1.5 Types of Atomic Bonds

There are a great number of solids in nature but all of them are formed by no more then a hundred of chemical elements. All the difference between them is due to interaction between their atoms, which in its turn depends on the construction of electron shells of the interacting atoms. The bond between the shells almost totally depends only on the *forces of electrostatic attraction and repulsion.*

The presence of stable bonds between atoms of a crystal makes it possible to assume that the total energy of crystal is less than the energy of other configuration including that one when all the atoms are very far from each other. The difference between these two quantities is called the *binding energy.* This quantity is from about 0.1eV/atom for solids with the Van-der-Vaals interaction up to about 8eV/atom for covalent and ionic compounds and metals. In covalent compounds, the angular directions are essential. All the other bonds have the tendency to increase the coordination number (the number of the closest neighbors).

There are four principal bonds in crystal: the Van-der-Vaals, covalent, ionic and metallic.

1.5.1 Vav-der-Vaals Interaction

The weak interaction between neutral atoms and molecules is called the Van-der-Vaals interaction. Though the average electric dipole moment of neutral atoms and molecules is zero, the heat oscillations of atoms produce the fluctuation dipole moment. Assume that the nuclei of two atoms are at the distance r. An instant dipole moment p_1 produces at the center of the second atom, the electric field $E = 2p_1/r^3$. That field polarizes the second atom and generates an instant dipole moment $p_2 = \alpha E = 2\alpha p_1/r^3$, α - electric polarizability.

The dipole-dipole potential energy is (see [1]):

$$U(r) = \frac{(\mathbf{p}_1 \cdot \mathbf{p}_2)r^2 - 3(\mathbf{p}_1 \cdot \mathbf{r})(\mathbf{p}_2 \cdot \mathbf{r})}{r^5} \tag{1.73}$$

The vector $\mathbf{p}_1$ и $\mathbf{p}_2$ are parallel, so the energy of their interaction can be written as follows:

$$U(r) \approx -\frac{2p_1 p_2}{r^3} = -\frac{2\alpha p_1^2}{r^6} \tag{1.74}$$

It is the energy of attraction. The magnitude of the energy is calculated in [2].

$$U(r) \approx -\frac{4e^2 r_0^5}{r^6} \approx -\frac{10^{-58}}{r^6} \text{ (erg). } r_0 \approx 10^{-8} \text{ см.}$$

In general case, the energy of the Van-der-Vaasls interaction:

$$U(r) \approx -\frac{A}{r^6} \tag{1.75}$$

If $A \approx 10^{-58}$ erg·cm^6 = 6.25·10^{-47} eV·cm^6 and $r = 4$ Å, the interaction energy of krypton $U \approx 2 \cdot 10^{-14}$ erg = 1.25·10^{-2} eV.

The calculations show that when r is about 1 Å, the interaction energy of two dipoles is ~10eV. But when the atoms with completed electron shells are approaching each other,

the interaction energy caused by reciprocal superposition of atomic shells is the energy of repulsion. Mainly it is due to the Pauli exclusion principle.

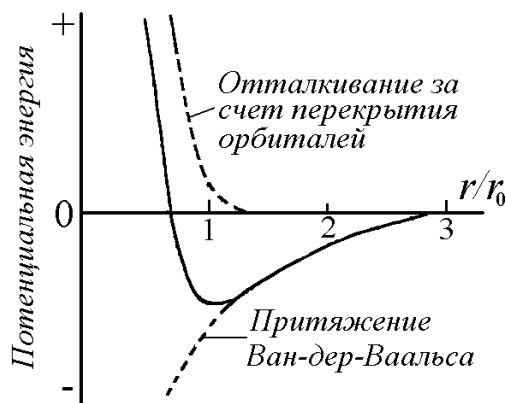The repulsion potential of inert gases can be written as B/r^{12} (B – a positive constant). The total potential energy of two atoms at a distance r:

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{1.76}$$

ε And σ are constants: $4\varepsilon\sigma^6 \equiv A$, $4\varepsilon\sigma^{12} \equiv B$. The quantity (1.76) is known to be the Lenard-Jones potential.

Using the characteristic length, we can write the total energy in the form:

$$U(r) \approx -\frac{A}{r^6} + \lambda\exp\left(-\frac{r}{\rho}\right). \tag{1.77}$$

The dependence is shown in Fig.1.12. The resultant bonding energy and the equilibrium distance r_0 between the atoms under consideration depends on parameters A, B, and ρ. The crystals of inert gases can be considered as solids in which the bonds are produced exclusively by the Van-der-Vaals forces.

Fig.12 *The Van-der-Vaals potential energy.*

1.5.2 Covalent Bonding

Covalent (homopolar) bonding is build up between two electrons when they simultaneously belong to two neighbor atoms. As a result, in the region between two atoms, the high density of the electron charge is produced. The covalent bond is a strong one. For example, the bonding energy of two neutral carbon atoms of a diamond is 7,3 eV. The covalent bonding is strongly angular dependant. Thus, in crystals of carbon, silicon, and germanium with the structure of diamond, every atom is in the center of tetrahedron, which is formed by four closest neighbor atoms.

Two electrons belonging to two of neighbor atoms usually form the covalent bonding. Electrons making the bonding have a tendency to partial localization in the space between two interacting atoms. The electron spins are anti-parallel.

A molecule of Hydrogen (H_2) is the simplest. An electron in both Hydrogen atoms is in 1s-state. When the atoms are brought together, the interaction between them splits the 1s-state into two states with different energies. σ_g (bounding) molecular orbital is build up as the result of summation of 1s-orbitals. σ_u (anti-bounding) molecular orbital is build up as the result of subtraction 1s-orbitals. In a molecule H_2, both electrons having the anti-parallel spins are in σ_g –state and build the strong bond.

Composition of many electron atoms is more complicated, but in general is like the previous one. In all cases, the approaching of atoms to each other is limited by Coulomb repulsion. In heavy atoms, we observe repulsion, which is cause by superposition of filled intrinsic electron shells

The compounds with covalent bond are subdivided as follows:
1) A great number of organic compounds;
2) Solids and liquids, the bounds of which are build between halogen atoms (and between the pairs of atoms of hydrogen, nitrogen and oxygen);
3) Elements of the third period (for example boron), elements of the fourth group (for example diamond Si, Ge, α-Sn), elements of the fifth group (for example As, Se, Te);
4) Semiconductors (for example $A^{III}B^{V}$, $A^{II}B^{VI}$);
5) Many oxides and sulfides of metals (for example, Cu_2O, PbS).

Sometimes when the crystallization of substances with covalent bonds is being performed, crystalline structures can be formed, the bonding energy of which is almost the same. The initial structure can be substituted by energetically more profitable one by variation of the pressure and temperature. That property is known as *allotropy or polymorphism*. For example, the structure of ZnS can be cubic or hexagonal.
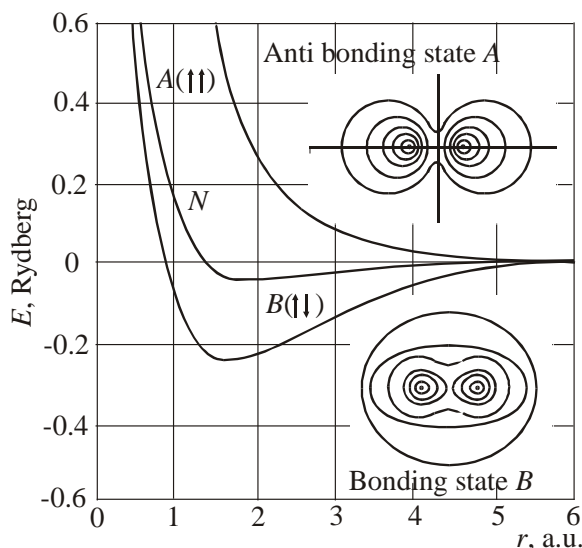
Fig.1.13 The energy of a Hydrogen molecule as function of the distance between its atoms. The state *B* is stable (the electron spins are anti-parallel). Contour lines represent the charge distribution in states *A* and *B*.

1.5.3 Ionic Bond

Ionic bond is due to electrostatic interaction of the ions of opposite electric charges. An ionic crystal is compounded of positive and negative electric charges. The typical representatives of ionic crystals are halogenides of alkaline metals (for example NaCl, crystallizes as Na^+Cl^-).

The structure of sodium chloride is shown in Fig.1.14. The electron shells of ions of a simple ionic crystal are identical to those ones of the atoms of inert gases. Approximately the charge distribution in an ionic crystal is spherically symmetric. In crystal NaCl, an electron of Na transits to Cl.

As the result of this process, a cation Na^+ (the ionization energy 5.1 eV) and anion Cl^- (energy 3.61 eV is liberated) are produced. Their electron configurations are typical for neon and argon atoms (Na^+ - $1s^22s^22p^6$, Cl^- $1s^22s^22p^63s^23p^6$).

The bond energy of a NaCl crystal is due mainly to the Coulomb interaction and is 7.9eV per molecule. The crystalline structure is formed as the result of the Coulomb attraction between charges of the opposite sign and repulsion between charges of the same sign.

The interaction energy of Na^+ and Cl^- is the sum of the Coulomb attraction energy $U_{кул} = e^2/4\pi\varepsilon_0 r$ and repulsion energy $U_{отт} = B \cdot \exp(-r/\rho)$, which is due to the Pauly

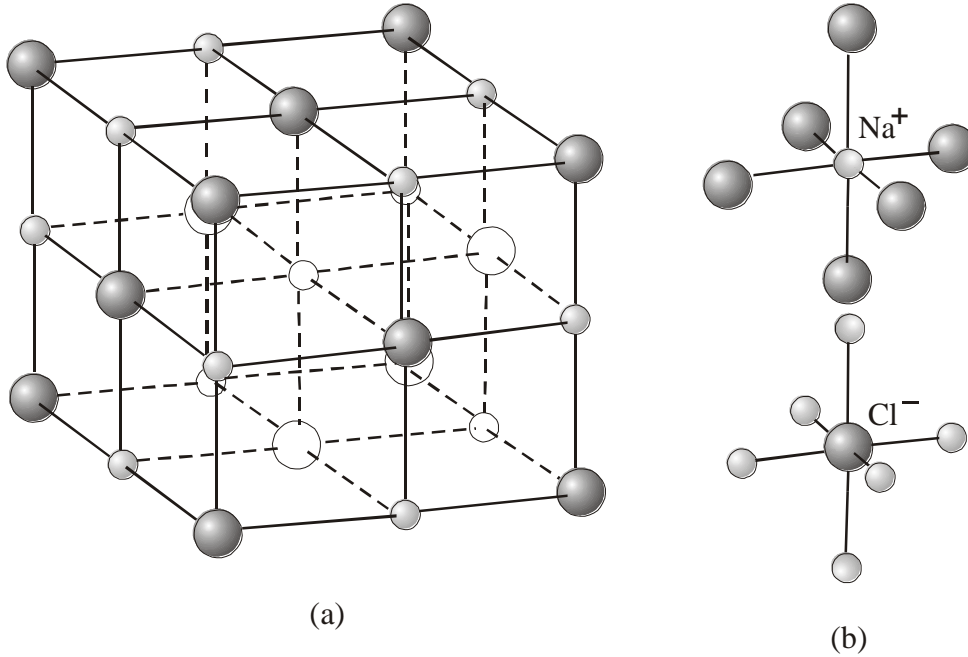exclusion principle. The bonding between Na^+ и Cl^- is stabile if the energy is minmal.

(a)

(b)

Fig1.14. (a) Crystalline structure of NaCl. Space lattice is a side-centered cube, Na+-ion with coordinates 000 and Cl-ion with coordinates $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ form the basis. **(b)** In the crystal, every ion is surrounded by the six closest neighbors having the charges of the opposite sing.

$$U(r) \approx -\frac{e^2}{4\pi\varepsilon_0 r} + B\exp\left(-\frac{r}{\rho}\right) \qquad (1.78)$$

The Coulomb repulsion and total energies are shown in Fig.1.15.
Taking into account the geometric concepts, we can use these rules when describe the bond between ions Na^+ и Cl^- inside a NaCl crystal. A cation Na^+ is surrounded by the six closest neighbors of Cl^-, twelve anions Na^+ at a distance $\sqrt{2}r_0$, eight cations following Cl^- at a distance $\sqrt{3}r_0$ and others. Thus, the total energy of the Colomb attraction per *an ionic pair* can be represented as the sum of an infinite series

$$U(r) \approx -\left(\frac{e^2}{4\pi\varepsilon_0 r_0}\right)\left\{6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \cdots\right\} =$$
$$-1,748\left(\frac{e^2}{4\pi\varepsilon_0 r_0}\right) = -\alpha\left(\frac{e^2}{4\pi\varepsilon_0 r_0}\right) \qquad (1.79)$$

A factor α is called the *Modelung constant*. The quantity α for a given lattice depends on its geometry. For the cubical structure of ZnS $\alpha = 1.638$; for CsCl $\alpha = 1.763$.
In order to find the Modelung constant, we have to summarize the series (1.78), which is a rather tiresome procedure. Evald (1921) and Evien developed the methods of

summation. The methods are based on subdivision of the space around an ion into zones, which are confined between the sequence of polyhedrons. The surfaces of polyhedrons are chosen in such a way that the total charge of every zone is zero and the charge of an ion at the interface between two zones is uniformly distributed.

Using the expression for the repulsion energy of two ions and equation (1.78), we get that the total energy of formation of a single molecule of ionic crystal can be written in the form:

$$E_i = -\frac{\alpha e^2}{4\pi\varepsilon_0 r} + C\exp\left(-\frac{r}{\rho}\right) \tag{1.80}$$

The quantities C и ρ are found by solution of a Schrödinger equation. It should be noted that the energy is minimal when the distance between two closest neighbors is equilibrium (r_0). By differentiating equation(1.80), we arrive at:

$$\frac{dE_i}{dr} = \frac{\alpha e^2}{4\pi\varepsilon_0 r^2} + \frac{C}{\rho}\exp\left(-\frac{r}{\rho}\right) \tag{1.81}$$

Using condition $\left(dE/dr\right) = 0$ when $r = r_0$, we get:

$$C = \frac{\alpha\rho e^2}{4\pi\varepsilon_0 r^2}\exp\left(-\frac{r_0}{\rho}\right) \tag{1.82}$$

Thus: $E_i = -\frac{\alpha e^2}{4\pi\varepsilon_0 r}\left[1 - \left(-\frac{r\rho}{r_0^2}\right)\exp\left(-\frac{r_0 - r}{\rho}\right)\right] \tag{1.83}$

When the distance is equilibrium i.e. $r = r_0$

$$E_{равн.} = -\frac{\alpha e^2}{4\pi\varepsilon_0 r}\left[1 - \left(-\frac{\rho}{r_0}\right)\right] \tag{1.84}$$

The bonding energy depends mainly on the magnitude of Modelung energy because the constant ρ is small in comparison with r_0.

The constant ρ can be found if the coefficient of volume contraction χ is known. Let dv be the volume increment per molecule at the pressure p. We can assume that the volume of a pair of sodium chloride ions $v = 2r^3$. Its increment $dv = 6r^2 dr$. The contraction work produced is $dE = pdv = 6pr^2\,dr$. The pressure:

$$p = -\frac{1}{6r^2}\frac{dE}{dr} \tag{1.85}$$

$$\frac{dp}{dr} = -\frac{1}{6r^2}\frac{d^2E}{dr^2} + \frac{1}{3r^3}\frac{dE}{dr} \tag{1.86}$$

$\left(dE/dr\right) = 0$ if $r = r_0$ (i.e. when the distance between ions is equilibrium). Thus, the second addend in the right part of equation (1.83) is zero

Contraction 𝔪 depends on pressure and volume as follows:

$$\chi = -\frac{1}{v}\frac{dv}{dp} = -\frac{3}{r}\frac{dr}{dp} \tag{1.87}$$

Representing the quantity *dp/dr* in terms of χ and having in mind equation (1.84) we get:

$$\left(d^2E\middle/dr^2\right)_{r_0} = 18r_0\middle/\chi \tag{1.88}$$

Having differentiated equation (1.82) two times and comparing the result with equation (1.88) we find that

$$\rho/r_0 = \left[1 + \left(72\pi\varepsilon_0 r_0^4\middle/\alpha e^2\chi\right)\right]^{-1}. \tag{1.89}$$

Thus, the bond energy can be evaluated if the period of lattice, Modelung constant and contraction constant are known.

Many authors describe the properties of ionic crystals. In particular, Mott and Herny have an opinion that for all twenty crystals of halogenides of alkaline metals, $\rho = 0,345$Å, but the factor *C* of equation (1.80) varieties in a wide range. It is due to the fact that the positive ions of alkaline metals and negative ions of halogens with the totally filled electron shells are very like the ideal solid spheres having contact at the equilibrium distance.

The radii of some ions are given in the Table 1.1.

Table 1.1. Radii of ions of halogenides of alkaline metals

cations	r_c, Å	anions	r_a, Å
Li^+	0.475	F^-	1.110
Na^+	0.875	Cl^-	1.475
K^+	1.185	Br^-	1.600
Rb^+	1.320	I^-	1.785
Cs^+	1.455		

1.5.4 Electric Negativity of Atoms

Interaction of electron shells of atoms is the essence of intrinsic atomic interaction. The type of interaction depends on the ability of atoms to take or to give electrons. That ability can be characterized from one hand by the *ionization potential* and from the other hand by the *cohesive energy*.

The first ionization potential depends periodically on the chemical element number. The ionization potentials of alkaline metals are minimal $(I = 3 - 5)$ eV. The ionization potentials of inert gases are maximal ($I_{He} = 24,5$ эВ).

When an electron is approaching a neutral atom, the forces of interaction (mainly the forces of attraction) are produced. The number of generated energy levels in this process is finite. If the stable states are possible, then the atom would have the tendency to capture the extra electron and to transform into negative ion. It that, the cohesive energy is positive. The cohesive ability of haloide atoms is the greatest $(E = 3 - 5)$ eV. The atoms of heavy one-valence atoms have the maximal cohesive energy $(E_{Cu} \approx 1.0$ eV, $E_{Au} \approx 2.4$ eV).

The ability of atoms to take or to give their valence electron is called the *electric negativity*. The electric negativity is a relative characteristic. The half of the sum of the ionization potential and cohesive energy represents it:

$$X = \frac{1}{2}(I + E) \qquad (1.90)$$

If to arrange the chemical elements in accordance with electric negativity, then this series will begin with the more electric positive elements (alkaline metals). These metals can form positive ions rather easily. The series will end with electric negative elements. These elements in its turn can form negative ions easily (halogens).

In order to build up the practical scale of atomic electric negativity, the special units are used. Let us assume that the unit bonds between two different atoms bind a molecule *AB*. If these two atoms are rather like, the covalent bond between them is produced. If the difference is essential (for example one is more electrically negative than the other), then according the theory of chemical bonds, the energy of the actual bond is more greater then that one which would correspond to the usual covalent bond between these atoms.

The additional energy is due to the ionic component of the chemical bond. The decrement ΔE between the actual bonding energy *A-B* and the energy calculated for normal covalent bond under condition that the last is equal the arithmetical mean of energies *A–A* and *B-B*, increases with decrement between the electric negativity of atoms *A* and *B*: $\Delta E = E(A - B) - \frac{1}{2}[E(A - A) + E(B - B)]$ (1.91)

The bond energy of two-atomic molecule is identical with the dissociation energy needed to split the molecule into atoms. It can be found by thermal chemical and spectroscopic methods.

When the decrement ΔE between the actual and calculated energies is found, then it is possible to build up the scale of electric negativity. In such a way, the difference between of electric negativity for different pairs of atoms can be determined. Thus, the evaluated quantities ΔE do not follow the additivity principle, i.e. they can not be represented as decrements of addends characterizing both bonding atoms. The square roots of these quantities hold those conditions. Thus, it is possible to chose such magnitudes of electric negativity when their difference approximately equals $\sqrt{E}$:

$$X_A - X_B = \sqrt{\frac{\Delta E}{23,06}} = 0,208\sqrt{\Delta E} \ \ \text{эВ.} \qquad (1.92)$$

Notice that ΔE is identical with the heat liberated in reaction $\frac{1}{2}A_2 + \frac{1}{2}B_2 \to AB$. At normal condition, the great number of chemical elements is bound by unit covalent bonds..

The electric negativity is shown in the Table 1.2.

Table 112 Electric negativity

Element	☜	Element	X	Element	X
Li	1,0	B	2,0	As	2,0
		Al	1,5	Sb	1,9
Na	0,9	Ga	1,6	Bi	1,9
Au	2,4	C	2,5	O	3,5
Be	1,5	Si	1,8	S	2,5

Mg	1,2	Ge	1,8	Se	2,4
Ca	1,0	Sn	1,9	Te	2,1
Sr	1,0	N	3,0	H	2,1
Ba	0,9	P	2,1	F	2,0
Zn	1,6			Cl	3,0
Cd	1,7			Br	2.8
Hg	1,9			J	2,9

The electric negativity can not be considered as the actual physical quantity that can be measured directly. The magnitude of electric negativity depends on an electric charge of ion. The concept of electric negativity is mainly used for evaluation the ionic characteristics of the bond under investigation.

The decrement of electric negativity is really of interest. An atom can be electric positive in one circumstance and electric negative in the other circumstance. It depends on properties of surrounding atoms. Having in mind the additivity principle, which is widely used in theoretical chemistry, we can say that concept of electric negativity testifies that the chemical bond of molecules and crystals is not ideal. It is not pure ionic or covalent but of some intermediate kind.

In pure covalent bond, the electron density is distributed between atoms symmetrically. In pure ionic compounds, the maximum of electron bond cloud coincides with the center of an ion. For the intermediate polar bond, the center of electron cloud is displaced from the central position between atoms towards one of the atoms. This displacement (in per cents) describes the degree of bond ionicity. The degree of polar bond (*A–B*) ionicity is proportional to the differential of electric negativity.

The crystals with the pure covalent bond (diamond) or pure ionic bond (LiF) are considerably rare than that one with the bond of an intermediate character. Thus, speaking about the substances with ionic or covalent bond, we have in mind not the ideal bond but the bond, which can be approximately considered as ionic or covalent.

To form the pure ionic bond in a compound, two components are necessary: electric positive charge (cation) and electric negative charge (anion). The halogenides of alkaline metals hold those requirements very good. In compounds with not so strong electric positive or negative properties, the degree of transition of the charge from a cation to anion is less than 100%.

For example, the ionization energy of noble metals is greater than that one of alkaline metals. Thus, the bond in the halogenides of silver is not so ionic as in the halogenides of alkaline metals. In the series of compounds with diminishing difference of electric negativity, the continuos transition from pure ionic bonds to pure covalent bonds is observed.

When the partial generalization of electrons takes place, the bond can be considered as the result of *resonance* of ionic and covalent charge configurations. In this situation, the wave function of an electron building this kind of a bond can be written as:

$$\psi = \psi_{cov.} + \lambda\psi_{ion.} \qquad (1.93)$$

The function ψ_{cov} and ψ_{ion} are normalized wave functions for pure covalent and ionic bond correspondingly. A parameter λ characterizes the degree of ionicity.

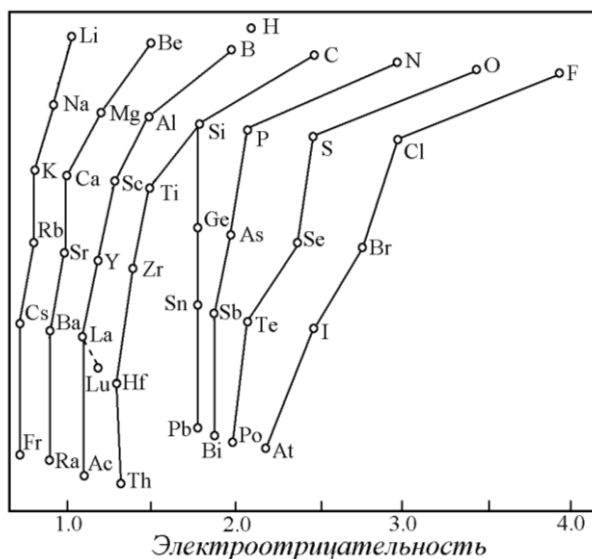$$Ionicity, \% = \frac{100\lambda^2}{1 + \lambda^2} \qquad (1.94)$$

Fig.1.16 Electric negativity (Polling, 1960). The x-axis scale is chosen to satisfy the condition (1.95).

The magnitude of λ is evaluated by solution of quantum equation. The mixed bond leads to additional bond energy

$$\Delta = E_{cov.} - E , \qquad (1.95)$$

This quantity is called the **ion covalent resonance energy.**

For evaluation λ and Δ the scale of electric negativity is used (Table 1.2 and Fig 1.16).

According to Polling, ionicity can be described with sufficient accuracy:

$$Ионность,\% = 100\left\{1 - \exp\left[-\left(\frac{x_A - x_B}{2}\right)^2\right]\right\} . \qquad (1.96)$$

1.5.5 Hydrogen Bond

A Hydrogen atom with one electron besides the covalent bond can form the additional electrostatic bond with the second atom having the strong electric negativity. The atoms of fluorine, oxygen and in a less degree the atoms of nitrogen are of that type. The additional bond is called the *Hydrogen bond.* The energy of the hydrogen bond is 0.1–0.5eV.

The hydrogen bond unites the molecules H_2O in crystals of ice. The distance between the neighbor oxygen atoms is 2.76 Å. This magnitude is more than two times greater than the distance between the nuclei of oxygen and hydrogen (0.96 Å) in an isolated molecule of water. There is an opinion that the molecule of water is partly bond by the hydrogen bonds. Unusually high boiling and evaporating temperatures of this compound with molecular mass of only 18 are due to hydrogen bonds. The high dielectric properties of water and ice are due to hydrogen bonds too. Those bonds play the great role in polymerization of HF, HCN and like. The Hydrogen bonds are responsible for the signet-electrical properties of the compounds of the type of KH_2PO_4. The hydrogen bonds are to be taken into consideration to understand the properties of many organic and biological substances. For example the compound C_2H_6O is found in the form of two isomers: dimethyl ether $(CH_3)_2O$ and ethyl alcohol CH_3CH_2OH. In ethyl alcohol, the hydrogen bonds are formed between a hydrogen atom of a hydroxyl group and the oxygen atom of the neighbor molecule. The configuration of ether molecule handicaps to form the hydrogen bond. As the result of it, the boiling temperature and evaporation heat of ether alcohol is higher than that one of dimethyl ether.

1.5.6 Metallic Bond

In ionic and covalent crystal, valence electrons are bond with certain atom. In a metal, the bond between atoms is a result of generalization of electrons. In a typical metallic structure, every atom has many neighbors and bonds. Every bond is week, but the metal is stable because the number of bonds is great.

The distance between nuclei in metallic structures is great too. The properties of the three typical metallic structures are shown in Table 1.3.

Table 1.3. **Three most common metallic structure**

Structure	Metal	Number of the closest neighbors	r_0
v.c.c..	Lithium	8 atoms at a distance r_0 6 atoms at a distance $2r_0/\sqrt{3}$	3.04 Å
s.c.c. (c.t.p.)	Copper	12 atoms at a distance r_0	2.56 Å
(s.t.p)	Zinc	12 atoms at a distance r_0	2.66 Å

In order to build a metallic bond of a number of metals, it is sufficient to take an electron from every atom and then to generalize the produced electrons. Such situation takes place for lithium in the external shell of which there is only a single electron. A lithium crystal can be considered as the lattice of Li^+ ions (radius 0.68 Å) surrounded by the *electron gas* with the density of one electron per atom.

In accordance with quantum mechanics, a metal is the set of positive charged 'ionic islands' with big cavities between ions filled by the electron gas in such a way that all macro-system is electrically neutral. The wave functions of electrons that form this gas are strongly superposed (the Bloch functions). The bonding of the metallic crystal is associated with the fact that the *mean* energy of a valence electron is less than the energy of an electron of the isolated atom. In order to discus the situation in details, it is necessary to take into consideration: the electrostatic repulsion of electron centers (screened by the electron gas); the Van-der-Vaals attraction between ions and their repulsion produced by the interposition of electron shells (those interactions are rather weak); the bond produced by the internal shells, which are not filled (it is very important for transitional elements); the correlation of electrons inside the electron gas.

The main properties of a metallic crystal are follows.

1. Periodic distribution of atomic residuals or ions. Every ion consists of atomic nucleus and electrons, which form the filled shells. In accordance with the Pauly principle, the electron of the filled atomic shell is bond only with its atom.

2. Quasi-uniform density of a negative charge is due to the external electrons moving with heat velocities. They form the gas of free electrons uniformly distributed in space. The collective action of the electrons produces the bonds in a solid. The density of free electrons can be from one electron per atom ($2 \cdot 10^{28}$ м$^{-3}$) to more great quantities. It depends on the valence of atoms forming the metal. A set of atomic residuals and electrons is shown in Fig.1.17

The *mean* charge density of the combination shown in Fig.1.17 is zero (having in mind the electric neutrality of solid body). But we can assume that the charge density ☐ of the *local* distribution is to have the periodic maximums that are interposed on the uniformed distribution of negative charge of the electron gas. As a rule, the atomic residual, which consists of the filled shells is less than the distance between atoms.
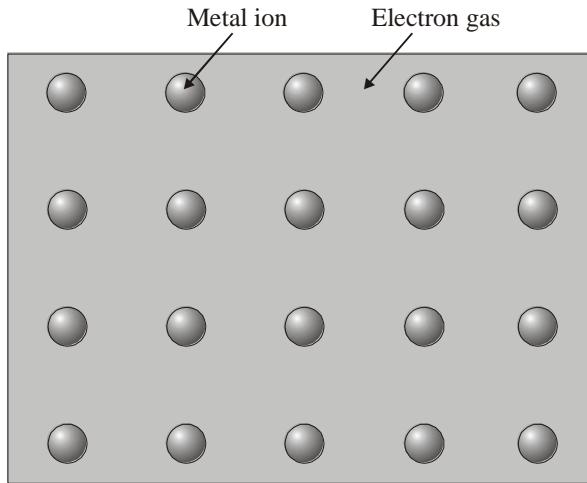

Fig.1.17 Two-dimensional metallic crystal Periodically distributed atomic residues and electron gas are uniformly distributed.

Thus, the ions fill only the small part of a total volume. The maximums of density are also small but concentrated in small volumes.

In accordance with the Poison equation:

$$\nabla^2 U = -\rho/\varepsilon_0 \qquad (1.97)$$

It follows that in a metallic crystal there is a three-dimensional periodic distribution of electrostatic potential (see Fig.1.18). The form and height of each potential maximum depends on the charge distribution inside of atomic residual.

According to model of *free electrons,* the influence of periodicity of electrostatic potential can be neglected. The calculations are being made under assumption that the motion of electrons is free in entire volume of metal. The electrons only strike the potential barrier on the metal interface. This barrier corresponds to the work of exit. The density of free electrons is of order of 10^{28} m$^{-3.}$ This quantity depends on the atomic number.
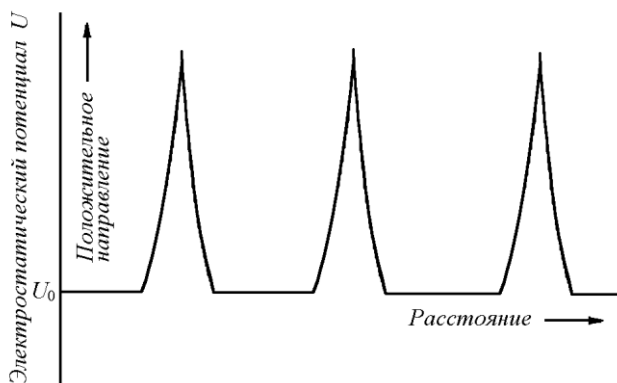

Fig.1.18. Periodical variations of an electrostatic potential produced by the density charge distribution.

The statistic approach to study those electrons (when totally neglect the inter-atomic potential) is of success for alkaline metals. Those methods describe correctly in the first approximation the properties of multi-valence metals (Aluminum, Lead).
Properties of solids with a different kind of chemical bonds are shown in the Table 1.4.

Table 1.4 Bonds in solids

Kind of the bond	Examples			
	Substance	Crystalline structure	Bond energy, eV/molecule	Distance between the closest neighbors, Å
Van-der-Vaals	Argon	S.c.c	0.1	3.76
	Chlorine	Tetrogonal	0.3	4.34
Covalent	Si	Cubical (diamond)	3.7	2.35
	InSb	Cubical (ZnS)	3.4	2.80
Ionic	KCl	Cubical (rock salt)	7.3	3.14
		Cubical (fluorite)		
	BaF_2		17.3	2.69
Hydrogen	Ice	Hexagonal	0.5	1.75
Metallic	Na	V.c.c.	1.1	3.70
	Ag	S.c.c.	3.0	2.88