

CHEMICAL BOND AND CTRENGTH OF SOLIDS

V.Ya. Khentov¹, E.Yu. Shachneva^{1*}, B.E. Kudinova²

¹Federal State Budgetary Educational Institution of Higher Education “South-Russian State Polytechnic University”, Novocherkassk, Russia

²JSC «Thermo Fisher Scientific», Saint Petersburg, Russia

Abstract. It is shown that the strength properties of a solid are connected with the energy of the chemical bond. Theoretical strength is many times greater than the technological strength. This is for non-metallic materials, containing non-polar covalent bonds. The most important areas of materials use are mechanical engineering and construction practice. Strength is associated with the evolution of the earth's surface relief. The classification of solids into three main classes is given. The graph of energy dependence as a function of the distance between the lattice sites is presented. The dependence of Young's modulus of elasticity on the binding energy is described. The values of the theoretical and technological strength of solids are calculated using the example of inorganic materials.

Keywords: Chemical bond, theoretical and technological strength, Hooke's law, dislocation, Young's modulus of elasticity.

Corresponding Author: E.Yu. Shachneva, Federal State Budgetary Educational Institution of Higher Education «South-Russian State Polytechnic University», 346428, Novocherkassk, Russia,
e-mail: evgshachneva@yandex.ru

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1. Introduction

The concept of chemical bond is fundamental in the study of the matter structure. From the material science point of view, it seems quite interesting to study the role of chemical bonds in connection with the problem of the strength of a solid.

The strength of a solid is the most important property of the material used by mankind to manufacture machine parts and create various mechanisms or constructions. The most important areas of materials use are mechanical engineering and construction practice. Strength is associated with the evolution of the earth's surface relief. The methods of mechanical handling of a solid are closely related to its strength characteristics. The concept of strength is associated with the creation of new structural and functional materials. The matter of particular importance is the problem of maintaining the strength characteristics of a solid surface under various physical and chemical effects on the surface (mechanical, chemical, thermal, radiation and other influences).

The type of chemical bond determines the ability of a crystal to undergo plastic deformation or brittle fracture.

In crystals with a covalent bond (atomic lattice), a slight displacement of atoms relative to each other leads to the fact that bonds are destroyed faster than new ones are formed. Such crystals include diamond, germanium, arsenic, etc. After reaching the elastic limit they are susceptible to brittle fracture. Such crystals do not demonstrate plastic deformation.

In crystals with a metal bond, which does not have a strict directivity, high plasticity is manifested. The movement of atoms relative to each other within the slip plane does not lead to the destruction of the metal bond, and the displacement of the planes can occur up to several thousand atomic distances. Crystals with an ionic bond are at an intermediate position. They can be subject to both brittle fracture and plastic deformation (Xu & Xue, 2006; Zewail, 2000; Nahum *et al.*, 2010; Vybornyi *et al.*, 2019; Sada *et al.*, 2007).

2. Discussion

It is determined to divide all solids into three classes – crystalline, amorphous and nano-dispersed. An order in the arrangement of neighboring atoms in solids is specific and can be limited by short-range order. This applies to the environment of this atom. Short-range order is limited for amorphous bodies. But the vast majority of crystal lattices are characterized by a long-range order. That means the crystal lattice is extended.

The crystalline state is characterized by a structural order in the spatial arrangement of the nodes of the crystal lattice. The transition from crystalline state to liquid occurs abruptly (Fig. 1a). The temperature changes stepwise and is called the melting point of a solid. The crystalline state is characterized by the presence of a substance in a monocrystalline or polycrystalline state. Polycrystalline substances are built from individual small crystals connected by intermolecular forces. Monocrystals are characterized by anisotropy of properties in different directions. This applies to the manifestation of such properties as electrical conductivity, thermal conductivity and strength.

A disordered arrangement of atoms or molecules is observed for an amorphous state. The transition from an amorphous body to a liquid state occurs gradually. The temperature when supplying thermal energy to a solid varies in the temperature range. There is a melting range for amorphous solids (Fig. 1b). This is a significant concept that is important for the process of thermal processing of crystalline and amorphous bodies. And finally, amorphous bodies are isotropic.

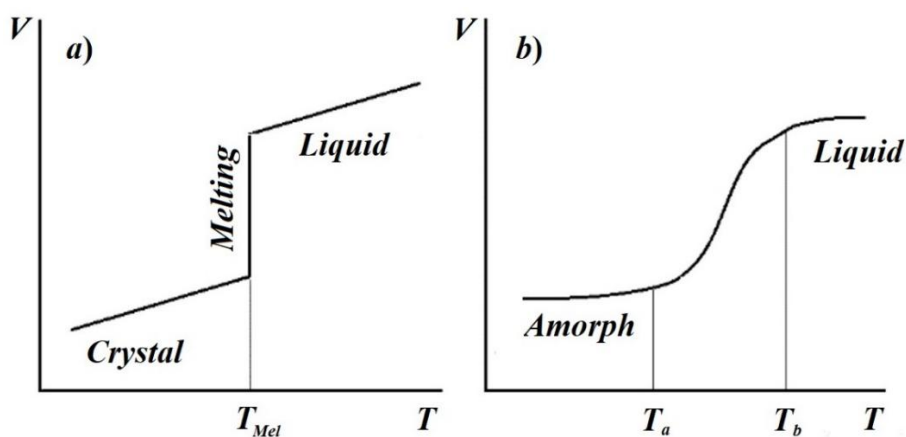


Fig. 1. Change in the volume V of crystalline (a) and amorphous (b) substances during heating (T_{Mel} - melting point; $T_a - T_b$ - melting range)

Examples of an amorphous body include glass, resins, polymers, etc. Properties such as internal energy, heat capacity and density do not depend on direction.

Polycrystalline substances are characterized by statistical averaging of properties in different directions – the phenomenon of isotropy appears. A substance may be in an amorphous and crystalline state (Karapetyants & Drakin, 2000). Amorphous compounds are less stable than crystalline ones. Some amorphous substances, for example polymers of organic substances, cannot be crystallized. Crystallization is prevented by high melt viscosity. Usually amorphous bodies are considered as supercooled liquid. Silicate glass is an example of an amorphous body that after a long time can suddenly become crystallized. Therefore, amorphous bodies are often called glassy. Amorphous bodies include, for example, sulfur, selenium, oxides of a number of substances – B_2O_3 , SiO_2 , GeO_2 .

If the particle sizes of a solid do not exceed 100 nm (nanostate of a substance), the so-called size effect appears for such particles of a substance. Nanoscale crystals have unique physical and chemical properties that are of particular interest to the technology.

A solid can be characterized by the crystal lattice nodes motion shape (fig. 2). The solid aggregation state of a substance is characterized by the oscillatory form of motion of lattice particles (nodes) of a solid body. With the formation of a crystal lattice, a curve with a potential well appears on the graph of the energy dependence in the function of the distance between nodes. This graph resembles the formation of a chemical bond between atoms.

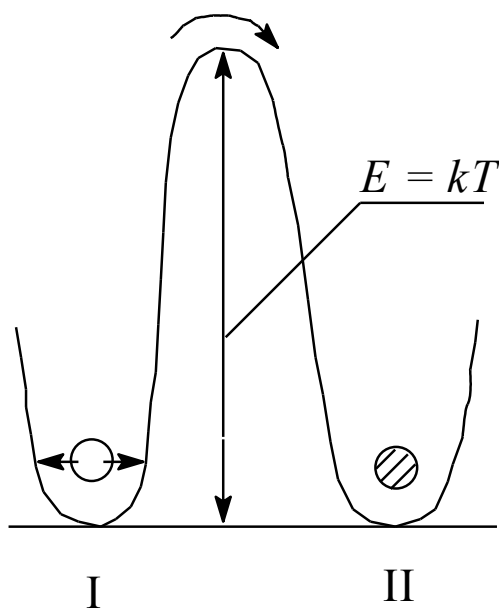


Fig. 2. Scheme of particle (lattice node) activated leaps from equilibrium I to equilibrium II (Barrier height: $E = kT$, where E –energy; k – constant; T – temperature)

A particle oscillates indefinitely in a potential well (Fig. 2). With increasing temperature, the particle creeps out of the potential well and the amplitude of the oscillations increases. Thus, a solid aggregation state is characterized by an oscillatory form of particle motion. Then the particle overcomes the energy barrier E and moves from position I to position II. This form of motion is called translational motion or self-diffusion and is specific for the liquid aggregation state of a matter.

The solid and liquid state of a substance is called the condensed state.

A further increase in temperature leads to chaotic motion of particles and the

distance between them increases. This form of motion is a characteristic of the gaseous state of a matter.

Table 1 shows the classification of substances in various aggregation states (Kuhling, 1985). Each state is characterized by a certain internal structure of a substance, which leads to the manifestation of certain properties.

Table 1. Properties of a substance in three aggregation states

Property	State		
	Solid	Liquid	Gaseous
Crystal lattice	Yes	No	No
Form constancy	Yes	No	No
Intermolecular interaction	Yes	Yes	No
Volume constancy	Yes	Yes	No

The most common solids are metals. They are about $\frac{3}{4}$ of all Periodic system elements. The bond strength of a valence electron with an atomic nucleus can be calculated by the formula:

$$F = ne^2/r^2, \quad (1)$$

where n is the number of the group of the Periodic system, e is the elementary charge, r is the radius of an atom.

There are no clear differences between metals and non-metals. Moreover, many non-metallic elements are able to transform into a metallic state at high pressure.

There is a classification of solids based on the formation of chemical bonds. The structure of a crystal as well as its physicochemical properties are determined by the nature of chemical bonds. This area is of peculiar interest to physicists, chemists and is a matter of concern to the technology of processing substances.

Solids are often classified by the type of chemical bond. It is determined to distinguish five types of solids: ionic, covalent, metallic, molecular and compounds with hydrogen bonds. But there are cases when several types of chemical bonds are combined in solids.

Strength is the resistance of a solid to fracture that is determined by the nature of the chemical bond and the defects in the crystal lattice, primarily dislocations. Dislocations are responsible for the appearance of microcracks preceding to the fracture process.

The experimentally observed pattern of solid extension (the dependence of the voltage P applied to a solid on the relative elongation of the body ε) is shown on Fig. 3. The section of curve AB corresponds to the elastic deformation area and obeys Hooke's law:

$$P = E \cdot \varepsilon \quad (2)$$

where P is voltage, $\varepsilon = \Delta l/l$ is the elongation; l is the initial body length; Δl is the increment of the body length at an applied load; E is the coefficient of proportionality, called Young's modulus of elasticity.

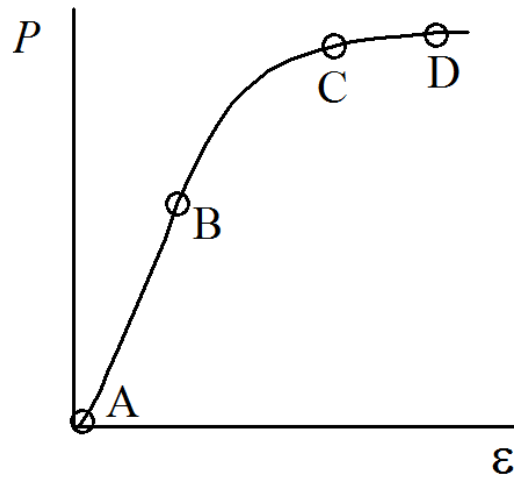


Fig. 3. The diagram of solid extension

Hooke's law is valid up to a certain limit of voltage P that is called the elastic limit. In the area of AB dislocations remain at rest. In the area of BC plastic deformation or fluidity (displacement of one plane relative to another) is observed. Dislocations obtain mobility. Unloading does not lead to the initial state in the crystal.

During plastic deformation, the accumulation of dislocations begins to slow down their motion. The crystal is deformed, but its hardening occurs (area CD). With a further increase in load, tensions are concentrated in the dislocation zone. A microcrack appears. A slight increase in tension splits the crystal. Such tension is called strength limit.

3. Results

A matter of particular interest is the calculation of the theoretical strength of a solid. It can be assumed that an external tensile force F acts on a rod of length L and cross section S (Fig. 4). In this case the rod is extended by a value ΔL and the distance between the nearest atomic planes 1 and 2 will increase by a value x .

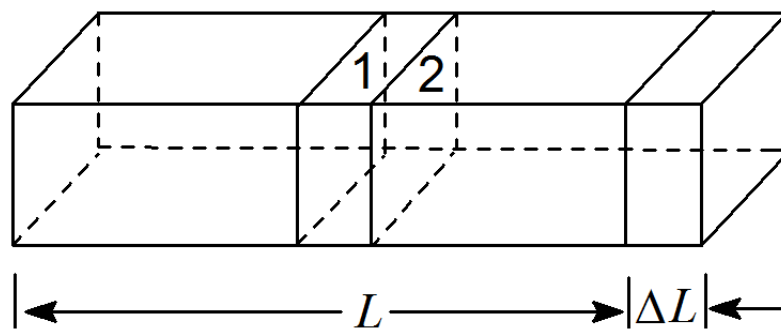


Fig. 4. Scheme of rod extension

The external force F must be balanced by the internal force F_{BH} . To calculate the internal force, it is necessary to know the number of chemical bonds n penetrating the cross-sectional area of the rod, as well as the force f , acting between adjacent particles of the crystal lattice. Then:

$$F_{BH} = fn = \beta xn, \quad (3)$$

where β is a parameter characterizing the rigidity of the bond between two particles. In fact, this value is proportional to the energy of the chemical bond.

The voltage that occurs when the rod is stretched is determined according to the formula:

$$P = \frac{F_{BH}}{s} = \frac{\beta xn}{s} \quad (4)$$

The right side of equation (4) should be multiplied and divided by the distance between the atomic planes a :

$$P = \frac{a\beta n}{s} \cdot \frac{x}{a}. \quad (5)$$

The first factor of this equation is called Young's modulus of elasticity:

$$E = \frac{a\beta n}{s}. \quad (6)$$

The second factor is called the relative elongation of the rod:

$$\varepsilon = x/a. \quad (7)$$

The relationship between P and ε ($P = E\varepsilon$) is called Hooke's law.

The coefficient of proportionality E (angle of inclination) characterizes the strength features of a solid, which are determined by its chemical nature.

The elastic modulus is proportional to the energy of the chemical bond. The dependence of Young's elastic modulus (Dobronravov *et al.*, 1928; Kay & Laby, 1962) on the binding energy of the U bond (Kittel, 1978) is given on fig. 5 for 27 s -, p and d -elements of various groups of the periodic system (Li, Na, K, Be, Mg, Ca, Al, Ge, In, Sn, Sb, Pb, Bi, Ti, V, Cr, Fe, Co, Cu, Zn, Mo, Ag, Cd, Hf, Ta, W, Os). Binding energy is meant to be the energy that should be spent to separate a solid into separate atoms at temperature of 0 K. This dependence is described by a linear equation:

$$E = -4.4241 + 0.2068U_{\text{bond}}. \quad (8)$$

It should be noted that this is a good result, since when the correlation coefficient is close to 1, pair dependencies are described only for elements of the same type. For example, the dependence of the isothermal volumetric elastic modulus B on the binding energy of the U bonds for s -elements of group I is perfectly described by the equation (correlation coefficient is 0.99, significance level is 0.0016):

$$B = -0.0711 + 0.005 U_{\text{bond}}. \quad (9)$$

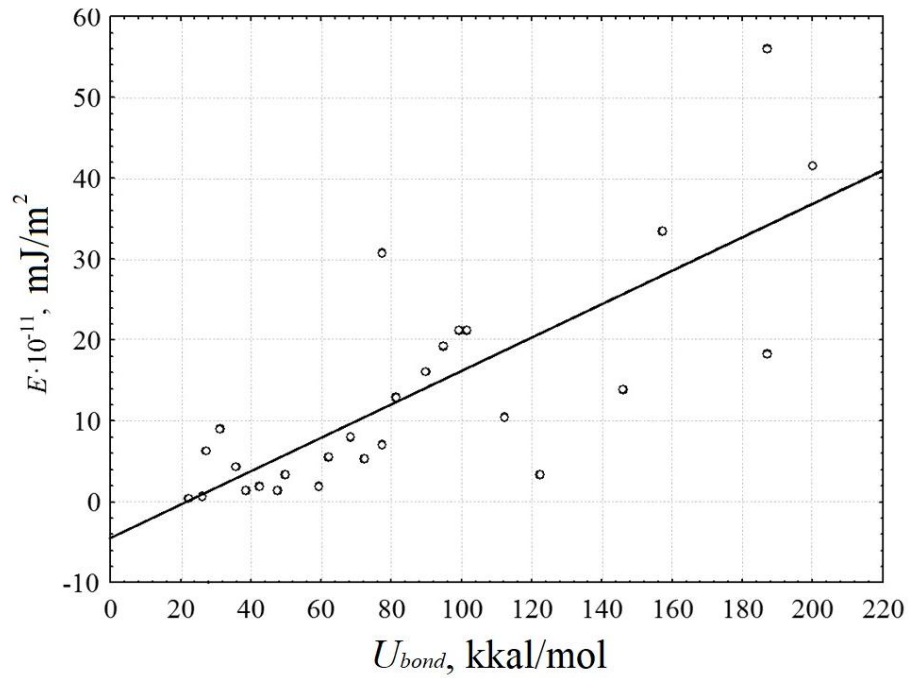


Fig. 5. The dependence of Young's modulus of elasticity E on the binding energy U bonds. Correlation coefficient is 0.78, significance level is 0.000002

When calculating the strength of a crystal, it should be taken into account that when a solid is destroyed along a section plane, chemical bonds between particles, located in the nodes of the crystal lattice, are broken.

The work of one connection breaking can be calculated according to the formula:

$$A = F \cdot l, \quad (10)$$

where F is the gravity force between adjacent nodes of the lattice, l is the distance by which two planes must be moved apart so that the gravity force between adjacent nodes of the lattice ceases to act. This distance is estimated as 1 \AA and corresponds to the length of the chemical bond.

The work of the formation of two surfaces can be calculated as follows:

$$A_s = A \cdot n, \quad (11)$$

where n is the number of bonds penetrating the cross-sectional area of the rod.

The surface energy can be calculated as:

$$\sigma = \frac{1}{2} A_s = \frac{1}{2} F l n. \quad (12)$$

The tension required to open the microcrack is:

$$P = F n \text{ or } P = \frac{2\sigma}{l}. \quad (13)$$

To simplify the calculations, the value of l can be taken equal to the lattice parameter a . Then:

$$P = \frac{2\sigma}{a}. \quad (14)$$

As an example, the surface tension and strength of an ionic crystal of sodium chloride will be calculated. The parameter $a = 2.78 \text{ \AA}$. From geometric considerations it can be concluded that $n = 1/a^2 = 1.3 \cdot 10^{19}$ ions are located in an area. The same number of bonds permeates the section plane. The force of interaction between two charges of anion and cation is calculated in accordance with the Coulomb's law:

$$F = e^2/\epsilon a^2, \quad (15)$$

where e is the elementary charge ($1.602 \cdot 10^{-19} \text{ C}$). For breaking one bond, $F = 2.98 \cdot 10^{-9} \text{ N}$. Thus, $\sigma = 1.931 \text{ Pa}$, $P = 3.9 \cdot 10^8 \text{ Pa}$. It is assumed that the elastic energy of a solid at the moment of destruction is equal to $\frac{1}{2}P\epsilon$, then the strength (tension) can be calculated using Young's modulus of elasticity. So $\frac{1}{2}P\epsilon = 2\sigma$. For an elastic body in accordance with Hooke's law:

$$P = \epsilon/aE, \quad (16)$$

Combining the previous two equations:

$$P = (2E\sigma/a)^{1/2} \quad (17)$$

Equation (17) allows to calculate the theoretical strength of a solid. Table 2 shows the values of the technological strength and the theoretical tensile strength of a solid, calculated according to equation (17).

Table 2. Theoretical P_{theor} and technological P_{tech} strength of inorganic materials (Kelly, 1972; Khentov, 1992)

Material	$P_{\text{theor}}, \text{ kg/cm}^2$	$P_{\text{tech}}, \text{ kg/cm}^2$	$P_{\text{theo}}/P_{\text{tech}}$
Iron	180	69	2,6
Copper	94	21	4,5
Aluminum	51	10	5,1
Boron	250	7	35,7
Graphite	500	2	250,0
Corundum(Al_2O_3)	500	2	250,0

It should be noticed that the theoretical strength is many times greater than the technological strength. The theoretical strength of inorganic materials of non-metallic nature significantly exceeds the theoretical strength of metals. This can be explained by greater strength of covalent non-polar chemical bonds in comparison with the metallic bond.

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