of the phases, all phenomena of oriented nucleation can be divided into two types – topotactic and epitaxial. Both require structural correspondence between the two phases. In the case of epitaxial reactions, such correspondence is observed only directly at the interface.

The readiness of a nucleus of the new phase to form also depends on the structure of the particular contact surface of the reacting phases. In most cases, the

surface structure cannot be the same for the whole crystal. The reactivity of crystals in individual regions of their surface that differ in structure is also different. The reactivity of solids also depends to a great extent on the presence of structural defects. The presence of crystal structure defects such as vacancies, interstitial ions and dislocation pipes sharply accelerates diffusion.

Self-assessment questions

1. Which reactions are classified as topochemical? Give examples.
2. Explain the terms "reaction zone" and "reaction front" as applied to topochemical reactions.
3. What factors affect the rate of a topochemical reaction?
4. Explain the mechanism of oxidation of metals and alloys.
5. Explain the mechanism of the reduction of metals from oxides.
6. Name the features of the mechanism of spinel formation.
7. Name the features of topotactic and epitaxial reactions.
8. How do crystal lattice defects affect the rate of topochemical reactions?

LECTURE 9

AMORPHOUS SOLIDS

9.1 THE AMORPHOUS AND VITREOUS STATES OF SOLIDS

Amorphous solids (from the Ancient Greek α - "not" and μορφή "shape, form") are substances in the condensed state whose atomic structure has short-range order but lacks the long-range order characteristic of crystalline structures. Compared with crystalline bodies of the same chemical composition, they have a higher energy content.

Unlike crystals, amorphous substances do not solidify with the formation of crystal faces and exhibit isotropy of properties, i.e. they do not show different properties in different directions.

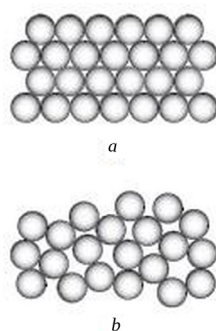


Figure 9.1 – Comparison of the atomic structure of crystals (a) and amorphous bodies (b)

Amorphous modifications of many elements of the periodic table are known – boron, arsenic, antimony, selenium, and others (Bi, Ga, Zn, Hf, V, Nb, Ta, Cr, Mo, W, Re, Fe, Ni, Al). The interaction of chemical elements produces vitreous compounds, which leads to an enormous diversity of systems with a non-periodically organised structure.

Amorphous solids can exist in two states – amorphous and vitreous (glassy). The concept of the "amorphous solid state" is broader than that of the "vitreous state". A glass is always amorphous, but amorphous substances are not always glasses. For example, highly dispersed powders obtained by precipitation from aqueous solutions may be amorphous, but they cannot be called glasses. The amorphous state of many substances is obtained at high rates of solidification (cooling) of the liquid melt, or by condensation of vapour on a surface (substrate) cooled well below the melting point, as well as by amorphisation of crystalline substances, for example by ion-beam bombardment. Amorphous substances do not have a definite melting point. As the temperature rises, stable amorphous substances gradually soften and, above the glass transition temperature, pass into the liquid state. Substances that normally have a

polycrystalline structure but are strongly supercooled during solidification may solidify in the amorphous state and crystallise on subsequent heating or with time.

The vitreous state is a metastable state of matter in which elements of crystallisation are observed only in very small clusters. It is usually a supercooled liquid in which the formation of a crystalline solid phase is hindered. The reversibility of the transition from the vitreous state to the melt and from the melt to the vitreous state, i.e. vitrification, is the characteristic feature that distinguishes the vitreous state from other amorphous states. Practically any substance can be converted from the molten state into the vitreous state. A substance capable of passing into the vitreous state is characterised by a critical, i.e. minimum permissible, cooling rate at which, after cooling, it is able to pass reversibly into the vitreous state. Some melts of glass-forming substances do not require rapid cooling for this. However, substances such as metal-containing melts require very rapid cooling to avoid crystallisation.

One of the most important parameters characterising the transition to the vitreous state is the glass transition temperature. The higher it is, the wider the temperature range in which a glass exists without changing its shape. Substances with any type of chemical bond can pass into the vitreous state. In particular, the glass-forming oxides SiO_2 , B_2O_3 , GeO_2 and P_2O_5 have bonds of mixed ionic and covalent character. However, regardless of chemical composition and the temperature range of solidification, a glass has the physical and mechanical properties of a solid while retaining the ability to pass reversibly from the vitreous to the liquid state. Owing to the short-range order existing in amorphous solids, energy bands can arise. Most glasses, in particular silicate glasses, are dielectrics in terms of their electrical properties, but there are also amorphous metals and amorphous semiconductors.

9.2 SILICATE GLASSES

The term "vitreous state" owes its origin to glass, a widely used inorganic material that is in an amorphous metastable state. The three main types of inorganic silicate glass are soda–lime (soda) glass, potash–lime (potash) glass and potash–lead (lead) glass. The basic method of producing silicate glass consists in melting a mixture of quartz sand (SiO_2), soda (Na_2CO_3) or potash (K_2CO_3), and lime (CaO). The main constituent of glass (70–75 %) is silicon dioxide (SiO_2). Calcium oxide (CaO) makes the glass chemically resistant and enhances its lustre. The proportion of the alkali metal oxides of sodium (Na_2O) or potassium (K_2O) is 16–17 %.

An important parameter that must be taken into account in the production and service of glass is the viscosity of the glass-forming components. This parameter

determines the choice of the melting temperature and the time during which the raw materials are heated until a homogeneous melt is obtained. To ensure high product quality, the melt must be refined, i.e. gas bubbles must be removed from it. The lower the viscosity, the easier the refining.

Potash glass is more refractory and harder, less plastic and less easily shaped, but has a strong lustre. Lead glass (crystal glass) is fairly soft and fusible, but rather heavy; it is distinguished by a strong lustre and a high refractive index, dispersing light into all the colours of the rainbow and producing a play of light.

9.3 METALLIC GLASSES

The electrical resistance of amorphous metals is considerably higher than that of crystalline metals and, in certain temperature ranges, is characterised by a weak temperature dependence, sometimes even decreasing with increasing temperature.

In analysing the resistance features of amorphous metals, three groups are distinguished:

- simple metal – simple metal;
- transition metal – metalloid;
- transition metal – transition metal.

Metallic glasses of the simple metal – simple metal group have a low resistivity (less than $100 \mu\Omega \cdot \text{cm}$). As the temperature rises, the resistance of different materials of this group may either increase or decrease.

The resistivity of materials of the transition metal – metalloid group lies in the range $100\text{--}200 \mu\Omega \cdot \text{cm}$. The minimum resistance is observed at a temperature of about 300°C . The temperature coefficient of resistance is positive up to $\sim 150 \mu\Omega \cdot \text{cm}$ and then becomes negative.

Some amorphous alloys exhibit superconductivity while retaining good ductility. The main method of producing metallic glasses is rapid cooling of the melt, as a result of which it passes into the solid state while avoiding crystallisation. Technologies are known that make it possible to obtain amorphous metals in the form of powder, thin wire, thin ribbon and platelets. To obtain platelets weighing up to several hundred milligrams, a drop of melt is shot at high speed onto a cooled copper plate; the cooling rate then reaches 10^9 K/s . To obtain thin ribbons with a width from fractions of a millimetre to tens of millimetres, the melt is extruded onto a rapidly rotating cooled surface. To obtain wires from a few to hundreds of micrometres thick, the melt is drawn through a tube passing through a cooling aqueous solution (the cooling rate being $10^4\text{--}10^5 \text{ K/s}$), or a jet of melt enters a cooling liquid held on the inner side of a drum by centrifugal force.

Alloys with a low critical cooling rate have been developed, which has made it possible to produce bulk metallic glasses. The use of corrosion-resistant amorphous alloys in various industries is promising. In the defence industry, interlayers of aluminium-based amorphous alloys are used in the manufacture of protective armour to absorb the energy of a penetrating projectile owing to the high fracture toughness of such interlayers. Owing to their magnetic properties, amorphous metals are used in the manufacture of magnetic screens, read heads of audio and video tape recorders, data recording and storage devices in computer technology, transformers and other devices. The low temperature dependence of the resistance of some amorphous metals allows them to be used as reference resistors.

9.4 AMORPHOUS (VITREOUS) SEMICONDUCTORS

Since amorphous solids have short-range order, one can speak of the existence of a band structure different from that of crystalline bodies. Some substances in the amorphous state exhibit semiconducting properties. In amorphous (vitreous) semiconductors, both electronic and ionic conductivity may occur. The most studied are the elemental tetrahedral amorphous semiconductors germanium and silicon; chalcogenide semiconductors – alloys of sulphides, tellurides and selenides of various metals, for example As–S–Se, As–Ge–Se–Te, As–Sb–S–Se and Ge–Pb–S; oxide semiconductors, for example V_2O_5 – P_2O_5 –BaO, V_2O_5 – P_2O_5 – Li_2O and V_2O_5 – P_2O_5 – Ag_2O ; and others.

Amorphous Ge and Si are most often obtained by ion sputtering in various hydrogen-containing atmospheres, as well as by the dissociation of the gases SiH_4 and GeH_4 in a high-frequency discharge. Chalcogenide amorphous semiconductors are obtained by cooling the melt or by evaporation in vacuum. Amorphous (vitreous) semiconductors have a low sensitivity to impurities and a low charge-carrier mobility, interact in a characteristic way with various kinds of radiation, and find diverse applications – in optical instrument making, electrophotography, light-recording media for holography, and in photo-, electron- and X-ray resists.

Films of amorphous silicon and other elemental amorphous semiconductors are used to manufacture solar cells and various image converters.

Self-assessment questions

1. Name the fields of application of corrosion-resistant amorphous alloys.
2. Name the structural features of amorphous bodies.
3. In what states can amorphous solids exist?
4. Under what physical conditions is the amorphous state of solids achieved?
5. What features characterise the vitreous state of solids?

6. Explain the concept of the "glass transition temperature".
7. Describe amorphous metals (metallic glasses).
8. Name the types of amorphous glasses of the "metal–metalloid" and "metal–metal" type.
9. Amorphous semiconductors: their properties and methods of production.
10. Fields of application of amorphous semiconductors.

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