05

Theory of the structure of icosahedral quasicrystals: general principles

© A.E. Madison,[1] P.A. Madison[1,2]

[1] HSE University,
190121 St. Petersburg, Russia
[2] St. Petersburg State Electrotechnical University „LETI“,
197022 St. Petersburg, Russia
e-mail: alex_madison@mail.ru

Received June 28, 2024
Revised October 30, 2024
Accepted October 30, 2024

A unified theory of the structure of icosahedral quasicrystals is proposed, within the framework of which it is possible to describe all three types of quasilattices (P, I, F) and both icosahedral symmetry groups. The theory is based on the combined use of three types of tilings, each of which is characterized by its own basis set of unit cells and its own substitution rules. By analogy with ordinary crystals, the problem of describing the structure of a quasicrystal splits into two stages: filling space with cells and filling cells with atoms, with the only difference that instead of one elementary cell, cells of several types are used, and to fill space with cells, instead of translations, an iterative algorithm of inflation and deflation is used.

Keywords: icosahedral quasicrystals, substitution rules, packings.

DOI: 10.61011/TP.2024.12.60432.216-24

Introduction

This article starts a series of papers on the theory of icosahedral quasicrystals. In this paper, we consider possible structure types of icosahedral quasicrystals, a unified approach to the construction of icosahedral packings, as well as properties common to all structure types. In subsequent papers, we intend to separately consider in detail the features of constructing quasilattices of various types and the enantiomorphism phenomenon in them.

Icosahedral quasicrystals were discovered by D. Shechtman [1], for which he was awarded the Nobel prize. The editors of Nature journal ranked this discovery as one of the key milestones in the development of modern crystallography [2], emphasizing also the contribution of A. Mackay, who predicted the existence of quasicrystals based on simulation of the diffraction pattern of the Penrose tiling [3], and P. Steinhardt, who gave the first theoretical explanation of the quasicrystalline long-range order [4,5].

Structure analysis of quasicrystals is still an unresolved problem [6]. It is known that icosahedral quasicrystals can be of three types: P, I, F [7,8]. They are the analogues of the primitive, body-centered and face-centered cubic lattices and should be obtained by projecting appropriately centered six-dimensional cubic lattices from 6D-space. However, no any clear illustrations of the corresponding 3D-quasilattices have been provided so far. Generally speaking, projection from the higher-dimensional metric spaces (not necessarily Euclidean) opens the way to the design of potentially possible hierarchical structures of the most general type, while the true chemical or physical nature of the subunits being packed should be considered as a secondary factor [9].

Historically, the first way to describe the structure of quasicrystals was based on the tiling theory. Socolar and Steinhardt showed that the entire space can be filled in a natural way with four types of zonohedra according to the face-to-face principle without gaps and overlaps [5]. Surprisingly, zonohedral tiling has almost never been used in practice when solving real structures. Later, Danzer introduced the space tiling into four types of tetrahedra, which also has global icosahedral symmetry [10], and then published a paper stating the complete equivalence of both tetrahedral and zonohedral tilings [11]. In fact, it was only about their mutual local derivability, i.e. that the tiles of one of them can be dissected into smaller pieces, which can then be regrouped into tiles of the second tiling [12]. Below we show that Socolar–Steinhard tiling and Danzer tiling are characterized by different inflation factors, contain different number of nodes, and generate quasilattices of different types (P and F, respectively). An interesting fact: in Danzer's fundamental study [10], namely in section „Open problems“ yet another tetrahedral tiling is casually mentioned, which has since virtually gone unnoticed in the scientific literature. We examined it [13] and came to the conclusion that it is the missing third tiling, which generates a quasilattice of I-type.

The tiling into prolate and oblate rhombohedra, also called 3D-Penrose tiling or Amman–Kramer–Neri tiling [14], is often used in practice as a model for structure refinement of multicomponent alloys [15,16]. The main problem in this case is the ambiguity of the projection procedure from 6D-space, since certain regions of space can be filled with two types of rhombohedra in several equivalent ways at once. The exact icosahedral symmetry of the structure is violated and preserved only in the average. Such defects are called phason flips [17]. On the other hand, for both, zonohedral and both tetrahedral tilings, the projection procedure from 6D-space is quite straightforward, and no

phason flips occur. Then, a question arises: are phasons inherent in the true structure of a quasicrystal, or are they a consequence of an improper model?

There is an opinion that quasicrystals cannot be represented as packings of identical unit cells at all, so the most stable, energetically favorable atomic configuration corresponds to an aperiodic arrangement of mutually overlapping clusters [18]. One or more characteristic clusters can be used, the structure of which is determined as a result of diffraction experiments either on the basis of projection of 6*D*-lattices, or using the analogy with the structure of crystalline approximants [19–22].

The main method of structure analysis of quasicrystals today is the method of projection from 6*D*-space (strip projection); in its modern form, it is outlined in detail in [23,24]. The method comprises two steps: first, based on the experimental data, a 6*D*-model of icosahedral quasicrystal is created as a distribution of six-dimensional hyper-atoms in a six-dimensional hypercube (unit cell of the periodic 6*D*-lattice), and then a certain slice of it is projected into a physical 3*D*-space (cut-and-project). The resulting projection is analyzed within the framework of a pre-selected structure model, the parameters of which are refined by fitting the computed intensities to experimental data. It should be emphasized that different authors choose specific structure models based on their own personal intuitive preferences. The following types of models are known: model based on two types of rhombohedra [15,16], model based on an incomplete set of zonohedra [25], model of mutually overlapping triacontahedra [26,27], model of canonical cells [28] and several others based on incomplete and mixed sets.

Projection is considered to be the best alternative to tiling [29]. In particular, Senechal is of the opinion that „mathematicians explored tiling models, but they turned out to be unrealistic. Further, she notes, In the second stage of the quasicrystal revolution, tilings are receding to the background and clusters moving to the foreground. We will still need polyhedra: not to tile space, but to hang the clusters on“ [30].

What problems may arise in the projection method? First, to build a 6*D*-model, we need Fourier coefficients. This implies that the material under study has already been synthesized. On the other hand, the major, central direction of modern materials science is the creation of new materials that have no analogues in nature. In particular, the photonic and phononic crystals, as well as metamaterials have attracted a growing interest recently [31]. The projection method is hardly applicable for design of potential structures of photonic quasicrystals [32] or quasicrystals from non-atomic subunits [33].

To understand the next problem, consider the simplest case — obtaining a one-dimensional *LS* Fibonacci sequence by projecting a square lattice tilted at an irrational angle onto a straight line [34]. All edges of the square that served as a unit cell in 2*D*-space were equivalent, but after projection, one of them produces a long segment (L) while the other one produces a short segment (S), and the rest two edges should be discarded. The edges are inclined with respect to the projection line at different angles and undergo distortions with different aspect ratios. If we swap the counted and discarded pair, we get a phason flip. Another important issue: the result of projecting two adjacent squares is different!

In the case of $6D \rightarrow 3D$ projection a similar situation takes place. For example, in the root lattice D_6 all nodes are equivalent, whereas in Danzer tiling generated by it there are 3 types of non-equivalent nodes with local icosahedral symmetry [10]. Another example is the generation of Socolar–Steinhardt tiling from a simple cubic 6*D*-lattice. When an elementary hypercube is located at the origin, its projection is a rhombic triacontahedron. In the region next to it, a 3-fold cluster is obtained formed by three rhombic dodecahedra and four rhombohedra. When neighboring identical unit cells get projected, the projection results can differ drastically from each other depending on their position with respect to the projection window. If this is ignored, the structure model is likely to be reduced to the overlapping triacontahedra with statistically disordered tetrahedra inside, and the exact icosahedral symmetry will be lost.

The central problem of X-ray diffraction analysis is the phase problem. How can it be solved for non-centrosymmetric structures in a six-dimensional space? Indeed, the transition from Patterson function to the atomic distribution is based on stereochemical criteria, and different degree of distortion when projecting equivalent directions makes their applicability questionable. The typical problems that can arise when solving the structures of classical crystals and the characteristic „symptoms“ of frequently made mistakes are discussed in the review paper [35], namely: incorrectly selected symmetry groups, incorrect identification of atoms in certain positions, incorrect determination of Bravais lattice, errors in determining local symmetry of the lattice sites etc. At the same time, the wrongly assigned structures are generally noticed to have very good values of *R*-factor. The task of determining the true structure of quasicrystals is no less problematic.

Analyzing various versions of the higher-dimensional approach, we came to a conclusion that implementation of this approach does not exclude the risk of forced fitting of the experimental data to an incorrect structure model. In our opinion, the refusal from the use of icosahedral Socolar–Steinhardt tiling and Danzer tiling is unjustified and was caused by insufficient study of theoretical aspects of the problem. Recently, we derived the substitution rules for the zonohedral Socolar–Steinhardt tiling and an algorithm of its construction was developed on their basis [36–38]. A similar approach was applied to Danzer tiling and to the third, previously missing tiling [13], which, within the unit cells concept [39], allowed us to describe the structures of icosahedral quasicrystals of all three types P, I, F and of both symmetry groups (I, I_h). The basic principles of our proposed unified theory are outlined below.

1. General principles

If we change the order of operations — first, we project the „empty" lattice, and only then fill the cells of the resulting tiling with specific atoms — then a complete analogy arises with ordinary periodic crystals, with the only difference being that instead of one unit cell, cells of several types are used [39]. Three types of quasilattices become analogues of Bravais lattices (P, I, F). To fill the space with cells, an iterative inflation and deflation algorithm is used instead of translations, while copies of cells may have different orientations. The equivalence of the opposite faces of a parallelepiped unit cell gives place to the local matching rules. Similar to the way how the general and special Wyckoff positions are considered in the unit cell of a periodic crystal, it is also possible to systematize the atomic positions with a certain local symmetry and multiplicity in the unit cells of quasicrystalline packings, but due to the requirements of local matching, some positions may simultaneously be present in cells of several types at a time. The common approach is applicable to both icosahedral groups (I, I_h). The internal symmetry of the atomic distribution inside an individual cell is determined by the stabilizer subgroup, and its possible orientations in space are determined by the corresponding orbit according to Burnside lemma (also known as the Cauchy–Frobenius lemma). Taking into account the local matching rules leads to the symmetry increasing for some positions on the faces of the zonohedra compared to the symmetry of the stabilizer subgroup, and in case of a non-centrosymmetric group, even their multiplicities may increase. With the software implementation of the algorithm for constructing icosahedral packings, any fragment of it and the packing itself as a whole are given by lists of cells, for each of which its type, position, and orientation are specified (substitution rules and starting configurations are also given by lists of cells). Despite the mentioned differences, the essence remains unchanged — quasicrystal is a packing of cells.

Our approach is based on the simultaneous use of three tilings. The first of them is Socolar–Steinhardt tiling [5]. The basis set of unit cells for it consists of 4 types of „golden" zonohedra: prolate rhombohedron (GR), Bilinski rhombic dodecahedron (RD), Fedorov rhombic icosahedron (RI), Kepler rhombic triacontahedron (RT). For the other two, Danzer tetrahedra are used as unit cells: A, B, C, K [10]. The building algorithm for Danzer $ABCK$-tiling is described in detail in paper [40].

It should be noted that a six-dimensional cubic lattice Z^6 (with minimal norm 1) was used to derive zonohedral tiling [5], while an integer root lattice D_6 (the so-called „chessboard" lattice) with enlarged basis vectors was used to derive tetrahedral $ABCK$-tiling [10]. It is necessary to bring all the lattices to a single scale. Instead of tetrahedra A, B, C, K we use their reduced in τ times copies, where τ is the golden ratio. For the reduced tetrahedra we use designations a, b, c, k [13]. An increase in scale by a factor of τ corresponds to a single inflation, which is accompanied by a cyclic change of node types at the vertices of the tetrahedra C → B → A → C. Danzer used Roman numerals [11] to denote the nodes, and we used alphabetic symbols [36–39]. To avoid confusion, we use italic font to denote the tetrahedra (A, B, C, K) and normal font to denote the nodes (A, B, C, F). By decreasing the scale, we not only formally reduce the linear dimensions of the tetrahedra, we also have to cyclically (in reverse order) change the types of vertices. Once again, we note that Danzer pointed out the existence of two basis sets of tetrahedra: $\{A, B, C, K\}$ and $\{A, C, K, \tau K\}$, but he didn't pay much attention to the second version [10]. After downscaling we obtain $abck$- and $ackK$-tilings; they both have a fundamental importance [13].

2. Three types of quasilattices: P, I, F

The quasilattices in the theory of quasicrystals play the role of Bravais lattices. Three types of icosahedral quasicrystals are illustrated in Fig. 1. Three types of cubic lattices are shown on the left: primitive or simple cubic (sc), body-centered (bcc) and face-centered (fcc), and on the right are their six-dimensional analogues (P, I, F).

The three types of quasicrystals correspond to three different schemes for centering polytopes in 6D-space, which are subjected to projection to produce three types of tilings, each with its own basis set of unit cells and its own substitution rules. Primitive 6D-lattice generates zonohedral Socolar–Steinhardt tiling, centering of I-type results in tetrahedral $ackK$-tiling, centering of F-type results in Danzer $abck$-tiling. Centering polytopes does not affect the vertices of the elementary hypercube of the initially selected primitive lattice, it only leads to the addition of new nodes inside. Therefore, the quasilattices of I and F-types should contain all the nodes of the quasilattice of P-type as a subset. By grouping and combining the corresponding tetrahedra, we shall obtain the zonohedra again. In other words, all three types of tilings are consistent with each other, the types of nodes and substitution rules are consistent too.

In a three-dimensional space, a simple cubic lattice (sc) is generated by the vector [1 0 0] and the vectors equivalent to it. Similarly, the simple cubic 6D-lattice (the integer lattice Z^6) is generated by the unit basis vector [1 0 0 0 0 0] and the vectors equivalent to it by cyclic permutations of coordinates. Their projection yields six vectors directed along 5-fold axes (towards the vertices of the icosahedron). If the center of the projection window is combined with the center of the 6D-hypercube, then the projection result will be a triacontahedron with two types of vertices (A and B). All its edges represent the projections of [1 0 0 0 0 0] and equivalent vectors. If the center of the projection window is combined with one of the vertices of the 6D-hypercube, then the projection will form a star of rhombohedra (hexecontahedron); 12 edges coming out of the center of the star represent the projections of [±1 0 0 0 0 0] and equivalent vectors.

A rhombohedron is a distorted projection of a 3D-cube, a rhombic dodecahedron is a projection of a 4D-hypercube

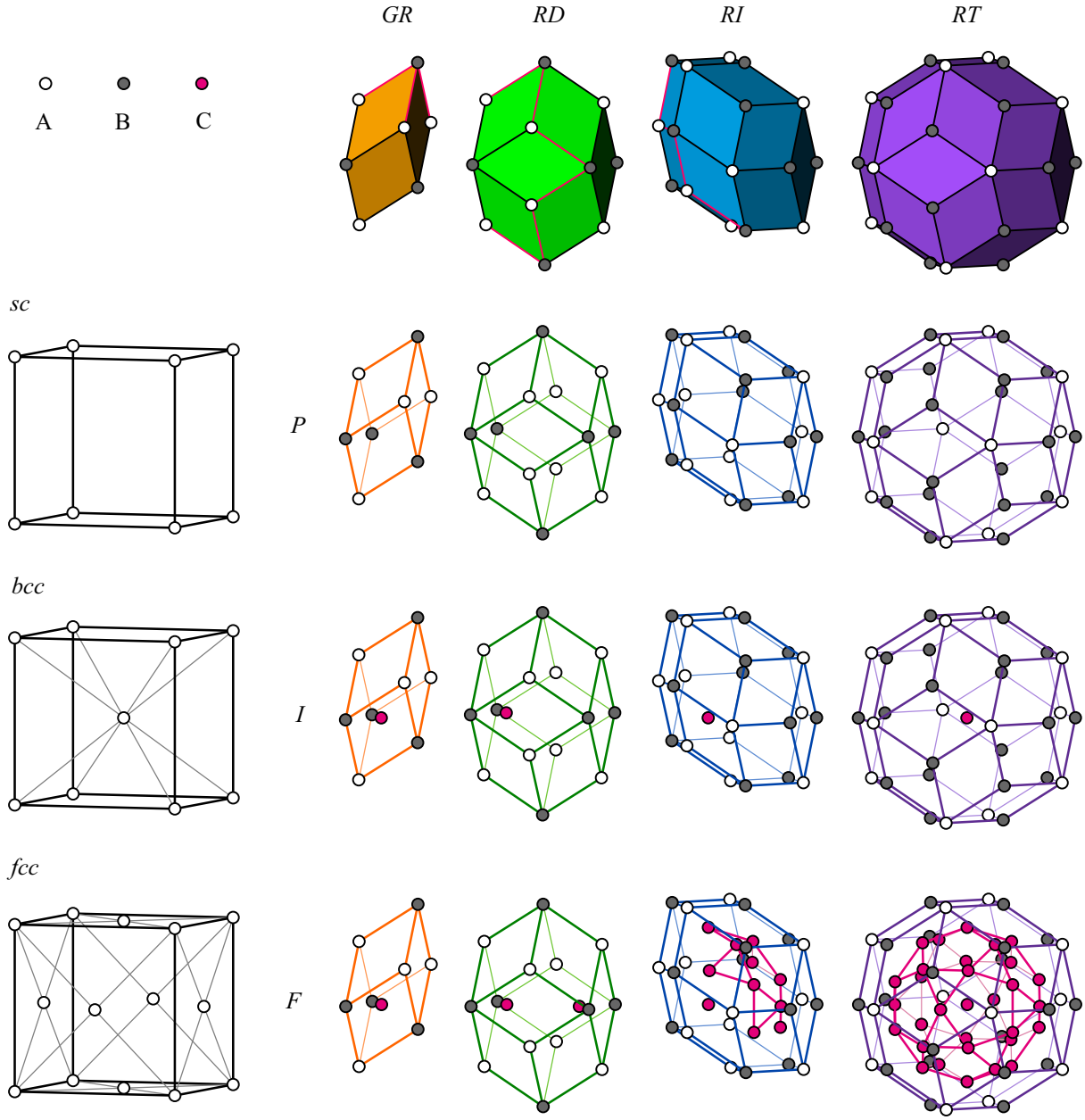

Figure 1. Three types of icosahedral quasilattices (P, I, F) considered as packings of zonohedra. Top — zonohedra GR, RD, RI, RT; thee types of non-equivalent nodes (A, B, C) are highlighted in color (white, black and red, respectively); specific edges of zonohedra are also highlighted in color (see explanation in the text); on the left — unit cells of simple (sc), body-centered (bcc) and face-centered (fcc) cubic lattices; on the right — zonohedra of quasilattices P (vertices of zonohedra are represented by nodes A and B, there are no additional nodes inside zonohedra), I (a new additional node C appears inside each zonohedron) and F (the clusters consisting of nodes C in the form of icosidodecahedron or its fragments appear inside the zonohedra).

(tesseract), a rhombic icosahedron is a projection of a $5D$-hypercube, and finally a triacontahedron is a projection of $6D$-hypercube. The cube has $2^3 = 8$ vertices, and all of them are mapped to the corresponding vertices of the rhombohedron. Tesseract has $2^4 = 16$ vertices, but only 14 of them are mapped to the corresponding vertices of Bilinski dodecahedron. Projections of the two remaining vertices fall inside the rhombic dodecahedron and, moreover, coincide with each other. If we take them into account, we get a subtiling of the rhombic dodecahedron into prolate and oblate rhombohedra (as in Ammann–Kramer–Neri tiling), which inevitably leads to ambiguity of projection and occurrence of phason flips. When projecting $5D$-hypercube, only 22 of its 32 vertices are mapped to the vertices of the rhombic icosahedron, and when projecting $6D$-hypercube, only 32 of its 64 vertices are mapped to the vertices of the triacontahedron. If we do not remove „extra“ sites, the icosahedral symmetry will inevitably be broken. Therefore, the following rule is applied — only the convex hull of the projected polytope and all its substructures should be

taken as the base polyhedron of the tiling. As a result we obtain zonohedral tiling.

In quasilattice of P-type there are only 2 types of nodes (A and B). All edges have the same length, but despite this, there are 2 types of edges. The edges of different types should not adjoin in the final global packing. Specific edges of the second type [36] are highlighted by color in Fig. 1. The edges are always parallel to 5-fold axes and connect nodes of alternating types. Generally speaking, there are no C-type nodes in this quasilattice. Strictly speaking, C-type positions are not the nodes of a quasilattice but special points. We added them to Socolar–Steinhardt tiling, which greatly simplified the procedure for its construction and made it possible to correctly take into account all three types of characteristic icosahedral clusters [36,37]. The points C located inside different zonohedra in P-type quasicrystals are not equivalent to each other. The first two characteristic clusters occur at A and B sites. The points C inside the triacontahedra have icosahedral symmetry and are the centers of characteristic clusters of the third type. The points C inside other zonohedra do not differ in any way from the neighboring points on the corresponding symmetry axes. Later, we will continue to refer to C-type points as nodes if we are talking about general properties of different types of quasilattices, and will delineate them as special positions only in relation to a primitive quasilattice and only if necessary to emphasize the differences in strict interpretation of these concepts in terms of crystallography.

In a three-dimensional space, a body-centered cubic lattice (bcc) can be obtained as a union of a simple cubic lattice with its copy shifted by the vector $\left[\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\right]$. Similarly, in a six-dimensional space the centering of I-type can be obtained as a union of a simple cubic $6D$-lattice with its copy shifted by the vector $\left[\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\right]$. Only one sublattice is added. After projection onto $3D$-space, the centers of the triacontahedra and equivalent C sites appear in addition to A and B — one node C inside each zonohedron. It is obviously that if $6D$-hypercube is mapped to the triacontahedron, then the center of the hypercube gets projected onto the center of the triacontahedron. If one or another $6D$-hypercube is located not exactly in the middle of the projection window and partially extends beyond its frame, then not the entire polytope should be projected, but only its lower-dimensional part entirely falling within the window. As a result, we get smaller zonohedra differently oriented in space, each of which with an asymmetrically located single C site inside.

If we add F points at the centers of the faces of a triacontahedron and equivalent positions (strictly speaking, they are not the nodes themselves), and then connect A, B, C nodes and F points accordingly, we'll get a tetrahedral $ackK$-tiling [13]. Rhombic faces will be dissected into parts depending on their type (Fig. 2). Rhombuses of the first type will be divided into four parts, and F-type points will appear at the intersection of the diagonals. Rhombuses of the second and third types will be divided in halves by long and short diagonals, respectively.

Tetrahedral $ackK$-tiling is a subtiling of the zonohedral tiling. Zonohedra are made up of tetrahedra according to the composition equation (see Fig. 2, top view):

$$\begin{pmatrix} GR \\ RD \\ RI \\ RT \end{pmatrix} = \begin{pmatrix} 0 & 6 & 12 & 0 \\ 8 & 12 & 4 & 4 \\ 10 & 10 & 0 & 40 \\ 0 & 0 & 0 & 120 \end{pmatrix} \begin{pmatrix} a \\ c \\ k \\ K \end{pmatrix}.$$

Quasilattice of F-type is projected from the root lattice D_6 and is constructed based on Danzer tiling. Danzer tetrahedra are obtained by projecting its $6D$-Voronoi polytope [41,42]. The system of lattice roots D_6 is formed by vectors $[\pm 1 \pm 1\,0\,0\,0\,0]$ and all equivalent vectors obtained by cyclic permutation of six coordinates. The result of projecting the root polytope is an icosidodecahedron [43]. In order for all three types of quasilattices to be consistent with each other, it is necessary to change the scale of the lattice D_6, representing it as a union of a simple cubic $6D$-lattice with its copies shifted by the vector $\left[\frac{1}{2}\,\frac{1}{2}\,0\,0\,0\,0\right]$ and equivalent vectors.

The centering scheme is again similar to the three-dimensional case for which a face-centered cubic lattice (fcc) can be obtained as a union of a simple cubic lattice with its copies shifted by the vector $\left[\frac{1}{2}\,\frac{1}{2}\,0\right]$ and equivalent. However, there are some differences. The centering scheme of F-type in even-dimensional spaces includes centering of I-type as a subset. The consequence of this is that if the structure of a quasicrystal (not necessarily icosahedral) is derived by projection from a space of even dimension, then a quasilattice of F-type contains every single node of I-type quasilattice, and that, in turn, contains every single node of P-type quasilattice.

As a result of D_6 root lattice projection, with a consistent choice of scale, 30 C nodes in the form of an icosidodecahedron (projection of the root polytope of D_6 lattice) are added inside the triacontahedron (projection of the $6D$-hypercube). A fragment of an icosidodecahedron consisting of ten additional C nodes appears inside the rhombic icosahedron. One additional C node appears inside the rhombic dodecahedron, while the prolate rhombohedron remains unchanged (Fig. 1).

A quasilattice of F-type may be considered either as Danzer $abck$-tiling, or as a packing of zonohedra decorated with additional C nodes. As already noted, the set of nodes of F-type quasilattice includes all nodes of I-type quasilattice as a subset. Tetrahedral Danzer $abck$-tiling is a subtiling of $ackK$-tiling according to composition equation:

$$\begin{pmatrix} a \\ c \\ k \\ K \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \\ k \end{pmatrix}.$$

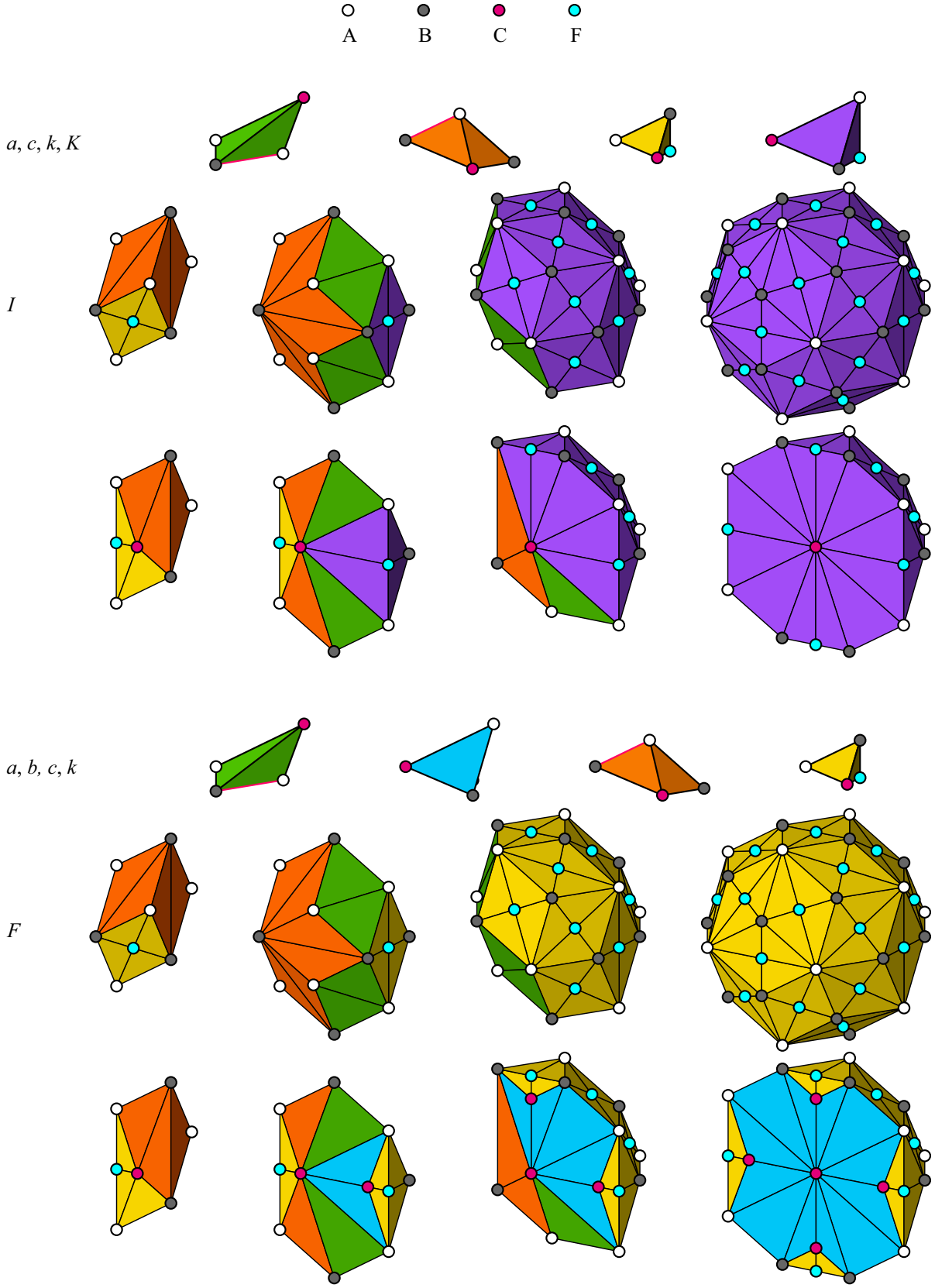

Figure 2. Tetrahedral packings of I and F-types: basis sets of cells, schemes of merging tetrahedra into zonohedra, schemes of zonohedra formation from tetrahedra (sectional view); top — for $ackK$-tiling (packing of I-type); down — for $abck$-tiling (packing of F-type). The tetrahedron's vertices of different types are highlighted in color: A — white, B — black, C — red, F — turquoise.

It is also the subtiling of the zonohedral Socolar–Steinhardt tiling (Fig. 2, bottom view):

$$\begin{pmatrix} GR \\ RD \\ RI \\ RT \end{pmatrix} = \begin{pmatrix} 0 & 0 & 6 & 12 \\ 8 & 4 & 12 & 8 \\ 10 & 40 & 10 & 40 \\ 0 & 120 & 0 & 120 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \\ k \end{pmatrix}.$$

Let's pay attention to one important common property of the unit cells of all three basis sets: the normals to all faces of all Danzer tetrahedra and all zonohedra are always directed parallel to the global 2-fold symmetry axes.

The procedure for deriving the three types of quasilattices and corresponding tilings is mutually consistent, unambiguous, and practically has no alternatives. Phason flips do not occur in any of the cases we have considered (although they can be introduced in an artificial way if desired). In our opinion, any other tiling will have limited applicability: it either represents a very specific individual case, or can be reduced to one of the three basic tilings. In particular, Mosseri–Sadoc tiling can be reduced to projection of the root lattice D_6 [44–46].

Thus, the structure of any icosahedral quasicrystal can be considered as a packing of zonohedra. The rules for constructing such packings [35–39] are common to all types; the only difference is in the way the unit cells are decorated with specific atoms. For quasicrystals of P-type, the methods of filling zonohedra with atoms are largely independent of each other. Only those atomic positions that lie on the faces which are shared by two adjacent unit cells should be consistent with each other to obey the local matching rules. For quasicrystals of I and F-types zonohedra are split into smaller subunits, namely Danzer tetrahedra. As a result, the atomic positions inside different zonohedra turn out to be completely matching each other so that the decoration of identical tetrahedra inside different zonohedra would be the same.

3. Enantiomorphism of icosahedral quasicrystals

Icosahedral quasicrystals can be characterized by two symmetry groups I_h and I, i.e. with and without inversion. The structure of experimentally obtained multicomponent quasicrystalline alloys is fitted, as a rule, under the assumption of a centrosymmetric group. There is usually no justification for such an assumption, and the theoretical basis for the alternative case has clearly not been worked out sufficiently.

A clear example of a polyhedron with I symmetry is a polyhedral compound of five tetrahedra. It was first described in M. Bruckner's monograph [47]. Its aesthetic appeal inspired M.C. Escher to create a small sculptural form (M.C. Escher, „Polyhedron with flowers", maple, 1958, wood carving) [48]. The right and left enantiomorphic forms of the polyhedral compound of five tetrahedra are shown in Fig. 3, *a*. From whichever side we look at the resulting polyhedra, we always see a pattern of only the right screws in one case, and only the left screws in the other. They can be mapped into each other by the mirror reflection, which, as is known, is absent in the non-centrosymmetric group I.

The question arises: is it possible to design an infinite quasicrystalline structure based on a given configuration of atoms or given polyhedra (including the asymmetric ones) by filling the unit cells with them? Our approach makes it possible to solve this problem. The simplest example is given in Fig. 3, *b*. A compound of five tetrahedra, whether right- or left-handed, can be inscribed inside a triacontahedron by identifying the vertices of the tetrahedra with the corresponding vertices of the dodecahedron. Triacontahedra decorated with right or left polyhedra can be used as unit cells for the packing generation. This way we can obtain the simplest right and left structures of P-type.

In general, any of three types of quasicrystals (P, I, F) may have symmetry of any of two icosahedral groups (I, I_h). The easiest way to explain this is using the example of quasicrystals of I-type and the corresponding tetrahedral $ackK$-tiling.

Let's start from the group I_h. There are three types of nodes with icosahedral symmetry (A, B, C). Therefore, to generate a packing, we need first create three starting configurations. We need to take three basis tetrahedra (c, k, K) in some orientation chosen as the initial one (Fig. 2), and subject them to the action of all 120 symmetry elements of the group I_h. We'll get 120 copies of each of the tetrahedra (orbits of cells in I_h symmetry group) joined into polyhedra with icosahedral symmetry. These are the required starting configurations (the basis tetrahedron a is not used for their formation). We only need to apply the iterative inflation and deflation algorithm to the tetrahedra and fill the cells of the resulting packing with specific atoms.

In the centrosymmetric group, all 120 copies of each of the tetrahedra are equivalent. For I group the cells, the orientations of which are obtained from the initial one by using proper and improper rotations, should be considered to be different. In I_h group there are 60 rotational symmetries (subgroup of proper rotations of an icosahedron I). The obtained in this way 60 orientations of basis tetrahedra c, k, K we'll consider as the „right" orientations while the rest ones as the „left". The exception is the basis tetrahedron a, for which either the initial orientation shall be changed (Fig. 2), or the order of determining the right and left orientations shall be reversed. As a result, tetrahedra will be packed according to the face-to-face principle, and the right tetrahedron will always be adjacent to the left and vice versa, regardless of its specific type (a, c, k, K). Now it is enough to fill the right and left unit cells in different ways, and the problem of designing the structure of a non-centrosymmetric icosahedral quasicrystal will be solved. If we set the reversed rules for filling the right and left cells, we'll get a twin (enantiomorphic) structure.

For quasicrystals of F-type, the procedure for constructing enantiomorphic forms is completely similar and does not

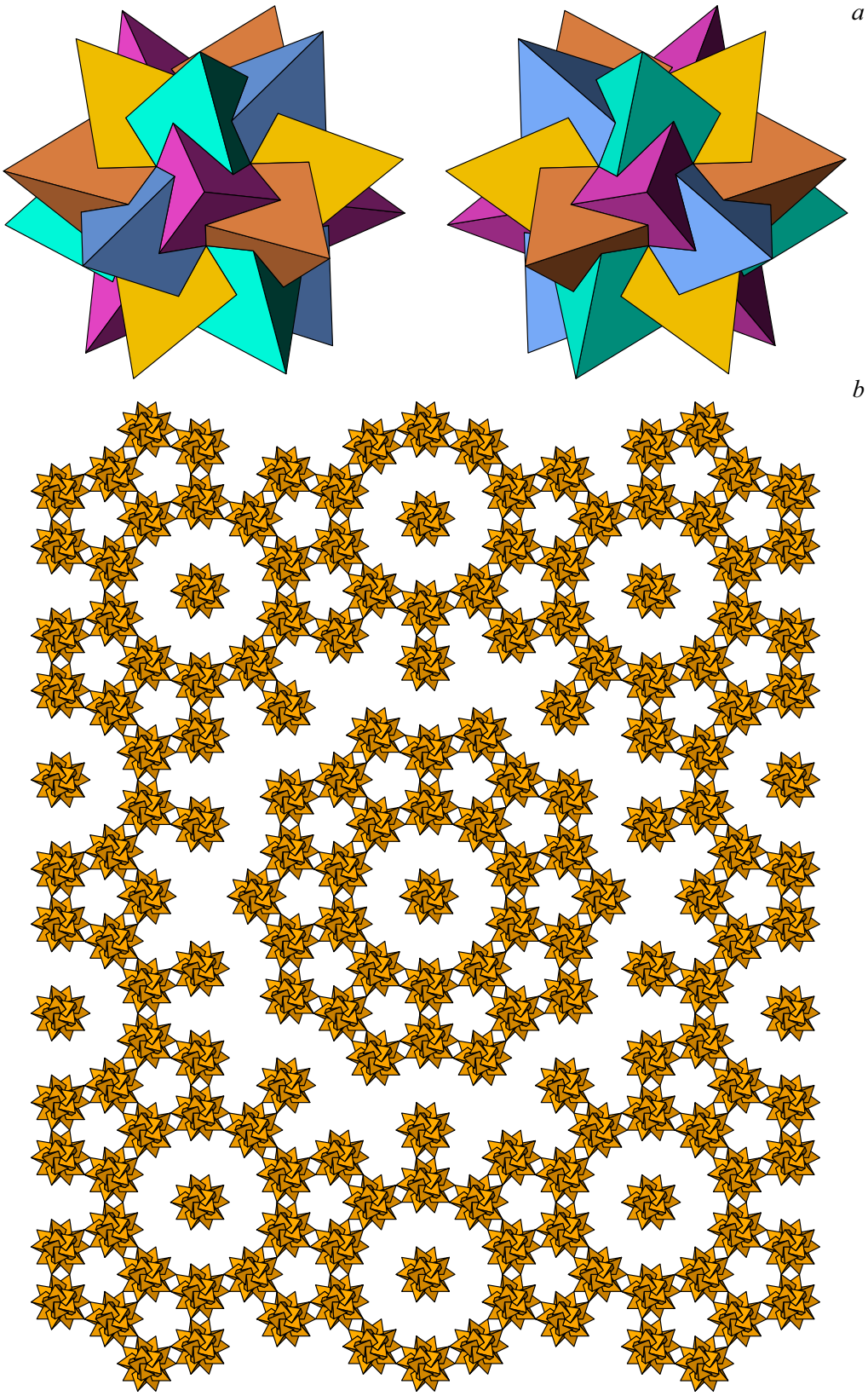

Figure 3. Enantiomorphism in icosahedral structures: *a* — polyhedral compound of five tetrahedra, right and left forms; *b* — an example of a non-centrosymmetric structure of a hypothetical icosahedral *P*-type quasicrystal (the left forms of the polyhedral compound of five tetrahedra are identified with triacontahedra, the layer is cut out perpendicular to the 5-fold axis, only the polyhedral compounds are shown in the layer).

require additional explanations. The only difference is that a different basis set of cells should be used. For quasicrystals of P-type, the rules for filling zonohedra should take into account their own intrinsic symmetry [38]. Another option is to introduce „fictitious" C positions and the so-called context-sensitive rules for tetrahedra that form different zonohedra.

4. Characteristic icosahedral clusters: three types of sites, three types of clusters

As we have already noted, in any icosahedral structure there are always exactly three types of sites with local icosahedral symmetry. Depending on the selected starting configuration, the iterative inflation and deflation algorithm generates three locally isomorphic variants of cell packings. Decoration of cells with atoms generates three types of characteristic clusters. Since, for any of the three types of icosahedral quasicrystals, the cells either are initially zonohedra (P) or can be grouped into zonohedra (I, F), the structural features of the three types of clusters can be analyzed based on zonohedral packing. The corresponding projections along the 2-fold, 3-fold and 5-fold symmetry axes are shown in Fig. 4. Large fragments of packings in the projection along the 5-fold axis have been discussed earlier [39].

If we direct the coordinate axes along the 2-fold symmetry axes and orient the packing so that the plane of the drawing coincides with xy plane, then one of the 2-fold axes will be perpendicular to the plane of the drawing and coincide with z axis. The 3-fold axis closest to it will be in yz plane, and the nearest 5-fold axis will be in xz plane. The layers shown in Figure 4 are cut out perpendicular to these specific axes and slightly rotated in space for clarity.

We shall explain an important general property of the characteristic clusters — their structures are not independent. The point is that the inflation factor and the self-similarity factor are two different concepts. The difference can be most easily explained using the Penrose tiling as an example. It contains two types of inequivalent sites and, hence, two types of characteristic configurations („star" and „sun"). The substitution rule for it is well known, the inflation factor is equal to τ. After the first iteration, the „star" and „sun" transform into each other, and only after the second iteration both characteristic patches coincide with themselves. Thus, self-similarity factor is equal to τ^2. Danzer tiling has a similar property. The inflation factor for it is equal to τ, whereas the self-similarity factor is equal to τ^3 [11]. According to the conclusions of [42], the self-similarity factor for icosahedral tilings of all three types is τ^3. Inflation factor shall be equal to τ^3 for P-type and τ for both I and F-types. We emphasize that our approach is completely compatible with these requirements.

If the atoms are localized at the positions A, B and on the faces of zonohedra, then these positions should always be occupied according to the common rules, regardless of the cluster type where they appear. For icosahedral quasicrystals of P-type, such atomic configuration form certain mutually consistent „scaffolds" in characteristic clusters. In all other aspects, the specific structure of the characteristic clusters remains significantly variable.

Much stricter limitations are imposed on the possible cluster structure in quasicrystals of I and F-types. After each inflation and deflation, the types of nodes should be cyclically changed C → B → A → C. Suppose we are interested in the idealized structure of a multicomponent alloy in which three types of sites are occupied by three types of atoms. Suppose there is a cluster centered at the A site, and at some distance r from it there are 12 B sites forming an icosahedron. The following substitutions will take place after the first iteration: $r \to \tau r$, A → C, B → A. It means that if the cluster A contains an icosahedron consisting of B atoms at a distance r, then, cluster C shall contain A atoms at a distance τr, and cluster B shall contain an icosahedron of C atoms at a distance $\tau^2 r$. After the third iteration, the global packing coincides with itself. This leads to the formation of super-clusters (clusters of clusters); characteristic configurations are reproduced on an enlarged scale at a distance of $\tau^3 r$. This property has been experimentally established for the mutual arrangement of Tsai clusters [26].

So, in the structure of any icosahedral quasicrystal, there are always exactly three types of characteristic clusters associated with three types of non-equivalent sites. Clusters that occur at sites of various types cannot be the same (see illustrations in paper [39]). If the structure of a quasicrystal is interpreted on the basis of only one or two characteristic icosahedral clusters, then such a structure should be considered as studied insufficiently. If the experimental method or theoretical approach does not allow identifying all three types of clusters, then this result, in our opinion, is negative and requires a critical rethinking.

Conclusion

We propose a unified structure theory of icosahedral quasicrystals, within which it is possible to describe all three types of quasilattices (P, I, F), both icosahedral symmetry groups (I, I_h), as well as right and left enantiomorphic forms for the non-centrosymmetric case. The theory is based on the simultaneous use of three types of tilings, for each of which the unique basis set of unit cells and unique substitution rules are established. By analogy with ordinary crystals, the task of describing the structure of a quasicrystal splits into two stages: filling the space with cells and filling the cells with atoms, with the only difference being that instead of a single unit cell, unit cells of several types are used, and the iterative inflation and deflation algorithm is used to fill the space instead of translations.

The design of a possible promising structure of a photonic or phononic quasicrystal being created (as well as the structural analysis of an experimentally synthesized quasicrystal) implies the following sequence of steps:

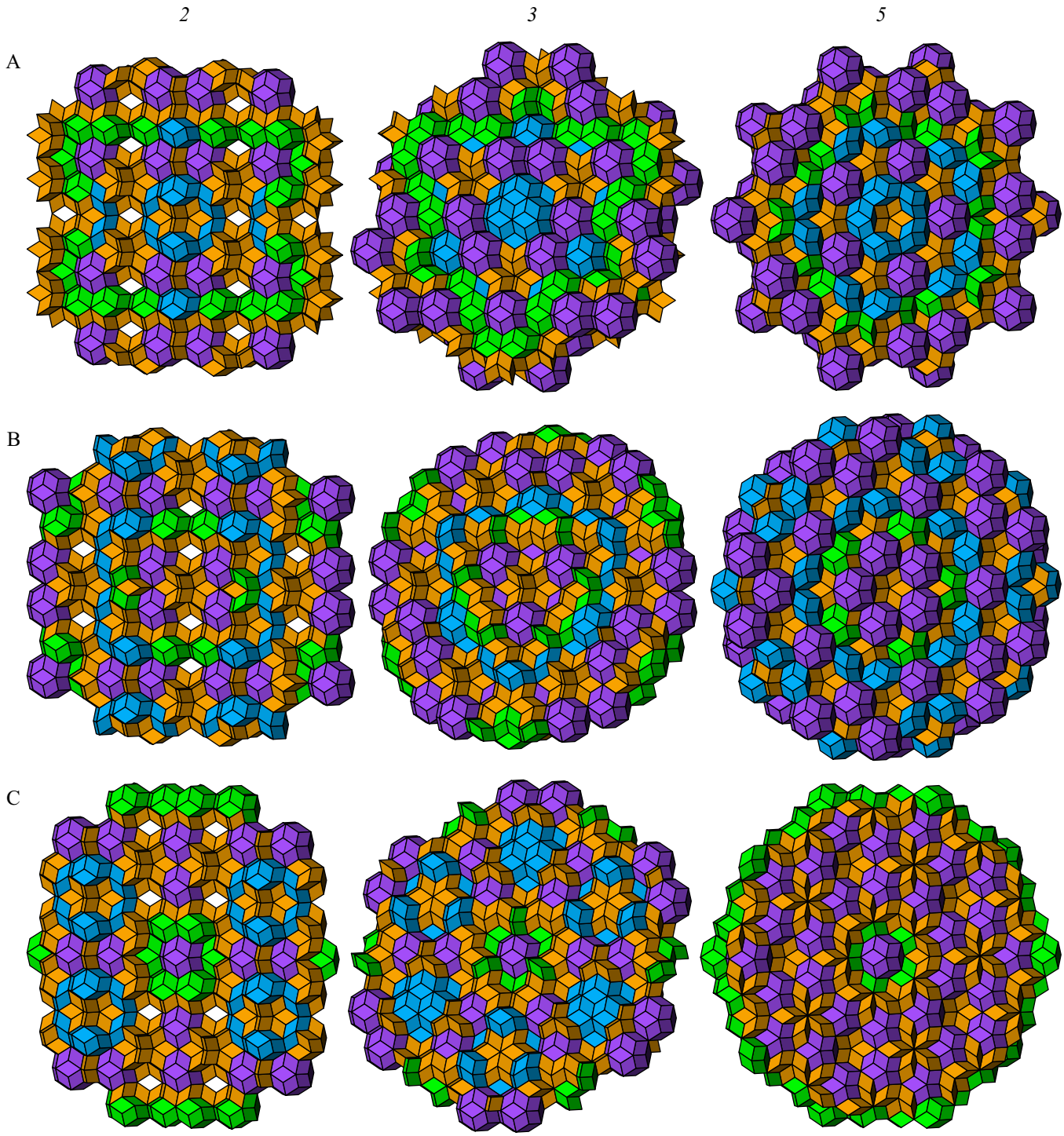

Figure 4. Three types of characteristic icosahedral clusters: in any icosahedral packing, three types of nodes (A, B, C) generate three types of characteristic icosahedral clusters; the layers of zonohedra are cut perpendicular to the 2-fold, 3-fold and 5-fold axes.

— Determining the type of quasilattice; it will determine the specific type of tiling used, the basis set of unit cells, and the substitution rules for them. When clarifying the structure of experimentally synthesized alloys the most probable type of quasilattice is determined based on the analysis of extinction rules.

— Analysis the intrinsic symmetry of cells; the stabilizer subgroup determines the intrinsic symmetry and the rules for filling the interior of cells with atoms, while the orbit determines their possible orientations in space. Note that for tetrahedral tilings and the symmetry group I_h, the stabilizer subgroup is trivial and contains a single identity element, and the unit cells' orbits are formed by 120 possible spatial orientations.

— Selection of standard cell orientations and starting configurations.

— Determination of the symmetry group of a quasicrystal (with or without inversion).

— Packing generation (space filling) based on substitution rules; the packing is given by a list of cells, for each of which its type, position and orientation are specified.

— Establishing the rules for atomic decoration of cells; they shall obey the symmetry of the stabilizer subgroup and the local matching rules between different types of cells.

— Filling of cells with atoms and structure generation; identification of characteristic clusters and characteristic motifs of their mutual arrangement.

— Analysis and refinement of obtained structure.

Acknowledgments

The authors would like to express their gratitude to S.V. Kozyrev and V.A. Moshnikov for helpful discussions of the investigation.

Funding

This study was supported by grant No. 23-23-00392 from the Russian Science Foundation № 23-23-00392, https://rscf.ru/project/23-23-00392/.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] D. Shechtman, I. Blech, D. Gratias, J.W. Cahn. Phys. Rev. Lett., **53**, 70 (1984). DOI: 10.1103/PhysRevLett.53.1951
[2] R. Daw. Nature, **511** (Suppl 7509), 18 (2014). DOI: 10.1038/nature13366
[3] A.L. Mackay. Physica A, **114**, 609 (1982). DOI: 10.1016/0378-4371(82)90359-4
[4] D. Levine, P.J. Steinhardt. Phys. Rev. B, **34**, 596 (1986). DOI: 10.1103/PhysRevB.34.596
[5] J.E.S. Socolar, P.J. Steinhardt. Phys. Rev. B, **34**, 617 (1986). DOI: 10.1103/PhysRevB.34.617
[6] W. Steurer. Acta Cryst. A, **74**, 1 (2018). DOI: 10.1107/S2053273317016540
[7] L.S. Levitov, J. Rhyner. JETP Lett., **47** (12), 760 (1988). http://jetpletters.ru/ps/1099/article_16620.pdf
[8] L.S. Levitov, J. Rhyner. J. Phys. France, **49**, 1835 (1988). DOI: 10.1051/jphys:0198800490110183500
[9] V.Ya. Shevchenko, A.E. Madison, A.L. Mackay. Acta Cryst. A, **63**, 172 (2007). DOI: 10.1107/S0108767307002723
[10] L. Danzer. Discrete Math., **76** (1), 1 (1989). DOI: 10.1016/0012-365X(89)90282-3
[11] L. Danzer, Z. Papadopolos, A. Talis. Int. J. Mod. Phys. B, **7** (6-7), 1379 (1993). DOI: 10.1142/S0217979293002389
[12] M. Senechal. *Quasicrystals and geometry* (Cambridge University Press, Cambridge, 1995)
[13] A.E. Madison. Tech. Phys. Lett., **50** (10), 13 (2024). DOI: 10.61011/PJTF.2024.19.58650.19962
[14] P. Kramer, R. Neri. Acta Cryst. A, **40**, 580 (1984). DOI: 10.1107/S0108767384001203
[15] S. van Smaalen, J.L. de Boer, Y. Shen. Phys. Rev. B, **43**, 929 (1991). DOI: 10.1107/S2053273319017339
[16] I. Buganski, J. Wolny, H. Takakura. Acta Cryst. A, **76**, 180 (2020). DOI: 10.1103/PhysRevB.43.929
[17] M. de Boissieu. Chem. Soc. Rev., **41**, 6778 (2012). DOI: 10.1039/C2CS35212E
[18] E. Abe, Y. Yan, S. Pennycook. Nature Mater., **3**, 759 (2004). DOI: 10.1038/nmat1244
[19] M. Duneau, D. Gratias. In: *Coverings of Discrete Quasiperiodic Sets*, ed. P. Kramer, Z. Papadopolos (Springer Tracts in Modern Physics, Springer, Berlin, Heidelberg, 2002), v. 180, p. 23, DOI: 10.1007/3-540-45805-0_2
[20] A.P. Tsai. Sci. Technol. Adv. Mater., **9**, 013008 (2008). DOI: 10.1088/1468-6996/9/1/013008
[21] P. Guyot, M. Audier. C. R. Phys., **15**, 12 (2014). DOI: 10.1016/j.crhy.2013.10.005
[22] S. Lidin. In: *Handbook of Solid State Chemistry*, ed. by R. Dronskowski, S. Kikkawa, A. Stein (Wiley-VCH, Weinheim, 2017), p. 73, DOI: 10.1002/9783527691036.hsscvol1002
[23] W. Steurer, T. Haibach. In: *International Tables for Crystallography Volume B*: Reciprocal Space, ed. by U. Shmueli (Springer, Dordrecht, 2006), v. B, Ch. 4.6, p. 486. DOI: 10.1107/97809553602060000568
[24] W. Steurer, S. Deloudi. *Crystallography of quasicrystals. Concepts, methods and structures* (Springer, Berlin−Heidelberg, 2009), DOI: 10.1007/978-3-642-01899-2
[25] A. Yamamoto, H. Takakura, A.P. Tsai. Phys. Rev. B, **68**, 094201 (2003). DOI: 10.1103/PhysRevB.68.094201
[26] H. Takakura, C. Pay Gómez, A. Yamamoto, M. de Boissieu, A.P. Tsai. Nature Mater., **6**, 58 (2007). DOI: 10.1038/nmat1799
[27] T. Yamada, H. Takakura, H. Euchner, C. Pay Gómez, A. Bosak, P. Fertey, M. de Boissieu. IUCrJ, **3**, 247 (2016). DOI: 10.1107/S2052252516007041
[28] M. Mihalkovič, M. Widom. Phil. Mag., **86** (3-5), 519 (2006). DOI: 10.1080/14786430500333356
[29] M. Baake, U. Grimm. Acta Cryst. A, **76**, 559 (2020). DOI: 10.1107/S2053273320007421
[30] M. Senechal. Proc. Steklov Inst. Math., **288**, 259 (2015). DOI: 10.1134/S0081543815010204
[31] A.R. McGurn. *Introduction to Photonic and Phononic Crystals and Metamaterials* (Springer, Cham, 2020), DOI: 10.1007/978-3-031-02384-2
[32] A. Poddubny, E. Ivchenko. Phys. E: Low-Dimens. Syst. Nanostructures, **42**, 1871 (2010). DOI: 10.1016/j.physe.2010.02.020
[33] Y. Nagaoka, J. Schneider, H. Zhu, O. Chen. Matter., **6**, 30 (2023). DOI: 10.1016/j.matt.2022.09.027
[34] W. Steurer. Angew. Chem. Int. Ed., **50**, 10775 (2011). DOI: 10.1002/anie.201107163
[35] R.L. Harlow. J. Res. Natl. Inst. Stand. Technol., **103**, 327 (1996). DOI: 10.6028/jres.101.034
[36] A.E. Madison. RSC Adv., **5**, 5745 (2015). DOI: 10.1039/C4RA09524C
[37] A.E. Madison. RSC Adv., **5**, 79279 (2015). DOI: 10.1039/C5RA13874D
[38] A.E. Madison, P.A. Madison. Struct. Chem., **31**, 485 (2020). DOI: 10.1007/s11224-019-01430-w
[39] A.E. Madison, P.A. Madison, V.A. Moshnikov. Tech. Phys., **69** (4), 528 (2024).
[40] A. Al-Siyabi, N. Ozdes Koca, M. Koca. Symmetry, **12**, 1983 (2020). DOI: 10.3390/sym12121983
[41] P. Kramer, Z. Papadopolos, M. Schlottmann, D. Zeidler. J. Phys. A: Math. Gen., **27**, 4505 (1994). DOI: 10.1088/0305-4470/27/13/024

[42] P. Kramer, Z. Papadopolos, D. Zeidler. In: *Symmetries in science V*, ed. by B. Gruber, L.C. Biedenharn, H.D. Doebner (Springer, Boston, 1991), p. 395. DOI: 10.1007/978-1-4615-3696-3_19
[43] J.C. Baez. Not. Am. Math. Soc., **70**, 821 (2023). DOI: 10.1090/noti2685
[44] R. Mosseri, J.F. Sadoc. In: *The Structure of Non-Crystalline Materials, 1982*: Proc. 2nd Int. Conf., Cambridge, 12-15 July 1982, ed. by P.H. Gaskell, J.M. Parker, E.A. Davis (London, NY., Taylor & Francis, 1982), p. 137, ISBN: 978-0800230777
[45] N. Ozdes Koca, R. Koc, M. Koca, A. Al-Siyabi. Acta Crystallogr. A, **77** (2), 105 (2021). DOI: 10.1107/S2053273320015399
[46] P. Kramer, Z. Papadopolos. Can. J. Phys., **72**, 408 (1994). DOI: 10.1139/p94-057
[47] M. Brückner. *Vielecke und Vielfläche — Theorie und Geschichte* (Leipzig, Teubner, 1900) M. Brückner. *Vielecke und Vielfläche — Theorie und Geschichte*. Classic Reprint Series (London, Forgotten Books, 2018)
[48] D. Schattschneider. In: *Proceedings of Bridges 2019: Mathematics, Art, Music, Architecture, Education, Culture*, ed. by S. Goldstine, D. McKenna, K. Fenyvesi (Phoenix, Tessellations Publishing, 2019), p. 347.

Translated by T.Zorina