The Effect of the Interatomic Distances Distribution Character on the Radial Distribution Function of Amorphous Solids

G.M. Ivanitska[1], V.S. Kovtunenko[2], M.M. Ryaboschuk[1,*]

[1] *Uzhgorod National Universiry, 3, Narodna Sq., 88000 Uzhgorod, Ukraine*
[2] *Cherkasy State Technological University, 460, Shevchenko Blvd., 18006 Cherkasy, Ukraine*

It is proposed parabolic assignment of the radial distribution function peaks shape. It is shown that this assignment is more in line with the real structure of disordered atomic networks, in comparison with the Gauss distribution. At the same time its application more adequately describes also the partial structural factors in diffraction studies of the amorphous solids. The analysis shows that the description of coordination spheres atomic networks of amorphous substances by parabolic distribution functions can significantly improve the resolution of the radial distribution function method.

Keywords: Disordered materials, Atomic short-range order, Radial distribution function.

PACS numbers: 61.43. – j, 61.43.Bn

1. INTRODUCTION

The necessity of a detailed understanding of the structure and properties of non-crystalline materials is due to the important role they play in the development of a relatively new class of materials, such as metallic glasses, amorphous semiconductors, disordered nanosystems. Therefore, their structural characteristics have become a rapidly growing area of experimental and theoretical research in the last decade [1].

The structure of disordered states of matter is characterized by the presence of a certain atomic short-range order and is traditionally described in terms of the coordination spheres (CS) [2]. They define the geometric configuration of the location of the nearest neighbors in the space around a "central" atom. The most common characteristic of presentation of the structure of disordered materials is a radial distribution function of the atoms (RDF) $W(r)$ [3]. Such information is extracted mainly from either direct diffraction experiments or atomic networks obtained by different methods of mathematical modeling.

By definition, RDF can be represented as the sum of the distributions of the atoms of individual CS defined by certain functions $W_k(r)$ [4]:

$$W(r) = \sum_k W_k(r), \qquad (1)$$

In the ideal case, each CS in the atomic network is allocated so that all of its atoms are arranged at the same distance from the central atom. But this situation does not occur even in crystals. In the crystal lattice the atoms uniting into the coordination sphere are located at very close distances from the central atom [5]. In amorphous atomic networks the deviations of the interatomic distances within coordination sphere are considerably larger [6]. Therefore, their presence is necessarily taken into account in the study of the short-range order of real amorphous solids.

Traditionally, in the structural analysis the above-noted topological disorder of structure is described by a Gaussian distribution functions within each of the CS [7]. Thus, for the CS with the coordination radius r_k and coordination number Z_k this function is:

$$W_k(r) = \frac{Z_k}{\sqrt{2\pi\sigma_k^2}} \exp\left[-\frac{(r-r_k)^2}{2\sigma_k^2}\right], \qquad (2)$$

where σ_k^2 is the standard deviation (variance) of the interatomic distances distribution in CS under consideration.

From a physical point of view, the use of the mathematical expression Eq. 2 to define the RDF within a fixed CS is not entirely correct. This is due to the fact that the Gaussian distribution describes the physical parameters of the systems with perfect disordering. Therefore, the graph of the distribution has long "tails" both towards lower and higher than r_k distances.

The real amorphous materials have a more ordered atomic network. It is due to the fact that the geometric parameters of such networks in condensed systems are set by the strict quantum mechanical laws of the interatomic interaction. As a result, these parameters are strictly defined within specified ranges. For example, for the first CS the interatomic distances correspond to the lengths of strong chemical bonds between atoms which are locked at the minimum of the potential energy of their interaction. This causes severe restrictions on the change in length of chemical bonds, and, respectively, on the variation of the interatomic distances within the first CS. For the second coordination sphere the same limitations are set by fixing the certain range of angles between chemical bonds due to chemical interaction of different atomic triplets in atomic network. Similarly, interaction between different numbers of atoms of the third, fourth and subsequent CS limits the range of variation of the interatomic distances in them also. In this study, we investigate the possibility of using a quadratic function to describe the topological disorder of atomic structure within each of the CS.

* mryaboshhuk@yandex.ua

2. MODEL CALCULATION

For the comparative analysis we shall calculate the limiting parameters of the first several CS of the atomic network of amorphous silicon films. Its second CS is formed by the second neighbors of the central atom. Chemical bonds between these three atoms form an angle θ (see Fig. 1). The minimum length of Si-Si chemical bond, according to the first peak parameters in experimental RDF [8] is $r_{1min} = 0.215$ nm, and the maximum is 0.245 nm. For the tetrahedral linking of silicon atoms together the average angle between the bonds may be taken as 109 °. Analysis indicates that for different atomic networks, this angle may vary widely, from 103 ° to 115 °, without causing any significant mechanical stress of an atomic network [9]. From these data we can find the smallest interatomic distance between second neighbors as $r_{2min} = r_{1min} (2 - 2\cos 103°)^{1/2} = 0.333$ nm. Similar calculations give the maximum distance between the second neighbors of $r_{2max} = r_{1max} (2 - 2\cos 115°)^{1/2} = 0.416$ nm. At the same time, in the Gaussian representation the second RDF peak is contributed by the atomic pairs with consi-?erably wider range of r_2 interatomic distances from 0.32 nm to 0.45 nm. The value $r_2 = 0.32$ nm can be obtained by decreasing the angle θ between bonds to 97 °, that is unlikely for the tetrahedral bonding of atoms [9]. The value of $r_2 = 0.45$ nm in real silicon networks is unattainable, even if the angle $\theta = 180$ °(for this angle $r_2 = 0.430$ nm).
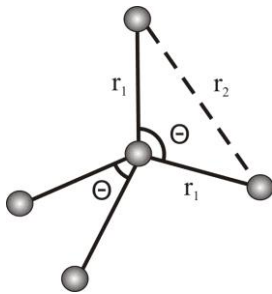

Fig. 1 – The geometry of the second CS formation for amorphous silicon

The variation limits for the values of distances between third neighbors of the central atom can also be easily identified. But it is necessary to take into acc?-nt the possibility of changes in the spatial arrangement of four atoms (see Fig. 2) linked by three chemical bonds. These changes are caused by two types of rotations of the terminal fourth atom with respect to chemical bonds between first and second, and second and third atoms. The rotations of the first type do not alter the interatomic distances r_2 and r_3. Therefore it is sufficient to analyze the influence on the r_3 of the second type rotation only. Such rotations will vary the r_3 value from a certain minimum value to a certain maximum one. These limiting cases correspond to the geometric configuration shown in Fig. 2, in which all four atoms under consideration lie in one plane. Simple mathematical calculations for these configurations give $r_{3min} = 0.244$ nm and $r_{3max} = 0.526$ nm.

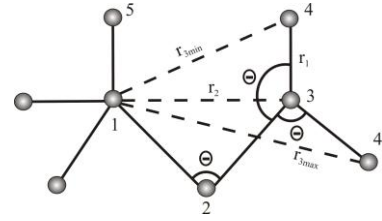The value of $r_{3min} = 0.244$ nm corresponds to the distance between the nearest neighbors. This means

Fig. 2 – The geometry of the third CS formation for amorphous silicon

that, in this configuration, the fourth atom spatially must be very close to the nearest neighbor 5 of atom 1 (see Fig. 2). But this is forbidden by the laws of formation of covalent chemical bonds in the disordered atomic network of silicon [9], and is not confirmed by their experimental diffraction study [8]. Therefore, the atomic configurations with r_{3min} in the structure of amorphous silicon are absent and do not contribute to the first CS. The same conclusion was made based on the results of mathematical modeling in [10].

The rotation of tetrahedrally arranged neighbors of atom 3 around the axis 2-3 from the position with r_{3min} will gradually increase the r_3 value. At a certain stage of this turn, the fourth atom will go away from the atom 5 for the distance in which formation of covalent chemical bond between the atoms may become energetically favorable. The result is formation of 5-membered ring. The existence of the local atomic configurations in the disordered atomic network of silicon is confirmed both by computer simulations [10] and experimentally [9]. But for the five-membered ring interatomic distance r_3 falls in magnitude into the second CS. Therefore, such geometric configurations will be manifested in the second CS in RDF.

So, the third CS of amorphous silicon may partially overlap with the second CS and comprises a range of distances from 0.416 nm to 0.526 nm. But in the Gaussian representation the third peak of the experimental RDF covers a wider range from 0.39 nm to 0.56 nm that is not consistent with physical and chemical principles of the construction of a disordered network from silicon atoms.

3. THEORY

To account for the marked restrictions, we have tried in the diffraction analysis to describe the variations of interatomic distances in atomic networks of amorphous materials within each CS not by a Gaussian distribution, but close to it mathematical function with a clear fixation of distribution "tails". Our analysis have shown that a simple quadratic function, with the domain of definition limited to a range of possible changes in the interatomic distances in each of the CS satisfies such conditions. So we have set RDF within a fixed CS in the simple form:

$$W_k(r) = A_k \left(r - r_k \right)^2 + B_k , \qquad (3)$$

where A_k and B_k are the values determined by Z_k and σ_k parameters of interatomic distances distribution in the relevant CS. In order to establish the correlation of A_k and B_k with Z_k and σ_k parameters we use physical conditions which must be satisfied by function Eq. 3.

From the physical meaning of $W_k(r)$ function it follows that when deviations of the interatomic distances from the CS radius r_k exceed a certain amount δ, the function should take zero values. That is,

$$W_k(r) = 0, \text{ if } r \leq r_k - \delta \text{ and } r \geq r_k + \delta. \quad (4)$$

At the same time the area under the graph of $W_k(r)$ function within its definition domain should be equal to Z_k. Thus,

$$\int_{r_i-\delta}^{r_k+\delta} W_k(r)dr = Z_k. \quad (5)$$

In addition, to maintain maximum consistency between Gaussian and quadratic distributions we impose the additional condition of peak heights equality for these distributions. Then, with $r = r_k$:

$$W_k(r_k) = \frac{Z_k}{\sqrt{2\pi\sigma_k^2}}. \quad (6)$$

From the relations Eq. 3 and Eq. 6 it follows that

$$B_k = \frac{Z_k}{\sqrt{2\pi\sigma_k^2}} = 0,399\frac{Z_k}{\sigma_k}. \quad (7)$$

Using the condition of Eq. 4, we obtain:

$$W_k(r_k - \delta) = A_k(r_k - \delta - r_k)^2 + B_k = A_k\delta^2 + B_k = 0. \quad (8)$$

The last expression gives a simple relation between the parameters of the quadratic distribution function: $A_k\delta^2 = -B_k$. We now apply the condition Eq. 5:

$$\int_{r_k-\delta}^{r_k+\delta}\left[A_k(r-r_k)^2 + B_k\right]dr =$$
$$= \left[\frac{1}{3}A_k(r-r_k)^3 + B_kr\right]_{r_k-\delta}^{r_k+\delta} = \frac{2}{3}A_k\delta^3 + 2B_k\delta = Z_k \quad (9)$$

From the last equation taking into account the ratio Eq. 7 we obtain:

$$\delta = \frac{3}{4}\sqrt{2\pi\sigma_k^2} = 1,88\sigma_k \quad \text{and}$$

$$A_k = -\frac{16Z_k}{9\left(2\pi\sigma_k^2\right)^{3/2}} - 0,113\frac{Z_k}{\sigma_k^3}. \quad (10)$$

Summarizing the performed mathematical calculations, we find that the quadratic function of the interatomic distances distribution for the certain k-th CS in analytical form is given by

$$W_k(r) = -0,113\frac{Z_k}{\sigma_k^3}(r-r_k)^2 + 0,399\frac{Z_k}{\sigma_k} \quad (11)$$

within the definition interval of $(r_k - 1,88\sigma_k) < r < (r_k + 1,88\sigma_k)$. Beyond this interval $W_k(r) = 0$.

4. DISCUSSION

To test the possibility of the use of quadratic functions in the description of CS interatomic distances distribution we consider model RDF for amorphous silicon films, shown in Fig. 3. They were obtained from experimental data taken from [8]. These model curves were constructed from the set of the peaks of different shape, each of which corresponds to a certain maximum in experimental RDF. The set of these peaks gives us some model RDF. In the case of Gaussian peaks we have got the first model RDF (see curve 1 in Fig. 3), which differs from the experimental one by 2-3 %.
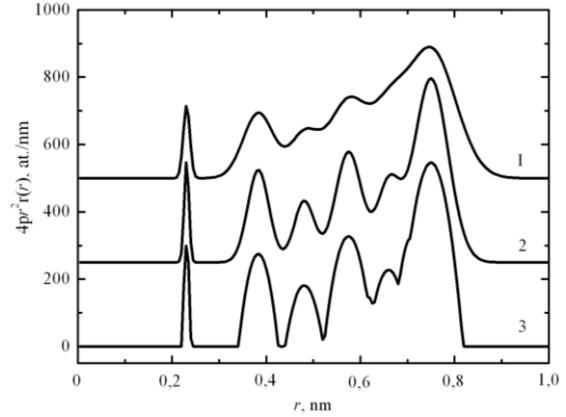

Fig. 3 – Model RDF graphs for the initial Gaussian (curve 1), adjusted Gaussian (curve 2) and quadratic (curve 3) distributions of CS interatomic distances for amorphous silicon films

Further we have taken into account that the RDF in [8] was obtained at the upper limit of the integral Fourier transform $s_2 \approx 150$ nm^{-1}. Therefore, its peaks are much broader than the real distribution of the atoms in the CS of the atomic network. According to the results of [11], the transition in the Fourier transform from $s_2 \approx 150$ nm^{-1} to $s_2 \to \infty$ the variances of the interatomic distances distributions in the CS are reduced by ~ 30 %. Taking into account this regularity, we have adjusted the model RDF of amorphous silicon films to the form that fits best their atomic structure. To do this, we have reduced the variances by ~ 30 % in the parameters of the Gaussian CS (see curve 2 in Fig. 3).

In the third step of the calculations of model RDF we have carried transformation of CS Gaussian peaks at the vertex of the parabolas (see curve 3 in Fig. 3). The parameters of the quadratic distributions within each of the CS were calculated from the corresponding parameters of Gaussian distributions adjusted by the above relationships.

As it is seen from the Fig. 3, the two functions set almost identical distribution of peaks in the central region. At the same time, there are no "tails" specific to Gaussian distributions for very large and very small interatomic distances, as compared to the respective CS radii on the graphs of quadratic function. Therefore, we suppose that in structural analysis of amorphous solids the use of quadratic distribution of interatomic distances within individual CS is physically justified.

As for the Gaussian distribution the half width Δ_Γ is associated with the dispersion by the simple relation $\sigma^2 = 0.18\Delta^2_\Gamma$. Let's find a similar relation for the introduced quadratic distribution of interatomic distances. For this purpose, we substitute in the expression Eq. 11 the values of $(r - r_k) = \Delta_K/2$ and we will take by definition that $W_k(r) = 0.5B_k$. As a result we obtain a simple equation:

$$0,5 \times 0,399 \frac{Z_k}{\sigma_k} = -0,113 \frac{Z_k}{\sigma_k^3} \left(\Delta_K\right)^2 + 0,399 \frac{Z_k}{\sigma_k}. \quad (12)$$

After the necessary transformations, we have find that for a quadratic distribution $\sigma^2 = 0.15\Delta^2_K$. The resulting expression is very close to the above formula similar to a Gaussian distribution. They differ only by a numerical coefficient. Since quadratic distribution at half-height is a little bit wider than the Gaussian one ($\Delta^2_K > \Delta^2_\Gamma$) (see Fig. 3), to obtain the same σ^2 value, the half-width of the peak of the quadratic distribution should be multiplied by a slightly smaller factor (0.15 instead of 0.18).

The results shown in Fig. 3 for different models of the interatomic distances distributions in CS show some differences in the overall total RDF relating peak width and depth of the valleys between them. In general, these differences accurately describe the natural discrete character of short-range order in amorphous solids. It was interesting to clear up the nature of the effect of such differences in the distribution functions of interatomic distances $W_k(r)$ on the interference functions of the CS. For this, we have calculated the functions for the first and second CS for amorphous silicon films by numerical methods for the two types of distribution: the adjusted Gaussian and quadratic. Analysis of the results have shown (see Fig. 4) that when using the same parameters in these distributions calculated interference functions are virtually identical to each other for the first CS and have slight differences for the second CS. In general, the identified differences lie within the accuracy of the interference functions determination in the diffraction experiments.
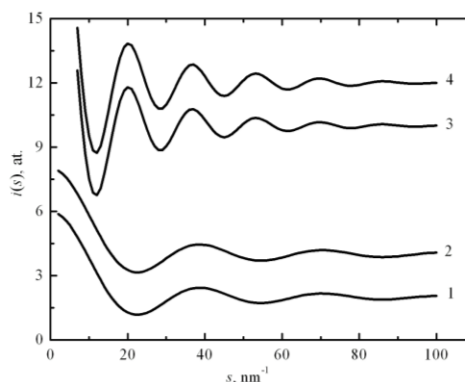

Fig. 4 – The interference function for the first (curve 1, 2) and second (curve 3, 4) CS of amorphous silicon films, calculated for the Gaussian (curve 1, 3) and quadratic (curve 2, 4) distribution of interatomic distances

5. CONCLUSION

The Gaussian distribution that often used in physics describes the physical parameters of the systems with perfect disordering. The graph of this distribution has long "tails" both towards lower and higher than average parameter. The real amorphous materials have a more ordered atomic network. And we have tried in the diffraction analysis to describe the variations of interatomic distances in atomic networks of amorphous materials within each coordination spheres not by a Gaussian distribution, but close to it mathematical function with a clear fixation of distribution "tails". It is shown that a simple quadratic function, with the domain of definition limited to a range of possible changes in the interatomic distances in each of the coordination spheres satisfies such conditions. The analysis shows that the description of coordination spheres atomic networks of amorphous substances by parabolic distribution functions can significantly improve the resolution of the radial distribution function method and more adequately describes the partial structural factors in diffraction studies of the amorphous solids.

Вплив типу розподілу міжатомних відстаней на функцію радіального розподілу аморфних речовин

Г.М. Іваницька[1], В.С. Ковтуненко[2], М.М. Рябощук[1]

[1] *Ужгородський національний університет, пл. Народна, 3, 88000 Ужгород, Україна*
[2] *Черкаський державний технологічний університет, бул. Шевченка, 460, 18006 Черкаси, Україна*

Запропоновано параболічне представлення форми піків функції радіального розподілу атомів. Показано, що таке наближення більш відповідає реальній структурі невпорядкованих атомних сіток, у порівняні з розподілом Гауса. Одночасно, його використання більш адекватно описує парціальні структурні фактори в дифракційних дослідженнях аморфних речовин. Аналіз показує, що опис координаційних сфер атомної сітки аморфних матеріалів параболічним розподілом може суттєво покращити розділення піків функції радіального розподілу атомів.

Ключові слова: Невпорядковані матеріали, Атомний ближній порядок, Функція радіального розподілу.

Влияние типа распределения межатомных расстояний на функцию радиального распределения аморфных веществ

Г.М. Иваницкая[1], В.С. Ковтуненко[2], М.М. Рябощук[1]

[1] *Ужгородский национальный университет, пл. Народная, 3, 88000 Ужгород, Украина*

[2] *Черкасский государственный технологический университет, бул. Шевченко, 460, 18006 Черкассы, Украина*

Предложено параболическое представление пиков функций радиального распределения атомов. Показано, что такое приближение больше соответствует реальной структуре неупорядоченных атомных сеток, в сравнении с распределением Гаусса. Одновременно его использование более адекватно описывает парциальные структурные факторы в дифракционных исследованиях аморфных веществ. Анализ показывает, что описание координационных сфер атомной сетки аморфных материалов параболическим распределением может существенно улучшать разделение пиков функций радиального распределение атомов.

Ключевые слова: Неупорядоченные материалы, Атомный ближний порядок, Функция радиального распределения.

REFERENCES

1. J.R. Telle, N.A. Pearlstine, *Amorphous Materials: Research, Technology and Applications* (New York: Nova Science Publishers Incorporated: 2009).
2. J.M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives* (Weinhiem: Wiley-VCH: 1995).
3. J.P. Hansen, I.R. McDonald, *Theory of Simple Liquids* (London: Academic Press: 2005).
4. H.P. Klug, L.E. Alexander, *X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials* (Weinhiem: Wiley Interscience Publication: 1974).
5. K.H. Grundzuge, *Der Anorganischen Kristallchemie* (Berlin: Verlag: 1968).
6. A. Feltz, *Amorphe und Glasartige Anorganische Festkörper* (Berlin: Academie – Verlag: 1983).
7. B. E. Warren, *X-ray Diffraction* (New York: Dover: 1990).
8. N.F. Mott, E.A. Davis, *Electronic processes in non-crystalline materials* (Oxford: Clarendon Press: 1971).
9. *Amorphous Silicon and Related Materials* (Ed. by H. Fritzsche) (Singapore: World Scientific: 1989).
10. P. Biswas, R. Atta-Fynn, D.A. Drabold, *Phys. Rev. B* **69**, 195207 (2004).
11. W. Wei, *J. Non-Cryst. Solids* **81**, 239 (1986).