The interference of electron waves scattered on the atomic pair of the substance in diffraction studies

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It was studied how the orientation of the atomic pair of the substance relative to an electron ray influences the general character of the distribution of interference intensity from the given pair as well as the qualitative contribution of atomic pairs with different orientation to the total diffraction pattern of the amorphous substance. It follows from here that experimental electron-diffraction data reflect the structure of amorphous substances which is predominantly characteristic for the directions oriented relative to the probing ray at angles $\alpha = 40°\text{-}90°$. The structure in the directions close to an incidence vector of the probing ray is not actually reflected in them.

1. Introduction

Nowadays studying the structure of amorphous substances many scientists often proceed from the fact that the latter do not demonstrate the perfect disordering at the local structural level. In many cases the tendency of amorphous substances to the predominating formation of some local atomic configurations in comparison with others becomes apparent. This is shown by such "thin" structurally-connected effects as the molecular-phase separation [1], natural and stimulated optical anisotropy [2,3], intermediate structural phases [4], reverse "thermal windows" [5] and so on. These effects can be seen in different amorphous states, particularly in glasses and thin films that can serve as an important supplementary moment for better understanding of the character and mechanisms of these effects to be realized.

On the other hand, the thin-film state of amorphous substances is just considered as the most promising one from the point of view of its practical application. That's necessary to widen the experimental studies of amorphous substances just in the form of thin films. For such objects the most effective methods of structural studies are the transmission electron microscopy and electron diffraction analysis. But electron diffraction methods with respect to amorphous substances are developed much less than X-ray ones and yield to them as to accuracy of the results obtained. This is due to the fact that the electron diffraction method for amorphous substances has been developed on the basis of simple "mechanical" application of many approaches of the X-ray diffraction method without taking into account the essential differences between them in full. Such a situation makes the problem of detailed analysis of reliability and accuracy of the results obtained by electron diffraction methods for amorphous substances very important. In connection with this, the true understanding of the essence of the interference process of electronic waves on amorphous substances which predetermines the formation of diffractograms becomes especially important because it may greatly influence correctness of the interpretation of the experimental results obtained and accuracy of the determination of structural parameters.

2. Modeling

It is very convenient to choose a pair of atoms (a two-atom molecule) as the simplest basic structural element for studying the formation process of the diffraction pattern [6] as the interference of waves on such a pair reflects the majority of peculiarities of the diffraction process most pellucidly. The diffraction pattern obtained is the result of averaging the interfering waves from atomic pairs with different spatial orientation. Each orientation of the atomic pair gives its specific interference pattern. Therefore the most important problem is how the orientation of the atomic pair of the substance relative to an electron ray influences the general character of the distribution of interference intensity from the given pair as well as the qualitative contribution of atomic pairs with different orientation to the total diffraction pattern of the amorphous substance.

The subject of our studies is an idealized model in the form of two similar atoms A_1 and A_2 whose mutual position in space is preset by an interatomic distance vector $\vec{r}$ (Fig. 1). The orientation of axes in the laboratory coordinate system xyz and the position of its origin are chosen so that one of the atoms (for example A_1) is at the origin of coordinates and a vector $\vec{r}$ is in the plane $x0z$. The probing electron ray in the form of a plane wave is incident onto the atoms along the axis z. The direction of its incidence is preset by a wave vector $\vec{k}$ so

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that $|\vec{k}_o| = \dfrac{2\pi}{\lambda}$ where λ is the wavelength of electrons of the probing ray. The orientation of an interatomic vector $\vec{r}$ relative to an incident electron ray will be preset by an angle α.

The coherent electron scattering intensity by such a pair of atoms will be analyzed in the arbitrarily chosen direction specified by a wave vector $\vec{k}$ of the scattered wave. The equality $|\vec{k}_o| = |\vec{k}|$ ensures the condition for coherence of the scattering process. The direction of the scattered wave propagation relative to the probing ray will be preset by a scattering angle 2θ. To set the mutual displacement of vectors $\vec{r}$ and $\vec{k}$ we build the projection OC of a wave vector of the scattered wave onto the plane x0y. Then an angle φ between the projection OC and axis x together with an angle α will specify the direction of electron scattering in space relative to an interatomic vector $\vec{r}$.

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In the general case the intensity of an electron ray scattering by the atomic pair of one sort [7] is

$$I(s) = F^2(s) \sum_{i=1}^{2} \sum_{k=1}^{2} \exp[j\vec{s}(\vec{r}_i - \vec{r}_k)] , \quad (1)$$

where $F(s)$ is an atomic factor of electron scattering by these atoms, $\vec{s} = \vec{k} - \vec{k}_0$ is the vector of electron scattering, $\vec{r}_i$ is the radius-vector of i-atom in the laboratory coordinate system. In accordance with the conditions accepted by us a vector $\vec{s}$ has the same projection onto the plane x0y as a vector $\vec{k}$ (Fig. 1). Simultaneously, the scattering vector $\vec{s}$ forms an angle θ with this plane that follows from geometric plottings in Fig. 1 (an angle between a vector $\vec{s}$ and segment O″C″). Besides, $|\vec{s}| = 2|\vec{k}|\sin\theta = \dfrac{4\pi}{\lambda}\sin\theta = s$.

The account of all mentioned conditions and simple transformations of the double sum (1) give the following

relation for the intensity of electron scattering on the atomic pair depending on their orientation in space relative to the probing ray:

$$I(s) = F^2(s)\{exp[\ j\vec{s}(\vec{r}_1 - \vec{r}_1)] + exp[\ j\vec{s}(\vec{r}_1 - \vec{r}_2)] + \\ + exp[\ j\vec{s}(\vec{r}_2 - \vec{r}_1)] + exp[\ j\vec{s}(\vec{r}_2 - \vec{r}_2)]\} = \\ = F^2(s)[2 + \exp(j\vec{s}\vec{r}) + \exp(-j\vec{s}\vec{r})] = \\ 2F^2(s)[1 + \cos(\vec{s}\vec{r})] .$$

Expanding the scalar product $\vec{s}\vec{r}$ we get the final relation for the intensity

$$I(s) = 2F^2(s)[1 + \cos(sr\cos\beta)], \quad (2)$$

where β is the angle between vectors $\vec{s}$ и $\vec{r}$. To represent an angle β in Fig. 1 it is convenient to parallelly shift a vector $\vec{s}$ into the position $\vec{s}\,'$ so that its origin will match that of a vector $\vec{r}$.
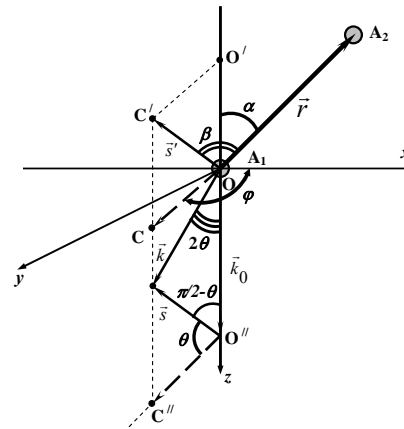

Fig. 1. The simplest basic structural element for studying the formation process of the diffraction pattern.

For general analysis of the pattern of electron scattering by changing the orientation of the atomic pair in space it is necessary to set the relation between angles α, β and θ. For this we will analyse geometric peculiarities of the scattering process in detail. As it is seen from Fig. 1 the cone of a scattering wave which is the result of the rotation of a vector $\vec{k}$ relative to the axis z for an angle φ from zero to 360 degrees corresponds to one and the same scattering angle 2θ. Such rotation of a vector $\vec{k}$ may be replaced by the identical rotation of a scattering vector $\vec{s}$ (or $\vec{s}\,'$) for the same angles φ. As a result a vector $\vec{s}$ being the generatrix will circumscribe its own cone (Fig. 2). The necessary constructions from Fig. 1 are plotted in this figure. From geometry some simple relationships follow: OB = OC′ = s; O′C′ = O′B = s·cosθ, OO′ = s·sinθ, O′E = OO′·tgα = s·sinθtgα, OE = OO′/cosα = s·sinθ /cosα. Then considering triangles O′C′E и OC′E it follows: s^{2}cos$^2\theta$ + s^{2}sin$^2\theta$tg$^2\alpha$ - 2s^{2}cosθ sinθ tgαcosφ = s^2 + s^{2}sin$^2\theta$/cos$^2\alpha$ - 2s^{2}sinθcosβ/cosα. Having done simple transformations in this relation we get that cosβ = =sinθ cosα + cosθ sinαcosφ. By substituting the value of cosβ into (2) we get in an explicit form the intensity of an electron ray scattering versus the

orientation of atomic pair in space (i.e. of an angle α) and versus the direction of scattering (i.e. of angles θ and φ):

$$I(s) = 2F^2(s)\left\{1 + \cos[\frac{4\pi}{\lambda} r \sin\theta(\sin\theta\cos\alpha + \sin\alpha\cos\theta\cos\varphi)]\right\}$$
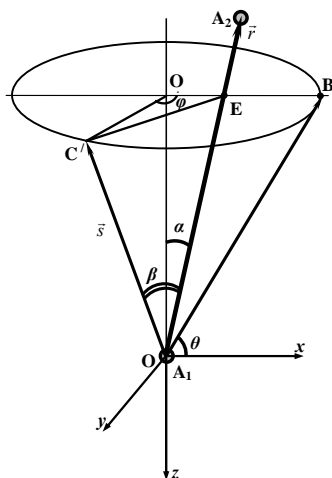(3)

Fig. 2. Reconstructed model of the simplest basic structural element.

The relation obtained shows that for each fixed orientation of one pair of atoms relative to an incident ray its own angular distribution of scattering intensity appears. The character of this distribution is set by a "structural" part of scattering (3) which is described by the relationship of complex argument cosine. To study the peculiarities of such scaterring in detail we have calculated the spatial distribution of the intensity of electron scattering on the atomic pair at its different orientation relative to the probing ray. While calculating we have taken the values r = 2 Å and λ = 0.1 Å typical for electron-diffraction studies. In accordance with symmetry of the scattering pattern an angle α changes from 0 to $\pi/2$ and angles θ and φ – from 0 to π. The calculations have been done for limit values of magnitude s = 100 nm^{-1} that complies with real conditions of the electron-diffraction experiment.

In diffraction experiments with amorphous substances a great number of atomic pairs with different orientation relative to an electron ray take part in the formation of diffraction pattern. It is reasonable that different diffraction patterns will be observed at different orientation of atomic pairs in space. For theoretical analysis of such patterns we have used an idealized model of a two-atom gas whose molecules can orientate in space with different ranges of orientation angles α.

In order to calculate the diffraction pattern of such gas it is necessary to average the intensity (3) for one molecule over all its orientations in space allowed by this or that range of angles α. When averaging, one of atoms of each molecule will be fixed in the origin of the laboratory coordinate system. Such simplification does not practically influence the results as the distances between separate gas molecules (nanometres) are much less than the one to the

plane on which the diffraction pattern is fixed (approximately a meter). At such simplification the other atom of any molecule will take its own position on the sphere surface with a radius r in the process of averaging.

From the mathematical point of view the averaging means the integration of intensities (3) over all the angles which specify the character of orientation of gas molecules relative to the probing ray. The limits of the change in these angles are determined by model conditions which are imposed on gas. From the point of view of the electron diffraction the condition is the most topical when an angle φ may change all over the range from 0 to 2π and the orientation angle α will be in the strictly defined range from α_1 to α_2 (see Fig. 1). For such a model the distribution of intensities in the diffraction pattern is symmetrical to the central ray and is set by relation

$$\overline{I(s)} = 2F^2(s)\left\{1 + \frac{1}{4\pi}\int_0^{2\pi} d\varphi \int_{\alpha_1}^{\alpha_2} \cos(sr\sin^2\theta\cos\alpha + sr\sin\theta\sin\alpha\cos\theta\cos\varphi)d\alpha\right\} =$$
$$= 2F^2(s)\{1 + i(s)\}$$
(4)

To take the double integral in (4) in an analytical form appears a very complicated problem. That's why for calculations of $\overline{I(s)}$ we have used the tabular integration method.

3. Results and discussion

In accordance with (2) the intensity of an electron ray scattering on the atomic pair is distributed in space by the relationship $\cos(s\cdot r\cdot\cos\beta) = \cos(\frac{4\pi}{\lambda} r\sin\theta\cos\beta$). That is at fixed position of an interatomic vector relative to the probing ray (a fixed angle α) the intensity of electron scattering in the definite position is preset by two independent angles: a scattering angle 2θ and angle β between a scattering vector $\vec{s}$ and orientation vector $\vec{r}$ of a molecule.

The generalized results of calculating the intensity are shown in Fig. 3. Here three-dimentional spatial profiles of a two-atom molecule electron-diffraction patterns at angles of its orientation α=0, 30, 60 and 90 degrees are depicted. Most likely the pattern of electron scattering critically changes with the change in an angle α. During the orientation of an interatomic vector along the probing ray (α = 0) the structural part of electron scattering in the form of peaks of interference intensification of waves is practically absent (Fig. 3a). The first peak for the given electron-diffraction pattern is within the region of 15 Å^{-1}, that is outside the limits of a routine experimental electron-diffraction pattern. In real electron-diffraction patterns the contribution to the structural part of scattering in the form of the first diffraction reflexes is initiated by atomic pairs only with the orientation beginning from α > 10 degrees (Fig. 3b). With further rise of an angle α such contribution greatly increases (Fig. 3c). With approaching the orientation of molecules with $\alpha \approx 90^o$ we

get the scattering pattern (Fig. 3d) in whose formation the reflexes of different orders of diffraction already participate.

The geometrical forms of separated reflexes in space appear very interesting (Fig. 3). Especially a strong increase in anisotropy of electron-diffraction patterns relative to an angle φ with increasing angle α from 0° to 90° draws our attention. As it is seen from Fig. 3 at orientation of molecules with $\alpha = 0°$ the interference pattern exhibit a wide bell-like cylindrically-symmetric unstructural distribution. With increasing α the interference pattern is transformed into extended corrugations along the axis y which approach a parallel wavy surface at $\alpha \rightarrow 90°$ relative to the axis y. Simultaneously an essential narrowing of the central scattering peak takes place.
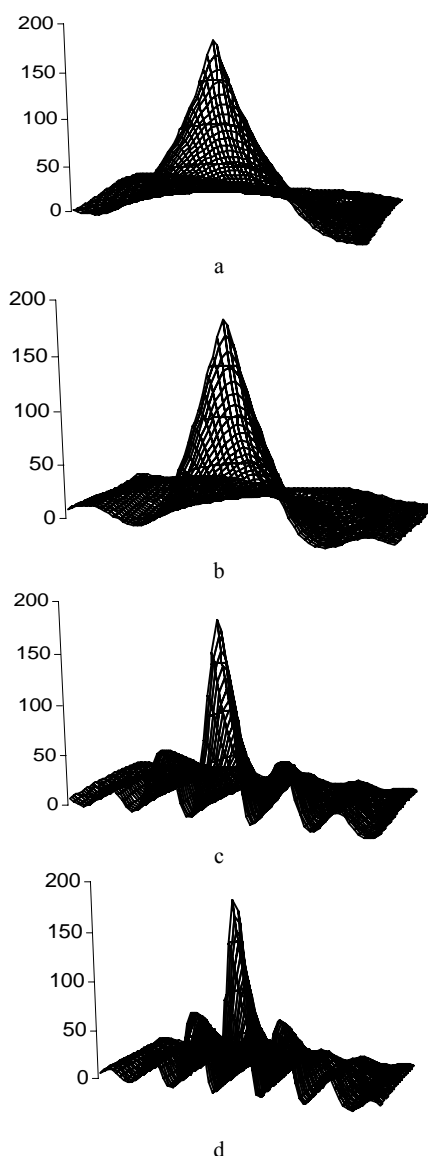

a

b

c

d

Fig. 3. Three-dimentional spatial profiles of a two-atom molecule electron - diffraction patterns at angles of its orientation α = 0°(a), 30°(b), 60°(c) and 90°(d).

The results obtained were compared with the diffraction pattern for a real disordered structure formed by a set of atomic pairs from their equiprobable orientation in space at different ranges of angles α. The electron-diffraction patterns of such a model will present the result of averaging the distributions of intensities over all corresponding orientation angles α of molecules and over all their 360-degree turn relative to the axis z (change in an angle φ) (Fig. 3). The following moment of averaging is important. In accordance with the general character of the magnitude of atomic factors $F(s)$ versus a scattering vector s the intensities of interference peaks sharply drop when they run away from the axis x. Therefore the formation of total interference pattern of the model takes place mainly at the expense of those parts of the lines of reflexes which lie near this axis. Such formation process of separate halos of electron-diffraction pattern presents the superposition of quite complex patterns of intensities of interference electron waves from differently oriented molecules.
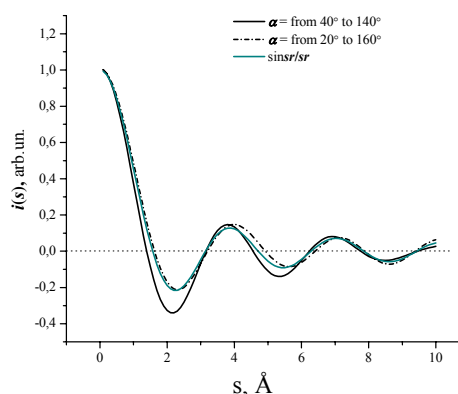

Fig. 4. Electron-diffraction patterns for real disordered structure formed by a set of atomic pairs from their equi-probable orientation in space at different ranges of angles α..

Within the specified limits of angles α and φ the averaged scattering pattern will be fully symmetrical relative to the change in an angle φ and will depend only on a scattering angle 2θ or on the scalar value of the scattering vector s. Moreover, in future it will be enough to consider only the informational structural part of the electron-diffraction pattern $i(s)$, which is preset by the integral in relation (4). In accordance with this, it is graphically convenient to present the results of averaging in the form of one-dimensional distribution of the averaged structural part of scattering intensity $i(s)$ depending on a scattering vector s. In this figure the interference function $\dfrac{\sin(sr)}{sr}$ of our model in the form of a two-atom gas with the equi-probable orientation of its molecules over all directions of space is given (Fig. 4c).

To analyze the structure of amorphous substances by electron-diffraction data it is important to elucidate the magnitude of contribution of molecules with different

spatial orientation to total averaged intensity (4). For this analysis we take into account that maximal scattering intensity by a molecule with any orientation α is observed in the directions with an angle $\varphi = 0$ (Fig. 1, 3). Therefore just for this direction we calculated scattering angles 2θ and scattering vectors s, which accounted for the position of maxima of the first three orders of diffraction from one molecule with changing its orientation α per 5 degrees. The results of such calculations are given in Table 1.

To visually compare the role of diffraction reflexes of separate molecules in the formation of interference function $\frac{\sin(sr)}{sr}$ the positions of these reflexes are "superimposed" on the plot of the given function (Fig. 5). In this figure the positions of the first diffraction reflexes are marked by long dashes, those of the second diffraction reflexes – by medium dashes, and of the third diffraction reflexes – by short ones. The analysis of the pattern in Fig. 5 shows that the main contribution to the formation of interference function is given by pairs of atoms whose interatomic distances are oriented relative to an incident ray at an angle from 40° to 90° (Fig. 5, table). All first diffraction reflexes from such pairs are within the region of the first maximum of interference function. Moreover, only these reflexes participate in the formation of the first peak. The second peak of interference function is mainly formed at the expense of contribution of the second diffractive reflexes from molecules with orientation from 50° to 90°. Here a slight contribution of the first-order reflexes from molecules with angles $\alpha = 20° - 25°$ is added. The form of the third peak, in its turn, is mainly preset by the third-order reflexes from the molecules with orientation at angles from 55° to 90° plus some second-order reflexes from the molecules with angles $\alpha = 30° - 35°$ and only one first-order reflex from the molecules with angles $\alpha = 15°$. Further peaks of the interference function are formed by reflexes of different orders from the molecules with different orientation angles.
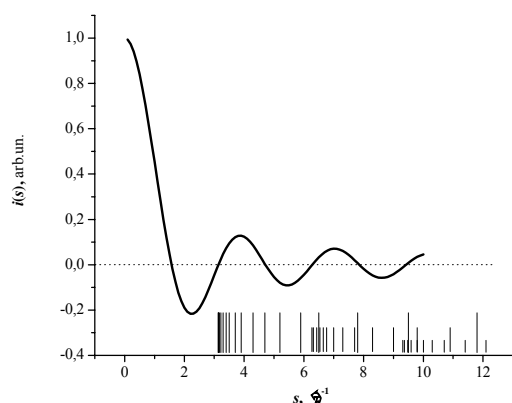

Fig. 5. Interference function and diffraction reflexes of separate molecules (see text).

Thus, at orientation of atomic pairs within the limits of an angle $\alpha < 40°$ their diffraction reflexes do not give the contribution to the first – main peak of the interference function. With gradual decreasing an angle α lower this magnitude, the contribution of their reflexes to next peaks of the interference function also sharply decreases. The contribution of atomic pairs with orientation at angles $\alpha < 10°$ in the experimental diffraction pattern is not practically fixed at all, as the position of their reflexes goes outside the limits of the third peak of experimental electron-diffraction patterns. It is taken into account that in a routine electron – diffraction experiment one can obtain reliable data only within the region of scattering vectors from 1 to 15 Å^{-1}.

More precise calculations of a number of diffraction reflexes whose position gets to the regions of forming the maxima of experimental interference function for our model give the following generalized results.

1. The first, most intensive peak of the interference function includes only more than 60% of the first-order diffraction reflexes.

2. The second peak of the interference function comprises only 10% of the first order-reflexes and more than 50% of the second order-reflexes.

3. The third peak of the interference function combines 5% of the first order-reflexes, 10% of the second order-reflexes and more than 40% of the third order ones.

4. On the whole, the electron-diffraction pattern of a two-atom gas is by 80% formed with atomic pairs oriented relative to the probing ray at angles $\alpha = 40°…90°$.

5. Only about 20% of information in the electron-diffraction pattern is conditioned by atomic pairs oriented relative to the probing ray at angles $\alpha = 15°…40°$.

6. Atomic pairs with orientations which account for angles $\alpha = 0°…15°$ in the formation of the experimental electron-diffraction pattern do not practically take part as their diffraction reflexes get to the region of scattering vectors which are not recorded in a routine electron-diffraction experiment.

The situation becomes more complicated if we take real amorphous substances in whose structure a large set of atomic pairs with different interatomic distances r is realized. The variation of magnitude r in our model of the amorphous structure does not change the general essence of the results obtained but only slightly shifts limit values of registered ranges of an angle α. But the relative contribution of atomic pairs with different interatomic distances to the experimental diffraction pattern greatly changes. In particular, if one takes the interference function for interatomic distance of 0.2 nm as the reference point, its decrease to 0.1 nm reduces the contribution of diffraction reflexes to the interference function within the region of scattering vectors to 100 nm^{-1}, i.e. almost to half. Yet the basic part of short distances participates in the formation of the interference function within the region of scattering vectors which are more than 100 nm^{-1}.

Table 1. The values of scattering angles 2θ and scattering vectors s, which account for the position of diffraction reflexes of different orders from one atomic pair with an interatomic distance r = 2 Å at its different orientations α relative to the probing electron wave with λ = 0.1 Å (angle φ = 0°).

α, degr.	Diffraction order					
	1		2		3	
	2θ, degr.	s, Å^{-1}	2θ, degr.	s, Å^{-1}	2θ, degr.	s, Å^{-1}
0	18.3	20	-	-	-	-
5	13.8	15	21	22.7	-	-
10	10.8	11.8	18	19.5	-	-
15	8.7	9.5	15	16.3	20	21.7
20	7.2	7.8	13	14.1	17.8	19.3
25	6	6.5	11.3	12.3	15.9	17.3
30	5.4	5.9	10	10,9	14.2	15.4
35	4.8	5.2	9	9,8	13	14.1
40	4.3	4.7	8.3	9,0	12	13.1
45	3.9	4.3	7.6	8,3	11.1	12.1
50	3.6	3.9	7.1	7,7	10.5	11.4
55	3.4	3.7	6.7	7,3	9.9	10.7
60	3.2	3.5	6.4	7,0	9.5	10.3
65	3.1	3.4	6.2	6,76	9.2	10.0
70	3	3.3	6.1	6,65	9	9.8
75	2.95	3.22	6	6,54	8.8	9.59
80	2.91	3.17	5.9	6,43	8.7	9.48
85	2.89	3.15	5.8	6,32	8.6	9.37
90	2.87	3.13	5.75	6,27	8.55	9.31

The mentioned tendency of reducing the contribution of atomic pairs with small interatomic distances becomes significantly stronger due to the fact that chemical bonds with such lengths are formed by light atoms which have essentially less atomic factors of electron scattering. Therefore weak oscillation intensities of interference functions from such pairs will "be lost" against the background of strong oscillations conditioned by the pairs with large *r*.

4. Conclusions

The interference function of complex amorphous substances obtained under routine conditions of the electron-diffraction experiment reflects the contributions of different interatomic distances not in proportion to their number in the real structure. Correspondingly, RDF methods give reliable data only for isotropic amorphous substances strictly in the respect of structure. Moreover, to obtain reliable data on the structure of such substances by electron-diffraction methods it is necessary to comply with some important statements:

1. Widening the registration region of the electron-diffraction pattern up to the values not less than 20 Å^{-1} that accounts for an equal contribution of different interatomic pairs with accuracy up to 10 %.

2. Increasing the sensitivity of registration methods to reliably record weaker contributions from atomic pairs with small interatomic distances at large *s* and from light atoms on the total electron-diffraction patttern.

3. Making measurements of the intensity of electron scattering with different orientation of the sample under study relative to the probing ray in order to extend the information density of experimental electron-diffraction patterns.

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