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Development of Model Representations of Materials with Ordered Distribution of Vacancies

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Abstract: This paper presents an overview of research results on the physical and technological features of crystal formation with an ordered distribution of vacancies. It is noted that the composition and properties of complex chalcogenide phases are not always described by the traditional concepts behind Kroeger's theory. Model concepts are considered in which the carriers of properties in the crystalline state are not molecules, but an elementary crystalline element with a given arrangement of nodes with atoms and vacancies. It is established that the introduction of the term "quasi-element atom" of the zero group for a vacancy allows us to predict a number of compounds with an ordered distribution of vacancies. Examples of the analysis of peritectic multicomponent compounds and solid solutions based on them are given. Quasi-crystalline concepts are applicable to perovskite materials used in solar cells. It is shown that the photoluminescence of perovskite lead-cesium halides is determined by crystalline structural subunits i.e., the anionic octets. This is the reason for the improvement in the luminescent properties of colloidal quantum $CsPbBr_3$ dots under radiation exposure conditions.

Keywords: chalcogenide; perovskite; vacancy; triangulation; tetrahedration; quasi-element; radiation resistance

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Citation: Muratova, E.N.; Moshnikov, V.A.; Zhilenkov, A.A. Development of Model Representations of Materials with Ordered Distribution of Vacancies. *Crystals* **2024**, *14*, 1095. https://doi.org/10.3390/cryst14121095

Academic Editor: Rajratan Basu

Received: 9 November 2024
Revised: 9 December 2024
Accepted: 11 December 2024
Published: 19 December 2024

1. Introduction

This work is devoted to a crystal-chemical model capable of describing a set of materials with an ordered distribution of vacancies.

At present, the concepts developed by Kroeger F., Novoselova A.V., Zlomanov V.P. and others are used almost everywhere [1,2]. These concepts allow for describing changes in electrophysical properties with a change in deviation from stoichiometry within the homogeneity region and ensuring control over the properties of the resulting materials. The essence of the model is based on finding the equilibrium concentrations of defects, both neutral and charged. When a new type of defect is introduced, additional equations appear in the complete system of equations. These include the equation of electroneutrality and the equation of effective masses for describing the concentration of charge carriers, as shown in Equation (1).

$$n\,p = n_i^2 \tag{1}$$

It is important to note that point defects in the sublattice of a metal and non-metal during ionization produce defects of different charge types. When extending these concepts to multicomponent materials (ternary, quaternary, etc.), the approximation devised by Goryunova N.A. works well [3].

In the middle of the 20th century, Goryunova N.A. proposed an effective method for predicting new multicomponent semiconductor materials with a diamond-like lattice. In such cases, the structure-forming crystalline element should be characterized by the presence of four electron bonds per individual atom of the structure, as well as an effective number of corresponding filled electron shells with eight electrons per atom in the non-metal sublattice. The problem of predicting a semiconductor with a diamond-like lattice is solved by a geometric thermodynamics method. For example, when constructing ternary compounds in the Gibbs triangle with the vertices of these three elements, the "four" line (for an average number of electrons per atom equal to four, conditions «4») and the "eight" line (eight electrons per atom on the non-metal lattice, conditions «8») are constructed.

Let us explain this using the example of Ag-In-S. The lines of the "four" line and "eight" line (Figure 1) intersect inside the triangle, indicating a single ternary compound corresponding to the formula composition $AgInS_2$. At the same time, a whole family of compounds corresponding to the formulas $AB_{2n+1}C_{3n+2}$ (for example, $AgIn_5S_8$) is known for these materials. This family of compounds are called "materials with an ordered distribution of vacancies" [4]. Thus, predicting the compositions of these materials does not follow Goryunova's rules.

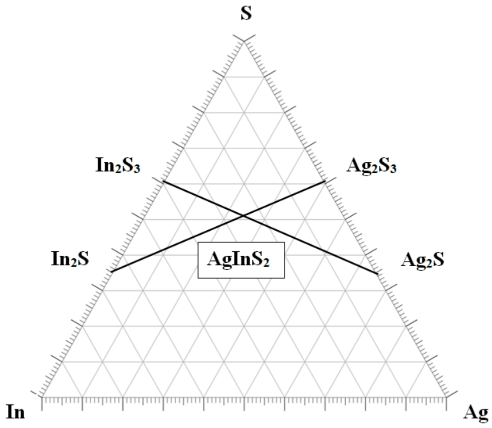


Figure 1. Triangulation of the ternary system Ag-In-S, (In_2S-Ag_2S_3 is the "four" line, In_2S_3-Ag_2S is the "eight" line).

The purpose of this work is to develop model concepts that provide an explanation for the emergence of a material class with an ordered distribution of vacancies.

2. Materials and Methods

2.1. Materials with an Ordered Distribution of Vacancies

A modified crystal chemical model is proposed to describe materials with ordered vacancies and built-in interstitial atoms. It is a continuation of the concepts of defective crystals developed by Professor Ormont B.F. [5]. This model considers the application of these concepts in modifying Goryunova's model.

In Kroeger's model all interactions are described by the quasi-chemical reactions of substances in molecular form. In contrast, in the Ormont's model [5,6] the carrier of the properties of materials is a small volume of the crystal lattice. Only in rare cases can molecular approximations be used to describe the properties of molecular crystals.

The system of equations for calculating the defectiveness of crystals according to Kroeger's model is based on the interaction of molecular forms. Kroeger's approach allows all defect concentrations to be calculated when setting the pressure values of the control component in cases where distributed defects (vacancies or interstitial atoms) do not arise in the systems. But many scientists, for example, Ormont B.F. [6], noted that molecular interactions cannot be used in all cases for defect analysis in the crystalline state of a solid. The carrier of the properties of the crystal is the structural element with all the resulting dependencies of point symmetry and translation. In the cases we are considering, this means the following. There are materials containing elements of different valence in different sublattices. When analyzing their crystalline state, structural vacancies may arise that are not vacancies in the Kroeger's theory. In other words, according to the condition of the completeness of valence bonds, in the structure-forming element of the crystal such a vacancy will not play the role of a point defect associated with deviation from stoichiometry.

We propose to consider such a vacancy as an element of the zero group with the preservation of all subsequent calculation operations.

Thus, the "initial stoichiometric composition" contains structure-forming vacancies. In this case, similar to Kroeger's concept, the formation of excess elements in the metal and non-metal sublattice will lead to a change in stoichiometry and a change in electrophysical properties during the ionization of excess defects.

Let us consider the crystal structure of a ternary system formed by binary compounds consisting of elements with different valence states. Empty nodes may arise in the structure-forming crystalline volume of such a system. These nodes cannot be considered vacancies in the traditional Kroeger's approximation. An empty node is an integral part of a crystalline structural element. It does not contribute its electrons to the formation of chemical bonds, but it participates in the redistribution of electron density. Thus, the charge is fractional.

The proposed model introduces a new concept for a quasi-element. It is responsible for an unfilled node in the crystal-forming volume. This expands the predictive capabilities of Goryunova's approximation. In old terms, this is an "atom of the zero group" for structure-forming vacancies.

The simplest example of the binary compound In_2S_3 is shown in Figure 2. The formula composition has an unequal number of atoms in the metal and non-metal sublattices. If we want to consider the possibilities of forming a crystal structure with an equal number of atoms in the metal and non-metal sublattices, we must admit the existence of empty sites as an element of zero valence (quasi-zero group). As can be seen, under the conditions of «4» and «8», there is also an intersection on the triangulation of the pseudo-ternary system. It corresponds to an ordered vacancy. Taking into account the concentration of structural vacancies of the zero group [V], the crystallochemical composition will look like $[V]_1In_2S_3$ or in a simplified form of writing, $[V]In_2S_3$.

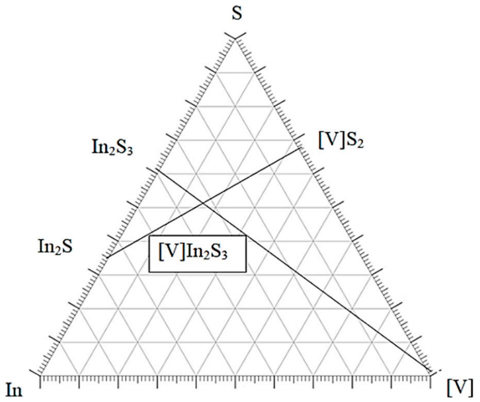


Figure 2. Triangulation of the pseudo-triple system [V]-In-S, (In_2S-$[V]S_2$ is the "four" line, In_2S_3-[V] is the "eight" line).

It can be seen that the triangulation of the pseudo-ternary system also has an intersection that corresponds to the ordered vacancy $[V]In_2S_3$. Thus, it becomes clear that this system is not a binary, but a quasi-ternary compound, with ordered vacancies.

In the Ag-In-S system, compounds with an ordered distribution of vacancies over the metal sublattice should be considered not as a ternary quasi-chemical system, but as a quaternary system with a structural vacancy (an element of the zero group), [V]-Ag-In-S (Figure 3). Then, the triangulation conditions turn into the tetrahedration condition.

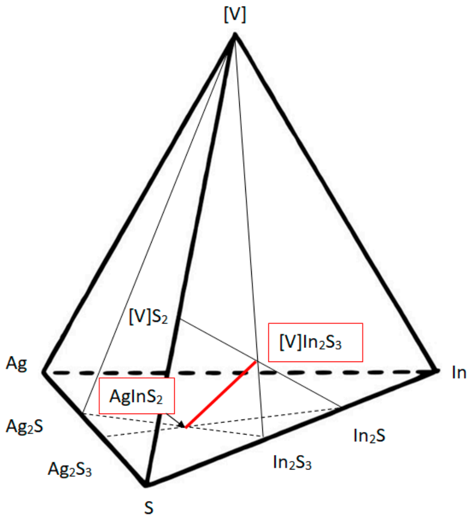


Figure 3. Tetrahedration of the pseudo-quaternary system [V]-Ag-In-S. The arrow points to a known chemical compound that we have marked in Figure 1.

On the lower face there is a point satisfying conditions "4" and "8"; this is $AgInS_2$ and there is no element [V] on it. To satisfy Goryunova's condition (Figure 1), it is necessary to consider the lateral face. This condition corresponds to the completeness of the connections in the presence of a crystal-forming zero element—an In_2S_3 vacancy. Therefore, the solution that satisfies conditions «4» and «8» will lie on the line connecting these points.

Since this article is a review, it is appropriate to note the almost forgotten fact of the registered discovery of V.P. Zhuze et al. [7]. This is based on the fact that the introduced metal atoms that fall into the nodal vacancy of the metal sublattice do not participate in the formation of chemical bonds and do not change the conductivity of the semiconductor. Thus, it would seem that there is a violation of the most important of semiconductors—their sensitivity to doping. From the point of view of the completeness of valence bonds, the inertness of metallic impurities in semiconductors with distributed vacancies is quite understandable. Then, a red line is formed in the tetrahedron, on which the conditions of «4» and «8» are satisfied at any point.

Let us continue to consider the pseudo-quaternary system [V]-Ag-In-S. Using the obtained data, the authors [8] derived a discrete series in which changes in the ordering of vacancies occur, as shown in (Equation (2)).

$$V_{i/(i+1)}Ag_{1/(i+1)}In_{(2i+1)/(i+1)}S_{(3i+2)/(i+1)} \tag{2}$$

where $AgInS_2$ is the stoichiometric composition:

i = 0 − stoichiometric $AgInS_2$;
i = 1 − $[V]_{1/2}Ag_{1/2}In_{3/2}S_{5/2}$ − $[V]AgIn_3S_5$;
i = 2 − $[V]_{2/3}Ag_{1/3}In_{5/3}S_{8/3}$ − $[V]_2AgIn_5S_8$ etc.;

It should also be noted that systems with ordered vacancies most often arise along quasi-binary sections. In this case, the formation of such materials in multicomponent structures formed during peritectic reactions is especially relevant. During peritectic reactions, there is an equilibrium $L_{ж} + S_1 \rightarrow S_2$. Obtaining such materials is difficult. This is due to the fact that the compound does not form at a temperature above the peritectic temperature. However, at temperatures significantly below the peritectic temperature, the formation of a crystalline framework is difficult.

As an example, let us consider the peritectic compounds $PbGa_6Te_{10}$ and $SnGa_6Te_{10}$ and solid solutions based on them [9–11]. These materials are currently finding increasing application as promising thermoelectric materials and materials for nonlinear optics [12–14].

For clarity, Figure 4 shows a phase diagram along the PbTe-Ga_2Te_3 section. It follows from this that S_1 is a limited solid solution based on Ga_2Te_3 with a small content of PbTe; L is a liquid containing Pb, Ga, and Te; and S_2 is a peritectic compound with a formula composition close to $PbGa_6Te_{10}$. The figure shows experimental points and boundary lines of stable states of existence of individual phases.

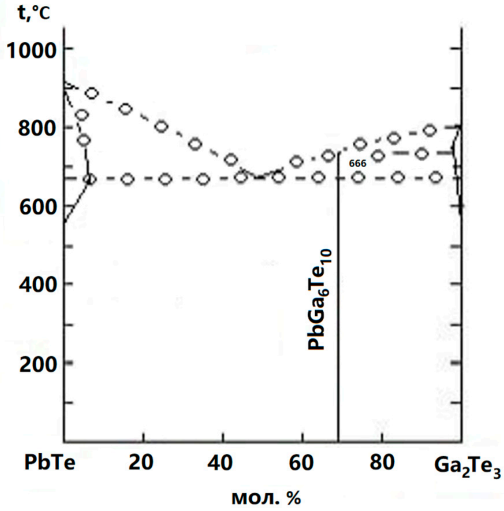


Figure 4. State diagram of the PbTe-Ga_2Te_3 system.

By definition, the peritectic phase diagram is characterized by incongruent melting of solid-phase $PbGa_6Te_{10}$ (S_2) with the formation of a new solid phase of a limited solid solution based on the compound Ga_2Te_3 (S_1) and a melt containing Pb, Ga and Te. At temperatures above the peritectic temperature, the compound $PbGa_6Te_{10}$ is not formed. At temperatures below the peritectic temperature, the formation of $PbGa_6Te_{10}$ compounds is also unlikely due to the limitation associated with the need to satisfy the complex composition condition (17 elements per basic $PbGa_6Te_{10}$ formula).

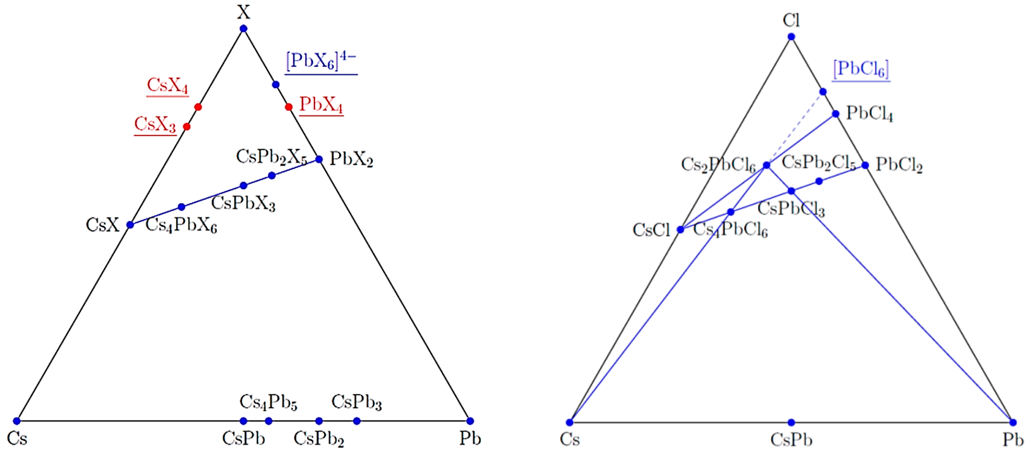
As already noted, there is a complexity of the analysis in the solid part of the phase diagrams along the quasi-binary sections of multicomponent compounds obtained from the peritectic reaction. In fact, it is necessary to order the crystal lattice. The brevity of the formula composition for a cell of the crystal lattice according to the X-ray structural analysis data is 2.

The first tasks for a more thorough analysis of the PbTe-Ga_2Te_3 phase diagrams were set after the discovery of microinclusions with a predicted composition of $PbGa_6Te_{10}$ in PbTe crystals doped with Ga. The analysis of microinclusions was carried out by X-ray spectral microanalysis. However, unlike traditional methods of quantitative analysis, the work used the proposed method of the ratio of relative intensities (RRI), which is discussed in more detail in [15].

This method is based on the fact that with certain relationships between the energy parameters of the analytical lines of the characteristic X-ray radiation of the elements in the analyzed system, it is possible to significantly expand the functional capabilities. In this case, the energy of the analytical K-alpha line of gallium is close to the energy of L-alpha line of lead. This allows the composition to be determined from the RRI of gallium and lead with a weak dependence on the size of microinclusions, the value of the accelerating voltage and the change in the selection angle of the X-ray radiation. Inclusions in which the RRI was almost constant and corresponded to the formula composition $PbGa_6Te_{10}$ were found.

2.2. Quasi-Crystalline Representations for Perovskite Materials

Perovskites are another example of the importance of the crystal-chemical hierarchical structure, for example, $CsPbX_3$. In these, photoluminescence (PL) is associated with the octet $[PbX_6]^{4-}$ and is preserved at high irradiation doses, as well as during the formation of mixed crystals. In this case, the equilibration of the multicomponent system is not required, and the replacement occurs with “bricks” or octets. Figure 5a shows a section that was most often obtained using the example of the Cs-Pb-X_3 system [16–18]. It is evident that a number of specific compounds are formed. According to the triangulation theory, if two quasi-binary sections intersect, then a compound is located at their intersection. Therefore, the study of cuts suggests that there must be cuts that pass through this point. In order to find this cut, it was proposed to add a crystal-chemical structure-forming element—the octet $[PbX_6]^{4-}$ (Figure 5b)—as a configuration point. Then, if in the Cs-Pb-Cl system, the lines $[PbCl_6]$–Cs and CsCl–$PbCl_4$ are drawn, two points will appear at the intersections. According to the hypothesis proposed by the authors of this article, in this case there should be compounds at the intersection points.



(**a**) (**b**)

Figure 5. The main compounds of three-component systems of lead-cesium halides on the Gibbs triangle (underlined binary compounds do not exist for all halogens X from the series Cl, Br, I) and partial triangulation of the system using the example of $CsPbCl_3$) [17].

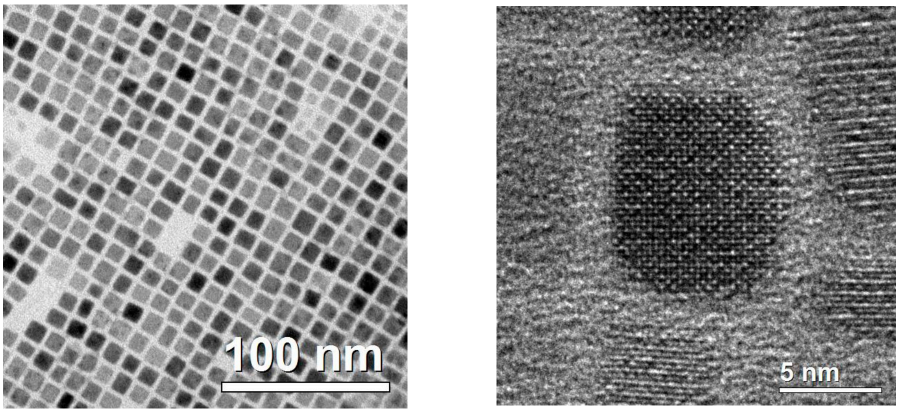
The possible compounds for halogens are highlighted in red. The structural unit highlighted in blue is geometrically an octahedron of a complexing lead ion coordinated by six halogen atoms. This is an element that is not typical for the classical consideration of triangulation. The blue dots represent the compounds that can form at the intersection of the line emanating from this structural unit.

Figure 5b shows examples of the determination of new compounds, including the compound $CsPbX_3$. The presence of these compounds was confirmed by the authors of [19] in 2000.

3. Results and Discussion

The TEM images (Figure 6) show that the structure of the $CsPbBr_3$ nanocrystal is composite. Individual atoms can be distinguished, rows of atoms are well formed, and a ligand shell of 12 C chains is visible in the images.

TEM images were obtained on a JEM-2100F microscope at an accelerating voltage of 200 kV and a resolution of 0.19 nm. The cubic shape of the nanocrystals can be noted. The light “layers” between the nanocrystals are the coating of oleic acid and oleylamine. The contrast of the image is determined by the fact that, unlike the organic shell, the main material of the nanocrystal consists of heavier elements. The different contrast of the nanoparticles in the TEM image can be explained by the fact that the nanocrystals are composed of a different number of planes.



(**a**) (**b**)

Figure 6. High-resolution transmission electron microscopy images of $CsPbBr_3$ nanocrystal [17]. (**a**) TEM images with 100 nm resolution; (**b**) TEM images with 5 nm resolution.

Improving the triangulation of the system made it possible to explain the observed experiments, including the rapid change in the composition of solid solutions, and as a consequence, the rapid change in optical properties [17]. This is explained by the fact that diffusion occurs according to the intouchment principle. In other words, not just atoms, but entire octets, are exchanged with the solution.

With such an exchange process, a sharp drop in intensity can be observed (insert in Figure 7). However, when some octets are completely replaced by others, the intensity increases again. With a decrease in intensity, the half-width of the spectrum increases.

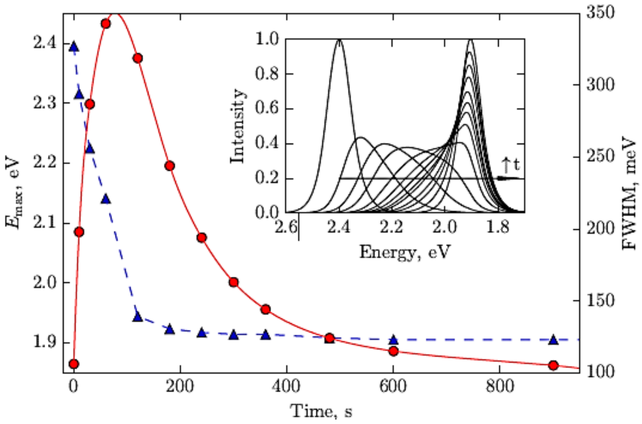


Figure 7. Dynamics of changes in photoluminescence spectra during the anionic substitution of Br–I: triangles represent the time dependence of the energy corresponding to the maximum PL intensity, and dots represent the time dependence of the half-width of the PL line [17].

The proposed PL model of lead cesium halides perovskite determined by the structural units of anionic octahedra was confirmed by experiments on the radiation stability of $CsPbBr_3$ nanocrystals [16]. In these experiments, the stability of the PL properties of perovskites was shown to be higher in the $CsPbBr_3$ sample compared to commercial samples of CdSe/ZnS nanocrystals. With increasing absorbed dose, a gradual decrease in the absolute value of luminescence was observed. At a dose of 2.3 MGy, a significant decrease in PL was observed with the appearance of an additional short-wave band.

The physicochemical features of the lead cesium halide system and the absence of bands associated with defect states in the PL spectra allow us to make an assumption about the implementation of stability with respect to the formation of defects in this system. The effect of rapid anion exchange also indicates that the system tends to restore the structures of anionic octahedra. These anionic octahedra are the basic crystal chemical structural units and are responsible for PL.

4. Conclusions

This paper presents the results of the modernization of physicochemical methods based on the triangulation of systems. A tetrahedration model is presented for nanostructures in I-III-VI systems taking into account the participation of ordered vacancies with the redistribution of electron bonds in the structure formation. The model predicts and explains the formation of families of compounds with ordered vacancies in these systems.

It is shown that the physicochemical triangulation patterns of the Cs-Pb-X system (X = Cl, Br, I) and the growth of $CsPbX_3$ nanocrystals are determined not only by binary compounds on the edges of the Gibbs triangle, but also by configuration points corresponding to the anionic octahedra $[PbX_6]^{4-}$. The proposed model of the PL of lead cesium halide perovskites, determined by the structural units of anionic octahedra, makes it possible to explain the effect of the radiation stability of $CsPbBr_3$ nanocrystals.

Author Contributions: Methodology, E.N.M. and V.A.M.; software, A.A.Z.; validation, E.N.M.; formal analysis, E.N.M. and V.A.M.; investigation, V.A.M.; resources, E.N.M., V.A.M. and A.A.Z.; data curation, E.N.M.; writing—original draft preparation, E.N.M.; writing—review and editing, V.A.M.; funding acquisition, A.A.Z. All authors have read and agreed to the published version of the manuscript.

Funding: The study was supported by the Russian Science Foundation Grant No. 23-42-10029, https://rscf.ru/en/project/23-42-10029/ (accessed on 20 December 2022). The research is partially funded by the Ministry of Science and Higher Education of the Russian Federation as part of the World-class Research Center program: Advanced Digital Technologies (contract No. 075-15-2022-312 dated 20 April 2022).

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

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