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A special class of simple 24-vertex polyhedra and tetrahedrally coordinated structures of gas hydrates

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It is established that the eight-dimensional lattice E_8 and the Mathieu group M_{12} determine a unique sequence of algebraic geometry constructions which define a special class of simple 24-vertex, 14-face polyhedra with four-, five- and six-edge faces. As an example, the graphs of the ten stereohedra that generate most known tetrahedrally coordinated water cages of gas hydrates have been derived *a priori*. A structural model is proposed for the phase transition between gas hydrate I and ice.

1. Introduction

The possibility of realizing ordered solid structures in three-dimensional Euclidean space E^3 is determined to a considerable extent by its topological properties, one of which is the non-integer nature of the maximum number, equal to 5.104 . . . , of regular tetrahedra with a common edge. Ultimately, this allows one to approximate the densest non-lattice sphere packing by statistical partitions into simple (three edges meeting at every vertex) 14-face polyhedra with four-, five- and six-edge faces (Coxeter, 1961; O'Keeffe, 1998; Delgado-Friedrichs & O'Keeffe, 2005; Komarov *et al.*, 2007). One such polyhedron is a truncated octahedron $[4^6, 6^8]$ with six square and eight hexagonal faces that make up the Dirichlet polyhedron for the body-centred cubic (b.c.c.) lattice. A dual to the $[4^6, 6^8]$ polyhedron is the subdivision of the sphere into 24 triangles, which serves as a basis for the derivation of the simple 24-vertex, 14-face polyhedra $[4^n, 5^{12-2n}, 6^{n+2}]$ given by Delgado-Friedrichs & O'Keeffe (2005).

In 1887 William Thomson (Lord Kelvin) considered the possibility of partitioning E^3 into polyhedra of fixed volume and minimal surface area. The partition he found consisted of (slightly curved) $[4^6, 6^8]$ parallelohedra and corresponded to the structure of sodalite or gas hydrate IV. The local minimality of the surface (which determines conservation of volume under small perturbations) is an important factor in the stability of the structure. The search for the solution to Kelvin's problem has continued and it was established by Weaire & Phelan (1994) that the partition made up of $[5^{12}]$ dodecahedra of equal volume and $[5^{12}, 6^2]$ tetrakaidecahedra is closer to the solution and corresponds to the (distorted) structure of gas hydrate I. Kelvin's $[4^6, 6^8]$ polyhedron and the polyhedron $[5^{12}, 6^2]$ belong to the class of simple 14-face polyhedra $[4^n, 5^{12-2n}, 6^{n+2}]$. In particular, this class contains ten stereohedra (n = 2, 3, 4, 6), which generate 23 crystallographic tetrahedrally coordinated partitions of E^3 (Delgado-Friedrichs & O'Keeffe, 2005). A mathematical formalism based on algebraic geometry constructions for the derivation of such crystallographic tetrahedrally coordinated networks has been put forward by Delgado-Friedrichs *et al.* (1999).

Kocian *et al.* (2009) demonstrated that the symmetry of crystalline and discrete ordered structures can be described within a unified formalism of the theory of manifolds (differential geometry). The apparatus of algebraic geometry has been used to determine the graph of a special polyhedron, the truncated icosahedron (Kostant, 1995). The latter required the extension of the rotation group of the icosahedron $Y = T \cdot C_5$, isomorphic to the projective special linear group $PSL_2(5)$, to the product $T \cdot C_5 \cdot C_{11}$, isomorphic to $PSL_2(11)$, where T is the group of rotations of the tetrahedron, and C_5 and C_{11} are cyclic groups. Kostant (1995) pointed out the correspondence between the icosahedral group and the root system (formed by the 240 vectors of the first coordination sphere) of the root lattice E_8 of the maximal semi-simple exceptional Lie algebra e_8 (Humphreys, 1975; Conway & Sloane, 1988).

The vector space E^3 forms a Lie algebra with respect to the vector product, so ultimately it determines a connection between manifolds, topological invariants of polyhedral surfaces and invariants of the corresponding algebras. In the approach developed by the authors, one of the constructions for realizing this connection is an 'algebraic' polytope. Vertices of this polytope (on the sphere S^3, situated in E^4) are determined by the subsystem of $8I_n$ vectors of the system E_8; I_n = 2, 8, 12, 14, 18, 20, 24, 30 are invariants of the E_8 lattice. These structures include the polytope {5, 3, 3}, which is a locally minimal manifold determined by the system H_4 (obtained from E_8) and generates a partition of S^3 into 120 dodecahedra {5, 3}. Algebraic polytopes allow one to define a special class of helicoids – Gosset helicoids (Samoylovich & Talis, 2007*c*) – with screw axes (crystallographic and non-crystallographic, integer and non-integer), which contain the well known (Coxeter, 1973; Mosseri *et al.*, 1985) non-integer axis 30/11 of the polytope {3, 3, 5}. The Gosset helicoids, determined by invariants of E_8, are realized in ordered (crystalline and non-crystalline) structures, in particular in gas hydrates. For example, Gosset's rod assembly of tetrakaidecahedra and dodecahedra with 12/5 and 10/3 axes determines the crystalline structures of the I and II types (Samoylovich & Talis, 2007*c*; Samoylovich *et al.*, 2009).

The discussion above suggests that this formalism may be employed for *a priori* derivation of a special class of 14-face polyhedra $[4^n, 5^{12-2n}, 6^{n+2}]$, whose 'progenitor' is Kelvin's polyhedron $[4^6, 6^8]$ – the Dirichlet polyhedron of the b.c.c. lattice. The solution of this problem is the main objective of this work, whose results, in particular, allow us to propose a model of structural phase transitions in gas hydrates.

2. The incidence table of the graph of Kelvin's polyhedron and constructions of algebraic geometry

Kelvin's polyhedron $[4^6, 6^8]$ has the symmetry group $O_h = T_h \cup m_d T_h$, and its vertices belong to two congruent right icosahedra,

$$[4^6, 6^8] \cong \{3, 5\}_{\rm r} \cup m_d\{3, 5\}_{\rm r}, \qquad (1)$$

where m_d is a diagonal symmetry plane of the cube and T_h is the symmetry group of the right icosahedron $\{3, 5\}_{\rm r}$ (a right icosahedron has eight regular triangles and 12 isosceles ones). Every vertex of $\{3, 5\}_{\rm r}$ is surrounded by three vertices of $m_d\{3, 5\}_{\rm r}$ and *vice versa*; hence $[4^6, 6^8]$ may be viewed as a three-dimensional analogue of the polytope {240} (Mosseri *et al.*, 1985) – the union of two right icosahedra *via* a second-order symmetry element (Fig. 1*a*).

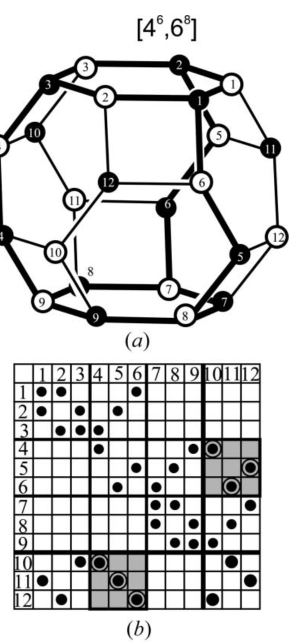

Figure 1
(*a*) White and black vertices of the parallelohedron $[4^6, 6^8]$ are also vertices of 'white' and 'black' right icosahedra. (*b*) The incidence table (IT) determining the graph of the parallelohedron (*a*). The columns of the IT correspond to white vertices of the parallelohedron and give black neighbours of a white vertex. The rows of the IT correspond to black vertices, and black dots correspond to edges. Bold lines distinguish in the IT a 9 × 9 diagonal block that determines an 18-vertex sub-graph of the parallelohedron shown in bold lines. Thinner bold lines distinguish the 3 × 3 sub-blocks. A black dot within a circle signifies an edge, dividing a side-face octagon of the parallelohedron into a square and a hexagon; the sub-blocks containing such symbols are shown in light grey.

According to Galois' proof, the set of p involutions is invariant with respect to the $\mathrm{PSL}_2(p)$ group, p = 3, 5, 7, 11. It was shown by Kostant (1995) that the set of vertices of the icosahedron is isomorphic to a collection of cosets of the maximum possible (p = 11) group $\mathrm{PSL}_2(11)$:

$$Y/C_5 \leftrightarrow \mathrm{PSL}_2(11)/B = \bigcup_{i=1}^{12} g_i B, \quad g_i \notin B = C_5 \cdot C_{11}, \qquad (2)$$

where $\mathrm{PSL}_2(11)$ is the automorphism group of the projective line PL(11), which lies in the Mathieu group M_{11} as a subgroup of index 12. The parallelohedron $[4^6, 6^8]$ is the union [equation (1)] of two congruent 12-vertex (right) icosahedra. Thus, for the analogous [equation (2)] symmetry of its graph one has to use the maximum subgroup of the symmetric group S_{12} (of permutations of 12 symbols) that corresponds to equation (1) and equation (2). The group $2M_{12}$ is such a group (an extension of the Mathieu group M_{12} by the second-order element), whose set of cosets by M_{11} is isomorphic to a collection of vertices $[4^6, 6^8]$,

$$O_h/C_{1v} \leftrightarrow 2M_{12}/M_{11} = \bigcup_{i=1}^{12} 2g_i M_{11} = \bigcup_{i=1}^{144} g_i 2\mathrm{PSL}_2(11), \qquad (3)$$

where 2 is a cyclic group of the second order, whose non-trivial element maps two non-conjugate subgroups M_{11} of the group M_{12} onto each other. The group $2M_{12}$ is the automorphism group of the manifold Q, which uses the basis vectors x_i, $i \in$ PL(11) over the Galois field GF(3) (Conway & Sloane, 1988). The group M_{12} contains the subgroup $M_n \cdot S_{12-n}$, n = 8, 9, 10, 11, which maps a certain subset of vectors from Q onto itself and determines the following representation. It may be shown that there exists a parabolic subgroup of an algebraic group (Humphreys, 1975) isomorphic to $M_n \cdot S_{12-n}$, which is generated by involutions corresponding to a certain subset of root vectors of the system E_8. In the end, this allows one to establish an isomorphic correspondence between a subsystem of the system E_8 and a subset of vectors from Q. A parallelohedron is called M-equivalent to the parallelohedron $[4^6, 6^8]$ if it is mapped onto $[4^6, 6^8]$ by a transformation which preserves the number of vertices, edges and faces and is included in $2M_{12}$.

A particular case of the space of the main fibration $E \to S^4$ (the S^3 fibre) is the Hopf fibration $S^7 \to S^4$ (the S^3 fibre). In the case of the vector fibration one must use the fibration with the edge ∂E which is homeomorphic (and is not necessarily diffeomorphic) to the S^7 sphere only when the first-class homology $\chi \in H^4$ (S^4, Z) is true. One can show that the structure on a sphere is guaranteed to be smooth by the use of the root vectors of the E_8 system limited onto S^7; these vectors determine vector sets which, in turn, determine polytopes onto S^3. The root lattice E_8 corresponds to the densest packing of spheres S^7 in E_8. The sphere S^7 is, in its turn, the main fibration space for the group SU(2), which as an algebraic variety corresponds to S^3 (Manton, 1987; Dubrovin *et al.*, 2001). The fibration $S^3 \to S^2$ (the S^1 fibre) is not reduced to the direct product $S^2 \times S^1$; therefore, it does not ensure a direct transition to substructures on S^2. In the approach of Mosseri *et al.* (1985), a transition from S^3 to structures in E^3 is implemented, for example, by an additional operation of a polytope rolling over E^3.

Let us show that a direct transition from E_8 substructures to substructures on S^2 (in E^3) is possible. The construction of the main fibration over the sphere S^n may be viewed as a union of two discs D^n_+ and D^n_-, intersected by the equator S^{n-1}. If the elements of the manifold lie on geodesics (analogue of straight lines in Euclidean space), then any vector tangent to a geodesic lies in this manifold. The sphere S^2, considered as such a geodesic and a locally minimal submanifold in SU(2), is denoted by S^2_0. From S^2_0 one may move to the union of two discs (hemispheres) D^2_{+0} and D^2_{-0}, which are intersected by the equatorial circumference S^1_0, corresponding to a one-parameter group SU(2). The disc D^2_0 can be chosen as the central section of the sphere S^7 by the plane E^3, drawn through the origin in E_8, and the circumference S^1_0 (the equator of the disc) can be put in correspondence with a great circle in the sphere S^7 (Dubrovin *et al.*, 2001). If fundamental vectors of the system E_8 are restricted on the sphere S^7 while S^1_0 is defined as a subgroup of the diagonal matrices (torus subgroup) of the group SU(2), then invariants of E_8 can be put in correspondence with elements of D^2_0. Any transformations of D^2_0 without loss of local minimality are reduced to rotations about S^1_0, which are automorphisms of the group SU(2). Therefore, the D^2_0 disc is also used for setting vectors from the E_8 system and (as distinct to S^1_0) in the final construction of polyhedra on S^2. The above allows one to consider the algebraic submanifold, corresponding to a manifold of vectors directed to edge centres of such a polyhedron on S^2, as a discrete subset of a homogeneous symmetric space:

$$S^2 \cong \mathrm{SU}(2)/\mathrm{U}(1) \cong S^3/S^1 \to [(D^2_{+0} \times S^1) \cup (S^1 \times D^2_{-0})]/S^1_0. \tag{4}$$

The relations in equation (4) allow one to move from the Hopf fibration $S^3 \to S^2$ (the S^1 fibre), used traditionally, to consideration of algebraic varieties (covers) taking into account the discrete nature of S^1_0 and S^2_0, as well as a certain manifold M, given on S^3,

$$M(S^3) \to S^1_0 \text{ (the } S^2_0 \text{ fibre)}, \tag{5}$$

where $S^2_0 = D^2_{+0} \cup D^2_{-0}$. Setting the S^3 sphere as $(D^2 \times S^1) \cup (S^1 \times D^2)$ permits one to use the foliation as a variant of a fibration. While $\partial(D^2 \times S^1)$ is a torus T^2, we use corresponding vectors of the E_8 lattice to set a fibre of co-dimensionality 1 onto an S^3 sphere: by such consideration one obtains a closed diffeomorph to the T^2 fibre restricted by the domain $(D^2 \times S^1)$ with a two-dimensional fibre.

Under the mapping of S^3 into the complex projective line CP^1, corresponding to equation (5), any point of S^3 is in correspondence with its equivalence class in CP^1 and, simultaneously, the inverse image of every point in CP^1 is a circumference $S^1 = [\exp(i\varphi)]$. In such an approach, the symplectic group $\mathrm{SP}(1) \cong S^3$ consists of unitary transformations of two-dimensional complex space C^2, preserving a skew-symmetric Hermitian form. For real vectors, the condition of skew symmetry in fact defines a two-form Ω (Daniel & Viallet, 1980). For two-dimensional real surfaces the Euclidean scalar square coincides with the Hermitian one and then Ω actually coincides with it. It can be shown that Ω is in correspondence with one-parameter subgroups, given by invariants of E_8, and, therefore, the definition of Ω (as a square) corresponds to equations (4) and (5). A symplectic structure on S^3 can be obtained using coincidence of the group SP(1) of unitary quaternions with SU(2). The following conversion to real form according to $C^2 \to \mathrm{CP}^1 \to M(\mathrm{CP}^1) \to \Omega$ [where $M(\mathrm{CP}^1)$ is a discrete structure on CP^1] allows one to put in correspondence with a two-form Ω a discrete 12-element submanifold as well as the corresponding symplectic discrete 24-element structure.

A manifold furnished by a simplectic structure (a closed differential non-singular two-form onto the smooth even-dimensional manifold) is called symplectic. It is significant in the local algebraic approach that a tangent space in each point of such a manifold is a vector space $[\mathrm{SP}(V^{2n})]$, and the condition for closeness makes a correspondence in it between an askew-symmetric product and nearby points in such a way that the local geometry of symplectic manifolds is a universal one. Each dense commutative group of the $\mathrm{SP}(V^{2n})$ type lies in some T^n torus with elements of this torus being conjugated in the symplectic group. The unit S^3 sphere is determined by unit quaternions (q) as the projective manifold and corresponds to three-dimensional space E^3, while transformations of the type qxq^{-1} (x-quaternion) describe rotational operations of the Euclidian space E^3. In the framework of such an approach the symplectic group $\mathrm{SP}(1) \cong S^3$ consists of unitary transformations of a complex space C^2, such transformations conserving the askew-symmetrical form. In accordance with the Darby theorem (see Arnold & Givental, 2000) the symplectic manifolds having the same dimensionality are local diffeomorphs (locality is described by the algebras only for the groups considered) and transformed into each other by symplectic transformations (Arnold & Givental, 2000). Using integral submanifolds (Dubrovin *et al.*, 2001) permits one to use corresponding collections of hyperplanes (*i.e.* seven-dimensional planes) normal to the root vectors of the E_8 lattice in order to establish a correspondence between submanifolds of symplectic (even number of dimensions) and contact (odd number of dimensions) geometries.

In a $(2n + 1)$-dimensional contact manifold, an integral submanifold of the field of hyperplanes of dimension n is called Legendre's submanifold. Discrete Legendre's fibrations with Legendre's fibres contain fibrations of the type in equation (5). A choice of a Lagrange section [equation (5)] determines a cotangent fibration of the base, which gives as a result a subdivision to a subsystem of vectors of the E_8 system. For instance, for the 240 vectors of the system E_8 such partitioning leads to eight subsystems containing 30 vectors each. By shifting the origin into a deep hole of the E_8 lattice

(Conway & Sloane, 1988) one singles out 144 vectors from the 240, forming a subsystem E_8(hole), which corresponds to the second decomposition in equation (3). For E_8(hole) the partition defined in equation (5) leads to eight subsystems of 18 vectors. Summing up the above, we obtain the relations

$$E_8(\text{hole}) \rightarrow M_s(S^3) \rightarrow M_s(S_0^2) \leftarrow \Omega \leftarrow M(\text{CP}^1) \leftarrow \text{CP}^1 \leftarrow C^2, \quad (6)$$

where $M_s(S^3)$ and $M_s(S_0^2)$ are discrete symplectic structures on S^3 and the fibre of the Legendre fibration [equation (5)] corresponding to it on S_0^2, respectively.

An equatorial section (starting from a cell) of the 24-vertex polytope {3, 4, 3} by the 'plane' E^3 gives a cuboctahedron, and the sections of the north and south hemispheres parallel to it give + and − octahedra. The centres of all 96 edges of the {3, 4, 3} polytope represent the vertices of the sn-{3, 4, 3} polytope (Coxeter, 1973); while moving from the north to the south pole these vertices can be divided into 12 edge centres of the 'arctic' (+) octahedron, 24 north edge centres, 24 edge centres of the equatorial cuboctahedron, 24 south edge centres and 12 edge centres of the 'antarctic' (−) octahedron. In the case where the edge centres of the octahedra are omitted, one obtains a polytope having {72} vertices which is symmetric relative to the equatorial plane of the {3, 4, 3} polytope. The centres of 24 edges of the cuboctahedron are vertices of a rhombicuboctahedron which can be subdivided into subsets of 2(2 × 6) equatorial vertices. Similarly, the remaining nonequatorial 48 vertices of the {72} polytope can be subdivided into 2(2 × 12) subsets. In view of equations (5) and (6), the subsystem E_8(hole) of 2[2(2 × 18)] vectors of E_8 determines polytope {72} as an algebraic polytope situated on S^3 with 72 = 2(2 × 18) vertices, whose 2 × 18 vertices determine one of the two fibres of S_0^2, consisting of 18 vertices on the disc D_{+0}^2 and 18 vertices on the disc D_{-0}^2. It can be shown that the 18 = 6 + 12 vertices on the disc D_{+0}^2 (D_{-0}^2) correspond to six equatorial and 12 nonequatorial vertices of polytope {72}.

A transition to the fibration associated with equation (5) determines a redistribution of vertices on S_0^2 from 36 = 2(6 + 12) to 36 = 12 + 24, which corresponds to the sum of invariants 12 and 24, as well as to the structure of 24 elements, put in correspondence with Ω. The system E_8 is a seven-scheme lattice, according to which the invariant 24 can be written as 24 = 3(7 + 1), where 7 is the index of E_8 (Conway & Sloane, 1988). Summing up the above, we obtain

$$72 = 2 \times 2(6 + 12) = 2[(6 + 6) + (21 + 3)], \quad (7)$$

which reflects the partitions of the set of vertices of the algebraic polytope {72} considered above.

The sphere S^3 can also be given as a Stiefel manifold $V_{4,1}$, which (after complexification) is a universal cover for the Grassmanian manifold $G_{2,1}^c$. This manifold corresponds to midpoints of the minimal geodesics of the group SU(2); therefore, it is possible to bring into correspondence with the vertices on S_0^2 the midpoints of edges of the polyhedron, which also form minimal geodesic subsets. For the polyhedron representing a joining of two equivalent polyhedra, the set of edge midpoints can be given by an incidence table (IT), where a column is in correspondence with a 'white' vertex of one polyhedron, a row is in correspondence with a 'black' vertex of the second polyhedron, and the incidence symbol corresponds to the edge joining these vertices (Kraposhin *et al.*, 2008). In other words, an IT is a polyhedron connection table with two kinds of vertices (such as the IT of [4^6, 6^8], Fig. 1).

There is a single variant of an IT which satisfies the system of relations in equations (3), (6) and (7), namely, the 12 × 12 IT of a dichromatic graph of the parallelohedron [4^6, 6^8], where the incidence symbols fill 36 cells (Fig. 1*b*), corresponding to 36 vectors, reflected on S_0^2. The dichromatic pair of the graph's vertices is in correspondence with the involution; hence, the IT reflects the connection between an affine space and a vector representation (generated by an involution) of Weyl's group of the system E_8. The symplectic nature of the structure on S^3 is reflected in the right icosahedra (white and black) on S_0^2 and in placing only three incidence symbols into each row (column) of the IT. The icosahedron is the most symmetric triangulation of the sphere, in which five triangles meet at every vertex; hence every column (row) meets five columns (rows) in three rows (columns). The correspondence of E_8 to a subsystem Q from equation (3) determines a partition of the IT into 3 × 3 blocks, each of which can contain one or two triples of symbols, determined by the addition table of GF(3). The first decomposition in equation (7) corresponds to a partition of the IT into four 6 × 6 blocks, in which each of the two diagonal blocks contains 12 symbols. The second decomposition in equation (7) corresponds to the partitioning of the IT into 9 × 9 and 3 × 3 diagonal blocks (with 21 and three symbols in each), determined by the mapping of M_{12} into $M_9 \cdot S_3$ (Fig. 1*b*). It can be shown that the 24 symbols in the diagonal blocks are in correspondence not just with Horowitz's group, but also with the system of vectors (roots) D_4. The D_4 lattice is self-dual: $D_4 = D_4^* \supset D_3^* = A_3^*$, where A_3^* is a b.c.c. lattice (Conway & Sloane, 1988), and hence this relation determines [4^6, 6^8] as a parallelohedron – the Dirichlet polyhedron of b.c.c.

In Coxeter (1950) the configuration 12_3 of the finite projective geometry was introduced, formed by 12 (white) points and 12 'lines' (black points); here each 'line' consists of three points, and each point is traversed by three lines. The incidence graph of this configuration is {12} + {12/5} or a 'Nauru graph'. If there is a variety from v elements, a t-(v, k, λ) scheme is a set of subvarieties (blocks) from k elements so that each t element is contained in the λ blocks. If λ = 1 then the scheme is called a Steiner system $S(t, k, v)$ and the finite projective geometry PG(2, q) is a Steiner system $S(2, q + 1, q^2 + q + 1)$. The projective geometry prohibits the formation of rectangles out of incidence symbols in the IT – if they did form rectangles, two different straight lines would run through two points of the finite projective plane. In the IT in Fig. 1(*b*) this prohibition is satisfied only within the 9 × 9 diagonal block. This allows one to view the IT in Fig. 1(*b*) as IT $12_3(M_9 \cdot S_3)$, which could be inserted into the incidence table of the corresponding t-(v, k, λ) scheme (Samoylovich & Talis, 2007*b*).

3. Simple 24-vertex polyhedra with four-, five- and six-edge faces M-equivalent to the parallelohedron [4^6, 6^8]

The conservation of the algebraically essential part of the conditions in equations (4)–(6) (according to the unitary restriction principle) permits one to turn the graph of the parallelohedron [4^6, 6^8] into a simple 24-vertex graph M-equivalent to it. In particular, for IT $12_3(M_9 \cdot S_3)$ two requirements are algebraically essential: the inclusion of the 9×9 sub-table into the IT of the $(9_3)_2$ configuration of a finite projective geometry (Talis, 2004) and the equality of the number of symbols in diagonal blocks to the corresponding invariant of E_8. Taking into account equation (6) and the existence of the invariants of E_8 (18, 24, 30), all of them divisible by 3, the number of symbols in the diagonal blocks in IT $12_3(M_9 \cdot S_3)$ must be $\{(3(7+f) \cup 3(1+|f|)\}$, $f = 0, \pm 1$. The higher invariant 30 corresponds to the joining of 24 symbols of diagonal blocks in IT $12_3(M_9 \cdot S_3)$ with six symbols of two sub-blocks of non-diagonal blocks. If such sub-blocks are $10\text{–}12 \times 1\text{–}3$ and $7\text{–}9 \times 10\text{–}12$ then the 30-value sub-table IT $12_3(M_9 \cdot S_3)$ determines a hexagonal prism with two parallel hexagons as bases and six octagons as sides, each of which is divided by the interior horizontal edge into 4- and 6-gons. In the non-diagonal blocks in IT $12_3(M_9 \cdot S_3)$ such edges are determined by the symbols of the sub-blocks $10\text{–}12 \times 4\text{–}6$ and $4\text{–}6 \times 10\text{–}12$, which we shall refer to as horizontal (Figs. 1*a*, 1*b*). By connecting vertices having the same colour by the interior edge, the octagon can be divided into two 5-gons. The replacement of $2k$ dichromatic edges of the graph by monochromatic edges (between vertices of the same colour) requires one to discard $2k$ IT symbols and to introduce $2k$ arrows, which (in terms of projective geometry) determine the

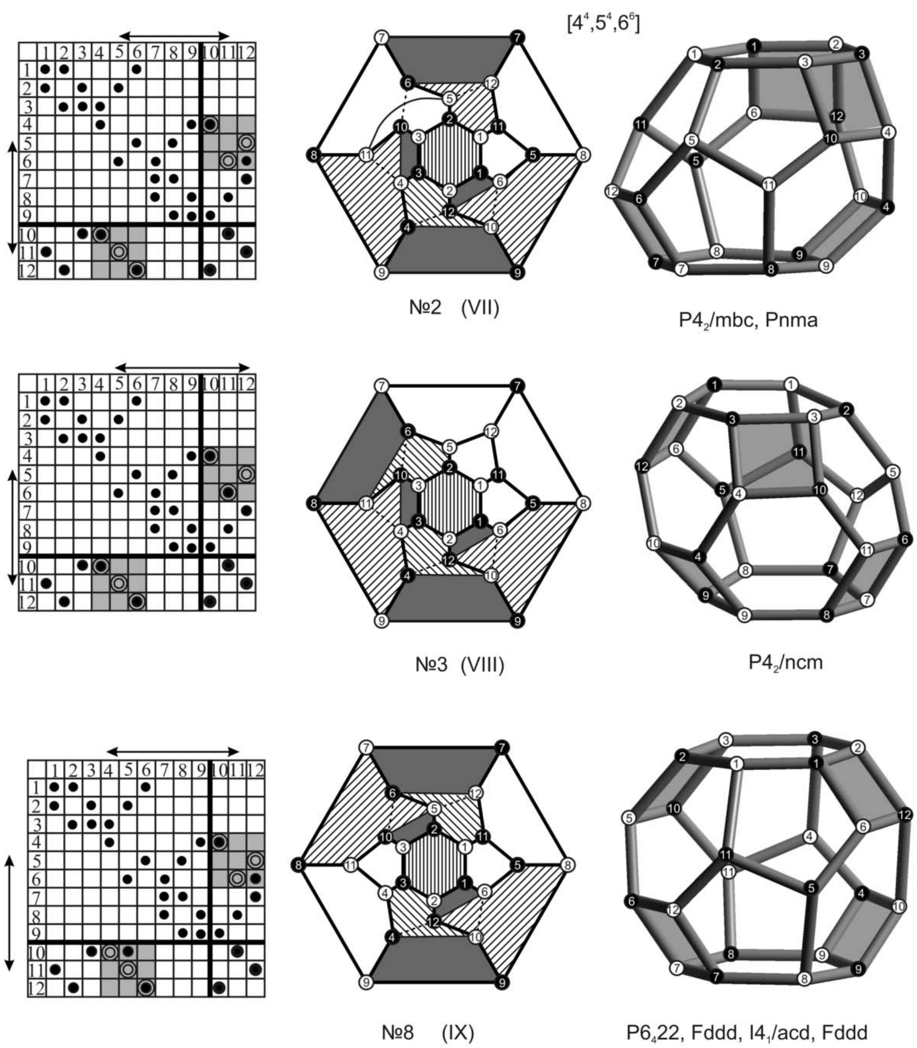

Figure 2
Incidence tables, Schlegel diagrams determined by them for graphs of stereohedra, and stereohedra [4^4, 5^4, 6^6]. Bold lines in the ITs distinguish diagonal blocks 9×9 and $10\text{–}12 \times 10\text{–}12$. The double arrow at the left (top) of each IT determines the 'incidence' of two rows (columns), which corresponds to an edge between vertices of the same colour. The ITs are different from one another only in the light-grey blocks, where there are circles within circles, denoting discarded (compared with the IT in Fig. 1*b*) incidence symbols. On the Schlegel diagrams determined by the ITs the quadrilaterals are shown in dark grey, hexagons are striped and the hexagon at the base is shown by vertical hatching. The edges of pentagons in the Schlegel diagram of the tetrakaidecahedron are shown as dotted lines. Under each diagram is given the number of the stereohedron (in which the quadrilaterals are shown in light grey) as determined by Delgado-Friedrichs & O'Keeffe (2005) and Komarov *et al.* (2007). The space groups according to Delgado-Friedrichs & O'Keeffe (2005) and Komarov *et al.* (2007) are given under each stereohedron.

'incidence' between a vertex and a vertex (a line and a line). Only diagonal blocks are algebraically essential, and hence a decrease of the number of incidence symbols is possible only in non-diagonal blocks. By skipping the interior (horizontal) edges in two adjacent side octagons, one of them can be divided by the new dichromatic edge into 4- and 6-gons while the second can be divided by a monochromatic edge into two 5-gons. The latter determines the possibility for the step-by-step skipping of symbols in the horizontal sub-block: firstly, one skips two symbols, corresponding to skipped edges, then a new symbol is introduced, corresponding to a new edge.

Summing up the above, let us determine the requirements for IT $12_3(M_n \cdot S_{12-n})$, which gives a simple 24-vertex graph M-equivalent to $[4^6, 6^8]$: the block $n \times n$ is inserted into the IT configuration n_3 of the finite projective geometry, and the structure of the entire IT is given by the relation

$$2[3 + (3 - k_i^j(f))] \cup \{(3(7 + f) \cup 3(1 + |f|)\} + \delta(k, f) = 36, \qquad (8)$$

where the square brackets and braces contain the number of symbols in the non-diagonal and diagonal blocks, respectively; $\delta(k, f) = 2k_i^j(f) - 3(f + |f|)$ is the number of monochromatic arrows. From here on, instead of representing a given IT with a symbol such as IT $12_3(M_n \cdot S_{12-n})$, we shall use the symbol IT $M_nS_{12-n}(f, k)$; for example, the graph of the parallelo-

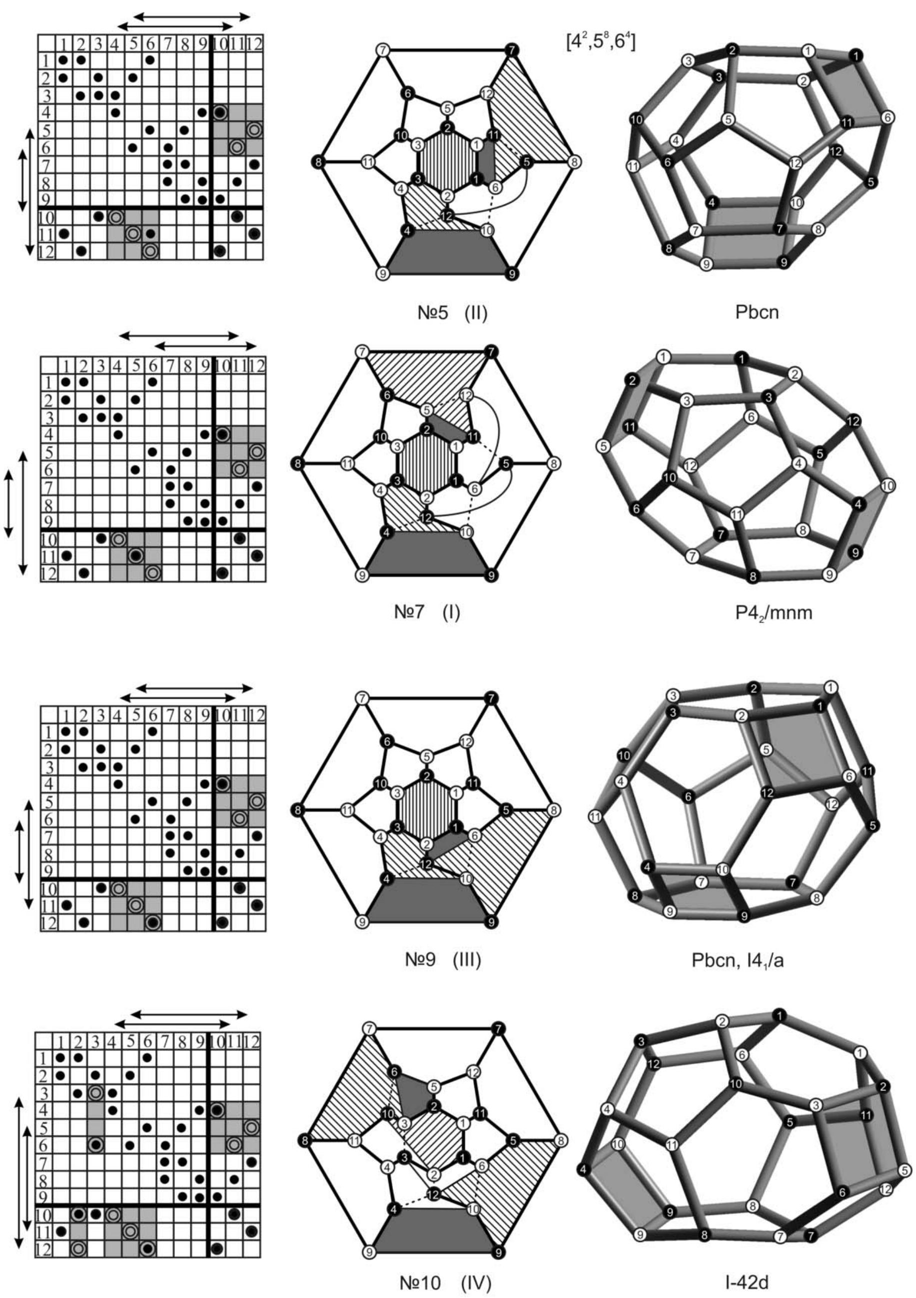

Figure 3
Incidence tables, Schlegel diagrams of graphs of stereohedra, and stereohedra $[4^2, 5^8, 6^4]$. The same notation as in Fig. 2 is used. In IT No. 10 light-grey stripes distinguish the shifts of incidence symbols, as compared with IT No. 9.

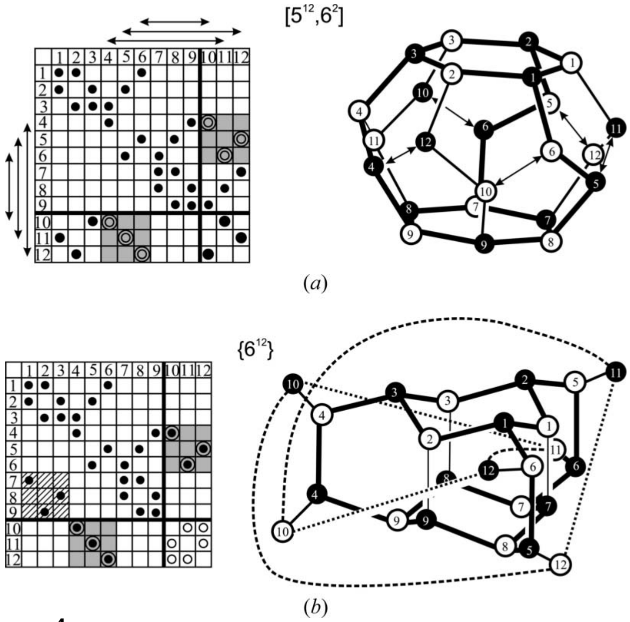

Figure 4
(*a*) An IT and the tetrakaidecahedron determined by it, in which the edges between vertices of the same colour are shown by double arrows. (*b*) An IT and the ice (or wurzite-type structure) cluster determined by it, whose hypothetical edges (dashed lines) are represented by empty circles in the IT. Without the dashed sub-block the 9 × 9 block in the IT coincides with the blocks in the IT in part (*a*) and the IT in Fig. 1(*b*), which determine an 18-vertex sub-graph of 24-vertex polyhedra (clusters) shown by bold lines.

hedron $[4^6, 6^8]$ will be characterized by the symbol IT $M_9S_3(0, 0)$.

Let us consider all *M*-equivalent polyhedra (clusters) whose graphs are determined by IT $M_9S_3(f, k)$, satisfying equation (8). The conditions $f = 0$, $k_i^j(0) = 0, 1, 2$, $\delta = 2k$ imply the replacement of $2k$ side faces $[4^6, 6^8]$ by $2k$ pairs of 5-gons according to

$$\begin{aligned}[4^6, 6^8] &\cong [(4\cup 6)^{6-2k}, (4\cup 6)^{2k}, 6^2] \leftrightarrow [((4\cup 6)^2)^{3-k}, ((5^2)^2)^k, 6^2]\\ &\cong [4^{6-2k}, 5^{4k}, 6^{8-2k}],\end{aligned} \tag{9}$$

where $(4\cup 6)^2$ and $(5^2)^2$ are 10-cycles, appearing upon uniting a pair of side octagons or two pairs of 5-gons. The variant $k = 0$ corresponds to the parallelohedron $[4^6, 6^8]$ (Figs. 1*a*, 1*b*); $k = 1$ corresponds to stereohedra Nos. 2, 3, 8 (Fig. 2); and $k = 2$ corresponds to stereohedra Nos. 5, 7, 9 (Fig. 3). The stereohedron No. 10 (Fig. 3) is determined by the IT that arises from the IT for No. 9 under the action of the element *m* of $2M_{12}(3)$; hence we denote this polyhedron by the symbol $[4^2, 5^8, 6^4]^m$. The transformation *m* is determined by the additional subdivision of 21 vertices in equation (7) into 20 (*i.e.* invariant of E_8) and 1.

By definition, IT $M_9S_3(0, 0)$ gives a parallelohedron; hence, the possibility for an *M*-equivalent polyhedron to be a stereohedron (that is, to generate a crystallographic subdivision of E^3) must be determined by conservation of some part of IT $M_9S_3(0, 0)$. In IT $M_9S_3(0, 0)$ the hexagons of the bases correspond with the symbols in the 9 × 9 block, and the three pairs of parallel squares correspond to pairs of symbols of two horizontal sub-blocks. The assemblage of $[4^6, 6^8]$ by parallel square faces in the sodalite structure leads to a rod with a symmetry axis, for instance, along the direction [100], belonging to the layer (001). It is evident that in order to obtain a three-dimensional structure one must place $[4^6, 6^8]$ along a direction not lying in (001), for example, along [111], that is, along the faces of parallel hexagons. Thus, in a three-dimensional crystalline structure, generated by an *M*-equivalent polyhedron $[4^6, 6^8]$, there must be rods assembled by 4-gonal as well as by 6-gonal faces. The $2(3 - k_i^j(f))$ horizontal symbols are responsible for the existence of 4-gonal faces. Therefore, IT $M_9S_3(f, k)$ may determine a stereohedron for $k \le 2$ and the tetrakaidecahedron $[5^{12}, 6^2]$ given by IT $M_9S_3(0, 3)$ is not a stereohedron (Fig. 4*a*). In the general case, this formalism is able to determine polyhedra *M*-equivalent to $[4^6, 6^8]$ that are not stereohedra (O'Keeffe, 1998).

The conditions $f = 1$, $k = 3$, $\delta = 0$ give an IT in which there are no rectangles formed by incidence symbols (not allowed in finite projective geometry). The latter means that the graph $[6^{12}]$ determined by such an IT may be isosceles in E^3 only after discarding a certain number of triplets of edges. Actually, assuming that the six symbols being discarded in the small diagonal block correspond to hypothetical edges, the graph $\{[6^{12}]\}^6$ is the graph of a 24-vertex (30-edge) stereohedron of crystalline ice (Fig. 4*b*), determined by IT $M_9S_3(1, 3)$.

The graph of the dodecahedron $[4^0, 5^{12}, 6^0]$ is determined by the 10 × 10 IT of a sub-configuration of the Desargues configuration (Talis, 2004). The 10 × 10 IT of another sub-configuration of the configuration 10_3 (Talis *et al.*, 2007) contains 24 incidence symbols and determines the 'minor' dodecahedron $[4^3, 5^6, 6^3]$ (Fig. 5*a*). By analogy with the above case of $M_9S_3(f, k)$, it is possible to show that the 10 × 10 IT $M_{10}S_2(f, k)$ block can be inserted in IT 10_3, and the structure of the entire IT is determined by the relation in equation (8), for $f = 0$ and by the value $k(0) = 4$, incompatible with M_9. The simple 24-vertex polyhedron $[4^3, 5^6, 6^5]$ determined by IT $M_{10}S_2(0, 4)$ is stereohedron No. 4 (Fig. 5*b*). Like the construction of stereohedron No. 10 by the IT of stereohedron No. 9, stereohedron No. 6 can be constructed by the IT $M_{10}^mS_2(0, 4)$, determining the stereohedron $[4^3, 5^6, 6^5]^m$ (Fig. 5*c*).

The 8 × 8 sub-table of the IT for a configuration 8_3 determines a 16-vertex isosceles polyhedron 2Z8 with seven nonplanar hexagonal faces (Talis, 2004). The polyhedron 2Z8 is determined only by the condition of minimality of the number of additional vertices and edges, which transforms a regular partition of the sphere into 4-gons (cube) into a non-regular one of seven hexagons. The graph 2Z8 is inserted in the graph of the polytope [4, 3, 3], whose symmetry group of order $2^4(4!)$ is inserted in the group $M_8 \cdot S_4$. Discarding a single edge and adding four leads to a simple ten-face polyhedron $[(4^2)^2, 4^1; 5^2, 6^3]$, in which two pairs of 4-gons have common edges (Fig. 6*a*). It can be shown that the extension of the 8 × 8 sub-table, determining $[(4^2)^2, 4^1; 5^2, 6^3]$ to IT $M_8S_4(-1, 2)$, gives simple 24-vertex 14-face polyhedra, containing isolated 4-gons. Thus, IT $M_8S_4(-1, 2)$ determines stereohedron No. 4 (Fig. 6*b*). By analogy, one can construct IT $M_8^mS_4(-1, 2)$, reducing stereohedron No. 6 to the polyhedron $[4^3, 5^6, 6^5]^m$ (Fig. 6*c*). The transformation m corresponds to the determination of the 18 invariant of the E_8 lattice by adding 1 to its exponent 17 [the algebraic polytope 136 = 8 × 17 has been considered in detail by Samoylovich & Talis (2008)].

4. Mutual transformations of *M*-equivalent polyhedra as a structural mechanism for local phase transformations

M-equivalence of the simple 24-vertex polyhedra given by IT $M_9S_3(f, k)$ determines the structural basis of the chain of (direct and reverse) local phase transitions, for example, gas hydrate↔ice (structure of bonded water). Actually, in all cases considered, the IT contains a 21-symbol 9 × 9 sub-table, insertable in IT $(9_3)_2$. The polyhedron given by such a sub-table arises within a prismatic treatment $[4^6, 6^8]$ upon joining [by equation (9)] pairs of side-face 8-cycles into 10-cycles. Discarding interior vertices and edges in 10-cycles leads to an 18-vertex 21-edge graph (of two base hexagons and three side-face 10-cycles) which is common to all the polyhedra (clusters) considered. The existence of such an invariant water cage allows one, in particular, to propose a model of (direct and reverse) local phase transitions for gas hydrate I↔ice.

According to Weaire & Phelan (1994), the surface of the 10-cycle $(4 \cup 6)^2$ in the parallelohedron $[4^6, 6^8]$ (Fig. 1*a*) is greater than the surface of the 10-cycle $(5^2)^2$ in the tetrakaidecahedron (Fig. 4*a*); hence for the exit of a guest molecule *via* a side-face 10-cycle it is necessary to transform the tetrakaidecahedron into one of the *M*-equivalent polyhedra according to the mechanism in equation (9). In general, different variants of transformations between polyhedral intermediates are possible (Figs. 1*a*, 2, 3), enabling the exit of the guest molecule. The remaining empty water cage 'implodes' into an ice cluster, decreasing the size of the inner cavity to the volume of the cluster $[(6 \cup 6)^3, 6^2]$, with the 18-vertex graph defined earlier,

$$\begin{aligned}[5^{12}, 6^2] &\leftrightarrow [4^{6-2k}, 5^{4k}, 6^{8-2k}] \\ &\leftrightarrow \{[6^{12}]\}^6 \supset [(6 \cup 6)^3, 6^2], \qquad (10)\end{aligned}$$

where the side-face 10-cycle consists of two 6-cycles, with a common interior edge (Fig. 4*b*). The relations in equation (10) also determine the reverse process of gas-hydrate formation, beginning with the increase in volume of the water cluster $[(6 \cup 6)^3, 6^2]$ due to discarding of interior edges in side-face 10-cycles. After the entrance of the guest molecule into the cavity thus formed within $\{[6^{12}]\}^6$, the molecule is 'fixed' due to formation of six additional bonds, transforming $\{[6^{12}]\}^6$ into one of the polyhedra $[4^{6-2k}, 5^{4k}, 6^{8-2k}]$. The chain of transformations [equation (9)] further leads to a tetrakaidecahedron with the guest molecule inside.

5. Conclusion

Space groups are the discrete groups of rigid motions in E^3, the elements of these groups acting on the structure as a whole. The need for the apparatus developed here is due to: firstly, the incompleteness (partiality) of the mapping of the symmetry for space subdivision into polyhedra by such groups;

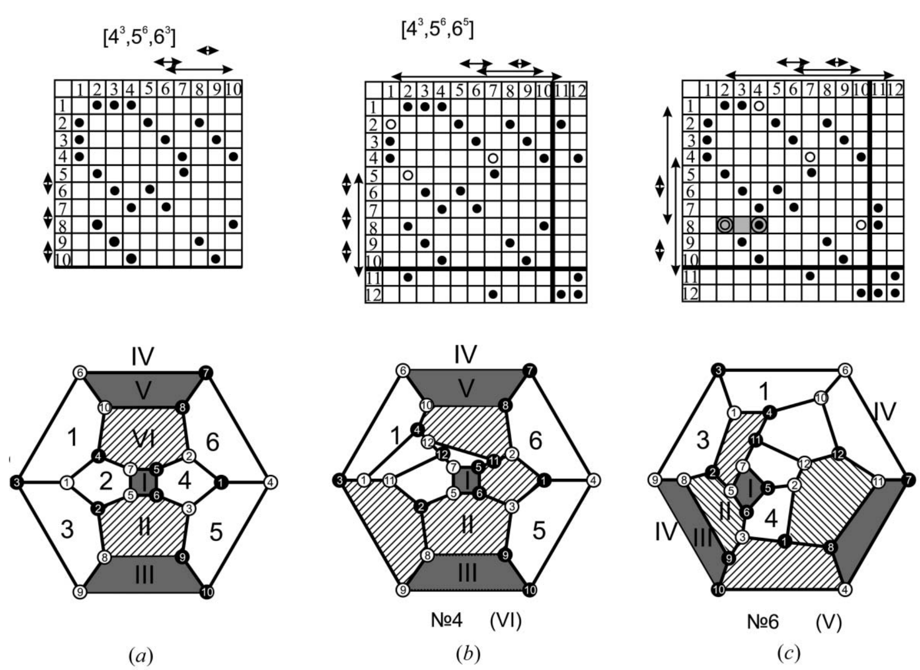

Figure 5
(*a*) The IT of a sub-configuration of Desargues configuration 10_3 and Schlegel diagram determined by it for a 'minor' dodecahedron $[4^3, 5^6, 6^3]$, whose triple axis goes through the white and black vertex 1. Roman numerals denote the 'equatorial' belt of squares and hexagons; triples of pentagons around the axis are shown by Arabic numerals. (*b*), (*c*) ITs and Schlegel diagrams of stereohedra $[4^3, 5^6, 6^5]$ determined by them. The 10 × 10 blocks differ from the IT in part (*a*) by the absence of three symbols, shown by empty circles. In the IT in part (*c*) the light-grey stripe marks the shift of the incidence symbol as compared to the IT in part (*b*). Similarly positioned polygons on Schlegel diagrams (*a*)–(*c*) are marked with the same numbers.

and, secondly, the incompleteness of the mapping of the polyhedral symmetry by their point subgroups. In fact, with the same point-symmetry group the simple 24-vertex and 36-edge polyhedra Nos. 5 and 9 with the same set $[4^2, 5^8, 6^4]$ of faces are distinguished by two edges only, corresponding to the incidence symbol and arrow in the incidence table (Fig. 3). Hence the mutual transformation of stereohedra is effected by a local (non-rigid) transformation which could not be determined at the level of the symmetry groups but is given by the incidence tables determined by the invariant of the algebraic geometry constructions. Crystallographic subdivisions of E^3 generated by given stereohedra have the same group *Pbcn*; hence their mutual transformation is effected by reconstructions conserving the invariants of constructions of algebraic geometry considered here, but not by the subgroup of the *Pbcn* group as in the classic theory of second-order phase transformations. It is evident that an adequate description of such structural phase transformations is impossible, in principle, in the framework of the space group apparatus.

The system of constructions of algebraic geometry allows one, in the end, to single out a special class of polyhedra whose 'progenitor' is Kelvin's polyhedron. Besides a more complete reflection of the symmetry of certain polyhedra, the proposed formalism is also necessary for describing the symmetry of polyhedra joining together. Examples include nanostructures, widely considered in recent times, for which, in contrast to crystals, there is no unique mathematical definition. In our approach to the definition of nanostructures, a local self-

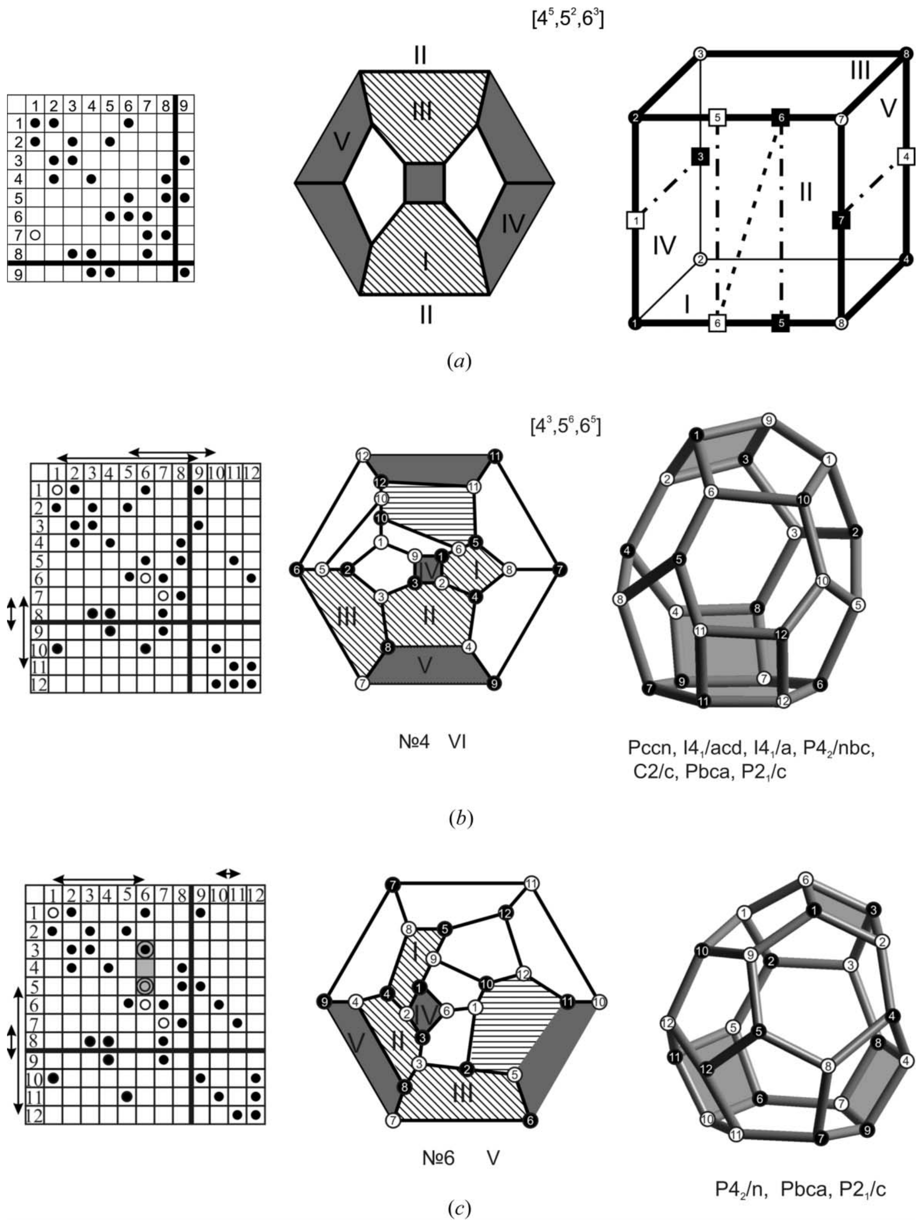

Figure 6
(*a*) The 8 × 8 block of the IT configuration $(9_3)_2$ determines a partition of the cube into seven hexagons, by decorating the edges by 'square' vertices and separating the face by a dashed edge. Discarding this edge and drawing dash–dotted edges leads to the polyhedron $[4^5, 5^2, 6^3]$, on whose Schlegel diagram the sequence of four- and six-vertex figures is shown in Roman numerals. (*b*), (*c*) When comparing 8 × 8 blocks in these ITs with the IT in part (*a*) and among themselves the notation is the same as in Figs. 5(*b*) and (*c*).

assembly principle may be proposed (Samoylovich & Talis, 2007*a*), where the initial (starting) elements of the system already contain the structural and self-organization rules which are determined by the condition of the maximum possible conservation of topological invariants of the system and its subsystems. Note that, in this case, all basic concepts of the standard approach are preserved and possible sets of vector representations of non-crystallographic groups are considerably extended (Humphreys, 1975; Shcherbak, 1988; Conway & Sloane, 1988); their use is inevitable in the study of nanostructures. In such a system the transitions between its subsystems, invariant with respect to various algebras, are difficult, which diminishes the system's susceptibility to instabilities of external conditions. The proposed approach is in full agreement with a well known quote by I. Prigogine (made in his Nobel lecture) concerning an amazing ability of structured systems to organize in similar ways under substantially different external conditions.

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