

§2. The Interaction of Atoms in Crystal (see [3]).

2.1.1 Some basis ideas about interatomic interactions.

The fact that under certain conditions atoms can form stable molecules and crystals proves that forces of attraction can act between them, being compensated at distances of the order of 10^{-8} cm by forces of repulsion. Almost in every case it appears more convenient to operate not with forces but with the potential energy of interatomic interaction $U(R)$, which we assume to be dependent only on the distance R between the atoms. The curves 1 and 2 in Figure 1 depict possible cases of interaction between two atoms, one of which is placed in the origin O , and the other atom A , can move along the R axis. Since the potential energy is determined to within a constant term, we can always put $U=0$ for $R \rightarrow \infty$. The force acting on atom A is $\vec{F} = -\hat{\nabla} U(R)$. Hence, often the forces of attraction act at those points where $dU/dR > 0$ (F is anti parallel to R), and the forces of repulsion

where $dU/dR < 0$ (F is parallel to R). It may be seen from Figure 1 that curve 1 corresponds to the case where the atoms repulse each other at all distances R , Curve 2 corresponds to a more complex case where the atoms attract each other at $R > R_0$, and repulse each other at $R < R_0$. The derivative $(dU/dR)_{R_0} = 0$ at $R = R_0$, i.e., $\vec{F} = -\frac{dU}{dR} \frac{\vec{R}}{R} \Big|_{R=R_0} = 0$, and the system of two atoms is in a state of stable equilibrium. In this case, as we the shape of curve 2, $(d^2U/dR^2) = \beta > 0$. For small deflections of atom A from the equilibrium position potential energy can be expanded to power series

$$U(R) = U(R_0) + \left(\frac{dU}{dR} \right)_{R_0} (R - R_0) + \frac{1}{2} \left(\frac{d^2U}{dR^2} \right)_{R_0} (R - R_0)^2 + \frac{1}{6} \left(\frac{d^3U}{dR^3} \right)_{R_0} (R - R_0)^3 + \dots \quad (1)$$

to within terms of the third order of smallness. If, as is actually the case, the forces of repulsion close to the point $R=R_0$ grow more rapidly with a decrease in R than the forces of attraction fall, then $(d^3U/dR^3)_{R_0} = -2\gamma < 0$. Denoting $U(R_0)$ by U_0 and the deflection of atom A from its equilibrium position $R - R_0$ by x , we obtain

$$U(x) - U_0 = \frac{1}{2} \beta x^2 - \frac{1}{3} \gamma x^3 \quad (2)$$

The force acting on atom A as it moves near its equilibrium position along the R axis is

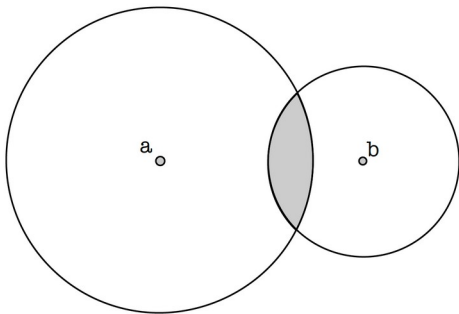
$$F = -\frac{dU}{dR} = -\beta x + \gamma x^3. \quad (3)$$

Often the non-linear terms can be omitted $F = -\frac{dU}{dR} = -\beta x$ (because of their smallness) and we have a so-called quasi-elastic or linear or harmonic approximation for interatomic forces. This approximation is very convenient for describing the vibrational properties of crystals and molecules. In this case, vibrating atoms can be represented as a set of independent harmonic oscillators or independent quantum of vibrations (formal particles) - phonons (analogical to photon - quantum of electromagnetic field). But important to emphasize that the nonlinear terms (3) play a decisive role in the phenomena of heat conduction.

2.1.2 Repulsion forces

A consistent theory of atomic (ionic) interaction should be based on a quantum mechanical treatment of the motion of their electrons. The atomic nuclei can be presumed to remain at rest because of their great mass (the adiabatic approximation). In this case the total energy of the electrons depends on the position of the nuclei as on parameters. When the distance between the atoms is varied, the total energy of the electrons, together with the Coulomb repulsion of the nuclei, plays the part of the potential energy of interatomic interaction. In some cases it is possible to get a rough idea about the atomic interaction from more elementary considerations based on a statistical analysis of the behaviour of the atomic

Figure 2



electrons.

Consider from this point of view the nature of the repulsion forces acting between the atoms (ions). Except in the trivial case of the Coulomb interaction between ions of like charge, which makes itself felt at great distances between them, the repulsion between atoms (ions) at short distances is the result of mutual penetration of their electron shells. This repulsion is due mainly to the rise in the kinetic energy of the atomic electrons on account of Pauli's principle.

To establish the nature of those forces we shall consider the electrons of the atoms (ions) as a degenerate Fermi gas at the absolute zero temperature. A simple calculation shows that the density of the kinetic energy of the electrons (kinetic energy per cubic centimetre) is $E(k) = (3^{5/3} \pi^{4/3} \hbar^2 / 10m) n^{5/3}$, where n is the electron concentration (at a specified point), $2\pi\hbar$ Planck's constant, and m the electron mass. As a zero approximation, we shall presume that the densities of electrons n_a and n_b in free atoms (ions) **a** and **b** (Figure 2) do not change as the result of mutual penetration of their electron shells. This assumption corresponds to the use in quantum mechanical calculations of unperturbed wave functions. In this case the variation of the kinetic energy density in the region of overlapping electron shells (shaded area in Fig. 2) is

$$\Delta E(k) = \frac{3^{5/3} \pi^{4/3}}{10m} [(n_a + n_b)^{5/3} - n_a^{5/3} - n_b^{5/3}] . \quad (4)$$

It may easily be seen that the effect of the overlapping of electron shells of atoms *a* and *b* is to increase the kinetic energy of the electrons in the system, i. e., to establish repulsive forces (the greater the smaller the distance between *a* and *b*). We should add to them the repulsive forces of a purely Coulomb origin between the atomic nuclei *a* and *b*, which appear when the nucleus of one atom penetrates the atomic shell of the other. A more detailed study shows that the inclusion of exchange effects into the statistical theory results in the appearance, as the result of mutual penetration, of certain attractive forces which, however, are unable to change the qualitative Fig. 2 picture described above. The quantum mechanical theory of interatomic repulsive forces yields for the potential energy an expression of the form $A \exp(-R/a)$, where *A* and *a* are positive constants.

2.1.3 Types of interatomic forces

For the formation of stable crystals there should be, in addition to the forces of repulsion between the atoms (ions), also forces of attraction acting between them. Usually four principal types of bonds in crystals are considered: (a) ionic or heteropolar, (b) covalent, (c) van der Waals or dispersion, and (d) metallic. It should be noted that in the majority of cases the bonds in crystals are of mixed character, therefore one often hears statements that a bond is covalent so many percent and ionic so many percent. When we speak of one type of bond, we mean that this type is prevalent. There is a special parameters determining this fact - degree of ionicity $\equiv r$. For NaCl $r=0.72$ and for CaF $r=0.92$ it means that interatomic bonds in NaCl on 72% ionic and on 28% covalent. For Si $r \approx 0$, the electron shell of the nearest atoms is completely separated.

The ionic bond in its purest form is realized in ionic crystals, for example, in alkali-halide compounds NaCl, KCl, CsCl. The interaction between the ions, in the first approximation, is considered as the interaction between point charges located at lattice sites. Since the ions of the first coordination group are always charged oppositely to the central ion, the Coulomb interaction of all the lattice ions results in some attraction, which provides for the stability of the lattice.

In a quantitative theory, because of the slow decrease of Coulomb forces with distance, we should take into account the interaction of the central ion with more distant ions of both signs. The next approximation takes into account the mutual polarization of the ions.

2.1.4 Covalent forces

The covalent bond occurs between closely spaced (10^{-8} cm) neutral atoms if certain conditions are fulfilled. In its simplest form, the covalent bond is realized between two hydrogen atoms in a hydrogen molecule H_2 (W. Heitler and F. London, 1927). The covalent bond cannot be interpreted in terms of classical physics. Special quantum mechanical features in the behaviour of a system of identical particles (electrons) are essential for the explanation

of the covalent bond. Classical physics was quite powerless to explain the properties of the saturated covalent bond, for example, the inability of a hydrogen atom to become attached to more than one other hydrogen atom. This property is characterized in chemistry by the concept of *valency*; it stems from the pairing of the electrons belonging to both atoms and the formation of a singlet state in which the electron spins are antiparallel (the curve of atomic interaction for the triplet state in which the electron spins are parallel is of the form $1/r$, i.e., the atoms repulse each other at all distances).

The covalent bond may occur not only between two hydrogen atoms but between other atoms possessing electrons capable of forming pairs with opposite spins. For instance, the nitrogen atom N has two electrons in the $1s$ -, two electrons in the $2s$ - and three electrons in the $2p$ -states, i.e., it has an electron structure denoted by $(1s)^2 (2s)^2 (2p)^3$. Spectroscopic data show that the spins of three electrons in the $2p$ -state are all parallel, i.e., there is no spin saturation, and, consequently, they are able to form three covalent bonds; hence, nitrogen is trivalent.

This is confirmed by experiment. Thus, for example, when nitrogen reacts with hydrogen, NH_3 is produced. The diatomic nitrogen molecule N_2 in which the atoms are bonded by three pairs of electrons with antiparallel spins is formed in the same way. The magnetic quantum numbers of the three $2p$ electrons in the nitrogen atom are $m = +1, -1, 0$, and the corresponding wave functions are of the form $\psi_{+1} = xf(r), \psi_{-1} = yf(r)$ and $\psi_0 = zf(r)$, i.e., the electron clouds of the three valence electrons are elongated in three mutually orthogonal directions x, y and z . The gain in energy accompanying the formation of a covalent bond depends to a great degree on the overlapping of the wave functions of the electrons forming the appropriate pair with antiparallel spins. Thus, it may be reasoned that the hydrogen atoms in an NH_3 molecule will be arranged in three mutually perpendicular directions with respect to the nitrogen atom (directed valencies). Experiment confirms that the NH_3 molecule, indeed, is of the shape of a pyramid with the HNH angle close to 90° (109° , to be precise). A somewhat greater angle between the directed valencies in the NH_3 molecule can be explained by the mutual repulsion of the hydrogen atoms.

The electron structure of the carbon atom C is $(1s)^2 (2s)^2 (2p)^2$. Since the spins in the s -states are saturated (antiparallel), the carbon atom should be bivalent. However, this conclusion is in contradiction with the data obtained in organic chemistry, according to which the valency of carbon is four. A more scrupulous theoretical and experimental investigation of the problem shows that the carbon atom takes part in the reactions not in its ground state but in an excited state: $(1s)^2 (2s)^1 (2p)^3$. In this case the spins of all four electrons are not saturated (the $2s$ electron has no partner, and the spins of the $2p$ electrons are parallel) and can participate in the formation of a covalent bonds.

More precisely, the carbon atom forms covalent bonds in the electron state, which is a superposition of one $2s$ - and three $2p$ -states. The coefficients (the weights) of each of those states in the linear combination and the directions of the four valence bonds are determined by the condition that the free energy of the molecule be

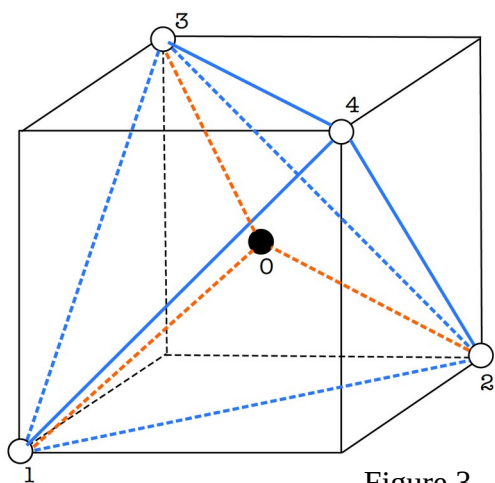


Figure 3

minimal. Mathematical analysis, which we are not in a position to carry out here, shows the directions of the valence bonds to coincide with the 01 , 02 , 03 , and 04 directions in a tetrahedron (Figure 3), and we know those directions to be $109,5^\circ$. Experiment shows that the methane molecule CH_4 does, indeed, have such a tetrahedral structure. The directed four valency of carbon atoms manifests itself in the formation of the diamond crystal, in which every carbon atom is located in the centre of a tetrahedron formed by four other carbon atoms. The silicon (Si) atom has four electrons in its M-shell in the $(3s)^2 (3p)^2$ -states, and, because the spins in its K - and L -shells are saturated, is expected to behave in a similar way to the carbon atom. The properties of the germanium (Ge) atom with four electrons in its N-shell in the $(3s)^2 (4p)^2$ -states, of the tin (Sn) atom with four electrons in its O-shell in the $(5s)^2 (5p)^2$ -states and of the lead (Pb) atom with four electrons in its P-shell in the $(6s)^2 (6p)^2$ -states are similar. Actually, silicon, germanium and grey tin all crystallize in the diamond-type lattice and belong to typical covalent crystals. As for normal (white) tin and lead, the covalent nature of atomic bonding in them does not make itself felt, because it is suppressed by the metallic properties of the material (see below).

Experimental studies in recent years have proved the chemical compounds of the $A^{\text{III}}B^{\text{V}}$ type, i.e., of the elements of groups III and V of the Periodic Table, to possess numerous properties (crystal lattice, electron band structure) typical for the elements of Group IV, germanium and silicon. InSb and GaAs belong to compounds of this type. Indium has three electrons in its O-shell in the $(5s)^2 (5p)^3$ states, and antimony five electrons in the $(5s)^2 (5p)^3$ -states. Hence, just as is the case with Ge or Si, there are four electrons in the s -state and four in the p -state. If one of the p electrons of Sb partly goes over to In, a covalent bond can be formed similar to that formed in Si and Ge crystals. The same is true of the GaAs compound. Of course, the bond InSb and GaAs is not purely covalent, being partly ionic.

2.1.5 Van-der-Waals forces

The covalent bond occurs only if certain conditions are fulfilled. First, the atoms should have electrons capable of forming pairs with opposite spins (singlet state). Second, the spacing between the atoms should be small enough for the quantum mechanical properties based on the indistinguishability of identical particles constituting the system to make themselves manifest. Calculation shows the covalent forces to decrease rapidly (exponentially) with the distance. At larger distances all atomic systems begin to display certain universal attraction forces. Those forces are termed van der Waals, or dispersion, forces because, on the one hand, they are the cause of the divergence in behaviour of real gases from the ideal and, on the other, their parameters determine the dispersion of light by atoms. The van der Waals interaction provides bonding between particles in solids (argon, krypton, xenon and molecular crystals) in such cases where for some reason (closed electron shells, saturated valence bonds in the interacting molecules, etc.) there are no covalent, ionic, or metallic bonds (see below).

If the distance between the atomic systems R a (a is the atomic system's dimension), the van der Waals (dispersion) forces can be calculated in the second approximation of the quantum mechanical perturbation theory. It can be demonstrated that the van der Waals interaction energy of two atomic systems is

$$U(R) = -W_0/R^6 \quad (5)$$

Here R is the distance between the systems, and

$$W_0 \approx \frac{3}{2} \frac{J_a J_b}{J_a + J_b} \alpha_a \alpha_b \quad (6)$$

where J_a, J_b are ionization potentials and α_a, α_b the polarizations of the atoms (molecules) a and b , respectively. The van der Waals forces, like the ionic forces, do not exhibit saturation effects characteristic for the covalent bond. In addition to the ionic, covalent, and van der Waals forces discussed above, there are also *dipole* and *induced forces* generated by the permanent electric dipole moment of some molecules. They may be of importance in the case of complex molecular lattices and shall not be considered here. The condition $R \gg a$ is not fulfilled in crystals in which the atoms or molecules are bonded by van der Waals forces (noble gases at low temperatures, molecular crystals).

2.1.6 Metallic forces

Typical metals such as, for example, Li, Na, K, Cu, Ag, Fe, Ni, have some characteristic electrical, optical and mechanical properties. They all feature a relatively high electrical conductivity and light absorption coefficient and high plasticity and malleability. These properties unambiguously point to the fact that the metals contain a large number (of the order of the number of atoms) of free electrons, i.e., electrons that can travel over macroscopic distances in the crystal already in weak external electric fields. The simplest model of a metal, proposed by Paul Drude, is made up of positively charged ions located at the sites of a crystal lattice and of an ideal gas of “free electrons” moving between the ions. Despite all the changes and complexities introduced into the modern electron theory of metals (which we shall in part touch on below), such a straightforward model has not lost its importance; we need only take into account that the ideal gas of free electrons is strongly degenerate at all practically attainable temperatures of a metal.

As was first demonstrated by Ya. I. Frenkel (we do not consider subsequent perfections of his idea to be essential), the forces of cohesion in a metal crystal can be explained on the basis of the original simple free electron model. Frenkel considers the total bonding energy in a metal as consisting of two parts: the negative energy of Coulomb interaction between the free electrons and the positively charged ions (it is proportional to $1/a$, where a is the lattice parameter) and the positive kinetic energy of the degenerate gas of “free” electrons (it is proportional to $n^{2/3} \sim 1/a^2$, where n is the free electron concentration).

The total bonding energy will obviously have a minimum value for some value of a as shown by simple calculation to be of the order of 10^{-8} cm.

Some characteristic properties of different materials.

Type of crystal	Example	Band energy(kcal/mol)	Properties
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Ionic	NaCl	150-200	Infrared absorption, dielectric for low temperature and ionic conductor for high.
Covalent	Ge, C, Si	200-300	High hardness, low conductivity for low temperature
Metal	Na, Fe, Cu	20-100	High conductivity
Molecular crystals	Ar, CH ₄	2-3	Low melting and boiling points. High compressibility.
Crystals with hydrogen bonds	H ₂ O, HF	~10	Tends to polymerisation. A little more stable than molecular crystal.

2.1.7 Ionic forces. An example of calculating the binding energy for ionic crystals.

In ionic crystals, atoms can be viewed as a set of point charges. For example, in CsCl, the Cs and Cl ions have a non closed electron shell. In process of creation of ionic chemical bond a single valence electron from the outer shell of Cs migrates to the Cl atom, and as a result we obtain Cs and Cl ions with completely filled electron shells. Electrons in an ionic crystal are completely localized and are in the valence band. To transfer an electron to the conducting zone (to tear it away from atom Cl), it is necessary to expend a lot of energy, more than 8 eV. That is why ionic crystals are dielectrics. The interaction energy for ion **i** and **k** can be equal to:

$$E_{i,k} = \pm \frac{Z_i Z_k e^2}{4 \pi \epsilon_0 r_{i,k}} + \frac{b}{r_{i,k}^m} \quad (7)$$

The first member is associated with classical Coulomb interaction. Due to the fact that in ionic crystals the minimum distance between ions with opposite charge signs is less than between ions with the same charge sign, this term describes the forces of interionic attraction. Second term is related to repulsion forces and associated to overlap of electron shells of ions and Pauli exclusion principle. In (7) Z -dimensionless charges of ions, b -unknown parameter, r -distance between ions, m -must be determined.

The potential energy of ion with number **i**:

$$E_i = \pm \sum_k \left(\frac{Z_i Z_k e^2}{4 \pi \epsilon_0 r_{i,k}} + \frac{b}{r_{i,k}^m} \right) = - \frac{\alpha_M e^2}{4 \pi \epsilon_0 R} + \frac{A}{R^m} \quad (8)$$

Here $A = \sum_k \frac{b}{q_{i,k}^m}$ and $\alpha_M = Z_i \sum_k \frac{Z_k}{q_{i,k}}$ - Madelung constant. When calculating the Madelung constant, a problem arises related to the very slow convergence of this sum. Therefore, to calculate this constant, it is necessary to use the special mathematical Ewald method. For NaCl $\alpha_M=1,7476$, CsCl $\alpha_M=1,7627$, ZnS $\alpha_M=1,638$.

The total internal energy can be calculated by multiplication of (8) on N – number of atoms.

$$U = N \left(-\frac{\alpha_M e^2}{4\pi\epsilon_0 R} + \frac{A}{R^m} \right) \text{ later we replace } \alpha_M \rightarrow \alpha_M / 4\pi\epsilon_0 \quad (9)$$

For T=0 atoms are located in equilibrium positions this means that $\left. \frac{dU}{dR} \right|_{R=a} = 0$. Calculation of derivative allow to calculate $A = \frac{\alpha_M e^2}{m} \cdot a^{m-1}$ and substitution one to (9) $U = -\frac{N\alpha_M e^2}{a} \left(1 - \frac{1}{m}\right)$.

The compressibility of crystal can be calculated by the following:

$$\frac{1}{k} = \frac{1}{V} \frac{d^2 U}{dV^2} \quad (10)$$

For NaCl crystal $V=2Na^3$ then for compressibility:

$$k = \frac{18a^4}{(m - Ne^2\alpha_M)} \quad (11)$$

Using data for NaCl gives for m=9,4. This is a fairly correct value and means that the overlapping of the shells leads to a very rapid increase in repulsive forces. For practical measurement of bonding energy the **Born-Haber cycle** can be used (https://en.wikipedia.org/wiki/Born%E2%80%93Haber_cycle).