Application of fragmentary model to analysis of the atomic structure of amorphous materials

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Abstract. Experimental atomic radial distribution functions, obtained from diffraction amorphous materials, are proposed to be interpreted using the model curves built upon the complete structural data of crystal analogues or upon the separate fragments of their structure. This modelling technique is called a fragmentary model. A model atomic radial distribution function is a radial cross section of the spherically symmetric function of interatomic distances. It characterises a nanodispersed diffraction amorphous polycrystal as uniquely as the values of interplanar spacings and intensities characterise a regular polycrystal. Comparing the model and experimental atomic radial distribution functions by the maxima positions we can perform the “identification” and “phase analysis” of nanodispersed diffraction amorphous polycrystals and define the crystalline compounds whose fragments form the structure of glass.

1. Introduction

With the development of nanotechnologies, more and more substances are obtained with a diffraction amorphous state, and more and more often the issue of their atomic structure arises. By diffraction amorphous we mean the materials whose X-ray diffraction pattern (electrons, neutrons) has several diffuse maxima. It has been shown [1] that the diffraction pattern of a nanodispersed polycrystal, the linear sizes of whose crystallites allow for 2-3 unit cells, is similar to the diffraction by classical types of glass.

Despite great advances in structural analysis, currently there are no generally accepted methods allowing to determine the atomic structure of amorphous materials similar to those used to analyse the atomic structure of crystals. The structure of amorphous materials is studied through models, built using any suitable coordinate system [2-6]. The adequacy of the model is checked by comparing the calculated values with the same as those obtained experimentally. The calculated and experimental intensities [5] or the model and experimental atomic radial distribution functions (ARDF)$4\pi\rho(r)$ can be compared [2, 4, 6-9]. The maxima of the experimental ARDF correspond to the most probable interatomic distances, taking into account the scattering ability of atoms.

In studies [2, 4] an equation is proposed which directly links the experimental ARDF (the left side of equation (1)) to the model ARDF (the right side of equation (1)), which is calculated using the method of pair functions

$$4\pi^2 \rho \sum_{f, c} Z_j \left( \frac{2r}{\pi} \int_{0}^{S_{\text{max}}} S \sin(Sr) \exp(-\alpha^2 S^2) dS \right)$$

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\[ \sum_{i} \sum_{j} \frac{N_{ij}}{r_{ij}} \int_{0}^{\infty} f_{i} f_{j} \frac{\sin(Sr_{ij})}{g^{2}(S)} \sin(S) \exp(-\alpha^{2}S^{2})dS. \]  

(1)

The summation is carried over the formula composition (f.c.) of the studied substance. \( \rho_{e} \) is the average electron density, \( Z_{j} \) is the number of electrons in the \( j \)-th atom; \( N_{ij} \) is the number of neighbouring atoms in the \( i \)-th layer, surrounding the \( j \)-th atom at a distance of \( r_{ij} \); \( \exp(-\alpha^{2}S^{2}) \) is the convergence factor, introduced to reduce the intensity at large values of the diffraction vector \( S = 4\pi \sin \theta / \lambda \), where the measurement accuracy is low. This factor is similar to the thermal intensity factor. Often a \( T(r) \) function is calculated instead of the ARDF, it is called a total correlation function \[4\].

It is almost impossible to build a correct model ARDF that is informative in the ordering region up to 1 nm for a closed disordered atomic system. All atoms near the boundary of such a system have defects of coordination spheres, which cause errors in the determination of coordination numbers \( N_{ij} \). To achieve maximum agreement between the calculated and experimental ARDF in the entire ordering region, \( N_{ij} \) is often used as an adjusting parameter.

In this study the atomic structure of amorphous substances is analysed using a fragmentary model that allows comparing the interatomic distances in amorphous substance in the ordering region of up to 1 nm with the interatomic distances of in their crystal analogues.

2. Theoretical basis of the fragmentary model

To interpret an experimental ARDF there is no need for the ideas regarding the coordination spheres of each atom in the cluster. It is easier and more convenient to use interatomic distances \( r_{ij} \), which are part of the well-known Debye formula (2) \[4, 10\]. From this equation it is easy to derive an equation analogous to (1)

\[ I(S) = \sum_{i} \sum_{j} f_{i} f_{j} \sin(Sr_{ij}) \frac{\sin(S)}{Sr_{ij}}. \]  

(2)

In this expression the intensity \( I(S) \) is normalised and coherent; \( N \) is the number of atoms in the irradiated volume; \( f_{i} \) and \( f_{j} \) are the atomic amplitudes, which are not identical or similar for different atoms. To make it possible to work with multicomponent systems Z- or K-approximation are used.

For Z-approximation the atomic amplitude per one electron of the formula composition

\[ \sum_{j} f_{j}(S) \]  

is considered the unit amplitude. \( Z_{j} \) is the atomic number of the element or its charge number \[2, 11\]. In this unit system the atomic radial distribution function represents the electron density distribution.

There are no electron scattering units in the electron diffraction. A study \[12\] suggests considering the scattering of the studied substance by the lightest element to be the diffraction unit. The relative scattering ability of other atoms is determined using the formula

\[ K_{j}^{2} = \frac{\int_{0}^{S_{\text{max}}} S^{2} f_{j}^{2}(S) dS}{\int_{0}^{S_{\text{max}}} S^{2} f_{0}^{2}(S) dS}. \]  

The integration is carried over the entire range of \( S \) values shown in the table, which is identical for both atoms. The product \( S^{2} f^{2}(S) \) is a bell-shaped function. The relative scattering ability of atoms is equal to the area ratio of these functions. If \( f^{2}(S) \) decreases not fast enough, which is typical for light elements, the “thermal” correction \( \exp(-\alpha^{2}S^{2}) \) can be introduced. The square of the unit atomic
amplitude is given by \( f_{\text{un}}^2(S) = \sum_{j} \frac{\sum_{f.e.} K_j^2}{N} \). The unit atomic amplitude is not identical to the atomic amplitude of the lightest element in the studied substance, but this is neglected in the calculation, assuming the \( K \) of the light element to be 1. In this study \( K \)-approximation is used for both electron and X-ray diffraction experiments. In the \( K \)-approximation, the atomic radial distribution function describes the density distribution of light atoms and is expressed in arbitrary units (a.u.).

Transforming the equation (2), we extract all the terms with \( i = j \) from the double summation, transfer them to the left side, and sum over the formula composition. There we also transfer from the right side the diffraction vector \( S \), as well as \( f_{\text{un}}^2 \), which we obtain by replacing \( f_i \) and \( f_j \) with their values with \( K \)-approximation of \( K_i f_{\text{un}} \) and \( K_j f_{\text{un}} \)

\[
\frac{I(S) - L \sum_{f.e.} f_j^2}{f_{\text{un}}^2} = \sum_{i} \sum_{j \neq i} \frac{1}{r_{ij}} K_i K_j \sin(S r_{ij}).
\]

We divide both sides of this expression by the number of formula units \( L \) in the irradiated volume. Given that \( I'(S) = I(S)/L \) is the intensity reduced to one formula unit, we write

\[
S \left( \frac{I'(S)}{\sum_{f.e.} f_j^2} - 1 \right) \sum_{j \neq i} K_j^2 = \frac{1}{L} \sum_{i} \sum_{j \neq i} \frac{1}{r_{ij}} K_i K_j \sin(S r_{ij}).
\]

The expression in brackets on the left we call an interference function \( i(S) \). In a real experiment the interference function is determined similarly: \( i(S) = \frac{m f_{\text{exp}}^2(S)}{\sum_{f.e.} f_j^2(S)} - \frac{m f_{\text{exp}}^2(S)}{\sum_{f.e.} f_j^2(S)} \) [13]. There \( m \) is a scale coefficient used to correct the experimental intensity values to the values close to the sum of the squares of the atomic scattering factors. The value of \( m \) is analogous to the number one in the writing of \( i(S) \) in the equation (3). It represents the scattering by independent atoms in a real experiment and eliminates the background radiation of any origin. It is called an average line and it is positioned so that the condition \( \int_{-\infty}^{0} i(S) dS = 0 \) is met.

Multiplying both sides of the equation (3) by \( \frac{2r}{\pi} \sin(Sr) \), we integrate with respect to \( S \) and add the small-angle term \( 4 \pi^2 \frac{d}{M \cdot 1.65 \rho_0} \left( \sum_{f.e.} K_j^2 \right)^2 \) to the left side, where \( M \) is the relative formula composition mass. We introduce a correction for the thermal vibrations of atoms \( \exp(-\alpha^2 S^2) \) to the right side, it is not necessary for the left side as the measurement is usually performed at room temperature. The result is:

\[
4 \pi^2 \rho_0 + \frac{2r}{\pi} \sum_{f.e.} K_j^2 \int_{0}^{S_{\text{max}}} S i(S) \sin(Sr) dS
\]
For each interatomic distance a pair function of the following type is calculated

$$P_{ij} = K_i K_j \frac{2S_{K_{ij}}}{r_{ij}^2} \int_0^{\infty} \sin(Sr_{ij}) \sin(Sr) \exp(-\alpha^2 S^2) dS.$$  

The sum of all pair functions is divided by $L$ so that the model ARDF is calculated for one formula unit, as well as the experimental ARDF. The equation (4) is strict when $N$ approaches infinity.

In this study the experimental ARDF was interpreted using a fragmentary model. In terms of the fragmentary model an amorphous substance is a complex mosaic that consists of the structural fragments of those crystalline phases whose formation is possible for a particular elemental composition. The structural fragments can be chains, layers in chained or layered structures, as well as crystalline nuclei whose linear dimensions allow for 2-3 unit cells. Diffraction of this nanocrystalline substance is similar to diffraction of a disordered atomic system [1]. However, the crystalline nuclei in the range of 2-3 unit cells retain the crystalline order and the quantitative ratio of the interatomic distances inherent in its structure. If the amorphous substance is a nanodispersed polycrystal, then the experimental ARDF maxima should correspond to the most probable interatomic distances of the crystalline phase (or phases) that originated in the studied amorphous substance. To confirm this point it is necessary to have model ARDFs built on the basis of complete structural data of all possible crystal analogues. In the analysis, the two independently obtained experimental and model ARDFs are compared, with particular attention to the maximum positions.

To build the model ARDFs of crystal analogues, the interatomic distances are calculated up to 1.5 nm, if the experimental ARDF has an ordering region of ~1 nm. For this purpose, the central unit cell is surrounded by a layer of 3-4 unit cells. The interatomic distances are calculated by spherical layers. Crystalline symmetry makes it easy enough to determine the number $2N_{ij}$ of the interatomic distances $r_{ij}$ per composition unit and simplify the calculation of the model ARDF. The interatomic distances are calculated for only one of each group of crystallochemically dependent atoms, choosing the one closest to the central unit cell coordinate origin. For each interatomic distance $r_{ij}$ the number $2N_{ij}$ in the compound with the composition $A_xB_y$ is determined using the formula

$$2N_{ij} = \frac{\sum q_i' \sum n_i' k_i' + \sum q_i' \sum n_i' k_i'}{\sum q_i' \sum k_i'} ,$$

where $q_i'$ is the number of independent atoms of $A$ type with the multiplicities of positions $k_i'$, and each of them has $n_i'$ identical interatomic distances $r_{ij}$ to the atoms of $B$ type. The denominator of the first summand is the sum of the multiplicities of the positions of all independent atoms $q_i'$ of $A$ type, i.e. the number of all $A$ type atoms in a unit cell. In the second term of the sum $q_i'$ is the number of independent atoms of $B$ type with the multiplicities of positions $k_i'$, and each of them has $n_i'$ similar interatomic distances $r_{ij}$ to the atoms of $A$ type. The denominator of the second summand is the number of all $B$ type atoms in a unit cell. Due to the bond completion, the first member of the sum is necessarily equal to the second. To calculate the number $2N_{ij}$ for the distances between the atoms of one type either the first (A-A) or the second (B-B) summand is used. The formula is universal and calculates the number of interatomic distances in compounds with three or more types of atoms.

The interatomic distances close in size and of the same type (A-A, A-B, B-B) are combined by Gaussian function, making sure that its dispersion $\sigma_{r_{ij}}^2$ does not exceed the thermal vibrations of atoms. The $2N_{ij}$ values of the combined distances are summarised. The model ARDF is calculated using the method of pair functions by the equation (5)
\[
4\pi^2 \rho(r)_{\text{mod}} = \frac{2r}{\pi} \sum_{ij} \sum_{l} \frac{2N_{ij}^l}{r_{ij}^l} K_i K_j \int_0^{S_{\text{max}}} \sin(Sr_{ij}^l) \sin(Sr) \exp\left(-\left(\alpha^2 + \frac{\sigma_{ij}^2}{2}\right)S^2\right) dS.
\]  

There \( r_{ij} \) is the expected value of Gaussian function, \( n \) is the number obtained after combining the interatomic distances of the same type. Summation over \( ij \) is performed over the types of interatomic distances, and summation over \( l \) is carried over the number of interatomic distances of the same type.

The pair functions are calculated individually for each type of interatomic distance, which allows seeing their partial contributions. On average, there are up to 300 pair functions for each type of interatomic distance (partial contribution). They are calculated with a step of \( r \) and \( S \) of no more than 0.01. The sum of partial contributions is the model ARDF of a perfect amorphised monocrystal. It is perfect because the interatomic distances are calculated based on a perfect crystal with no defects, a monocrystal, because the interface boundaries of crystallites are not taken into account, and an amorphised crystal because each interatomic vector has spherical symmetry. The lower limit of integration must be zero by necessity, and the upper limit is the same as in the calculation of the experimental ARDF or slightly larger. The model ARDF is calculated with the upper limit of integration over \( S \) being less than 1 Å\(^{-1}\). It is a parabola corresponding to the small-angle term \( 4\pi^2 \rho_0 \) that was introduced into the experimental ARDF earlier. This parabola is determined by the X-ray density of the crystal analogue \( D_x \), by the scattering ability of atoms and the formula composition of the compound. The model ARDFs, calculated for compounds of different composition within one system, have different parabolas. It makes them incompatible with each other or with the experimental ARDF. For the analysis, all model and experimental ARDFs are normalised to single atoms, that is achieved by simple division by the number of atoms in the formula composition. They are also normalised to an equal parabola (experimental).

Substituting the right side of the equation (4) (the calculated ARDF for a completely disordered atomic system) with the expression (5) describing the model ARDF, calculated based on the crystal structure data, we write

\[
\text{ARDF}_{\text{eq}} = \frac{2r}{\pi} \sum_{ij} \sum_{l} \frac{2N_{ij}^l}{r_{ij}^l} K_i K_j \int_0^{S_{\text{max}}} \sin(Sr_{ij}^l) \sin(Sr) \exp\left(-\left(\alpha^2 + \frac{\sigma_{ij}^2}{2}\right)S^2\right) dS.
\]

The approximate equation suggests that if the studied sample is a nanodispersed diffraction amorphous polycrystal, the experimental and model ARDFs will never fully coincide. The model ARDF is based on the structural data of a perfect crystal. So it is impossible to take into account neither the defects of the crystalline structure nor the interface boundaries of the crystallites, which are plentiful in the experimental sample. Therefore, the main characteristic of the ARDF is the position of its maxima.

3. Experimental

3.1. Atomic structure of nanodispersed materials

The nanodispersed diffraction amorphous polycrystals appeared to be the \( \beta \)-ZnP\(_2\) thin amorphous film [14] and the amorphous sediment, which was obtained upon decomposition of potassium oxofluoroniobate [15] in water.

The thin amorphous film of zinc diphosphide was obtained by explosive laser sputtering of a \( \beta \)-ZnP\(_2\) monocrystal in vacuum. All the maxima of the experimental ARDF (electron diffraction experiment) coincided in position in the entire ordering region with the maxima of the model, based
on the complete crystal structure data of $\beta$-ZnP$_2$ [16] (Figure 1). The model maxima, as expected, were higher and sharper than the experimental ones, except for the fourth maximum. This one and the previous maxima of the model ARDF are formed by Zn-Zn interatomic distances. The cleavage plane goes along them within the crystal. Consequently, this is where the preferential fracture of the crystal occurs during its dispersion [14]. The match in position of the maxima of the experimental and model ARDFs in the whole ordering region confirmed that the amorphous film was a nanodispersed polycrystal. The irregularity of the maxima allowed finding the place of the preferential destruction of the crystal.

![Figure 1](image1.png)

**Figure 1.** The experimental (1) and the model (2) ARDF of $\beta$-ZnP$_2$. Partial contributions of all the types of interatomic distances are given.

![Figure 2](image2.png)

**Figure 2.** The experimental ARDF of the sediment (1) and the model ARDFs of the crystalline analogues K$_{2-x}$Nb$_4$O$_{3(O,F)}$F (2) and N-Nb$_2$O$_5$ (3).

It was expected that when the composite crystal of potassium oxofluonibiobate K$_{2-x}$Nb$_4$O$_{3(O,F)}$F decomposed in water, the structural blocks of niobium oxide would precipitate and the blocks of potassium fluoride would dissolve [15]. When the model ARDF, calculated upon the structural data of
the K$_2$O$_3$(O,F)$_3$F compound, was compared with the experiment, the results showed (Figure 2, curves 1, 2) the absence of the maximum corresponding to the Nb-Nb interatomic distances ($r = 2.92$ Å). This distance is the edge of the niobium octahedron in the structure of the original crystal. The spectral studies have confirmed that the sediment is niobium oxide. Niobium oxides have many crystalline modifications. The fragmentary model revealed that there were structural fragments of $N$-form Nb$_2$O$_3$ in the sediment (Figure 2). The structure of this oxide [17] consists of the niobium-oxygen octahedra NbO$_6$. Most of them are connected by apexes and the smaller part of them by edges. In the amorphous sediment, both of those joints are approximately equal. Therefore, the fragmentary model allows not only for identification of the amorphous substance, but also for revealing the structural nature of amorphisation in some cases.

The model ARDF, built using the structural data of ZnAs$_2$ [18] could not account for the maxima of the experimental ARDF of the thin amorphous film of zinc diarsenide, that was obtained in the same conditions as the β-ZnP$_2$ film (Figure 3). The third maximum of the experimental ARDF is bifurcated, but in the model ARDF it is single. The divergence of the first maxima of both curves exceeds the limits of experimental error. There are other inconsistencies. Further studies have shown that the experimental ARDF correlates best with the model curve, based on the crystal structure data of arsenic [19]. Its nanodispersed particles form the basis of the thin amorphous film and explain most of the maxima of the experimental ARDF in the region up to 7 Å. The maxima of the experimental curve at $r > 7$ Å indicate the presence of zinc nanoparticles and the ZnAs$_2$ compound in the film. Despite the explosive laser sputtering the original compound was almost completely decomposed.

![Figure 3](image)

The given examples demonstrate that a kind of "phase analysis" of amorphous substances can be performed using the fragmentary model. From this point of view, the aluminium-based amorphous alloys we have studied are particularly interesting.

### 3.2. Atomic structure of the aluminium-based amorphous metallic alloys

We studied three amorphous metallic alloys (AMAs) in the most detail: Al$_{85}$Ni$_{10}$Nd$_5$, Al$_{83.5}$Ni$_{9.5}$Si$_1$L$_6$, and Al$_{84}$Ni$_{6}$La$_{10}$. To obtain the experimental ARDF with good resolution of its maxima the experiment was conducted with two types of X-ray radiation: copper and molybdenum. The data was processed in accordance with [1, 13, 20]. The ARDF was calculated with the upper limit of integration ~ 14 Å$^{-1}$. The entire composition of the alloy (100 atoms) was taken as the formula composition. To interpret the experimental ARDF within the framework of the fragmentary model, the
model ARDFs of pure aluminium and all known compounds of Al-Ni, Al-La, and Al-Nd systems were calculated. For the analysis all the model and experimental ARDFs were normalised to single atoms and to an equal parabola. The model ARDFs of some compounds based on Al-Ni and Al-Nd are given in Figure 4 and 5. Laying the model ARDFs over the experimental curve, we chose those whose maxima did not contradict the experiment. In Figure 6 the experimental ARDF of the Al$_{85}$Ni$_{10}$Nd$_{5}$ amorphous alloy is shown with the model ARDFs of Al$_3$Nd and Al$_3$Ni$_2$ compounds overlaid. The figure shows that the model ARDFs of these compounds explain the position of all the maxima of the experimental ARDF. We summarised the three model ARDFs of Al$_3$Nd, Al$_3$Ni$_2$, and Al, taken in proportions corresponding to the composition of the 5Al$_3$Nd + 5Al$_3$Ni$_2$ + 55Al alloy. We laid the total model ARDF over the original experimental curve and saw that this composition did not explain the position and filling of the experimental ARDF maxima well enough. The closest agreement with the experiment was obtained for the total model ARDF of the composition 5Al$_3$Nd + 4Al$_3$Ni$_2$ + 2Al$_3$Ni + 52Al (Figure 7).

![Figure 4](image1.png)

**Figure 4.** The model ARDFs of the crystalline analogues Al$_3$Ni (1), AlNi (2) and AlNi$_3$ (3).

![Figure 5](image2.png)

**Figure 5.** The model ARDFs of crystalline analogues Al$_2$Nd (1), Al$_3$Nd (2) and Al$_4$Nd (3).
Figure 6. The experimental ARDF of the Al<sub>85</sub>Ni<sub>10</sub>Nd<sub>5</sub> alloy (1) and the model ARDFs of the Al<sub>3</sub>Nd (2) and Al<sub>3</sub>Nd<sub>5</sub> (3) crystal analogues, normalised to a single atom and an equal parabola.

Figure 7. The experimental ARDF of the Al<sub>85</sub>Ni<sub>10</sub>Nd<sub>5</sub> alloy (1) and the total model ARDF (2).

The experimental ARDFs of the Al<sub>83.5</sub>Ni<sub>9.5</sub>Si<sub>1.4</sub>La<sub>5.6</sub> and Al<sub>84</sub>Ni<sub>6</sub>La<sub>10</sub> alloys were analysed the same way. First, we laid the experimental and model ARDFs over each other, normalised to single atoms and equal parabolas. This way we identified those model ARDFs that did not contradict the experiment in terms of the maximum positions. Combining them in various compositions and proportions we achieved the total model ARDF as close as possible to the experiment, which is described in detail in [1, 20]. The closest agreement with the experiment for Al<sub>83.5</sub>Ni<sub>9.5</sub>Si<sub>1.4</sub>La<sub>5.6</sub> alloy was obtained for the total model ARDF of the composition 3Al<sub>3</sub>La + 4.5Al<sub>3</sub>Ni + 2.96Al<sub>1</sub>La<sub>0.88</sub> + Al<sub>3</sub>Ni<sub>5</sub> + 51.72Al (Figure 8). The total model ARDF of the composition 6Al<sub>3</sub>La + 4Al<sub>3</sub>La + 2Ni<sub>3</sub>Al + 48Al explained the maximum positions of the experimental curve of the Al<sub>84</sub>Ni<sub>6</sub>La<sub>10</sub> alloy (Figure 9).

The interpretation of the experimental ARDFs of the amorphous metallic alloys using the fragmentary model proved that these objects are inhomogeneous [21]. This may be due to the presence of crystalline nuclei of different phases.
3.3. Atomic structure of classical glass

An interesting result was obtained when using the fragmentary model to analyse the atomic structure of spectrally pure quartz glass [22, 23]. The X-ray experiment was performed using monochromatised copper and silver X-rays. Silica is the most studied of all types of glass. The obtained experimental ARDF correlated best with the data [24] and had an ordering region of ~ 1 nm. The model ARDFs for all known crystalline modifications of silicon oxide were built [25-29] to interpret it, some of them are given in Figure 10. It can be seen that all model ARDFs have the same first three coordination spheres, but they differ well in position and filling of the maxima in the medium-range order region. The positions of the first and second coordination spheres are determined by the geometry of the SiO₄ tetrahedra. The third maximum is the distance between the silicon atoms, positioned in the neighbouring tetrahedra. It is considered [2] to be characterized by a "hinge" angle of Si-O-Si in the vitreous SiO₂. According to Figure 10, on average, this distance is the same for all crystalline SiO₂ modifications, except for stishovite, which has the octahedral coordination of silicon.
The first three maxima of the experimental ARDF of quartz glass are identical to the model maxima (Figure 11). The other maxima are best accounted for by the model ARDF, calculated using the structural data of β-quartz. A characteristic feature of the β-quartz structure is the silicon-oxygen tetrahedron helical chains running along the sixth-fold axis with interatomic distances specific to the helical step. In the studied glass at least three turns of such chain remain (maxima at \( r = 5.62 \text{ Å} \) and \( 7.54 \text{ Å} \)) [22]. However, the model ARDF of β-quartz could not account for all the maxima of the experimental ARDF of quartz glass. Further studies showed that the remaining maxima are best explained by the model ARDF, built on the basis of the crystal structure data of β-tridymite (Figure 11) [27]. Therefore, the studied quartz glass consists of β-quartz nanocrystallites, connected by β-tridymite structural blocks. This glass served as a substrate during the diffusion into silicon wafers in the manufacture of microcircuits. There was no crystallisation even during prolonged exposure at high temperatures.

**Figure 10.** The model ARDFs of different crystalline modifications of the SiO\(_2\) α-quartz (1), β-quartz (2), β-tridymite (3).

**Figure 11.** The experimental ARDF of the SiO\(_2\) glass (1) and the model ARDFs of β-quartz (2) and β-tridymite (3) crystal analogues.
The structure of crystal analogues remained largely in alkali borate glass. Two compositions LiB₃O₅ and CsB₃O₅ were chosen to examine their atomic structure [30]. Crystal analogues of these compounds have very similar structures. The great difference between the scattering abilities of alkali metals allows studying the boron-oxygen framework in lithium glass. It also allows studying the mutual arrangement of metal atoms and Cs-O interatomic distances in caesium glass.

The experimental ARDF of vitreous LiB₃O₅ had an ordering region of ~7 Å (Figure 12). It was compared with the model ARDF calculated using complete crystal structure data of LiB₃O₅ [31]. The first two maxima of both ARDFs were identical. It means that during glass transition the boron-oxygen tetrahedra and triangles in the glass remain the same as in the crystalline phase. The characteristic structural pattern of crystalline LiB₃O₅ are two triborate groups linked by an oxygen atom. The size of such a “link” amounts to ~7.5 Å, which corresponds to the ordering region of the vitreous LiB₃O₅. The maxima of the model and experimental curves correlate well in the entire ordering region, which indicates that the most probable interatomic distances of the boron-oxygen framework in the glass and crystal are very close. The interatomic oxygen-oxygen distances between the triborate groups bound by an oxygen atom are preserved in the glass. On the other hand, the similar oxygen distances between the unbound triborate groups are destroyed (the fourth maximum in the model is bifurcated, and in the experiment – single).

There is good correlation between all the maxima in the entire ordering region (~12 Å) of the experimental ARDF of the CsB₃O₅ glass and the model curve, built using the complete crystal structure data of caesium triborate [32] (Figure 13). The main contribution to the formation of maxima of the model ARDF is made by Cs-Cs interatomic distances, whose exact position is affected by Cs-O interatomic distances. The first maximum of the model and experimental ARDF is formed only by Cs-O interatomic distances. It is the same in both curves both in position and in filling. It means that, on average, the nearest oxygen environment of caesium atoms in glass and in crystal is the same. The experimental ARDF does not have the small maximum, formed exclusively by Cs-O interatomic distances, that is present in the model ARDF (position 5.52 Å). It follows that there is no crystalline order in the arrangement of triborate groups at this distance. The shortest distances between the caesium atoms, located within the crystal in the channels, which are located along the axis a (3.91 Å) and along the axis b (4.81 Å), form the maxima of the model. Their positions are 3.98 Å and 4.83 Å. They are positioned in the experimental ARDF at r amounting to 4.14 and 5.0 Å, respectively. It can be assumed that these distances increase in glass. The identical shape of both curves in the region of

![Figure 12. The experimental ARDF of the LiB₃O₅ glass (1) and the model ARDF of the LiB₃O₅ crystal analogue (2) with partial contributions of interatomic distances B-O and O-O.](image-url)
medium-range order \((r > 5 \text{ Å})\) (Figure 13) indicates that the arrangement of caesium atoms in glass and crystal is similar.

![Figure 13](image1.png)

**Figure 13.** The experimental ARDF of the CsB₃O₅ glass (1) and the model ARDF of the CsB₃O₅ crystal analogue (2) with partial contributions of interatomic distances Cs-Cs and Cs-O.

Until now, the analysed experimental ARDFs were compared with the model ones, built upon the complete structural data of a crystal analogue, i.e. a structural fragment meant the entire elementary cell. The necessity to calculate the model ARDFs for individual parts of the crystalline structure (structural fragments) has arisen in the analysis of the experimental ARDFs of classical semiconductor glass As₂S₃ [33].

![Figure 14](image2.png)

**Figure 14.** The experimental ARDF of glass (1), ARDFs built on the basis of the intralayer interatomic distances of the crystalline As₂S₃ (2) and the interatomic distances of the As₄S₅ fragment (3), corrected to the parabola.

Comparing the experimental ARDF, obtained from As₂S₃, with the model curve built upon the complete crystal structure data of orpiment [34], it was noted that some of the maxima, which are present in the model ARDF, are missing in the experiment. The analysis of the interatomic distances
showed that there were no model maxima formed by the interlayer interatomic distances in the layered structure of orpiment. The model ARDF built solely upon the intralayer interatomic distances did not explain all the maxima of the experimental ARDF. It was suggested that structural fragments of other phases of the As-S system may be present in the vitreous As$_2$S$_3$. The molecules of the As$_4$S$_5$ compound, orientated in a certain way, appeared to be such a fragment (Figure 14). A variant of the joining of orpiment corrugated layers by these molecules during glass transition was suggested [33]. Application of the fragmentary model to the analysis of the atomic structure of the vitreous As$_2$S$_3$ has shown that the structure of glass can be a mosaic of the structural fragments of those phases, whose formation does not contradict its elemental composition.

4. Conclusion
In the study the atomic radial distribution function (ARDF) is proposed to be considered as the function of the interatomic distances in the studied sample and not from the point of view of the coordination spheres around the atoms. In this case, the maxima of the experimental ARDF are the most probable interatomic distances, taking into account the scattering ability of the atoms that form them.

The authors interpret the experimental ARDF using a fragmentary model. According to it, any amorphous substance is a mosaic of the structural fragments of different crystalline phases, which can be formed with a given elemental composition of the amorphous substance. The structural fragments are represented by the whole unit cells as well as their parts (layers, chains, etc.) Model ARDFs built upon the complete structural data of crystal analogues allow for the identification of these fragments within the structure of the amorphous substance. A model ARDF characterises the hypothetical nanodispersed diffraction amorphous polycrystal as uniquely as a set of interplanar spacings and intensities characterises a regular polycrystal. When constructing a model ARDF neither the defects of the crystalline structure nor the interface boundaries of the crystallites are taken into account. Therefore, the model curve can not be exactly equal to the experimental.

It appeared that in many cases amorphous materials retain not only the short-range, but also the medium-range order, specific to crystal analogues. Thus, the structure of the $\beta$-ZnP$_2$-based thin amorphous film and amorphous sediment, which precipitates upon the decomposition of potassium oxofluronibate, has all the interatomic distances specific to their crystal analogues $\beta$-ZnP$_2$ and N-Nb$_2$O$_5$, respectively. This means that they are nanodispersed diffraction amorphous polycrystals based on these compounds. The structure of the amorphous metallic alloys and the thin amorphous film based on ZnAs$_2$ is a mixture of the crystalline nuclei in several phases. This made it possible to speak of the possibility of the “phase analysis” of amorphous materials using the fragmentary model. The study of classical types of glass proved that they also retain the structural fragments typical for crystals. Borate glass with lithium retains all the interatomic distances typical for the two triborate groups bound by an oxygen atom. Quartz glass has the spiral chains specific to $\beta$-quartz and the structural fragments of $\beta$-tridymite. Vitreous As$_2$S$_3$ consists of the structural fragments of orpiment (corrugated layers) that binds the molecules of the As$_4$S$_5$ compound.

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