STRUCTURE OF CONDENSED SOLID MATTER

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Abstract. In this contribution we have considered the main items of the history of ideas on the structure of condensed solid matter. They are divided into two principal groups; one is based on discreteness (numbers, atoms), the other on continuity (geometrical figures). The evolution of these ideas has led to such notion as crystals, long-range and short-range order, continuous and discrete space, quasicrystals, types of disorder, amorphous structure. In its turn the new notions generated new theories, such as group theory, topology, etc. Significant attention was given to molecular dynamics, a new powerful instrument for solution of many problems connected with the structure of disordered phases. Leaning on a molecular dynamics, we have developed the theory of deformation and fracture for amorphous materials.

1. Introduction: numbers everywhere

Numbers. According to the Russian Mathematical Encyclopedic Dictionary [1], "Number is one of the most important mathematical notions. Coming into being in a simplest form in a primitive society, the notion 'number' was changing over many centuries enriching its essence. The science of numbers is called *arithmetic* (Gr. αριθμητικη – skill of counting). In the course of development of arithmetic there appears a need to study properties of numbers as such, to seek out regularities in their interrelations caused by arithmetic operations."

Geometry. According to the Russian Mathematical Encyclopedic Dictionary [1], "Geometry (Gr. γεω-μετρια–land measuring, from γη– earth and μετρεω–measure) is a part of mathematics which studies spatial relations and shapes as well as other relations and shapes similar to special in their structure.

Pythagoras (Πυθαγορης, ~570–500 BC) used numbers as the basis for construction of the World [2]. "Prototypes and proto-bases baffle all clear description because it is difficult to comprehend their full meanings and to express clearly by words, that's why for teaching clarity sake one has to use numbers. All the things are numbers, the wisest is a number, and God is the number of numbers. Everything does not originate from a number, but in conformity with a number, since a number is a primary ordering, and in connection with it in countable objects, there ordered the first, the second and so on. All the nature phenomena should be explained with the help of numbers."

Numbers and symbols. According to Pythagoras, all the numbers are divided into categories and have a symbolic meaning. Number one is the universal beginning, since without a unity there is no any number. Number two is the beginning of an opposite and symbolizes a phenomenon polarity, e.g., light and darkness, good and evil, life and death,

right and left, even and odd, etc. Number three is the symbol of nature; it is the most prefect number, because it has the beginning, the middle and the end. The sum of these number gives

1+2+3=6,

so the number six is a divine number.

The symbol of constancy is number nine, because all the numbers which are multiples of nine have sum of ciphers equal to nine, i.e.

18→1+8=9,   27→2+7=9,   36→3+6=9.

A perfective number is equal to the sum of its own divisors, e.g.

6=1+2+3,   28=1=2+4+7+14.

Numbers and geometry. Pythagoreans distinguished triangular, quadratic and pentagonal numbers. The triangular numbers show the number of balls put in the form of a triangle, the quadratic numbers – in the form of a square, and so on, i.e.

1, 3, 6, 10, 15, 21, …   1, 4, 9, 16, 25, 36, …   1, 5, 12, 22, 35, 51, …

Pythagoreans considered also figurate numbers, analogous to triangular numbers, but in the three-dimensional space, so called pyramidal numbers. They show the number of balls which can form a regular pyramid, i.e.

1, 4, 10, 20, 35, 56, …

Pythagoreans reduced the space to numbers. A point has one dimension and it corresponds to number one. A line has two dimensions, because it can be drawn through two points. A plane has three dimensions, a volume has four. By summing all the plane figures one obtains

1+2+3=6.

By summing all the figures, corresponding to the geometrical shapes one obtains

1+2+3+4=10.

Again we see the divine nature of number six. However, there is the super-divine number, 36, because

36=1+2+3+4+5+6+7+8, $36=1·1·1+2·2·2+3·3·3$.

Numbers and harmony. According to the Longman Dictionary of English Language and Culture [3], harmony is 1) notes of music combined together in a pleasant sounding way; 2) a state of complete agreement (in feelings, ideas, etc.); 3) the pleasant effect made by parts being combined into a whole. A similar definition one can find in the Russian Dictionary of Foreign Words [4], besides it shows the origin of the word: harmony (Gr. αρμονια– consistency, consonance, concord). The Russian New Illustrated Encyclopedic Dictionary

enlarges this notion adding that in the ancient Greek philosophy harmony means the ordering of cosmos in contrary to chaos.

After such rather long definition, let us return to Pythagoreans. They discovered the following musical rule. In order to produce music in a pleasant harmonic way, a lyre must have the strings which lengths are in the ratios 1:2, 2:3, 3:4. So Pythagoreans combined the first four number into a tetrad. Their sum is

1+2+3+4=10.

And just the same number one has obtained by summing the numbers which correspond to the geometrical forms of different dimensions. Besides the sum contains the equal quantity of even and odd numbers. It means that the number ten is an ideal number, because this number expresses the space, musical and structural harmony of the World and therefore symbolizes the Universe. For this reason the sky must contain ten planets, including the Sun and the Moon, for which Pythagoreans introduced ten mobile spheres. The distances between the spheres must obey simple number relations. Rotating around the central Fire, the planets produce noiseless harmonic sounds creating the music of spheres. At that time only six planets were known, so Pythagoreans added a new sky body, the Anti-Earth. Later on Alexandrian mathematician and astronomer Αρισταρχος (the close of the 4th century–the first half of the 3rd century BC) excluded the central Fire and the Anti-Earth, placed the Sun in the center of Universe thereby creating the first heliocentric model of the Sun system.

Numbers rule our life. Some numbers tightly connected with definite sides of our life and nature. Their changing leads to fatal consequences. Consider some examples.

One: one king, one ruler, one president. Any increasing produces instability of the corresponding system and, as a consequence, there appear wars, revolutions, distempers etc.

Two: two eyes, dual highway with two-way traffic, etc. Decreasing leads always to disablement and frequently to road accidents.

Four: north-south-east-west, spring-summer-fall-winter. Nobody is able to change this number.

Six: types of usual movement: right-left-forward-reverse-upward- downward. It is possible to decrease, but impossible to increase.

It is worth noting that even in the modern life we deal sometimes with a whole system of numbers which conserved their symbolic sense. The cards used in card games come in *two red* suits, hearts and diamonds; and *two black* ones, clubs and spades; each suit has *nine* cards; the pack of cards contains usually *thirty-six* cards. Many people believe that the cards can tell fortunes.

2. Introduction: geometry everywhere

Geometry and elements. Mathematics is defined as the science of numbers and of the structure and measurement of shapes [1-5]. The term originates from the Greek word μαθημα [knowledge, science]. Just the same meaning has the word μαθησις, initially concerning to the knowledge obtained on the basis of clear thinking contrary to the knowledge received as a result of experience. "Study of mathematics approaches us to the immortal Gods" said Plato (Πλατων, 427–347 BC). In the antiquity, mathematics consisted of arithmetic and geometry. Above all ancient Greeks appreciated geometry. The entrance of the house, where Plato lived and taught, bore the inscription: "No-geometer does not come in."

Ancient Greeks believed that there were four substances (elements) earth, water, air, and fire from which everything material was made [2].

According to Ηρακλειτος (~544–483 BC) the elements transform into each other in the following manner. The downward way means changing as a result of condensation

$$fire \rightarrow air \rightarrow water \rightarrow earth.$$

The upward way means changing as a result of rarefaction in the opposite direction

$$earth \rightarrow water \rightarrow air \rightarrow fire.$$

The reason of transformation is a "fire measure."

Plato gave to these processes and elements geometric sense and forms. There are only five types of regular polyhedrons, all the faces of which being regular polygons; namely, tetrahedron, octahedron, icosahedron, cube, and dodecahedron. They are spoken of as Plato's bodies (Fig. 1). "The most movable body, according its nature and due to necessity, such one which has the least number of faces; besides it is the lightest because of it has the least number of initial parts. For this reason the form of a pyramid is a symbol and an element of fire." It should be mentioned that the Greek word πιραμις (pyramid) originates from the word πιρα (

"The second in birth order we name air, and we allot the middle body, an octahedron, for it. The largest body, an icosahedron, we allot for water. To earth we give the shape of a cube, because it is the most immovable out of four types and in the least degree is suitable to body transformation; that is why it must have the most stable basis. Demiurge (Δημουργος– creator) designated a dodecahedron for the Universe when decorating it." Later Plato confronted a dodecahedron with ether.

Aristotle (Αριστοτελης, 384–322 BC) considered that the Nature is twofold; it is a form and it is a matter, the form being leading and more active. We see that Plato connected the form with geometry.
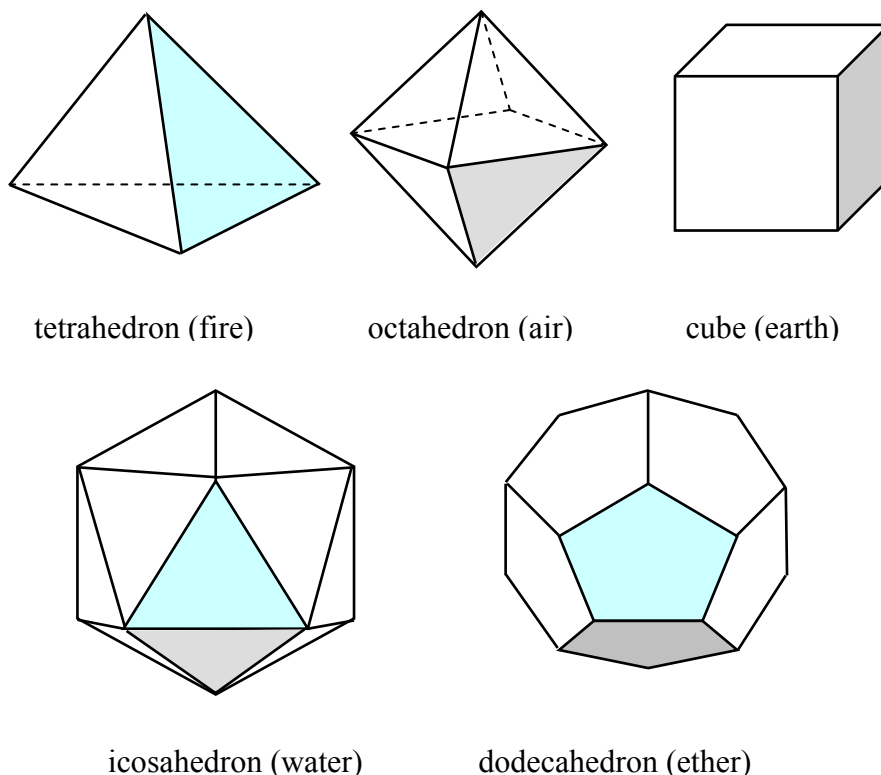

tetrahedron (fire)   octahedron (air)   cube (earth)

icosahedron (water)   dodecahedron (ether)

Fig. 1. Plato bodies.

Geometry and Universe. Johann Kepler (1571–1630) shared Pythagorean conviction: "Everything does not originate from a number, but in conformity with a number." He tried to find "the numerical harmony of sky spheres" and did it [6]. According to his geometric model of the Universe, Mercury sphere, the nearest to the Sun, is inscribed into an octahedron. In its turn, the octahedron is inscribed into the next sphere, Venus sphere. This sphere is inscribed into an icosahedron; around it, Earth sphere is located. Inscribing it into a dodecahedron, one obtains Mars sphere. Inscribing the latter into a tetrahedron, we come to Jupiter sphere. Putting it into a cube, we come to Saturn sphere. Therefore, we have five Plato bodies and six sky spheres which correspond to the six planets known at that time. The model gives the right quantitative relations between the radii of the planet orbits. It was published in the book under the name "Prodromos dissertationum cosmographicarum seu Mysterium cosmographicum" (Harbinger reasoning cosmographical or Cosmography mystery) in 1597. However, the most known achievement by Kepler is Kepler laws (1609), in particular his third law which connects the time of planet circulation with the planet distance from the Sun.

After these two introductions, pass on the structure of condensed solid matter. We did such rather long introductions with the purpose to show that numbers, geometry and structure are tightly connected with each other. However if to begin discussing structure of solids straight off, it will be difficult to understand why one or another type of model is used in modern science. Sometimes they seem rather artificial. In reality, "Multiform kinds of Greek philosophy have in embryo almost all the latest types of Weltanschauung. For this reason theoretical natural science is compelled to return to Greeks" (Friedrich Engels, 1820–1895).

3. Crystals

Principle of close packing. The majority of solids, which mankind confronted in ancient times with, are crystals. At first, the word crystal denoted only ice (Gr. κρισταλλοζ – ice), then rock crystal, because the Ancients believed that ice transforms to rock crystal in mountains under the action of the cold. In the XVII century, the scientists tried to explain the shape of crystals on the basis of the principle of close packing of spherical particles (Johann Kepler, 1611; Robert Hooke, 1685; Christian Huygens, 1690). Being a faithful follower of Pythagoreans, Kepler correlated the crystals with the Pythagorean pyramidal numbers.

His reasoning is as follows. Take a group of three contacting balls. Placing one more ball atop the group, one obtains a pyramid. If this pyramid is placed atop the triangle of six contacting balls, the pyramid form does not change. Let us increase successively the number of balls in the triangular basis, taking the group of 10 balls, then 15 balls and so on. The pyramid will grow holding the shape (Fig. 2). Inside the pyramid, each ball is in a contact with twelve other balls (its neighbors), at that six neighboring balls lie in the same plane, three neighboring balls lie in the plane above, and three neighboring balls below this plane. Using this line of reasoning, Kepler showed that the shape of a forming crystal can differ from the shapes of its constituent parts. Besides, Kepler has formulated the *principle of close packing*.
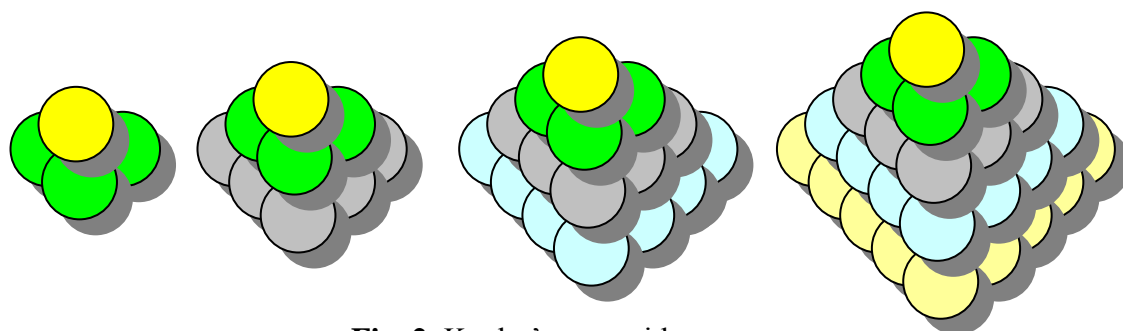

Fig. 2. Kepler's pyramids.

Atomic structure of crystals. The principle of close packing conserves its significance even today. Really, investigating the properties of condensed state, every so often an atom is modeled by a ball having diameter b. As a result, the real potential of interatomic interaction is replaced by the solid sphere potential

$$U(R) = \begin{cases} \infty, & R \le b \\ 0, & R > b \end{cases}.$$

The replacement of atoms by balls allows solve a whole series of tasks by pure geometry. For example, let us superimpose the ball layers one after another, as Kepler did. Then one obtains either the hexagonal or face-centered cubic structure depending on whether the arrangement order repeats every two or three layers (Fig. 3). Violation of the arrangement order creates stacking faults.

Take as a basis the group of four balls, each ball touching two neighbors. Putting one more ball atop the group, one obtains a pyramid, which base is a regular quadrangle. Increasing the basis size , we obtain the pyramid with the body-centered structure. This structure can be thought of as two simple cubic lattices inserted into each other (Fig. 4a). The structures considered are named h.c.p. (hexagonal close-packed), f.c.c. (face-centered cubic) and b.c.c. (body-centered cubic) structures. They are typical for metals and solid solution alloys.

Let us complicate the task. Suppose we have two-type balls which differ, for example, in color. Take as a basis the group of three balls of the same color. Build Kepler's pyramid in such a way as to create a two-layer periodicity. Then we obtain the structure in which it is possible to isolate a primitive cube of two tetrahedra inserted into each other, each tetrahedron having the balls of the same color (Fig. 4b). Such structure is typical for alkali-haloid compounds (ionic crystals A_1B_7), the balls of different colors corresponding to the ions of different signs. The f.c.c. structure obtained is called the structure of NaCl type.
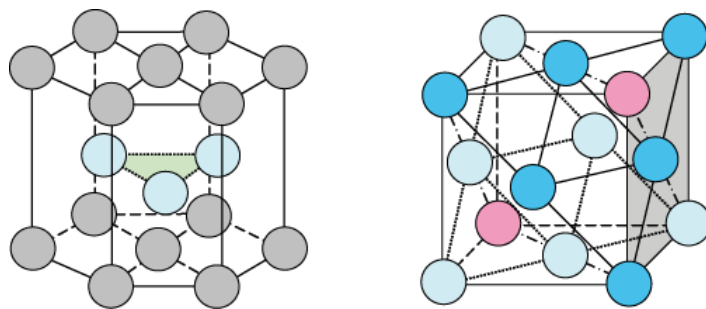

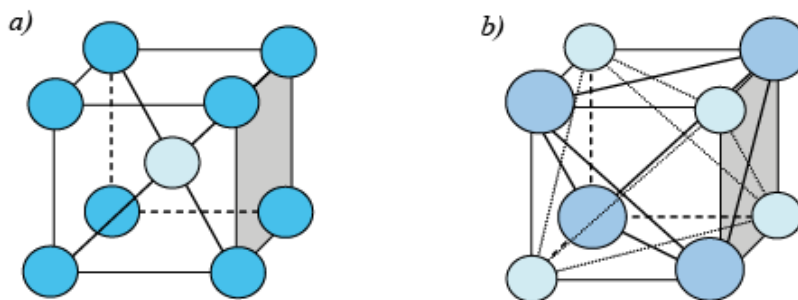**Fig. 3.** Hexagonal close packing (on the left) and face-centered cubic lattice (on the right).

Fig. 4. Body-centered cubic structure (*a*); tetrahedra of NaCl type structure (*b*).

If the pyramid basis has four balls of one color, then the two-layer periodicity of different colors corresponds to the structure of CsCl type. It is the b.c.c. structure which consists of two simple cubic structures inserted into each other, each structure having the ions of the same sign (Fig. 4a). More complex structures can be constructed, if we have three-type balls.

Electronic configuration of ions and the nearest to them atoms of inert gases is the same and has a spherical symmetry. Generally speaking, the distance between nearest neighbors in ionic crystals is not equal to the sum of the radii of different-sign ions, e.g. for sodium chloride we have

$$r\,(\,Na^+\,)+r\,(\,Cl^-\,)=0.095+0.181=0.276\,nm<b=0.281\,nm\,.$$

However, the difference is not large. That is why the solid ball model is a good approximation.

Consider the f.c.c. structure constructed from the balls having the same radius r. The structure contains "holes" or "interstices" between the balls. They are of two types: octahedral and tetrahedral ones (Fig. 5). The octahedral holes can contain a sphere of radius $0.41\,r$; the tetrahedral holes can accommodate spheres of radius $0.225\,r$.

Suppose that the f.c.c. structure consists of chlorine ions and all the octahedral holes are occupied by sodium ions. Then we obtain again the structure of NaCl type, with

$$r\,(\,Na^+\,)\,/\,r\,(\,Cl^-\,)=0.095\,/\,0.181=0.51\;>\;0.41\,.$$

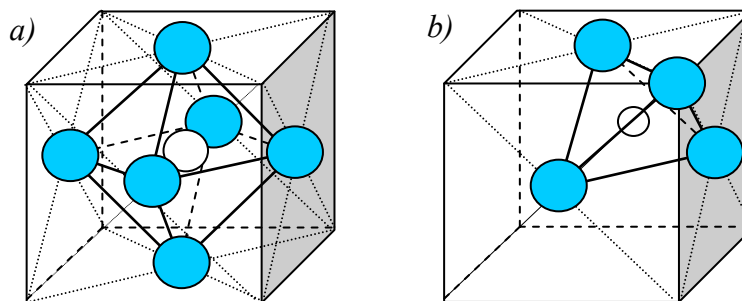It means that the large ions, in our case chlorine ions, do not touch each other.

Fig. 5. Holes in the f.c.c. structure: (*a*) octahedral, (*b*) tetrahedral.

Consider the tetrahedral holes of the f.c.c. structure (Fig. 5b). Inside the cube shown, eight holes also form a cube. Fill up by the same balls only four holes in such a way as to obtain a regular tetrahedron (Fig. 6a). To ensure that the new balls are able to find room in the holes, we need to reduce the radius r of the balls to the value $(r+0.225\,r)\,/\,2\cong0.61\,r$. At the same time the relative volume of all the balls decreases from 0.74 (initial cube with empty holes) to 0.34 (new porous cube). Natural and synthetic crystal of carbon has the structure obtained, so it was named the diamond structure. The length of the cube edge (lattice parameter) for a diamond crystal is equal to $0.357\,nm$. In addition to carbon, silicon, germanium and grey tin have the diamond structure, but their lattice parameter is significantly larger, $0.543,\,0.565,\,0.646\,nm$, respectively.

Let us replace all the internal atoms of the f.c.c. structure shown in Fig. 6a with the atoms of another kind, the external atoms being the same as before. Then we obtain the blende structure in which some compounds A_2B_6 and the most of compounds A_3B_5 crystallize.
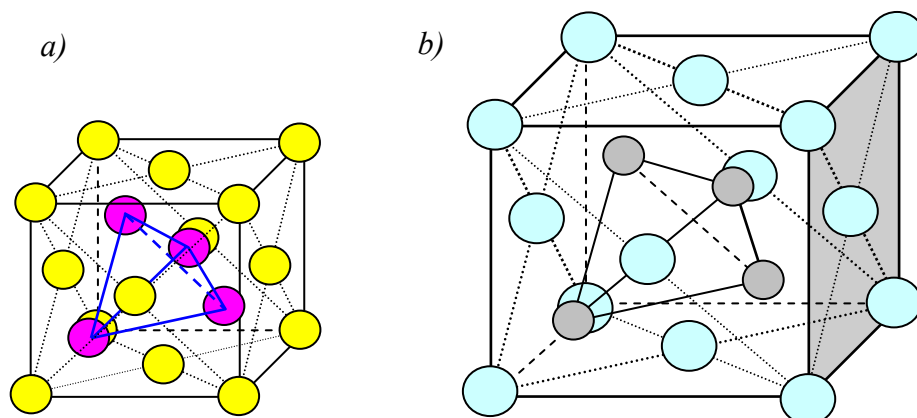
Fig 6. Diamond structure (a); blende structure (b). All the diamond atoms are identical; the atoms designated by dark color are located in tetrahedral holes. Dark and light balls of blende refer to atoms of different kinds. Lattice parameter of diamond is *0.356 nm,* whereas the lattice parameter of ZnS is *0.541 nm.*

It should be highly stressed that the loose diamond structure does not mean low strength. On contrary, diamond (from Gr. α-δάμας–hard, firm, steadfast) has the maximal hardness; on hardness testing by Vickers method, a diamond pyramid is indented by its spike into a material studied. In opposite to the f.c.c. structure, where each atom has 12 nearest neighbors, each diamond atom has 4 nearest (first) neighbors and 12 next nearest (second) ones. However, the distance between the first neighbors is *0.154 nm*; the second neighbors are at the distance

$$2 \times 0.154 \times sin\,(\,109^{0}28' \,/\, 2\,) \cong 0.25\;nm\;.$$

Just the same distance is between the nearest neighbors in nickel and copper which have the f.c.c. structure, the lattice parameters of nickel and copper, *0.352* and *0.361 nm*, coinciding practically with that of diamond. Synthetic diamond is produced under high pressure. Because of this procedure one is inclined to think that diamond resembles the interstitial solid solution of its own atoms in the f.c.c. lattice.

No crystal structures other than perhaps carbides, borides, and nitrides have such minimal distance between the nearest neighbors as diamond has. For example, in silicon carbide the distance between the nearest neighbors, *0.188 nm*, although is larger than in diamond, but significantly less than in silicon, *0.235 nm*. In essence, these nearest neighbors in diamond are ultra–nearest ones (Lat. ultra–beyond limit).

4. Long-range and short-range order

Bravais lattices. Consider an ideal crystal, in which the arrangement of atoms is specified with the help of lattice sites. The sites are given by the set of vectors

$$\boldsymbol{l} = n_{1}\,\boldsymbol{a}_{1} + n_{2}\,\boldsymbol{a}_{2} + n_{3}\,\boldsymbol{a}_{3}\,.$$

Here n_i are whole numbers, $\boldsymbol{a}_i$ are the noncomplanar base vectors having the least length in given directions. The word noncomplanar originates from two Latin words: com–together + planum–plane. Three base vectors form a primitive cell. All the crystal can be obtained by the translation of the primitive cell (translation is taken from Latin translatio–transfer). In this

case one might say on the translation invariance of a crystal lattice (in Latin in-variantia means dead-level, monotony). In other words, there is a translational long-range order which refer to the entire lattice.

Besides the transfer symmetry, crystals have also rotational symmetry around some axes, mirror symmetry of reflection relative some planes and inversion symmetry in some direction; inversion (Lat. inversio–permute, rearrange in a different order). All the symmetry operations must be compatible with each other. This condition is fulfilled only for five types of two-dimensional lattices (Fig. 7) and for fourteen types of three-dimensional ones. These lattice types were discovered by August Bravais in 1848, and are referred to by his name. The corresponding cells are spoken of as elementary cells (Lat. elementaris–initial).
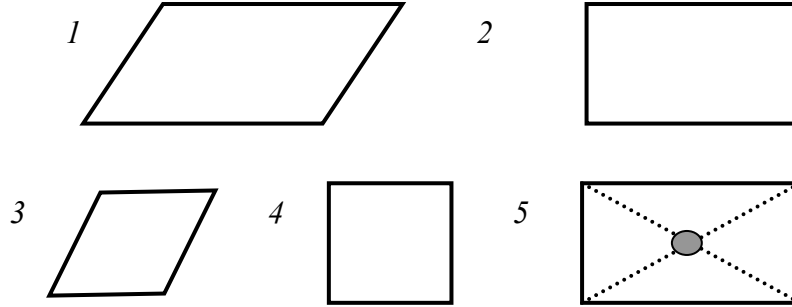

Fig. 7. Two-dimensional Bravais cells: 1) oblique-angled,
2) rectangular, 3) hexagonal, 4) square, 5) rectangular centered.

Elementary cell. If a crystal consists of one-kind atoms and the elementary cell contains only one atom, the crystal lattice is simple. In a general case, the elementary cell contains atom of different kinds, so the crystal lattice becomes complex. Consider, for example, ferroelectric $BaTiO_3$. In its elementary cubic cell barium atoms are located at the cube apexes, titanium atom – at the cube center, oxygen atoms – at the cube faces (Fig. 8a). Take the origin of coordinates at the cube center. Then the position of titanium atom will be characterized by the vector $r_0 = 0$, oxygen atoms will have the vectors $r_1 = a / 2 < 100 >$, barium atoms – the vectors $r_2 = a / 2 < 111 >$. In this case the atom arrangement in the elementary cell can be given with the help of the sum of δ–functions.

$$\rho(r) = \delta(r) + \delta(r - r_1) + \delta(r - r_2).$$

If the elementary cell has s different atoms having the coordinates r_s, $s=1, 2, ..., s$, then

$$\rho(r) = \sum_s \delta(r - r_s).$$

All the crystal can be obtained by the translation of the elementary cell, so the atom coordinates become equal to r_s+l, therefore the atom arrangement in an ideal crystal takes the form

$$\rho(R) = \sum_l \sum_s \delta(R - l - r_s).$$

It is a periodic function. Really, we have

$$\rho(R+l) = \sum_{l'}\sum_{s}\delta(R+l-l'-r_s) = \sum_{l'}\sum_{s}\delta\left[R-(l'-l)-r_s\right].$$

Introduce the new vector of translation $l'' = l' - l$. Then

$$\rho(R+l) = \sum_{l''}\sum_{s}\delta(R-l''-r_s) = \rho(R).$$

This formula shows that in an ideal crystal there is a strict periodicity over distances which are much larger than the size of an elementary cell.

Just the same approach can be used for an analysis of more complex structures, e.g. high-temperature superconductors (Fig. 8b).
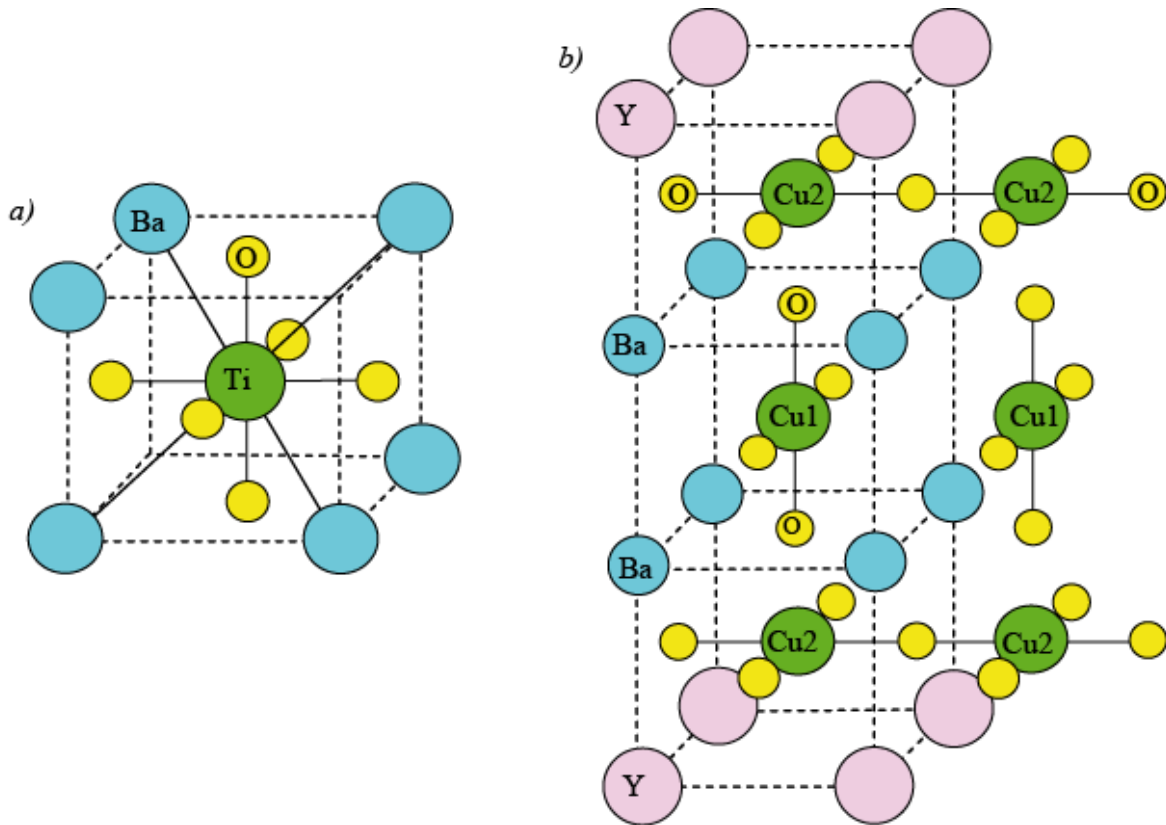

Fig. 8. Arrangement of atoms in elementary cells:
(*a*) ferroelectric $BaTiO_3$; (*b*) high-temperature superconductor $YBa_2Cu_3O_7$, $T_c \sim 91$ K.

Continuous and discrete space. An ideal crystal may be thought of as the structure which was formed as a result of transformation of continuous space into discrete one. In the modern mathematics the space is defined as a set of some objects. These initial objects are named elements. They may be geometric figures, functions, states of a physical system, etc. In its turn, the set is defined as an aggregate, collection of the elements having a common property. "A set is much thought of as a single whole" (Moritz Benedict Cantor, 1829-1920). For the set theory it is important to know not the nature of elements, but relations between them.

Fedorov bodies. Take the infinite set, its elements being points (point set). Consider convex polyhedrons of this set. A polyhedron is called convex if it is located on one side of the plane of any its face. Let these polyhedrons will be the bodies which parallel translation

allows fill up all the infinite space in the following way. The polyhedrons do not enter into each other and they do not leave holes between them. Then we obtain space partition into parallelohedrons. Only five types of convex polyhedrons satisfy to this condition. These polyhedrons were discovered by Evgraf Stepanovich Fedorov in 1881 and were named for the discover Fedorov bodies (Fig. 9). Most of them were known to ancient Greeks. They are:

- cube (κυβος – die in the form of a cube),
- regular hexagonal prism (πρισμα – literally sawed off; Εύκλειδης, 3rd century BC; Άρχιμήδης, ~ 287-212 BC),
- truncated hexagonal prism; two bases and two side faces are hexagons, eight oblique faces are rectangles,
- truncated octahedron (Θεαιτητος, 4th century BC),
- rhombic dodecahedron (ρομβος – peg-top, Άριστοτέλης, 384-322 BC; δώδεκα-εδρον – Θεαιτητος, 4th century BC).

The number of their faces is граней 6, 8, 12, 14 and 12, respectively.

In particular case, when all the faces of some Fedorov body are adjacent with the similar faces of neighboring bodies, the space partition is normal. Here the centers of Fedorov bodies form a lattice, i.e. a set of points having whole coordinates with respect to some Cartesian, not necessarily rectangular, system of coordinates.
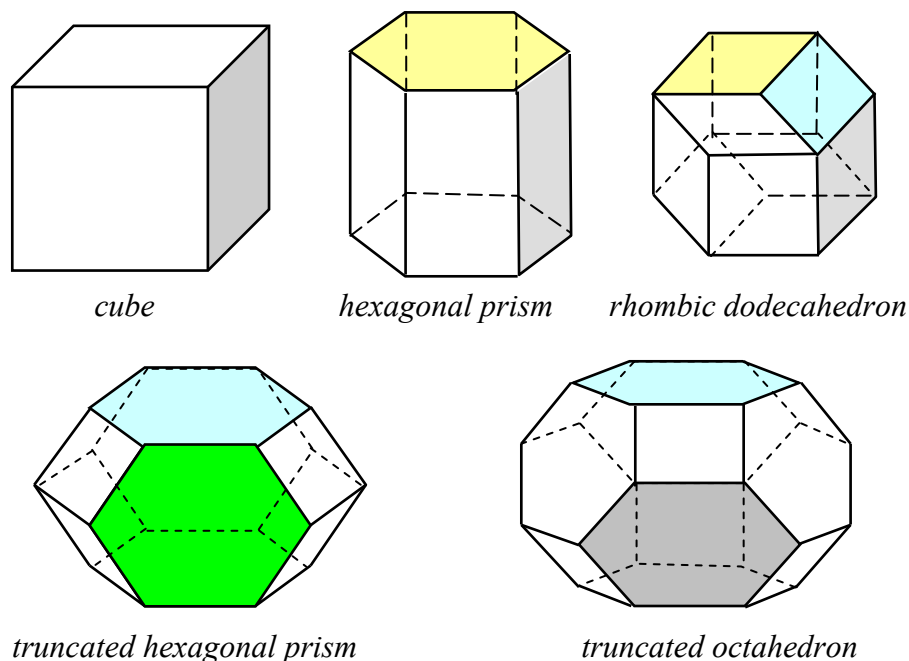

cube   *hexagonal prism*   *rhombic dodecahedron*

truncated hexagonal prism   *truncated octahedron*

Fig. 9. Fedorov bodies.

Voronoy polyhedrons. Global symmetry of a crystal is adequately taken into account by Bravais elementary cell in the form of a parallelepiped. The word parallelepiped originates from two Greek words: παρ-αλληλος–going alongside + επι-πεδον–plain, plane. However, it is difficult to understand local symmetry with the help of this cell. When one studies local symmetry, one examines an object from different sides, e.g. for an atom one defines the number of nearest neighbors of the first, second, and so forth coordination sphere. During the investigation one looks for the symmetry operations like rotation, reflection, inversion, which keep the distinguished atom immobile. In other words, the purpose of investigation is to discover the rotational short-range order which refer to this atom.

Let us construct an elementary cell which contains information on this order. Join the atom chosen with its nearest neighbors by lines, and then draw the panes through the middles of lines normal to these lines. The convex polyhedron obtained, having the chosen atom as a center, gives the elementary cell looked for. Consider, for example, two-dimensional hexagonal structure known in slang as "triangular lattice". It has an elementary translational cell in the form of a rhomb, whereas its rotational elementary cell is a hexagon (Fig. 10). Both cells are primitive since they contain only one atom. The rotational elementary cell better illustrates the regular arrangement of atoms in the vicinity of the atom considered, i.e. the rotational short-range order.

In three-dimensional space the rotational elementary cell has the form of polyhedrons. Their algorithm was developed by Georgy Feodosievich Voronoy in 1908, and these polyhedrons were named for the discoverer, Voronoy polyhedrons. In particular, Voronoy polyhedron in the f.c.c. and b.c.c. is a rhombic dodecahedron and a truncated octahedron, respectively. It must be emphasized that later on these polyhedrons were introduced in physics by E. Wigner and F. Seitz (1933). Probably, gaps in knowledge of foreign languages are the cause that in Wild West literature Voronoy polyhedrons is usually referred to as Wigner-Seitz cells.
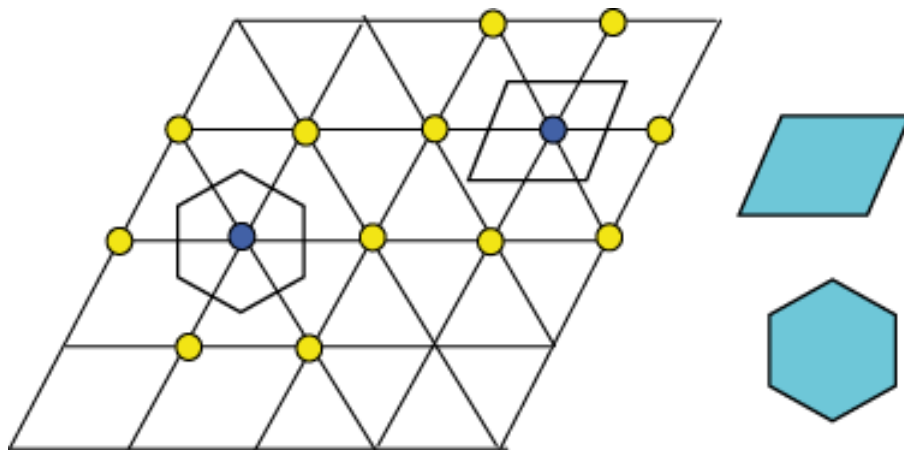

Fig. 10. Translational and rotational elementary cells
of two-dimensional hexagonal structure.

Group theory. We have considered an ideal crystal from two points of view, global and local symmetry, and introduced two types of order: long-range and short-range ones. These intuitive notions become more exact if one uses group theory, it being one of the parts of nonquantitative mathematics. Group theory investigates in the most general form the operations which are most often met with in mathematics, e.g. addition and multiplication of numbers, multiplication of vectors, symmetry operation and so on. In the general case a *symmetry operation* is defined as a displacement of a body into an *equivalent position*. What does it mean? Suppose that one sees a body before and after a symmetry operation, but not during its realization. If one is unable to say whether the symmetry operation is done or no, then the positions should be considered to be equivalent. Any crystal admits some symmetry operations, so it possible to state something on crystal properties even not solving the corresponding equations. With the help of group theory E.C. Fedorov solved the problem of classification of regular space systems of points (1890). Historically, it was the first case of the application of group theory directly in natural science.

The main idea underlies the *notion of group* is the *conception of structure*. Groups and their graphs are one of the forms of mathematical structure. The basic attributes of any group are a set of elements and a binary operation. The binary operation means one-to-one correspondence between a pair of elements A and B, and element C, which is named the multiplication of element A and B.

Consider some examples of groups which we will use in the subsequent text.

1) Set of all rotations of space around an axis. Multiplication of two rotations and β, i.e. the turn through angle α and then the turn through angle β, is defined as resulting rotation γ=α+β, i.e. the turn through angle α+β.

2) Set of all rotations of space around any possible axes, passing through a fixed point, is defined in a similar way. The set forms a *rotation group*.

Subgroup is defied as any subset if it is a group with respect to the same group operation. For example, rotations around one and the same axis in the rotation group; rotations around the cube center, as a result of which the cube coincides with itself.

3) Set of all rotations combined with the inversion of space points with respect the origin of coordinates gives an *entire orthogonal group*. If the turns occur through some fixed angles, one obtains a *point group*, which is a subgroup of the entire orthogonal group.

4) Set of all displacements of space such that the displacement of all points is equal. This is a *translation group*.

5) Set of all displacements, with the result that the distance between any pairs of points remains constant, forms *Euclidean group*. It contains two important subgroups: translation group and entire orthogonal group.

Suppose that one of the atoms is at the center of coordinates, which is immobile. Other atoms are arranged in an arbitrary way in the space. If interaction of atoms is of central character, the undirected valencies of any atom form an entire orthogonal group. Correlation of interatomic interactions during crystallization orders the chaos of interatomic bonds, which symmetry decreases. In fact, the bonds become ordered, since during crystallization takes place transition from the entire orthogonal group to one of the point groups. It is this transition that justifies the principle of close packing in the model of solid balls, where one implicitly takes into consideration the directedness of interatomic bonds.

5. Quasicrystals

Quasiperiodic lattices and functions. In parallel with crystals there are also solids having no translational long-range order, among which are quasiperiodic materials or simply quasicrystals. Consider a two-dimensional square lattice. Set off an elementary square. Let us displace it along a straight line *L* at some angle to a symmetry axis, e.g. to x-axis. The moving square generates a strip, which incorporates a part of sites of the square lattice (Fig. 11). Project these sites onto the line *L*. In doing so, one obtains a set of points which separate the line into two-type line segments, long and short. The set can be described by the expression

$$l = n_1 \, a_l + n_2 \, a_s \, ,$$

where n_i are whole numbers, a_l, a_s is a long and a short segment, respectively. If the tangent of the angle between the strip and a symmetry axis is a rational number, the long and short segments are linearly dependent, and the set is periodic. If the tangent is irrational, the segments are linearly independent, and one obtains a quasiperiodic one-dimensional lattice. The projection method considered was suggested N.G. de Bruijn (1981) and later on was developed for physical applications.
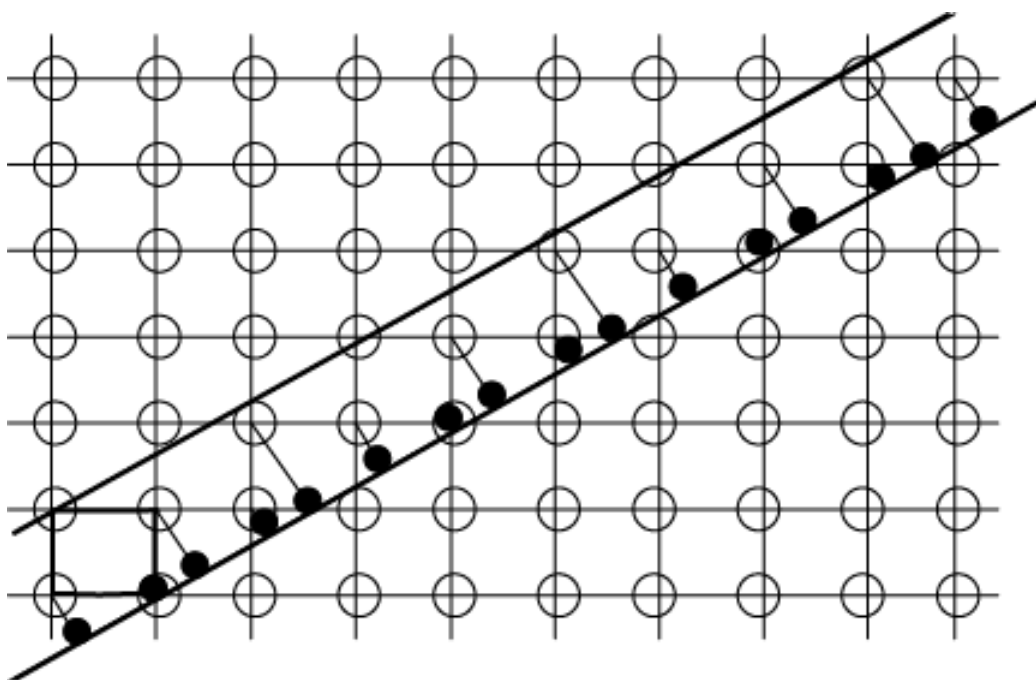
Fig. 11. One-dimensional quasiperiodic lattice as
a projection of a square lattice onto a line.

The function *l,* which defines such lattice, is quasiperiodic. The simplest quasiperiodic functions are obtained by adding finite number of periodic functions with incommensurable periods (Pirs Georgievich Bol, 1893), e.g.

$$y = sin\ x + sin\ \sqrt{2}\ x.$$

They have such property that if to add special constant numbers (almost periods) to their argument, the function values approximately recur. Therefore, the quasiperiodic one-dimensional lattice can be constructed also with the help of the functions, which have such property.

Fibonacci numbers. Consider, for example, Fibonacci numbers. They are defined in the following way (Leonardo Pisano Fibonacci, 1228)

$$F_{n+1} = F_n + F_{n-1}, \quad F_0 = 0, \quad F_1 = 1, \quad n = 0,\ 1,\ 2,\ \ldots,\ .$$

This gives the number sequence *1, 1, 2, 3, 5, 8, 13, 21, 34, 65, 99,...,* or Fibonacci series. In this case the ratio of antecedents to succedents gives the sequence of rational numbers, or Fibonacci sequence, *1,* $\dfrac{1}{2}, \dfrac{2}{3}, \dfrac{3}{5}, \dfrac{5}{8}, \dfrac{8}{13}, \dfrac{13}{21}, \dfrac{21}{34}, \dfrac{34}{65}, \dfrac{65}{99},...,$ converging to limit. Let us find this limit. Since

$$w_n = \frac{F_n}{F_{n+1}} = \frac{F_n}{F_n + F_{n-1}} = \frac{1}{1 + \dfrac{F_{n-1}}{F_n}}\quad,$$

then with $n \to \infty$ one obtains

$$w = \lim_{n \to \infty} w_n = \frac{1}{1 + w} \qquad \text{i.e.} \qquad w^2 + w - 1 = 0.$$

Therefore

$$w = (\sqrt{5} - 1) / 2 = 0.6180339.$$

One can consider the equality $w^2 = 1 - w$ as the product of extreme and mean terms of the proportion

$$\frac{w}{1} = \frac{1 - w}{w}.$$

In geometry, this corresponds to the division of a segment in such a way as to obtain the ratio of the greater part w to the whole length being equal to the ratio of the lesser part $1-w$ to the greater one. Such division is called harmonic division, division in the ratio of extreme to mean, divine proportion (Luca Pacioli, De divina proportione, 1509) or, following Leonardo da Vinci, golden section. The golden section was very popular in Antique and Renaissance architecture, so that the number w is called golden mean.

Fibonacci numbers characterize a quasiperiodic lattice of a given size. For example, in formula $F_n + F_{n-1} = F_{n+1}$, the first term is the number of long segments, the second is the number of short ones. One makes sure of it examining carefully Fig. 11. This allows construct a one-dimensional quasiperiodic lattice without using projective geometry. In the infinite quasiperiodic lattice, the number of long segments is equal to the golden mean w.

Penrose lattice. Consider two-dimensional quasiperiodic structures, a vivid example of which is Penrose lattice. Its sites are given by the set of the vectors

$$\boldsymbol{l} = n_1 \boldsymbol{e}_1 + n_2 \boldsymbol{e}_2 + n_3 \boldsymbol{e}_3 + n_4 \boldsymbol{e}_4 + n_5 \boldsymbol{e}_5 \ ,$$

where n_i are whole numbers, $\boldsymbol{e}_i$ is the set of unit vectors directed from the center of a regular pentagon to its apexes (star of vectors). The unit vectors satisfy the condition

$$\sum_{i=1}^{5} \boldsymbol{e}_i = 0,$$

so that one has only four linearly independent base vectors. However, as in the case of h.c.p. structures, it is conventional, for a better clearness, to use an odd vector.

Penrose lattice has two structural elements: a broad and a narrow rhombs (Fig. 12). The angles of the broad rhomb are equal to *$2\pi/5$, $3\pi/5$*; the angles of the narrow one are *$\pi/5$, $4\pi/5$*. The rhombs contain material atoms and play the role of elementary cells of an ordinary crystal. They are conjugated together according to definite rules so that the edges of rhombs were parallel to the symmetry axes of a regular pentagon. In doing so, there appears a quasiperiodic translational long-range order and simultaneously an orientation long-rage order with a symmetry axis of the fifth order which refer to the entire lattice.
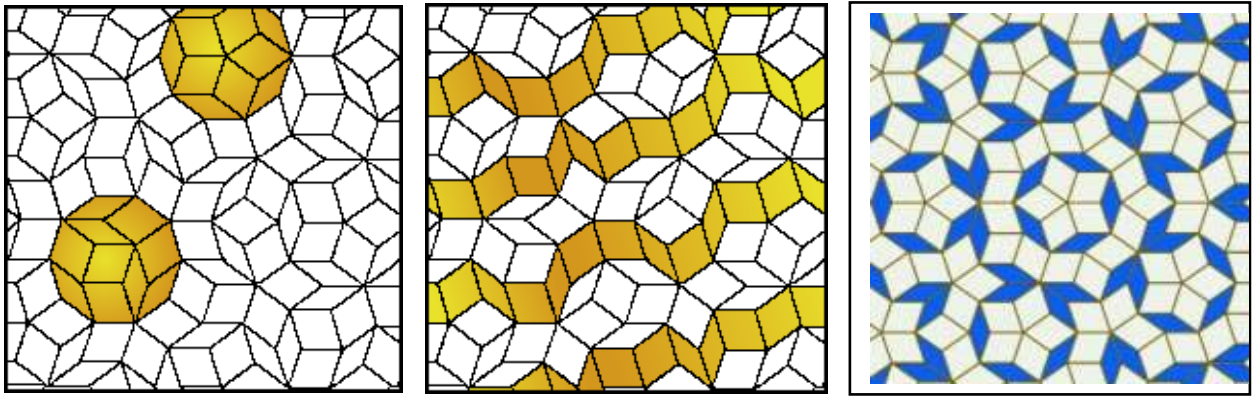
Fig. 12. Penrose lattices.

It should be emphasized that the formula giving the set of vectors defines the position of possible sites of a quasicrystal (a space of possible states), but a real lattice contains not all the sites, but only a part which is selected according to some rather complex rules, they being patented by Penrose as a method of wall-paper coloring (Fig. 13). In this case, the ratio of the number of broad rhombs to the number of narrow rhombs in the infinite Penrose lattice is equal to the golden mean, as in the infinite one-dimensional lattice.

Fig. 13. Penrose wall-papers.

Three-dimensional quasicrystals. These quasicrystals, with an orientation long-rage order, have the symmetry of an icosahedron (Fig. 1). The latter has 6 fivefold axes, 10 threefold axes, and 15 twofold axes. The first material of this type, a rapidly solidified aluminum alloy with *25–wt%* manganese, was obtained by Dan Shechtman in 1982. Then the orientation long-rage order was found in binary, ternary and quadruple transition-metal alloys. Generally these alloys have the symmetry of an icosahedron, so they are named icosahedral phases, although there are alloys having eightfold, tenfold, and even twelvefold axes.

Many viruses have also the form of an icosahedron (F.H.C. Crick, J.D. Watson, 1956). It is worth noting that before discovering the alloy quasicrystals there were known crystals with one fivefold axis. Among them there are copper dendrites having been grown under special conditions, whisker crystals of iron, nickel, platinum; cobalt crystals, synthetic diamonds, and so on (B.G. Bagley, 1965).

Nucleation and growth. Let us take up formation of quasicrystals. Take a group of five balls, each contacting with two others. Placing one more ball atop the group, one obtains a pyramid. Following Kepler, let us increase successively the number of balls in the pentagonal basis in such a way, as to ensure the pyramid growth keeping its form (Fig. 14). As will

readily be observed, in the act of forming there appear close-packed faces and close-packed directions (Fig. 15a).

Let us take 12 identical pyramids. Combine them with each other in such away that they have one common apex, two adjoining pyramids have one common face, and five adjoining pyramids have a common edge. Then we obtain a dodecahedron (Fig. 15b). Take again 12 identical pyramids and place each of them on one face of the dodecahedron. Then we obtain an icosahedron (Fig. 15c). Thus we can suggest the following model of nucleation and growth. At first, a quasicrystal nucleates and growths from one center simultaneously and evenly along 12 directions, similar to that of as snowflakes do in the beginning. As a result there appears a dodecahedron. Then the uniform growth gives way to a skeletal one, as the snowflakes do in the middle. As a result there appears an icosahedron. .

It is not surprising, since an icosahedron and a dodecahedron can be obtained from each other, if the gravity centers of one-of-them faces are accepted as the apexes of another, and vice versa. This property is called duality (Lat. dualis–two-fold). In the group theory, the point group of an icosahedron Y consists of all the rotations which superpose a pentagonal dodecahedron with itself.
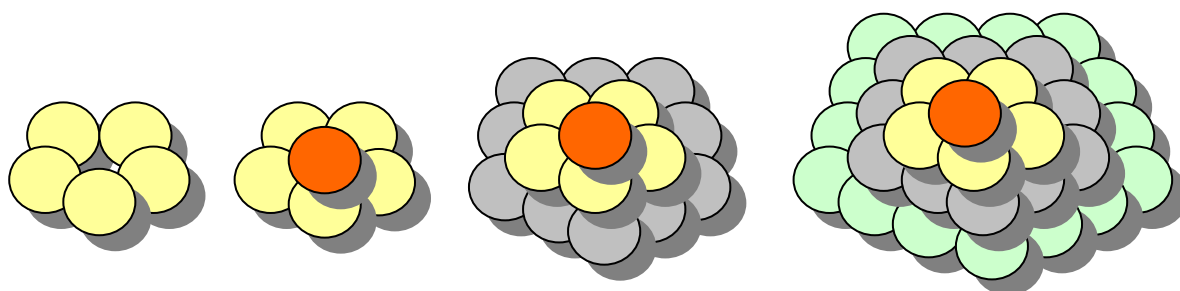

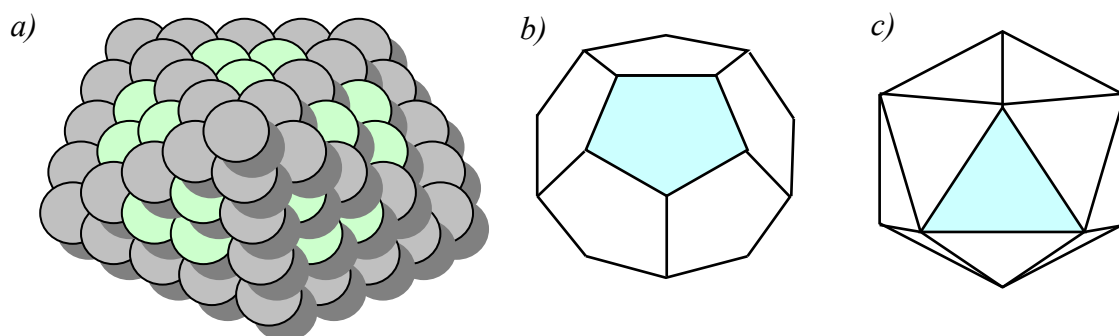**Fig. 14.** Growth of a pentagonal pyramid.

Fig. 15. a) Pentagonal pyramid, close-packed directions are distinguished
with dark color; b) dodecahedron; c) icosahedron.

Discovery. It is intriguing and instructively to note the history of quasicrystal discovery following its pioneer (Dan Shechtman, 1997). "Crystallographers, and other scientists who studied the structure of matter and its defects, relied on a series of laws and paradigms undisputed since von Laue performed his first x-ray-diffraction experiments in 1912. One leading paradigm stated that the atomic structure of a crystal is ordered and periodic. Explanation of this paradigm, based on *common sense,* could be summarized as, "It is periodic because it is ordered." Periodicity implies a set of specific rules, among them the allowed rotational symmetries – namely one-, two-, three-, four-, and sixfold. Fivefold rotational symmetry is excluded.

On April 8, 1982, I was studying – using electron microscope – a rapidly solidified aluminum alloy with *25–wt%* manganese. The specimen contained mainly a nodule-like phase. When I looked at the selected-area diffraction pattern taken from an orientation in which one such nodule was clearly diffracting many electrons (as the bright-field image was pitch-black), I saw for the first time the amazing tenfold diffraction pattern. My transmission-electron-microscopy (TEM) logbook from that day is a good record of what I felt. For plate number 1725 (Al–25% Mn)), I wrote, "10 Fold???"

At first glance, it was clear that the diffraction pattern was either taken from a multiply twinned crystal, or from something exciting. Within a couple of hours, I oriented the crystal in various orientations, and took a series of different diffraction patterns, a series of dark-field images, and several micro-diffraction patterns. No twins could be identified at the resolving power of the microscope, about 1 nm for the conditions of the specimen. With these results at hand, I inquired among my NBS colleagues about 10–fold symmetry in crystals. In doing so, I met a lot of ridicule, which came in different forms: from educated guess that the diffraction pattern was a result of multiple twins, which I knew clearly it was not, to fatherly advice about reading the x-ray crystallography text-books again. During 1982 and 1983, I discussed my fivefold diffraction patterns with many scientists. Although I communicated with many scientists and heard several wild guesses, nobody came up with a model or an idea explaining what that phase was.

I continued to work with rapidly solidified aluminum alloys for the rest of my stay at NBS. In the process, I observed the same set of symmetries in Al–Fe and Al–Cr alloys and started to believe it to be general for Al–transition-metal alloys. However when I tried to produce the symmetries in Al–Cu alloys, it did not work. In October 1983, I returned to the Technion and discussed my results with several colleagues. Only one of them, Ilan Blech, our X-ray expert who soon left academia to do business in California, believed in my results. Together we looked for structural models that would, when Fourier-transformed, gave the required patterns with the two-, three-, and five-fold symmetries as well as the proper angles between them. At a later stage, this became known as the icosahedral glass model. The model required that the icosahedra be joined by their spatial orientation.

My collaboration with Ilan resulted in a paper sent to the *Journal of Applied Physics* in the summer of 1984. The *Journal of Applied Physics* sent it back quickly, and the editor noted that the article was not suitable for the journal as it would not interest the community of physicists. Following their advice, I sent it immediately to *Metallurgical Transactions* where it ran a year later. While the paper was under review by *Metallurgical Transactions*, we wrote the second, shorter article, and sent it to *Physics Review Letters* where it was rapidly accepted and published very quickly in November of 1984. This article created a great wave of interest in the community of physicists contrary to the expectations of the editor of the *Journal of Applied Physics*. Quasiperiodic materials quickly drew a swell of attention. Today there are about 6,000 articles in the scientific literature as well as some 30 books, most of which are conference proceedings." It should be added that in 2011 Dan Shechtman became the Nobel Prize winner in chemistry.

6. Disorder

Defect types. In a real crystal atom arrangement differ from that of an ideal one. A distinction is made between the dynamic distortions connected with thermal vibrations of atoms and the static distortions produced by structure defects. The influence of defects on the properties of a real crystal correlates with their *dimensionality* by which is meant the number of dimensions defining the size of a defect. *A point defect* or zero-dimensional is one that is localized in a volume of the order of an atom. Usually it is a vacancy, an interstitial atom, or an impurity atom. If the regular arrangement of atoms is disrupted in the vicinity of some line, the defect

is named a *linear* or one-dimensional, e.g. a dislocation. Irregular arrangement of atoms along some surface generates a *surface* or two-dimensional defect. Among these are stacking faults, grain boundaries, cracks.

Ideal lattice. An ideal infinite crystal lattice is an abstraction which is convenient to use, as a first approximation, when crystals are analyzed quantitatively. Let us consider a real system of atoms being ordered, if its properties can be described on the basis of an ideal lattice and the distortions can be taken into account with the help of the theory of disturbances. If this assumption does not take place, the system is a disordered one.

Take up a simple ideal lattice. It has several attributes of ordering.
- All the atoms are identical,
- One and the same coordination number (equal number of nearest neighbors),
- There is a short-range order,
- There is a long-range order.

Types of disorder. Exclude the first attribute, i.e. take atoms of two kinds and distribute them randomly at the lattice sites. Then we obtain a binary alloy characterized by a composition irregularity or *composition disorder*. If the number of other type atoms is not too large, they can be considered as an impurity and an ideal lattice can be taken as a first approximation. However, with increasing of impurity atoms the first approximation becomes invalid. Perhaps this is the reason why up to now there is no the theory of disordered alloys.

Suppose that the second attribute is not realized. Then the atoms located in different places will have unequal number of nearest neighbors. As a result one confronts with a *topological disorder* (Gr. τοπος–place +λογος–doctrine). Almost all defects produce such type of disorder, namely, vacancies, interstitials, dislocations, disclinations, grain boundaries, except stacking faults.

Thermal vibrations eliminate a short-range order and, as a consequence, generate a *positional disorder*. If the vibrations are small, an ideal lattice, as before, is a good first approximation. In doing so, the coordinates of atoms can be represented by the formula

$$\boldsymbol{R} = \boldsymbol{l} + \boldsymbol{r}_s + \delta\,\boldsymbol{r}_{sl}.$$

Here $\delta\boldsymbol{r}_{sl}$ is the displacement of atom s from its equilibrium position in the elementary cell $\boldsymbol{l}$.

Let us take up how a long-range order is compatible with crystal defects. Take a real crystal with defects, say dislocations. Strictly speaking, the translational long-range order, which is characteristic of an ideal lattice, takes no place in such crystal, so the translational invariance is observed only at a distance of the order of a mean distance between the defects; so called a *mean or local order*. At the same time, many dislocations of different signs produce different distortions which compensate each other, and so one applies the notion of long-range order to real crystals. However, to emphasize the distinction from an ideal crystal, this order is named a *topological long-range* order, at that the defects divide all the real crystal into lesser parts with the translational order of the ideal crystal.

Paracrystals. A short-range order disappears not only due to thermal vibrations; it can be removed with the help of static distortions. Consider, for example, a paracrystal (Gr. παρα–near), where the sites of a crystal lattice are given by random way (R. Hosemann, 1950). In one-dimensional case these sites are found according to the following algorithm

$$x_0 = 0, \quad x_1 = a + \delta x_1, \quad x_2 = x_1 + a + \delta x_2 = 2a + \delta x_1 + \delta x_2$$

$$\sum_{i=1}^{n} \delta x_i = \delta x_\Sigma \qquad x_n = na + \sum_{i=1}^{n} \delta x_i = na + \delta x_\Sigma \;.$$

Here a is the lattice parameter, the value δx_i can be either positive or negative, whereas the variance δx_i^2 is always positive, so

$$\overline{\delta x_\Sigma^2} = \sum_{i=1}^{n} \overline{\delta x_i^2} = n\,\overline{\delta x^2}\,.$$

At the same time, for an ordinary crystal

$$\overline{\delta x_n^2} = \overline{\delta x^2} = const\,.$$

Therefore, for a paracrystal the mean-square deviation of an atom from its equilibrium position is proportional to the distance from the coordinate origin. It is the inventor's opinion that this model represents the structure of the state which intermediate between an ordinary crystal and a liquid.

Two-dimensional paracrystals can be classified into two groups: laminar (Lat. lamina–leaf, plate) and turbulent (Lat. turbulentus–stormy, violent). The laminar paracrystals have no static displacements along the axis parallel to one of non-coplanar base vectors. In the turbulent paracrystals, static displacements take place along all the base vectors. The structure of a paracrystal contains defects which are call paracrystalline.

Global disorder. At last, when there is no both short-range order, and long-range order, the structure, as a whole, is disordered. This global disorder is characteristic for amorphous materials.

7. Amorphous materials

Glass transition. It is customary to assume that matter can exist in four states (plasma, gas, liquid, and solid) depending on external conditions. The equilibrium state of matter, which differ in properties from other possible equilibrium states, is named a phase (Gr. φασις– appearance, showing up). Usually the transition from one phase to other due to changing external conditions (temperature, pressure, etc.) produces a stepwise change of physical properties at any particular value of an external parameter. For example, there is the stepwise change of liquid volume while crystallization (Fig. 16a), however, for glasses this rule is invalid (Fig. 16b). In the latter case, solidification develops gradually. In order to distinguish solid state from liquid, one is compelled to introduce a special temperature; the *temperature of glass transition*, whish is defined as the intersection point of two asymptotes (Fig. 16a). From the thermodynamics standpoint, liquid and *glass state* is the same, but technological properties of materials in these states are so much unlike that is necessary to introduce new notions.
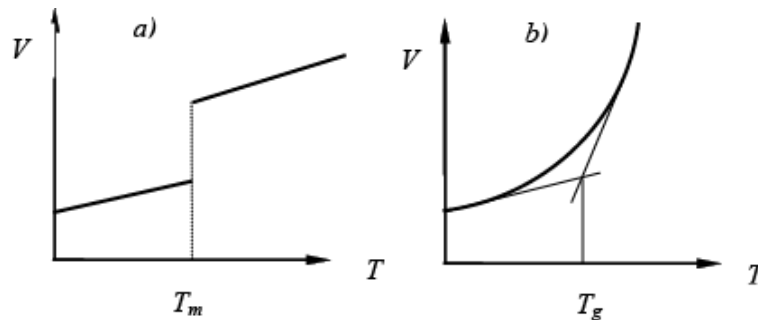

Fig. 16. Dependence of volume on temperature:
a) for crystals, b) for glasses.

Structure of amorphous materials. Glass refers to non-equilibrium disordered phases of solids which are known under different names: noncrystalline solids, common and metallic glasses, amorphous materials. We will use the last name. Amorphous materials have no long-range translational and rotation order, but they have a short-range order that is observed experimentally. It is thought that during cooling structure begins to lag from temperature. As a result, we obtain a glass (nonequilibrium structure) which fixes a liquid (equilibrium structure), i.e. practically we freeze the liquid without changing its structure.

The question arises what elements of order are present in the structure of this frozen liquid. The early models of amorphous materials are based on a random packing, at first of solid and then of soft balls (John Desmond Bernal, 1960). It turns out that the structure contains clusters of almost regular tetrahedra with common faces. The tetrahedra are rather small so it is not possible to insert one more ball of the same size into it. It should be remembered that a regular tetrahedron, the simplest Plato body, is a structure element of some crystals. In f.c.c. crystals these tetrahedra have no common faces, in h.c.p. crystals the tetrahedra are connected by pairs (one common face; Fig. 3, on the right). B.c.c. structure can be thought of as composed of four tetrahedra, two neighboring tetrahedra having a common edge. However, these tetrahedra are irregular, the common edge equals the lattice parameter *a*, whereas remaining edges are less and equal to *a√3/2*. Therefore we can introduce a *non-crystallinity parameter,* which can be formulated in the following way. If a cluster has three and more tetrahedra, such structure is non-compatible with a crystal and the solid is an amorphous material.

Besides tetrahedra, one can take other polyhedrons as a structure element, e.g. a tetragonal pyramid (semi-octahedron), of which it is possible to construct non-elementary polyhedrons (Fig. 17). Their inner holes resemble vacancies in crystals. For example, a polyhedron of three identical semi-octahedra gives a trigonal prism, two semi-octahedra on the bases of a square Archimedes antiprism form a polyhedron of 16 triangles etc. Combinations of various polyhedrons form create a lot of structures, having no long-range order with almost equal distances between the nearest neighbors. This geometric modeling satisfies Rudyard Kipling's principle: "There are 66 ways to compose the songs of tribes, and all are right," but usually it is in rather poor agreement with the principle of least action, so we do not dwell on it.
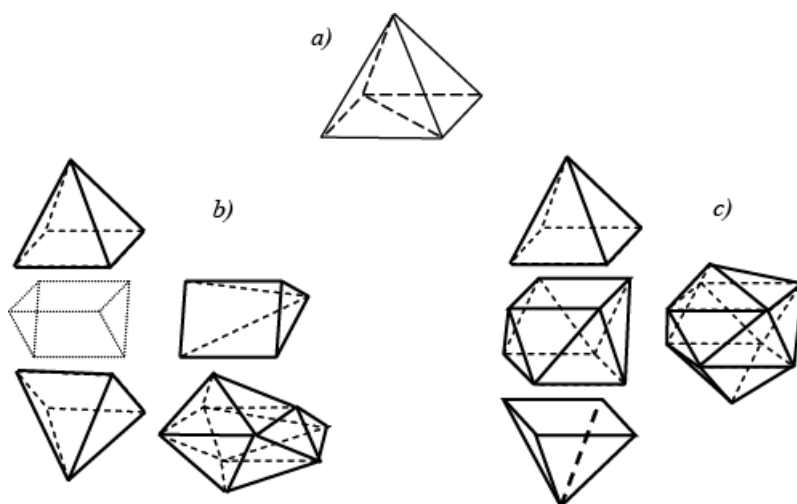

Fig. 17. Close-packing of atoms in Bernal pseudo-nuclei:
a) semi-octahedron of two adjacent tetrahedra,
b) triangular prism of three semi-octahedra,
c) Archimedes antiprism with two semi-octahedra.

Molecular dynamics and topology. The first rather new method of investigation is based on the conservation laws, so it allows obtain structures which incorporate both principles. Consider one of the most successful studies in this field (V.A. Likhachev, A.I. Mikhailin, L.V. Zhigilei, 1994 [7]). F.c.c. crystallite of 864 atoms was heated beyond the melting temperature up to total disappearance of the crystal structure, and then was quickly cooled. The amorphous structure obtained was divided into tetrahedrons, which were analyzed by a topological method.

The method consists in the following. Put some point in conformity with each tetrahedron (Fig. 18a). If two tetrahedrons have a common face, one connects the corresponding points with a line (Fig. 18b). As a result, one obtains a net describing a structure of amorphous material. The distance between neighboring points can be given arbitrary; the lines can be right, curves and even broken. In other words, when constructing the net, one does not use the notions of classical geometry, such as distance, straightforwardness, smoothness. The net can be stretched, compressed, but in any case one will obtain similar forms. The type of geometry that allows such transformations is named topology, so the net is a topological figure.

The topological analysis shows that the structure of amorphous material contains five-linked tetrahedron rings (Fig. 18c), branched chains of tetrahedrons (Fig. 18e), their combinations (Fig. 18f), and sometimes more complex figures such as an icosahedron (Fig. 18d). The atomic configuration of tetrahedron chains is such that they represent helices. The potential energy of atoms entering into these structures is even less than that of at sites of a crystal lattice. These regions of amorphous material are more dense and rigid. They create a skeleton of amorphous material and ensure its stability. Topological figures reveal common features of the real rigid structures of a material and simplify their analysis (Fig. 19).

Amorphous metallic alloys, metallic glasses, consist of by 80% transition metals and 20% polyvalent non-metals (boron, carbon, nitrogen, silicon, phosphor, etc. The latter play the role of glass-forming elements. The materials have high strength and large plasticity. They are metastable systems which crystallize when being heated up to the temperature approximately equal to half the melting temperature.
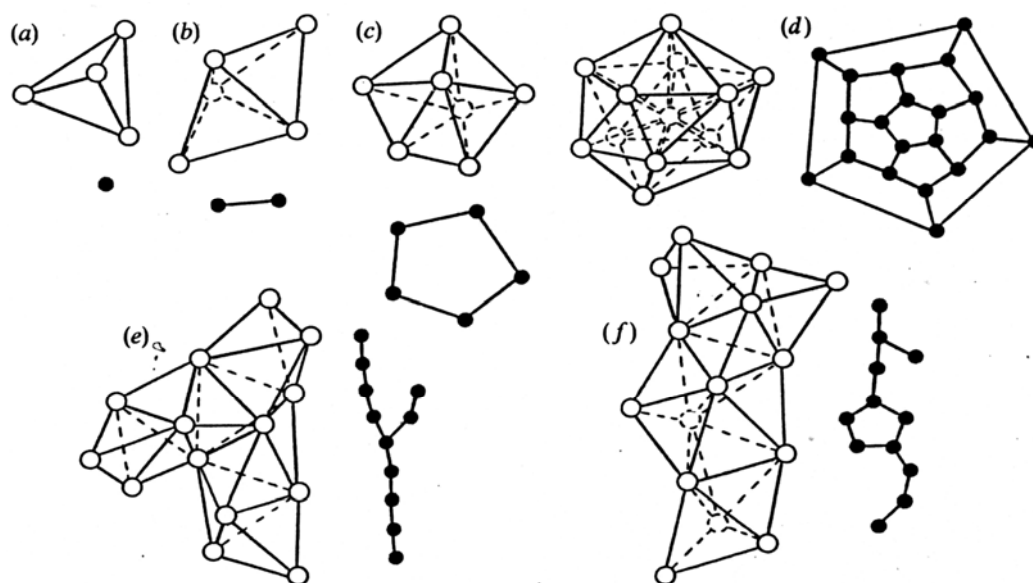

Fig. 18. Tetrahedron clusters and corresponding topological figures:
a) tetrahedron, b) two adjacent tetrahedrons, c) decahedron, d) icosahedron, e-f) chains.
[V.A. Likhachev, A.I. Mikhailin, L.V. Zhigilei, Phil. Mag. A69 (3), 421 (1994)].
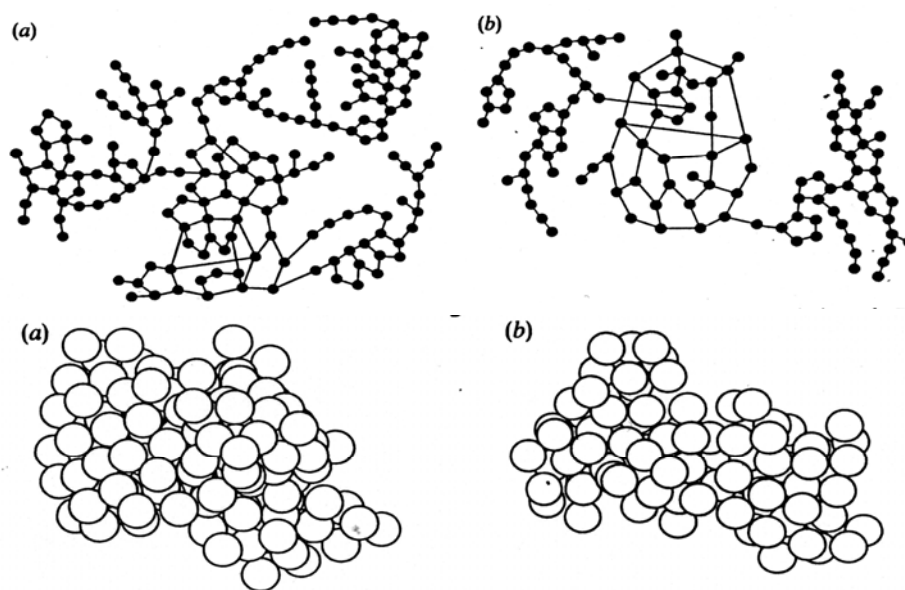
Fig. 19. Topological figures (up) and corresponding atomic structures (bottom). [V.A. Likhachev, A.I. Mikhailin, L.V. Zhigilei, Phil. Mag. A69 (3), 421 (1994)].

Disclination model and molecular dynamics. In parallel with the model of random closed-packed structure, there also have been other models of amorphous state. Among them the disclination model is very popular, because it has a higher degree of generality [8]. Indeed, the disclination model can describe various physical phenomena: mechanics of liquid crystals, glass structure, large plastic deformation of common crystalline materials, etc. The model is based on the approach which considers any glass as a crystal in curved space. It should be mentioned that the drawback of such approximation is connected with the necessity to introduce in a system considered a large number of disclinations, to a certain extent in a rather artificial way. Besides, the disclination model, in a pure form, does not take into account point amorphous defects, similar to vacancies in crystals, topological disorder defects, etc.

Obviously, it is not easy to study a subject which nature is not well defined either by analytical or experimental methods. In addition, analytical methods of continuum mechanics are ineffective for investigating defects at the atomic level, e.g. crack tips, since those methods lead to infinite values of strains and stresses in the vicinity of such defects, what has no physical sense. Using special postulates, those divergences can be avoided, but the question remains how to verify the validity of the postulates introduced. For this reason molecular dynamics seems to be the most promising approach for investigating deformation and fracture of amorphous materials. This method of computer simulation consists of solving Newton equations of motion for an N-body system. It allows investigate plasticity and fracture of materials without introducing special postulates. But even molecular dynamics needs a model. From what has been said, it follows that the disclination model, in spite of its drawbacks, more closely parallel amorphous state than other models.

For the sake of simplicity, we restrict ourselves with a two-dimensional model. Generally speaking, two-dimensional models allow better present the results, and, as a consequence, give a better insight into the mechanism of a process, especially at an early stage of investigation. As a starting point, the disclination model of amorphous structure

developed by V.A. Likhachev, A.I. Mikhailin, V.E. Shudegov [8, 9]. In this model the initial structure is obtained from a perfect crystallite having a closed-packed triangular lattice at first of 1599 atoms. Twelve positive and eleven negative wedge disclinations having the strength $\omega = \pi/3$ are incorporated into the lattice. As a result, the structure lost a long-range order, there appeared 18 atoms with the coordination number $z=5$ and 16 atoms with $z=7$. It should be noted that the initial amorphous structure is extremely nonequilibrium, so the model must be improved.

The upgrade was done as follows [10]. The structure is allowed relax to an equilibrium static configuration with the help of molecular dynamic procedure which dissipates the kinetic energy. The procedure consists of equating atom velocities to zero whenever the kinetic energy reaches a maximum. Since the initial structure is extremely nonequilibrium, the first calculations were made with a very small time step, less than one thousandth of an atomic vibration period. During the relaxation, there appeared an excluded volume. In order to prevent its formation, excess atoms were inserted into low-density regions; to the end of relaxation their number attained 60.

The amorphous structure obtained is shown in Fig. 20. The atoms within compressed regions are denoted by dark circles, and those of stretched regions by light circles. The structure contains two types of atoms; the atoms with the coordination number $z=6$ that corresponds to a close-packed triangular lattice, and the atoms with $z \neq 6$, namely $z=5$ or $z=7$. At the same time for the atoms with $z=6$, the variation of the distances between the nearest neighbors is significantly larger than that of due to thermal vibrations for common crystals. We can say that the amorphous structure contains a topologically crystalline phase in which domains of a real amorphous structure are incorporated.
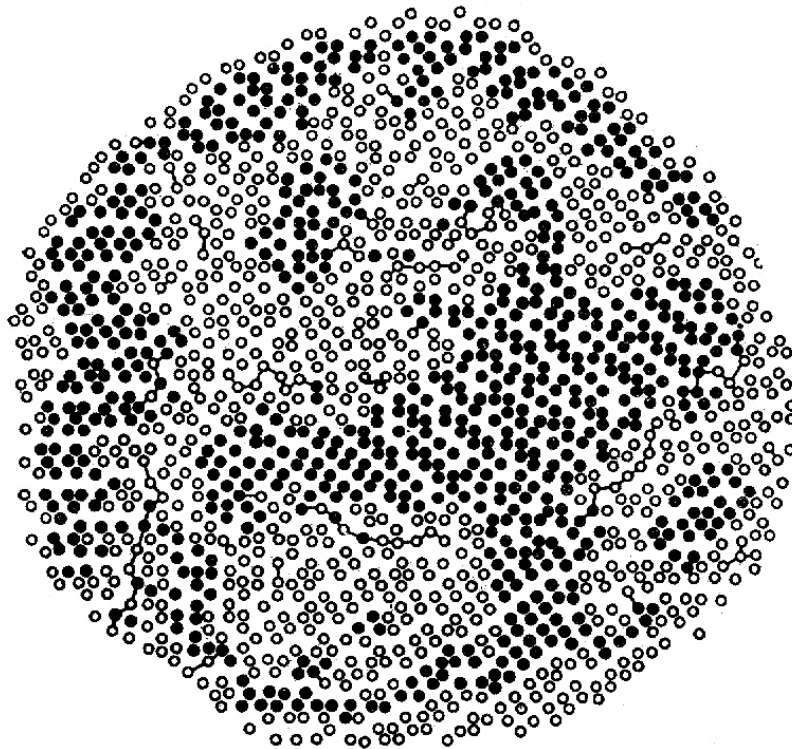

Fig. 20. Two-dimensional amorphous structure obtained from a disclination model [8].

We understand under the topologically crystalline phase the atoms with the coordination number $z=6$ which form domains having no short-range order but having curved translational invariance. Briefly we will name this phase a "topocrystalline." All the atoms with $z \neq 6$ belong to the genuine amorphous phase. The domains of topocrystalline phase either pass smoothly into each other or are separated with disorientation boundaries composed of the genuine "amorphous atoms" with $z \neq 6$; they are joined with solid lines. It should be emphasized that the entire specimen incorporates compressed and stretched regions which do not correlate with the domains of topocrystalline and amorphous phases.

Molecular dynamics, deformation and fracture. The specimen obtained is stretched along the y-axis in the following manner [10, 11]. The coordinates of every atom are changed from *x, y* to *x (1–v ε), y (1+ε)*, the strain *ε* being equal to 0.5 or 1.0 %. Such strain step allows observe structure changes in detail. Since Poisson ratio *v* for amorphous state is unknown, it is accepted being 1/3 as for an isotropic solid. Then the specimen is allowed relax to the temperature within five degrees of absolute zero. For boundary atoms, two types of boundary conditions are used. Either all the boundary atoms are fixed (Fig. 21, at the left), or only a part of the boundary atoms, which are located at the regions approximately normal to the stretch direction, are fixed; other boundary atoms taking part in relaxation (Fig. 21, on the right).

During stretching one can observe various structural changes which are connected with formation, rearrangement and disappearance of the disorientation boundaries (Fig. 21, beginning). Such changes can be understood in the framework of the theory of dislocations. At the same time, there appear a large number of so-called amorphous point defects (amorphous vacancies) in the vicinity of the disorientation boundaries located preferentially normal to the stretch direction. In due time, they transform into cracks which grow by a zigzag way; some cracks can disappear, others coalesce, forming a main-line crack (Fig. 21, end).

It should be emphasized that simultaneously the atoms of the topocrystalline phase are displacing in such a manner as if its different parts were rotated around the axes normal to the plane. This process leads to decreasing the curvature of the topocrystalline phase and to transformation its domain into domains of a common crystalline phase separated by small-angle boundaries. Using the macroscopic language, one can say that large plastic deformation of an amorphous material is realized via rotation modes of its mesoscale parts. The stress-strain diagram for a specimen with the rigid boundary conditions is shown in Fig. 22.

Mechanics or Kinetics? To construct a comprehensive amorphous structure and to do computer simulation is half the work; it is necessary to translate the discrete-model results obtained into more usual continuum equations, paying special attention to nonlinearity of atomic interactions. The traditional approach goes back to Claude L.M.H. Navier [12] and consists in the following [12-16]. The equations of motion for a system of particles are converted into the equations of the elasticity theory with the help of different postulates and approximations. Then various mechanical models of deformation and fracture, based on the concept of lattice defects, are developed. This approach is applied with success for common solids, but did not lead to success in the case of amorphous materials.

To our mind, the reason is connected with two circumstances: amorphous material is not a common solid, and defects are not a crucial point in the deformation of amorphous materials. On the basis of the molecular dynamics study considered, one can see that the main feature of the deformation is a forced phase transition from a frozen liquid state to a crystalline one, so the approach must differ from a purely mechanical. We suppose that it must be kinetic, similar to that of [17].
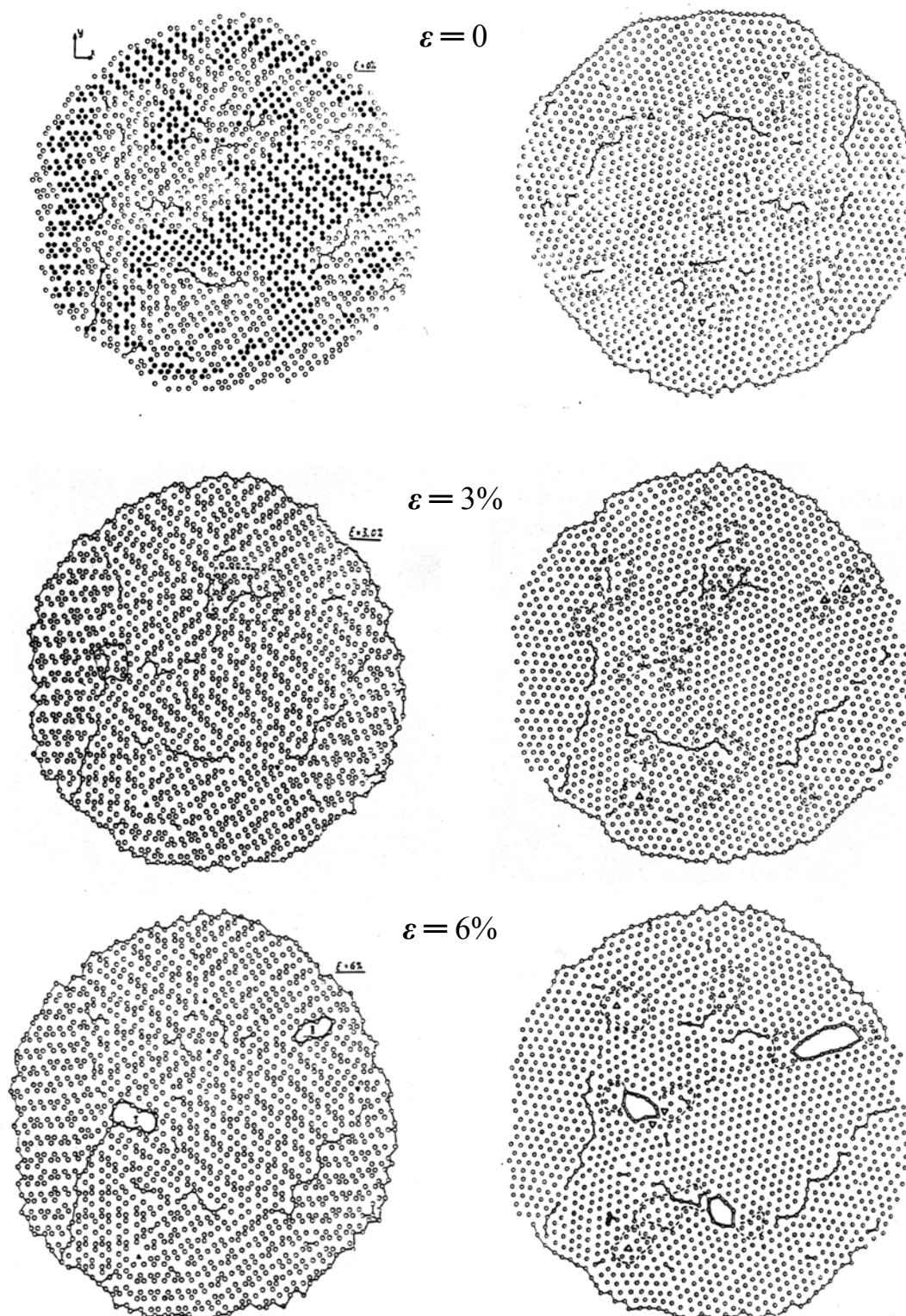
$\varepsilon = 0$

$\varepsilon = 3\%$

$\varepsilon = 6\%$

Fig. 21. Stretching two-dimensional amorphous structure under different boundary conditions: rigid conditions at the left and semi-rigid ones on the right (beginning).
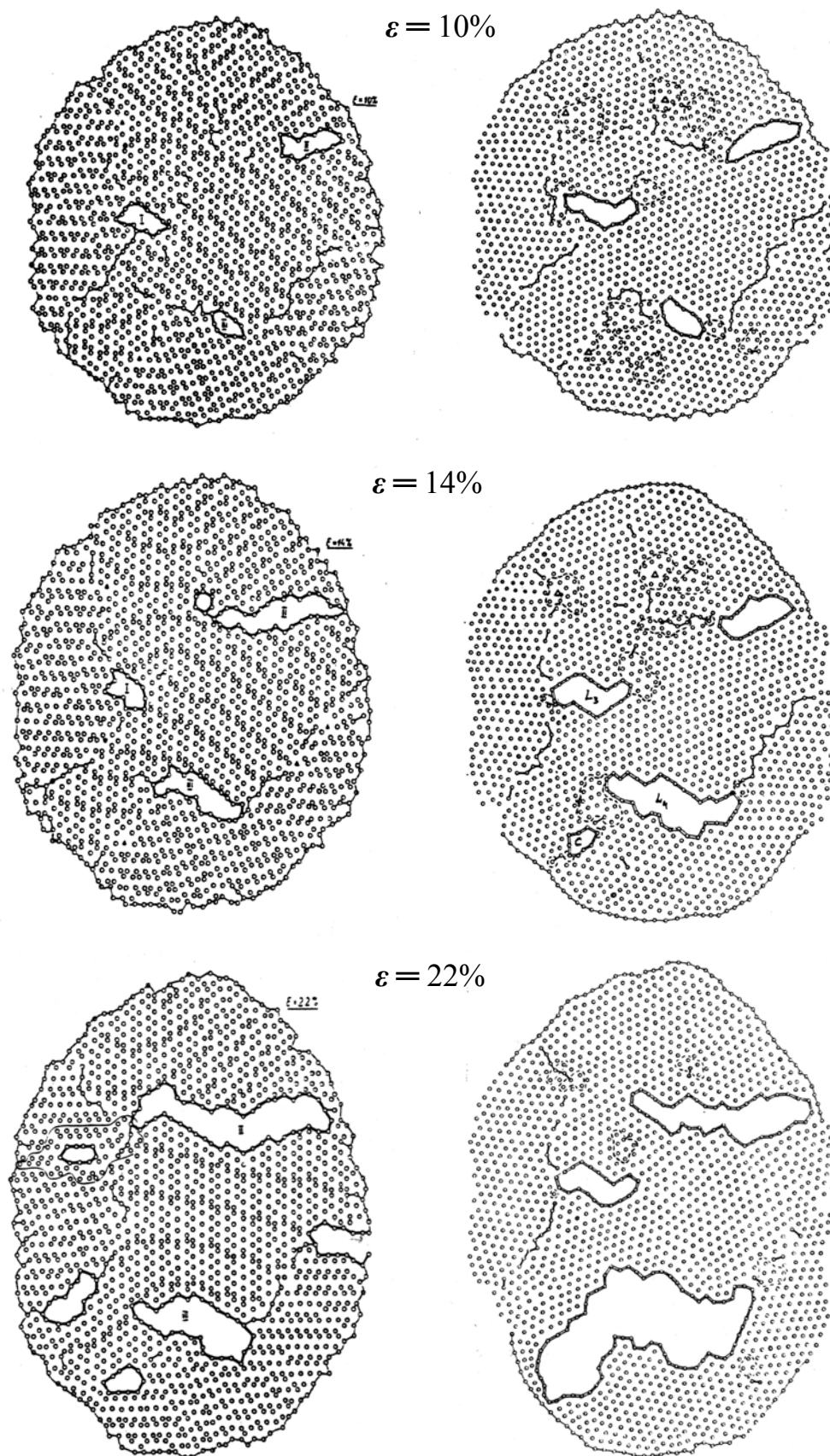
$$\varepsilon = 10\%$$

$$\varepsilon = 14\%$$

$$\varepsilon = 22\%$$

Fig. 21. Stretching two-dimensional amorphous structure under different boundary conditions: rigid conditions at the left and semi-rigid ones on the right (end).
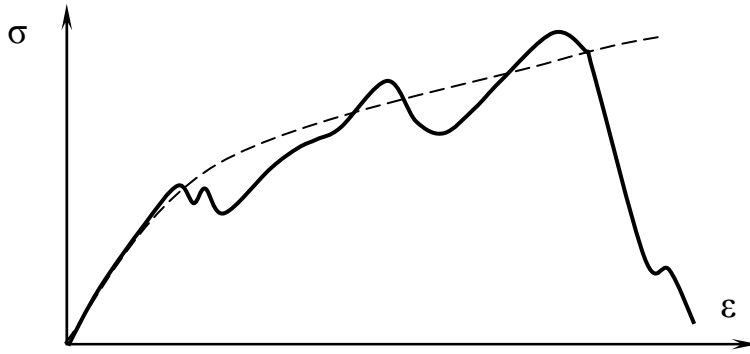
Fig. 22. Stress–strain diagram for two-dimensional amorphous structure
under rigid boundary conditions [8].

Kinetic theory of deformation. The computer simulation results give atomic "bottom-up" data for developing a kinetic theory of amorphous-materials deformation. Let us single out the structural elements responsible for the deformation. They are: atoms with z=6 of the topocrystalline phase (n_1), atoms with z=6 of the common crystalline phase (n_2), and atoms with z ≠ 6 of the amorphous phase atoms (n_3). Therefore we have three kinds of topologically different atoms (*i=1, 2, 3*) which are in different state with their own energy E_i. The rate equations relate the occupation probabilities of atoms in various states. The change in the corresponding states is caused by application of a load, and can be written in the form

$$\frac{d n_1}{d t} = -n_1 \left(v_{12} + v_{13} \right) + n_2 v_{21} + n_3 v_{31}$$

$$\frac{d n_2}{d t} = -n_2 \left(v_{21} + v_{23} \right) + n_1 v_{12} + n_3 v_{32}$$

$$\frac{d n_3}{d t} = -n_3 \left(v_{31} + v_{32} \right) + n_1 v_{13} + n_2 v_{23}$$

Here v_{ij} is the frequency with which an atom jumps from state i to state j. As follows from Fig. 21, the number of atoms with z ≠ 6 has a small share during extension, so assume that n_3 ≈0, v_{13}≈0, v_{23}≈0. Therefore the set of equations reduced to

$$\frac{d n_1}{d t} = -n_1 v_{12} + n_2 v_{21}$$

$$\frac{d n_2}{d t} = -n_2 v_{21} + n_1 v_{12}$$

,

Since now $n_1 = N - n_2$, where *N* is the total number of atoms without the small share, we have for state 2

$$\frac{d n_2}{d t} = -n_2 v_{21} + \left(N - n_2 \right) v_{12} = N v_{12} - n_2 \left(v_{12} + v_{21} \right).$$

From this it follows that

$$\frac{d\,n_2}{d\,t} = (v_{12} + v_{21})\left(N\,\frac{v_{12}}{v_{12} + v_{21}} - n_2\right) = b(a - n_2).$$

provided $n_2\big|_{t=0} = 0$. Separating variables, we have

$$\frac{d\,n_2}{a - n_2} = b\,d\,t.$$

Integrating with respect to time, we obtain

$$ln\,(a - n_2) = -b\,t + ln\,c.$$

Therefore

$$a - n_2 = c\,exp(-b\,t) = a\,exp(-b\,t),$$

and finally

$$n_2 = a[1 - exp(-b\,t)] = N\,\frac{v_{12}}{v_{12} + v_{21}}\left[1 - exp\left(-(v_{12} + v_{21})t\right)\right].$$

For $t \to \infty$, we have

$$n_2 = N\,v_{12}\,t.$$

The jump frequency is assumed to be thermally activated with the activation energy E

$$v = v_0\,exp\left(-\frac{E}{k\,T}\right),$$

where k is Boltzmann's constant, T is the absolute temperature and v_0 is a constant. The action of the applied load σ is assumed to decrease the activation energy for the transition of atoms from the topocrystal to the common crystal by $\Delta E = \gamma\,\sigma$; here γ is the activation length. As a consequence, the jump frequency v_{12} increases a little, and the jump frequency v_{21} decreases a little, so that

$$v_{12} = v\,exp\left(\frac{\gamma\,\sigma}{k\,T}\right), \qquad n_2 = N\,v\,t\,exp\left(\frac{\gamma\,\sigma}{k\,T}\right),$$

Suppose that the occupation of state 2 is proportional to the observed strain ε, i.e. $\varepsilon \sim n_2$. In this case

$$\varepsilon = \varepsilon_0\,exp\left(\frac{\gamma\,\sigma}{k\,T}\right),$$

where $\varepsilon_0 \sim N\,v\,t$ for $t = 1/v$.

The inverse function has the form

$$\sigma = \frac{kT}{\gamma} \, ln\left(\frac{\varepsilon}{\varepsilon_0}\right).$$

Therefore we have two input parameters, γ, ε_0, to describe stress-strain diagrams of amorphous materials. It is interesting to note that similar situation takes place for polymers; however the dependence of stress on strain is a little different [18]

$$\sigma = (kT/\gamma) \, ln\left((\varepsilon/\varepsilon_0) + \sqrt{(\varepsilon/\varepsilon_0)^2 + 1}\right).$$

Fracture as a parametric resonance. The kinetic theory developed governs the stress-strain diagram of amorphous materials under the conditions when there is only deformation and no fracture. In other words, it gives a trend (Fig. 22, dotted line). However, from Fig. 22 it follows that large divergent vibrations are superimposed on the trend. Consider this oscillating stress component. It has the following form

$$x = A \, exp(\beta t) \, sin(\omega t + \delta).$$

Here A is the amplitude of vibrations; β is the divergence factor; ω is the frequency, and δ is a phase. This means that the vibration part of the stress is the solution of the equation [19]

$$\ddot{x} - 2\beta \dot{x} + \omega_0^2 x = 0$$

where ω_0 is the eigenfrequency of a system in the absence of divergency and $\omega = \sqrt{\omega_0^2 - \beta^2}$. In this case it is supposed that the vibration frequency is constant. However, from Fig. 22 we notice that the frequency is decreasing with strain. To overcome the contradiction, one has to consider the above reasoning only as a first approximation. The equation discussed refers to only to isolated systems. There are also unclosed systems for which external action, being periodic, leads to changing their parameters.

Consider, for example, a rode with built-in edges under the action of a vibrating force. It is shown that for such rode composed of discrete particles interaction of longitudinal and transverse vibrations produces a parametric resonance [19, 20] which can be described by Mathieu equation [21-23]

$$\ddot{x} + \omega_0^2 \, (1 - h \cos \nu t) x = 0.$$

Here ν is the frequency of an external force, $h \ll 1$. The periodic solutions of the equation are known as Mathieu functions and have the form

$$exp(\mu t) P(t)$$

where μ depends on ω_0 and h; $P(t)$ is a periodic function.

To characterize the vibration stress component, we will use the following equation

$$\ddot{x} - 2\beta x + \omega_0^2 \, (1 - h \sin \nu t) x = 0.$$

The equation can be named as Mathieu equation with negative friction. Suppose that $v << \omega_0$. In this case $sin\, vt \sim vt$, and the equation takes the form

$$\ddot{x} - 2\beta\dot{x} + \omega_f^2 x = 0,$$

where $\omega_f = \omega_0 \sqrt{1 - hvt}$, and hence

$$x = A\, exp\, (\beta t)\, sin(\sqrt{\omega_0^2 (1 - hvt - \beta^2}\, t + \delta).$$

The equation was investigated numerically with a positive friction coefficient for different combinations of β, ω_0, v [24]. It turned out that the equation correctly described self-organization of biopolymers. Just the same situation takes place in our case.

However the main question remains, why the friction coefficient is negative. Mathieu equation originates from the following equation [19]

$$\frac{d}{dt}(m\dot{x}) + k\,x = 0$$

where m, k are coefficients of Lagrange function. For $m = const$ one obtains the equation of a linear oscillator. Suppose that the mass m decreases with time, say as

$$m(t) = m(1 - 2\beta t).$$

Then we have

$$m\ddot{x} - 2m\beta\dot{x} + k\,x = 0,$$

or

$$\ddot{x} - 2\beta\dot{x} + \omega^2 x = 0,$$

and we have negative friction. In our case the apparent mass decreasing is connected with crack formation. The cracks grow and reduce the effective cross section of a specimen. As a result we have negative friction and divergent vibrations.

8. Conclusion

We have considered the main items of the history of ideas on the structure of condensed solid matter. They are divided into two principal groups; one is based on discreteness (numbers, atoms), the other on continuity (geometrical figures). The evolution of these ideas has led to such notion as crystals, long-range and short-range order, continuous and discrete space, quasicrystals, types of disorder, amorphous structure. In its turn the new notions generated new theories, such as group theory, topology, etc.

Significant attention was given to rather new science, molecular dynamics, which became a powerful instrument for solution of many problems connected with the structure of disordered phases; other methods had failed. Leaning on molecular dynamics prompt, we have developed kinetic theory of deformation for amorphous materials and mechanical theory of fracture of these materials based a parametric resonance.

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