

Specific character of the atomic structure of the disordered condensed state

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Abstract. It is grounded physical meaning of short-range order of amorphous materials based on its differences from the short-range order of crystals. Thus, the amorphous substance is the solid body with the correlation (probabilistic) topological short range order in the structural particle locations that excludes formation of long range order. And, respectively, the crystal is the solid body with the total functional order in the atomic locations that ensures realization of both short and long range orders. We shall especially emphasize that in order to understand the differences in the structure of the crystals and the amorphous solids one has to point out the physical and chemical parameters of short range order of the separate atoms and the whole substance. In crystals, all the atoms that occupy the similar positions in the crystalline lattice have completely identical short range order. In the amorphous substances the following averaged parameters of SRO are considered: the general character of interaction between the nearest neighbors; averaged geometric figures of mutual location of the nearest neighbors; average angles between the chemical bonds; types of the bonds and their average energies; the character of the distribution of the bonds over different types; the equilibrium average coordination spheres radius; the average coordination numbers; the dimensions of the coherent scattering regions. The statistical distribution of these short range order parameters even for the equivalent atoms of the atom network defines the differences of all the properties of the amorphous and crystalline solids.

Keywords: amorphous materials, atomic structure, short range order, long range order

The analysis of the atomic structure of any real solid-body system requires clear pointing out the ideal basic atomic network and its defects. Similarly to the crystals, this includes the introduction of the notion of the ideal amorphous substances. Considering the ideal systems, we suggested the amorphous systems of a certain chemical composition, in the disordered atomic network of which each atom realized all its chemical bonds. In this work, we shall analyse the specific features of the atomic structure of the ideal amorphous substances.

The description of the structure of the atomic network of the substance includes the transition to the scaling level comparable with the dimensions of the separate atoms. On this scaling level, the corresponding coordinate frame is introduced being related to the object space. The coordinates of atoms and the other structural elements are set with respect to this frame.

The general idea about the atomic structure of the substance is as follows. Consider a certain volume V , which contains, at fixed temperature T , N atoms of different m chemical elements bound by the chemical bonds, which demonstrate the thermal oscillations around the equilibrium position. The momentary position of each atom in this volume is determined by its coordinates or by the radius-vector \vec{r}_k (for the k -th atom) drawn to this atom from the origin of the coordinate frame. Thus, one may choose as the general characteristic of the whole sample the $3N$ -dimensional vector \vec{R} , the coordinates of which are the relevant spatial coordinates of all atoms of the system.

In the amorphous substances, like the crystals, the local spatial configurations with correlated 'correct' location of the closest neighbors are realized [1-3]. Short range order (SRO) corresponds to the certain regularity in the locations of interatomic distances and the valence angles between the nearest atoms and describes the consistency in the atomic locations on the distances of several interatomic distances [4]. And the atomic network SRO defines primarily the

basic physical properties of the amorphous substances [5, 6]. It should be noted that the most of researchers do not impose limitations on SRO [7], but only state the availability of certain SRO in the amorphous solids, not itemizing its peculiarities [4, 8]. In general, in the condensed systems in the region of SRO the structures with both Fedorov's and non-Fedorov's symmetry groups are realized [9].

When defining the atomic structure of the amorphous substances it is necessary not only to state that these systems have SRO. One has to provide this attribute with a strict physical sense. The key moment here is the difference between SRO in the amorphous substances and that in the crystals. Indeed, both the amorphous substances and the crystals have SRO. If one assumes that these short-range orders are the same, then it is not evident why at the SRO extension Long range order (LRO) arises in the crystals and does not arise in the amorphous substances. The reason for such behaviour is that SRO in the crystals and in the amorphous substances is essentially different. As mentioned in the previous section, SRO in crystals is defined by a strict functional dependence of the structural particle locations in the space (functional SRO), while SRO in the amorphous substances – only by the correlation dependence of structural particles locations (correlation or probabilistic SRO). The functional SRO at its 'extension' in the space 'automatically' provides the formation of the atomic network with LRO having properties typical for the crystals. The same 'extension' of correlation SRO results in the loss of ordering in the structural particle locations at the certain distances inherent in the amorphous substances. Thus, SRO of the substance is decisive, and the character of this SRO provides the possibility of the existence or lack of the system LRO.

In this context, the amorphous substance is the solid body with the correlation (probabilistic) topological LRO in the structural particle locations that excludes formation of SRO. And, respectively, the crystal is the solid body

with the total functional order in the atomic locations that ensures realization of both SRO and LRO (or translation periodicity) in the atomic locations.

Taking into account the above definitions, we can classify a great number of 'exotic' materials as the amorphous substances. The examples are the soft Alexander's phases [10] in a form of the molecular glasses, jells, pastes, concentrated emulsions, concentrated colloids, foams [11] and the athermic amorphous systems in a form of the granulated substances [12, 13].

Thus, SRO in the amorphous substances is due to the local correlations of the certain physical quantities $P(\vec{r})$ of their atomic network. Mathematically, to describe the local correlations of given physical quantity $P(\vec{r})$ for the discrete atomic network, the first spatial correlation function is used

$$\Phi(\vec{x}) = \overline{P(\vec{r})P(\vec{r} + \vec{x})} \quad (1)$$

where \vec{x} is the spatial variable [14]. Correlations of the physical quantity $P(\vec{r})$ in the system exist, if the introduced first correlation function is significantly non-zero in the certain local spatial interval $|\vec{x}| \leq L$. At $|\vec{x}| > L$ the correlations in the systems become not essential [14]. L is called the correlation length or the radius. It serves the spatial scale of the available correlations of the physical parameters of the substance and, respectively, characterizes the degree of its ordering. When studying SRO, the radius-vectors are the basic physical parameters, which specify the locations of the atoms in the space in the certain coordinate frame. In other words, when speaking about SRO the atomic network structure is meant only, i.e., in average similar topologies of the location of atoms around the arbitrarily chosen centre in the region with the SRO correlation radius L .

Note that in the structural sense SRO is always fixed with respect to a certain atom called the central one (fig. 1). The quantum-mechanical interaction between this atom and its nearest neighbors with the formation of different-type chemical bonds is the primary cause and the drive force of the SRO appearance. This means that different-intensity interatomic correlations are established in the substances due to the action of the internal (structural particles interaction) and external (for example, pressure) forces.

Let us give several definitions to emphasize these SRO peculiarities. According to Ref. [2], SRO is a number of the nearest neighbors surrounding the atom chosen as the central one. The main SRO parameters here are the number of the neighbors (coordination numbers) and the distances between them (radii of the coordination spheres). The similar statements could be found also in Refs. [15, 16]: SRO means the correct location of a certain number of the nearest neighbors close to the fixed atom, ion or molecule. Or in Ref. [17]: in the covalent bound materials, SRO is characterized by the number Z_j of the nearest neighbors of the j type bound mainly by the covalent bonds with the length r_{ij} from the initial atom i . These parameters describe well-defined coordination polyhedron (e.g., Si_4), which is a basic structural unit and, in several cases, may produce the whole structure.

We shall especially emphasize that in order to understand the differences in the structure of the crystals and the amorphous solids one has to point out the physical and chemical parameters of SRO of the separate atoms and the whole substance.

For a single atom (black circle in fig. 1) SRO is described by: the character of its interaction with neighbors (e.g., the presence of two types of bonds); the geometric location of the nearest neighbors around it (in fig. 1, the nearest neighbors are located in the pyramid vertices); the type and the length of the chemical bonds between this atom and its neighbors (As-As bond with the l_1 length and As-Se bonds with the l_2, l_3 lengths in fig. 1); the angles between the chemical bonds (angles $\varphi_1, \varphi_2, \varphi_3$ in fig. 1); the binding energy ($E(\text{As-As})$ and $E(\text{As-Se})$ in fig. 1); the number of different-type neighbors (in fig. 1, the nearest neighbors are two Se atoms and one As atom) and so on.

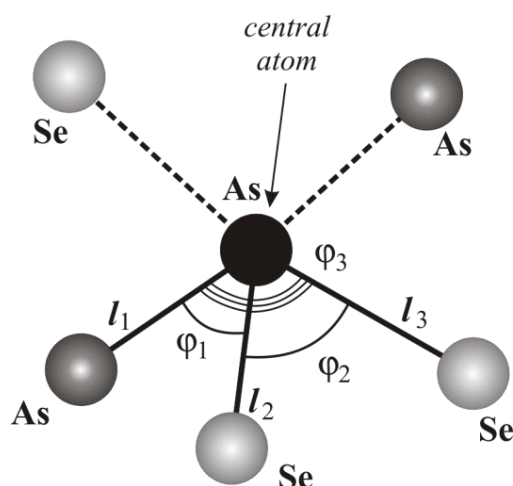


Fig. 1. SRO parameters of a single atom

- – dominantly covalent bonds;
- - - - - – Van-der-Vaals-type bonds

In crystals, all the atoms that occupy the similar positions in the crystalline lattice have completely identical SRO. Due to this, after the translation transfer of the central atom with its strictly fixed SRO, LRO arises in crystals. In the amorphous substances, the situation is changed drastically. Each separate atom in the amorphous substance also has its strictly determined SRO. Thus, a separate configuration of the close environment is related to each 'central' atom and the structure around each atom is individual and specifies the local atomic configuration (network) in its vicinity. Configurations of different closely located atoms are totally or partially overlapped.

However, different identical central atoms could have quite different SRO parameters. Due to this the agreement in the location of the neighbors decreases quite rapidly with the distance from the central atom and vanishes at the certain distances SRO around this central atom. Respectively, the possibility to form SRO also vanishes. Therefore, when describing the structure of the whole macrosample one has to carry out the statistical averaging of the above SRO parameters over the macroensemble of all the atoms of the sample, each of them being alternatively taken as the central one.

Such averaged parameters around the 'average' central atom describe the correlation SRO of the whole amorphous substance. The following parameters are considered the main averaged parameters of SRO: the general character of interaction between the nearest neighbors

(e.g., relation between the covalent, ionic and other types of the chemical bonds); averaged geometric figures of mutual location of the nearest neighbors; average angles between the chemical bonds $\bar{\varphi}_1, \bar{\varphi}_2, \bar{\varphi}_3, \dots$; types of the bonds and their average energies (for example, \bar{E} (As-Se), \bar{E} (As-As)...); the character of the distribution of the bonds over different types (e.g., 10% of the As-As, 70% – As-Se and 20% – Se-Se bonds); the equilibrium average coordination distances (coordination spheres radii R_1, R_2, \dots); the average coordination numbers (CN – Z_1, Z_2, \dots); the dimensions of the coherent scattering regions (i.e. the average distance L , at which the correlation in the nearest neighbors locations vanishes).

The above averaging results in the appearance of the statistical distributions of the physical and chemical parameters of the system. Therefore the basic parameters of SRO in the amorphous substances (being rigorously defined) must be presented in a form of such distributions. A number of the values that characterize the relevant statistical distributions are added here to the averaged parameters: the mean-square deviations (dispersion) of interatomic distances $\sigma_1, \sigma_2, \dots$ (fig. 2); the dispersion of the angles between the chemical bonds $\sigma_{\varphi_1}, \sigma_{\varphi_2}, \dots$ (fig. 3); the CN distribution dispersion $\sigma_{Z_1}, \sigma_{Z_2}, \dots$ (fig. 4); the chemical bond statistics and its changes with varying synthesis conditions (fig. 5);

the number, the types and the statistics of the basic coordination geometric figures that describe SRO etc. The most of researchers assume that this statistical distribution of the SRO parameters even for the equivalent atoms of the atom network defines the differences of all the properties of the amorphous and crystalline solids [18].

Each of the above SRO parameters of the amorphous substances determines certain peculiarities of their structure [16]. For example, the atomic coordination and the relative energy of the chemical bonds determine the topology of the disordered atomic network. Inclusion of only the first parameter results in the model of the chemically ordered network. Competition and, to some extent, interaction of these factors determine the final result for the specific substance.

From the viewpoint of the method of studying the structure of the atomic network in the complex amorphous substances, the especially unpleasant result of averaging is 'overlapping' of quite different individual SRO of different atoms: e.g., the tetrahedral for the Ge and Si atoms; the pyramidal for the As, Sb and Bi atoms; the linear doubly-coordinated for the S, Se, Te atoms and others. The experimental distinguishing of the above particular contributions from the general structural pattern is quite complicated task.

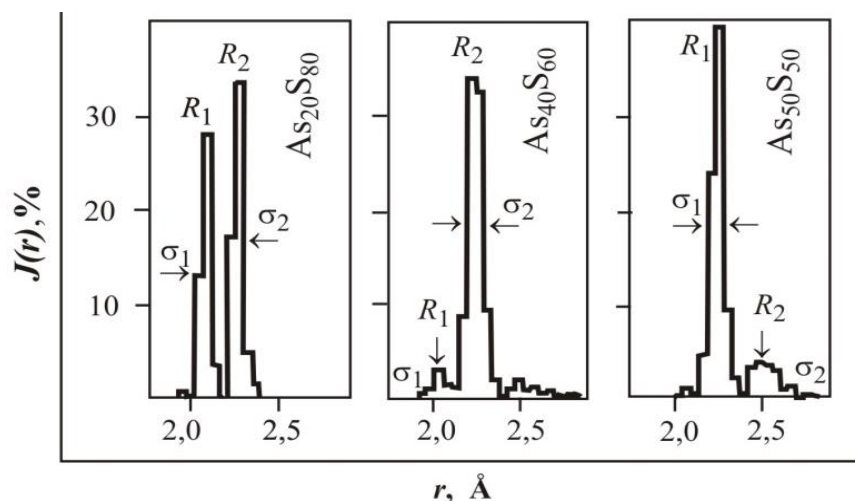


Fig. 2. Distributions of the probability $J(r)$ of realization of the chemical bonds between the nearest neighbors in the amorphous glasses $As_{20}S_{80}$ (a), $As_{40}S_{60}$ (b), $As_{50}S_{50}$ (c) [19]

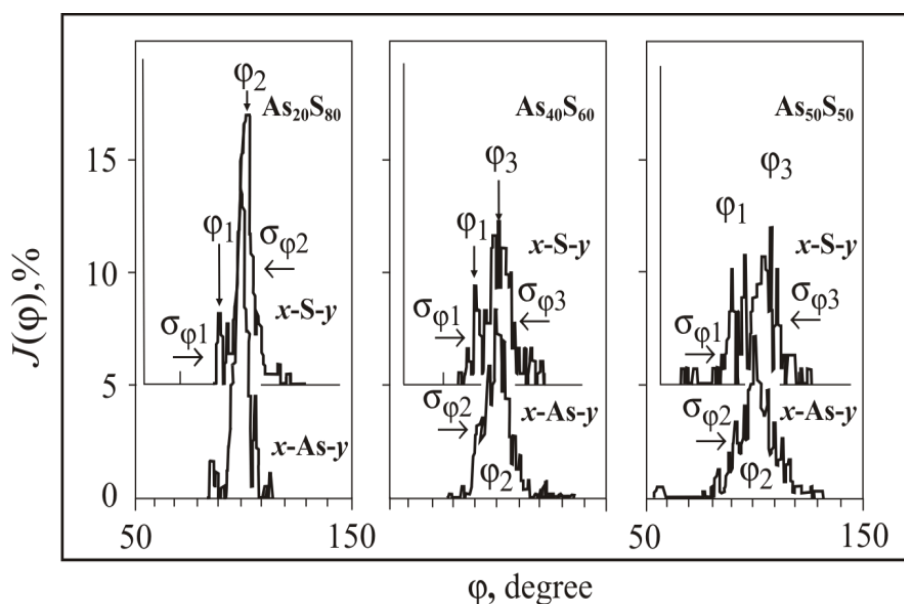


Fig. 3. Distributions of the probability $J(\varphi)$ of realization of the angle φ between the different chemical bonds in the amorphous glasses $As_{20}S_{80}$ (a), $As_{40}S_{60}$ (b), $As_{50}S_{50}$ (c) [19]. (Upper distributions – around the S atoms; lower – those around the As atoms; x and y can be either S or As atoms, respectively)

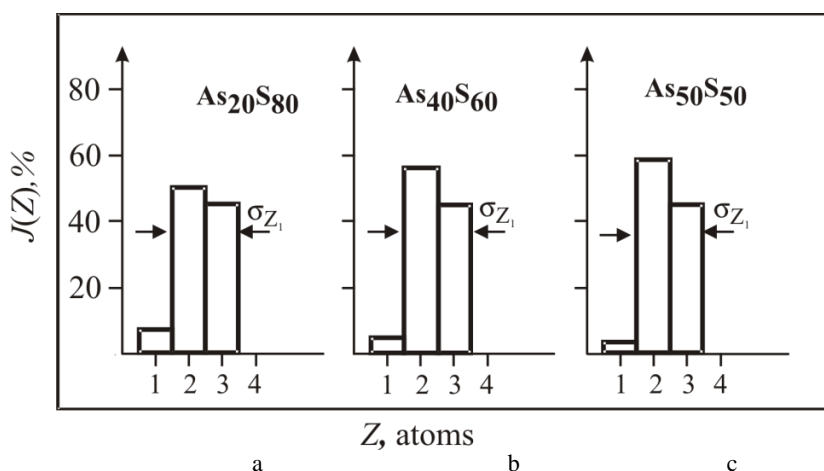


Fig. 4. Distributions of the coordination numbers of the first coordination sphere in the amorphous glasses As₂₀S₈₀ (a), As₄₀S₆₀ (b), As₅₀S₅₀ (c) [19]

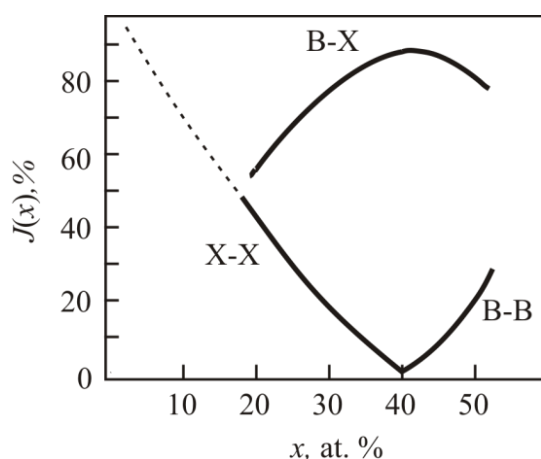


Fig. 5. Concentration dependence of the probability $J(x)$ of realization of the different-type chemical bonds in the model of the total chemical order in the amorphous substances $B_x^V X_{1-x}^{VI}$

By virtue of such peculiarities of SRO in the amorphous substances several local elements of the atomic network can be identical. However, it is impossible to 'eliminate' such identical and local areas by a certain set of translation operations. On the other hand, any limited macrovolume of the amorphous substance, which includes some hundreds of atoms, can be substituted by the same volume taken from the other part of the sample, not observing in this case a visible difference in the general structure and properties of this amorphous system. At the distances of such order the amorphous substance must be statistically homogeneous and one may use the continuous medium approximation to describe its structure at the above distances.

Depending on the physical parameters taken for consideration at the analysis of the structure of the amorphous substance, several types of its SRO are distinguished [2, 20]. The distant SRO specifies only the radii of the coordination spheres and the coordination numbers. The compositional (chemical, sorted) SRO describes the correlations in the mutual locations of different chemical elements. The topological (geometric or physical) SRO specifies the correlations of any parameter of the spatial location of the atoms and the chemical bonds between them. When considering this SRO one may not take into account the chemical nature of the elements. The orientation SRO is stipulated by the ordering of orientations of the structural particles, for example, it specifies correla-

tions in the orientation of several polymer fibres. Actually, the decisive is the chemical SRO, because the specific features of the atomic linkage and the parameters of this linkage are specified by the chemical nature of the atoms. The topological SRO is revealed as the result of formation of the chemical SRO and results from the chemical SRO in a form of certain geometric configurations and parameters of the atomic network.

The notion of the average or intermediate order is widely used in the analysis of the structure of the amorphous substances. This order is most often related to the existence of certain interatomic correlations or regularities in the mutual locations of the atoms at the distances exceeding the radii of the first two-three atomic coordination spheres. The existence of the first sharp diffraction peak (FSDP) in the neutron, electron and X-ray diffraction distribution is taken as the direct evidence of the occurrence of intermedium range order (IRO) in a form of certain regions of the structural configuration ordering at the scaling level of about 1 nm. This peak is inherent in the overwhelming number of the amorphous substances, though, the exceptions are possible (say, the amorphous Si films). The experimental pieces of evidence indicate the affinity of many amorphous substances by the FSDP parameters: intensity, half-width and position of this peak vertex [5, 21-23].

The existence of SRO and IRO in the amorphous substances requires elucidation of the quantitative scale of their manifestation. To do this, it seems expedient to use the introduced above radii of the atomic correlations of the atomic network L . SRO is the lowest scaling level of ordering in the disordered system structure. If the value L is proportional to the interatomic distances, only SRO does exist in the substance. It expands in space for 1 to 5 interatomic distances and is localized in the spherical region with the correlation radius L up to 1 nm.

At the considerable excess of the correlation radius L over the interatomic distances one may speak about the occurrence of IRO in the substance. IRO overlaps partially the scaling level of SRO. It expands in the space for 3 to 10 interatomic distances and is localized in the region of about 1 nm size.

The other criteria of the quantitative limits of ordering of these scaling levels are also suggested. For example, when studying the charge carrier dynamics in the unordered media, the SRO and IRO scales can be found in accordance with the relation of the two characteristic lengths: the Coulomb potential screening radius in the

condensed system R_e and the size of the coherent scattering regions R_k . If $R_k \leq R_e$, it is assumed that only SRO exists, whereas at $R_k \leq R_e$ both SRO and IRO occur.

When analysing SRO and IRO, the analysis of connectivity, dimensionality and other general topological characteristics of the atomic network is also important. There is an idea [24] that the differences in the structure of the amorphous and crystalline bodies are manifested only on the IRO level, while SRO in the most of the amorphous materials approximately corresponds to the crystalline SRO. Such conclusion was based on the analysis of the metal glasses only, and the presence of disclinations was considered to be its cause. Taking into account the above remarks on the specific character of SR in the amorphous substances, it seems probable that such a point of view is wrong, in particular, for the metal glasses.

The experimental studies of the structure-sensitive properties of the amorphous substances indicate their structural heterogeneity. This is related to the next scaling level of the atomic network structure called mesoscopic level, which is extended at the distances of several nanometres. In the diffractograms, this structural level is revealed, as a rule, in the region of the central peak, which covers the small-angle scattering and the part of the scattering intensity that rapidly descends to FSDP. It is assumed that for the mesoscopic level the correlation radius is $L = 1 - 10$ nm. The mesoscopic level is connected with the formation of a distinct hierarchy of the structural heterogeneities in the amorphous substances [21]: the chemical composition non-uniformities; the coexistence of different SU; molecular structure of the group of atoms of the amorphous network; the irregular structural cavities and fluctuations of the atomic density; the rings of different-length interatomic distances; the multi-phase associates of the fine crystalline particles etc. [21, 25, 26]. The structural and chemical heterogeneity of the nanoscale should be accepted as an inherent characteristic of the atomic network of the amorphous medium estimating it as one of the fundamental aspects that reflect and determine the metastable structural state of almost any amorphous substance.

Probably, there exists a relation between the mesoscopic and intermediate ordering. The structural particles, which make a basis of IRO manifestation, may simultaneously be revealed on the mesoscopic level as well. At the same time, the mesoscopic effects reflect the manifestation of a considerably wider spectrum of different structural polyatomic fragments as compared with the IRO effects. Therefore, when studying the mesoscopic structure parameters one have to take into account its correlation character and, respectively, to use different statistical distributions. One of them, for instance, can be the statistical distribution of the atomic rings (fig. 6).

The scaling levels of the nanostructure and microstructure with characteristic dimensions exceeding ten nanometers are the highest ones for the amorphous substances. Here the transition occurs from the discrete ideal atomic network to the amorphous substance structure on the qualitatively new level – the ideal continuous matrix. One may also note here the revelations of the macroscale heterogeneities with characteristic dimensions of several microns (the substructural heterogeneity). The indirect influence of the above heterogeneity may also be reflected in the peculiarities of the structure and the properties of

the amorphous substances. In the crystals, LRO is the highest structural level, which defines ordering of their structure at the infinitely large distances.

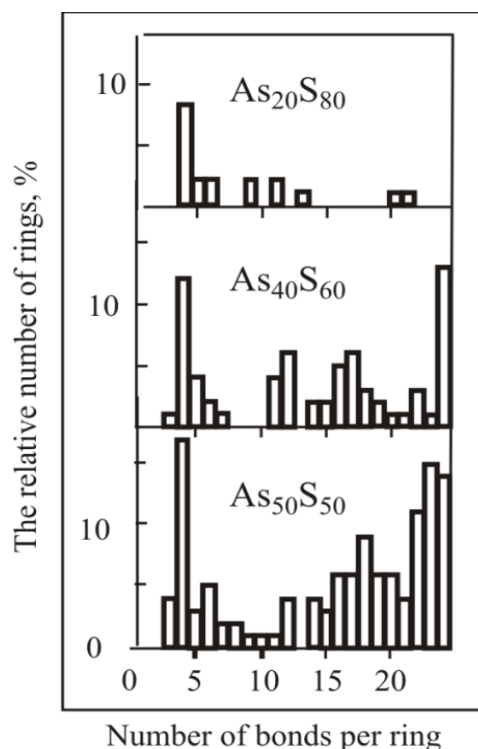


Fig. 6. Distributions of rings with different number of atoms in the As-S glasses [12]

In the process of physical and chemical analysis it is necessary to consider not only the chemical composition, structure and properties of the substance, but also to take into account its dispersibility [27]. At the crystal dispersion in the surface layers of the material the chemical bonds are broken and switched over, the angles between them are changed and new atomic configurations are distorted. Therefore, in the surface layers of the disperse particles LRO is broken, whereas the crystalline SRO is strongly distorted and in the boundary cases is completely destroyed. At some limiting size of the disperse particles all atoms become 'surface' atoms and their structure corresponds to the strongly distorted crystalline SRO. Since the SRO parameters distortion can be different, then SRO formed at the dispersion is called unlimitedly variational [27].

In accordance with such analysis, the conclusion is made [27] that the dispersibility is more determinant structural essence of the substance as compared with its SRO. In this case the dispersibility is considered the first cause of formation of a specific SRO of the amorphous films – the unlimited variational (twisted, surface-shell) SRO. In this relation, the dispersibility is also attributed the role of a forming factor of the amorphous non-glassy substances. As a result, V.S. Minaev gives the following definition of the latter: this is the ultramicrodisperse formation, the state of the substance of 'islets' (clots, monolite fragments, aggregates) with the dimensions varying from several units to tens angstrom, which accreted in spots with each other but on the large part of the surface are separated by the ultramicrohollows and are formed on the basis of unlimitedly variational SRO [27].

Supporting the idea of the necessity of taking into account the dispersibility when studying the properties of solids and its substantial influence on the peculiarities of their atomic structure, note that, probably, there are no sufficient grounds for its absolutization. Dispersibility is mainly the technological factor. It is the structure forming factor only indirectly, reflecting the conditions of their production in the peculiarities of the structure. Similarly, in the structure of the amorphous films, the technological conditions of their vacuum deposition are reflected.

It is also not reasonable to limit the amorphous state by the macrosystems of the 'ultramicrodisperse' formations, because the emphasis in such objects should be directed not to the parameters of the whole 'powder', but on the structure of some its disperse particles. Each of these particles is itself a particular subtype of the solid state. In turn, similarly to the case of the solid state, they can be either crystalline or amorphous. The fact that we construct of such particles the purely mechanical mixture (powder) makes no drastic changes in the structure of the particles but only adds certain specific features to their behavior due to the 'interaction' between them. In this relation, the hypothesis that dispersion of both crystal and glass of given chemical composition to the super-high degree of dispersibility (particles size is about 1 nm) will result in the formation of the disperse particles with identical structure [27] is not so trivial.

Many researchers of the amorphous states operate with such notions as the ordering degree, the disordering degree, the larger or the smaller order, ordering enhancement or weakening. In our opinion, the above and other equivalent formulations must concern SRO, IRO, mesoscopic structure or LRO definitely. This means that the 'intensity' of each order may vary within a wide interval from the total (ideal) order to the total (ideal) disorder. The descriptive abstract notions about the ordering value are often used to analyse different processes in the amorphous materials. At strict approach to studying the amorphous substances one has to operate legible quantitative criteria, which can define the ordering/disordering degree of the amorphous structure on any mentioned level.

One of such criteria can be the above correlation radius of the topologic order of the atomic network L . Other parameters of the structural ordering degree are also used. The most important of them are the symmetry elements of the first correlation function $\Phi(\vec{x})$, which completely succeeds the symmetry properties of the atomic network. In this case the structure with the higher symmetry is considered to be more ordered. Other ordering parameters can be the mean-square deviations (or dispersions) of the relevant topological parameters of the atomic network when setting their statistical distributions. If the system may transit by its whole volume to the totally ordered state, for example, due to crystallization, then the residual structural entropy that tends to a certain fixed value at the absolute temperature zero could be the measure of its disordering (and, respectively, ordering). One more approach to determine the ordering degree may be related to comparing this substance with the reference system.

The studies of the amorphous structure are complicated by the metastability of the amorphous state in general. This means that the character and degree of manifestation of different-type orders will depend not only on the type of

atoms included in the substance, but also on the external parameters (temperature, pressure). Due to the thermodynamical non-equilibrium, the structure of the particular amorphous substance will not be unique and will depend on the different kinds of the external influences after production. The number of the variables necessary for the unambiguous description of the structure of the amorphous state of certain substance is not known *a priori* [28]. For the same reason the structure of the amorphous substances is dynamical and could continuously vary with time [29], which is manifested in the relaxation of the principal physical and chemical properties of such substances. The similar liability also significantly complicates the studies of the structure of the disordered systems [5, 29, 30].

The structure of the atomic network of the crystals is formed under severe restrictions related to the necessity to realize the functional SRO, IRO, mesoscopic formations and LRO. Elimination of these restrictions in the amorphous substances expands considerably their 'creative capabilities'. This concerns both the freedom of realization of different new atomic configurations in the solids and formation of the homogeneous condensed systems in very wide limits of their chemical composition (for example, wide regions of vitrification in the chalcogenide systems). The possibility of large deviations from the stoichiometry allows the amorphous materials to be produced with chemical composition that by its structure and properties maximally corresponds to the particular problem of the material science.

In the amorphous substances, contrary to the crystalline ones, different atoms can be joined. The examples are the amorphous films of hydrogenated silicon Si:H, five-, six- and more component glass compounds. The atoms in such substances are not simply mixed mechanically, e.g. like the case of penetration of impurity atoms to the relevant places of the crystalline lattice. In the amorphous systems, new chemical linkage appears, which fixes new atomic configurations of disordered atomic network in the space [31].

The same atoms may manifest themselves differently in the amorphous and crystalline structure. The above-mentioned amorphous Si:H films are a bright example. The hydrogen atoms could be implanted into the silicon crystals as well. However, in the crystalline lattice they are the defects, whereas in the amorphous films the hydrogen atoms generate new structural configurations, which differ considerably from pure silicon ones [31]. These configurations are fixed as steric obstacles due to a large strength of the Si-H bonds and the geometric shape, which they acquire in the atomic network. Being distributed in the amorphous structure, they serve the effective barriers for the crystallization processes. At the same time the hydrogen atoms passivate the 'broken' silicon bonds and, thus, efficiently change the electro-physical properties of the amorphous Si-H films.

In the amorphous solids, the local 'oscillations' of the atomic coordination often exist [31]. Such behaviour of the atoms makes a basis for the appearance of new spatial distributions of the chemical bonds, new atomic configurations, which by their nature are non-crystalline and, thus, violate the tendency to the spatial periodicity of the atomic network. Therefore, formation of the amorphous state is especially peculiar for the substances comprising

atoms that are capable of changing the spatial coordination, i.e. B, C, S, Se, Te, transition metals and others [31].

Such peculiarity of the amorphous systems requires more comprehensive studies of not only the physical but also the chemical regularities of the solid body formation. And the lack of the chemical knowledge on the solids considerably restricts the development of the general theory of the structure of the amorphous systems [32]. As a result, the latter are often considered specific 'defective states' characterized by the deviation from the stoichiometry. Almost all amorphous substances are 'non-stoichiometric' compounds. In addition, though the stoichiometric rules are applicable in the amorphous solid chemistry, noncompliance with these rules is a characteristic attribute of these materials. The main cause of such properties of the amorphous substances is that in the most cases they have high-molecular structure [32]. Inclusion of such structures is also the necessary condition of studying the structure of their atomic network.

Consideration of the solid amorphous state as the polymer in many cases does not draw specific objections, though the covalent crystal could be considered the giant molecule with the three-dimensional carcass of the covalent bonds. The only doubt is caused by the use of this approach to the melts, when it is assumed that the glass forming compounds, unlike other ones, have the polymer structure that results in their high viscosity and, as consequence, in the ability of supercooling up to the transition to the solid amorphous state. This approach is more likely applicable for the high-molecular organic substances, though it is used in studying the inorganic solids as well. A bright example of this is the amorphous selenium. In Ref. [33], the high-molecular substances in the amorphous state are called the molecular amorphics. Certain molecules not being destroyed in the process of formation of the amorphous matrix are their basic structural elements. The size of the molecules in such substances can vary in a wide range.

Thus, the amorphous substance is not structureless, but it has a very complicated atomic network structure. Just for this reason, there are no clear unambiguous notions about the general structure of the amorphous state. In our opinion, the decisive point of the further structural studies of the amorphous substances is clarification of the peculiarities and role of the chemical bonds in the SRO and IRO formation in the disordered atomic networks. With this regard, it is necessary to give clear answers to a series of important questions. Does the certain ordering type of different scaling level occur in the amorphous substances due to the special chemical bonds action only, e.g., the bonds absent in the corresponding crystals of the same chemical composition? How are the topological peculiarities of the structure of the amorphous network related to the particular peculiarities of the chemical bonds realized in them? Do the qualitative distinctions between the bonds in the local sites with the continuous ideal atomic network and the bonds in the local sites of the network breaks exist? What does occur with the chemical bond network during the amorphous substance heating and at the phase transformations in them? In many cases one has to take into account the specific role of different defects in the realization of the particular properties of different-nature non-crystalline materials [22, 34-37].

In this context, we consider non-constructive the idea [38]. The authors state that the lack of LRO in the atomic network is not the most essential factor that defines the differences between the amorphous materials and crystals. More important role is played here by the own defects of the atomic network, the concentration of which in the amorphous materials can be quite large. Here we come to the important and poorly studied question of determination of the physical and chemical principles of clear distinguishing of different defects in the ideal disordered atomic networks. Note once more that above we analyzed the problems of the amorphous substance structure in the ideal network approximation. It was suggested to take the spatially topologically disordered atomic network as the above network, in which each atom realizes all its chemical bonds. It is obvious that any deviation from the ideal atomic network should be considered the defect provided that the concentration of such deviations is much less than the atomic density of this substance. This is due to the fact that the number of defects must be several orders less than the number of the atoms in the system. Otherwise, the 'defect' can be considered one of the possible structural fragments of the ideal disordered atomic network. More detailed analysis of the problems of the defects in the disordered atomic networks will be given in the next section.

Thus, the problems of studying the peculiarities of the disordered structure of the amorphous state lie in the different planes of the structural hierarchy, which are related to several scaling levels: SRO, IRO and the mesoscopic ordering of the atomic network and the nanostructure and microstructure (or substructure) of the matrix of the amorphous medium. Each of these levels is revealed specifically in the experimental results and reflects the interrelated and simultaneously specific processes of the structure formation in the amorphous substances.

Let us make some final comments concerning the relatively important methodic question: to what extent the amorphous and crystalline samples of certain chemical composition are structurally similar? Besides the mentioned above, here, in our opinion, one has to consider some crucial moments.

1. Only for a very limited circle of the amorphous substances there exist their crystalline analogs (basically, they are the elementary substances and compounds of the stoichiometric compositions of the complex systems). The overwhelming majority of the amorphous substances have no crystalline analogs and the question of the structural similarity has no sense for them. For example, what should we consider the crystalline analog of the $\text{Ge}_5\text{As}_{15}\text{S}_{80}$ glass?

2. If the substance exists both in the crystalline and in the amorphous state, one may surely find separate small structural fragments in the amorphous state, which have the structure almost identical (with certain accuracy) to the crystalline one. In this case the degree of distinction of these structures will be determined by the quantitative deviations of the functional and probabilistic SRO in them.

3. In any amorphous substance, which has the crystalline analog, separate structural fragments must necessarily occur with SRO, which both quantitatively and qualitatively differ from the typically crystalline fragments (e.g., in the region of the existence of the amorphous germanium and silicon with 5 and 7 atomic circles in the amorphous matrix).

4. The structural elements untypical for their crystalline analogs may occur in the amorphous substances (for example, the As_4S_4 molecules in the amorphous As_2S_3 films).

5. With increasing size of the structural fragments the degree of their similarity will decrease abruptly for the amorphous and crystalline substances. The spatial limits remain here very important and unclear question related to such structural similarity.

Also today the task is to extend the scheme of experimental investigations of unordered materials, i.e. full description of the initial state from which the amorphous sample is formed – the control of any technological parameters of this sample produced – the investigation of the structure and its relaxation at any level – the studies of

the structurally-sensitive physical and chemical properties and their induced and spontaneous changes – the construction of a rigorous model – the complex analysis of the data obtained on any aforementioned stage. These also involve elucidation of the role of different technological factors in the processes of structure formation in the amorphous substances; development of new methodological approaches at structural investigations of the amorphous substances, elucidation of specific features of the amorphous substance polymorphism and phase transitions in these substances, determination of the role of the initial structure of the amorphous materials in their physical and chemical properties as well as in the process of their structural relaxation etc.

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