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Unusual Permutation Groups in Negative Curvature Carbon and Boron Nitride Structures

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The concept of symmetry point groups for regular polyhedra can be generalized to special permutation groups to describe negative curvature polygonal networks that can be expanded to possible carbon and boron nitride structures through leapfrog transformations, which triple the number of vertices. Thus a D surface with 24 heptagons and 56 hexagons in the unit cell can be generated by a leapfrog transformation from the Klein figure consisting only of the 24 heptagons. The permutational symmetry of the Klein figure can be described by the simple PSL(2,7) (or heptakisoctahedral) group of order 168 with the conjugacy class structure $E + 24C_7 + 24C_7^3 + 56C_3 + 21C_2 + 42C_4$. Analogous methods can be used to generate a D surface with 12 octagons and 32 hexagons by a leapfrog transformation from the Dyck figure consisting only of the 12 octagons. The permutational symmetry of the Dyck figure can be described by a group of order 96 and the conjugacy class structure $E + 24S_8 + 6C_4 + 3C_4^2 + 32C_3 + 12C_2 + 18S_4$. This group is not a simple group since it has a normal subgroup chain leading to the trivial group C_1 through subgroups of order 48 and 16 not related to the octahedral or tetrahedral groups.

Key words: permutation groups, leapfrog transformation, negative curvature, polygonal networks, carbon nitride structure, boron nitride structure.

INTRODUCTION

Until the 1980's diamond and graphite were the only well-characterized allotropes of elemental carbon. However, during the 1980's new allotropes of carbon were discovered exhibiting finite molecular cage structures rather than the infinite polymeric structures found in diamond and graphite. The

first such molecular carbon allotrope was C_{60}, which was postulated and subsequently shown to have a truncated icosahedral structure with all 60 equivalent trigonal carbon vertices, 20 hexagonal faces, and 12 pentagonal faces.[1] The discovery of C_{60} was followed almost immediately by the discovery of other molecular C_n allotropes (*e.g.*, n = 70, 76, 78, 80, 82, 84, 86, 88, 90, and 96) exhibiting other polyhedral cage structures albeit with much lower symmetry.[2] Such molecular carbon cages, generally known as fullerenes in view of their resemblance to the architectural creations of R. Buckminster Fuller, were all found to have exactly 12 pentagonal faces; the remaining faces of all known fullerenes are hexagons. Such fullerenes may be regarded as topologically homeomorphic to a sphere, the prototypical surface exhibiting positive curvature and having genus zero. Thus the introduction of carbon pentagons into the flat graphite hexagonal lattices generates sites of positive curvature. Euler's theorem can be used to show that a closed polyhedron with all trigonal vertices and only pentagonal and hexagonal faces, such as all known fullerene polyhedra, must have exactly 12 pentagonal faces.

A question of interest is the favored shapes of networks of trigonal carbon vertices in which only heptagonal and hexagonal carbon rings are present. Such networks cannot form closed polyhedra of positive curvature homeomorphic to the sphere but instead must form infinite structures of negative curvature known as infinite periodic minimal surfaces (IPMS's).[3] The simplest and most symmetric IPMS's exhibit cubic symmetry and have unit cells of genus three. Negative curvature carbon allotropes based on IPMS's are conveniently called schwarzites, in honor of the mathematician H. A. Schwarz, who was the first to study IPMS's in detail. The possibility of negative curvature allotropes of carbon was apparently first recognized by Mackay and Terrones[4] in 1991 and in 1992 Vanderbilt and Tersoff[5] first postulated the so-called D168 structure with a unit cell of genus three containing 24 heptagons and 80 hexagons and a total of 168 carbon atoms. In this structure the heptagonal rings may be viewed as sites of negative curvature and are not necessarily planar but can be bent. Carbon allotropes with negative curvature IPMS structures have not yet been obtained experimentally. A major difficulty in designing a synthesis of schwarzites is how to selectively form carbon rings of the desired sizes (*e.g.*, hexagons and heptagons) without forming carbon rings of undesired sizes (*e.g.*, pentagons).

Boron nitride analogues of diamond and graphite are known with the stoichiometry $(BN)_x$ in which pairs of adjacent carbon atoms are replaced by isoelectronic BN pairs thereby suggesting the possible existence of negative curvature boron nitrides analogous to the schwarzites. In this connection, boron nitride structures $(BN)_x$ are most favorable energetically if they con-

tain only B–N bonds without any B–B or N–N bonds. However, the presence of carbon rings with an odd number of atoms (*e.g.*, pentagons in fullerenes and heptagons in schwarzites) makes impossible analogous $(BN)_x$ structures if only the most energetically favorable B–N bonds are allowed. Thus in order to obtain $(BN)_x$ with only B–N bonds only $(BN)_r$ rings with an even number of atoms are allowed with alternating boron and nitrogen atoms so that the most favorable positive curvature BN cage analogous to the fullerenes contains only $(BN)_2$ squares and $(BN)_3$ hexagons and the most favorable negative curvature IPMS boron nitride structure contains only $(BN)_4$ octagons and $(BN)_3$ hexagons. In this connection the truncated octahedral $B_{12}N_{12}$ structure has been shown computationally[6,7] to be a favorable structure for a cage $(BN)_x$ boron nitride.

The symmetry of the polyhedra of the fullerene cages such as C_{60} and $B_{12}N_{12}$ can be described in terms of the point group of the polyhedron, namely icosahedral (I_h) in the case of C_{60} and octahedral (O_h) in the case of $B_{12}N_{12}$. Generalizing this concept of point group symmetry to the permutational symmetry of the negative curvature IPMS carbon and boron nitride allotrope structures leads to permutation groups which were already known to mathematicians in the 19th century but are not familiar to chemists even today since they do not appear as symmetry point groups. Previous papers discuss the heptakisoctahedral group of order 168 arising from the D168 schwarzite structure.[8,9] This paper reviews these earlier observations in a group-theoretical context and extends them to the hypothetical IPMS boron nitride structure containing only hexagons and octagons.

GENERAL IDEAS

Negative Curvature and Infinite Periodic Minimal Surfaces

Consider a curved surface, such as one formed by a network of sp^2-hybridized carbon atoms. At each point such a curved surface has two principal curvatures k_1 and k_2. The mean curvature H and the Gaussian curvature K are defined as follows:

$$H = \frac{1}{2}(k_1 + k_2) \tag{1a}$$

$$K = k_1 k_2. \tag{1b}$$

A spherical or ellipsoidal shell has positive Gaussian curvature (*i.e.*, it is »convex«), a hyperbolic sheet has negative Gaussian curvature (*i.e.*, it is »concave«), and a cylinder or cone has zero Gaussian curvature. Minimal

surfaces are surfaces where the mean curvature H at each point is zero so that $k_1 = -k_2$ by equation (1a) and $K \leq 0$ by equation (1b). They are thus saddle-shaped everywhere except at certain »flat points« which are higher order saddles. The simplest example of a (non-periodic) minimal surface excluding the trivial case of the plane is defined by the following cubic equation:

$$F(x, y) = z = x(x^2 - 3y^2). \tag{2}$$

This surface (Figure 1) is called the *monkey saddle*,[10] since it has three depressions, namely two for the monkey's legs and one for the tail. The average curvature of the monkey saddle vanishes at every point so that at every point its »concavity« is equal to its »convexity.«

It is not possible to construct an infinite surface with a *constant* negative Gaussian curvature. However, H. A. Schwarz found before 1865 that patches of *varying* negative curvature and constant zero mean curvature could be smoothly joined to give an infinite surface with zero mean curvature which is periodic in all three directions. Such surfaces are called infinite periodic minimal surfaces (IPMS's). The finite surface element building block which is repeated periodically throughout space in an IPMS plays a role analogous to the unit cell in a crystal structure. The five classical IPMS's known by 1880 (Ref. 11) have octahedral, tetrahedral, cubic, trigonal prismatic, and triangular unit cells and are conventionally known as the P,

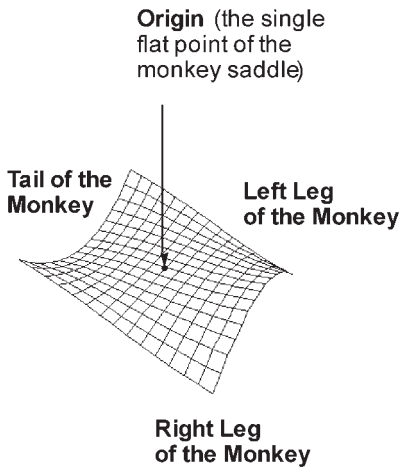
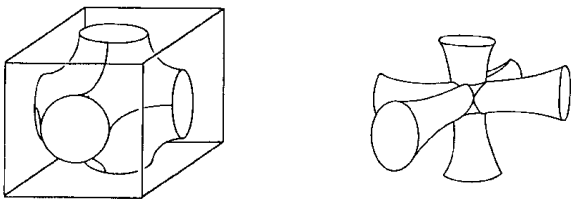


Figure 1. The monkey saddle generated by equation (2).

D, T, CLP, and H surfaces, respectively. Hyde and collaborators have used IPMS's to describe crystal structures.[3,12–16]

The IPMS's of particular interest for possible carbon or BN allotrope structures are those of the highest symmetry, namely the P and D surfaces, which have a genus of three. The unit cell of the P surface (the designation »P« refers to primitive cubic) can be viewed as an octahedral junction of six pipes or tubes (the »plumber's nightmare«) or equivalently as three hyperboloids whose axes meet at right angles (Figure 2). Connecting the open pipes emerging from each of the three pairs of adjacent faces of the plumber's nightmare thereby generating a closed surface leads to a sphere with three handles thereby indicating that a unit cell of this surface has genus 3.

The description of the unit cell of a P surface by the plumber's nightmare (Figure 2) suggests a natural division of the unit cell into eight equivalent octants, each corresponding to a face of the underlying octahedron so that the numbers of vertices, edges, and faces in a unit cell of a P surface are eight times those of an individual octant. All such octants of a P surface must be equivalent and contain the symmetry elements of the O_h point group describing the symmetry of the underlying octahedron or its dual cube. The local symmetry of an individual octant of the P surface is that of an equilateral triangle, namely D_{3h}. Thus in order to be compatible with the symmetry of the P surface the structure within an individual octant must contain a C_3 axis passing through the center of the octant and also must contain a reflection plane (σ_v in O_h) through each altitude of the triangle representing the octant corresponding to D_{3h} local octant symmetry. This symmetry clearly corresponds to that of a simple cubic lattice. The requirement of reflection planes in an octant of the P surface means that only achiral octants are suitable for P surfaces.



a) b)

Figure 2. Two descriptions of the unit cell of a P surface: (a) The »plumber's nightmare« octahedral junction of six pipes through the faces of a cube; (b) Three hyperboloids whose axes intersect at right angles.

The D surface is related to the P surface by reduction of the local symmetry from octahedral (O_h) to tetrahedral (T_d) (Figure 3). This means that the eight vertices of the underlying cube of the P surface are partitioned into two equivalent sets of four vertices for the D surface, each corresponding to the vertices of the two subtetrahedra making up the cube. The D surface can be seen to be related to the diamond lattice in that both consist of tetrahedral junctions imbedded into a cubic lattice (Figure 3). Three-fold symmetry is still required in the individual octants of the D surface but the reflection plane is no longer necessary. The D surface can thus accommodate chiral octants with the two sets of four vertices each corresponding to enantiomeric pairs of octants. The D surface bears an adjoint relationship to the P surface which is described in greater detail elsewhere.[3,8]

The relationship between the unit cells of P and D surfaces is depicted in Figure 2 as well as the face-centered cubic symmetry of a $2 \times 2 \times 2$ block of eight D surface unit cells. Thus the descent in unit cell symmetry from O_h for the P surface to T_d for the D surface can be depicted either by elongation of the »plumber's nightmare« octahedral junction (Figure 2) in the P surface to two tetrahedral junctions in the D surface[17] (Figure 3) or by the partitions of eight equivalent octants in the P surface unit cell (represented sche-

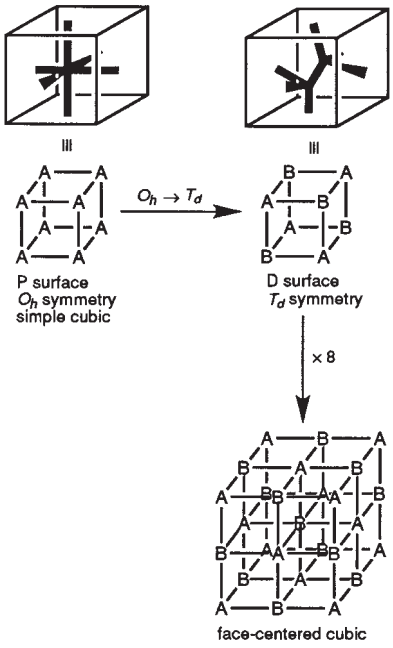


Figure 3. Relationships between the P and D surfaces and cubic structures showing the reduction of symmetry from the P surface to the D surface.

matically as A in Figure 3) into two complementary sets of tetrahedrally disposed octants in the D surface unit cell (represented schematically as A and B in Figure 3).

Euler's Theorem

The standard version of Euler's theorem relating the numbers of vertices (v), edges (e), and faces (f) is

$$v - e + f = 2 \ . \tag{3}$$

This theorem as stated in equation (3) applies to polyhedra which can be embedded in a sphere or a surface homeomorphic to a sphere and thus have genus zero. If such a polyhedron has all degree 3 vertices then

$$2e = 3v \tag{4}$$

since each edge connects exactly two vertices and each vertex is an endpoint of exactly three edges. In addition each edge is shared by exactly two faces leading to the relationship

$$\sum_n f_n = 2e \ . \tag{5}$$

Now consider regular polyhedra containing only triangular, square, or pentagonal faces so that

$$2e = 3v = 3\,f_3 + 4\,f_4 + 5\,f_5 \ . \tag{6}$$

Substituting this into Euler's equation (equation (3)) gives

$$\sum (6 - k)\, f_k = 12 \ . \tag{7}$$

Setting in turn $f_4 = f_5 = f_{>5} = 0$, $f_3 = f_5 = f_{>5} = 0$, and $f_3 = f_4 = f_{>5} = 0$ gives the solutions $f_3 = 4$, $f_4 = 6$, and $f_5 = 12$ for the regular tetrahedron, the cube, and the regular dodecahedron, respectively.

Euler's theorem can be generalized to polyhedra (or other polygonal networks) embedded in a surface of genus g by using

$$v - \ e + f = 2(1 - g) \ . \tag{8}$$

Note that if $g = 0$ (*i.e.*, for polyhedra homeomorphic to a sphere) equation (8) reduces to the familiar version of Euler's theorem (equation (3)). In the case of cubic IPMS's with genus 3, such as P and D surfaces, equation (8) becomes

$$v - e + f = -4 \ . \tag{9}$$

Now consider a cubic IPMS decorated with only trigonal atoms so that equation (4) applies as well as equation (5). Substitution of equations (4) and (5) into equation (9) gives

$$\sum (6 - k) f_k = -24 \ . \tag{10}$$

Now apply equation (10) to trigonal atom networks on genus 3 surfaces containing only hexagons and a single type of larger polygons leading to the following solutions of interest in this paper:

(a) Hexagons and heptagons $\Rightarrow f_{\neq 7} = 0 \Rightarrow f_7 = 24$ (*i.e.*, 3 heptagons per octant)

(b) Hexagons and octagons $\Rightarrow f_{\neq 8} = 0 \Rightarrow f_8 = 12$ (*i.e.*, 1 $^1/_2$ octagons per octant).

The Isolated Non-Hexagon Rule

The number of theoretically possible fullerene structures (*i.e.*, cage structures containing only pentagons and hexagons) for a given number of carbon atoms rapidly becomes unmanageable as the number of carbon atoms is increased above the minimum of 20 for the regular dodecahedron. Additional concepts must be introduced to select a limited number of preferred fullerene structures from this large number of possible fullerene structures and to rationalize the observation of C_{60} rather than C_{20} is the smallest isolable fullerene. In this connection an important additional concept for determining fullerene structures is the so-called *isolated pentagon rule* (IPR)[18] which avoids the unstable 8-membered pentalene-type cycle around any two pentagonal faces sharing an edge. Such pentalene units are undesirable for the following reasons:

(1) The Hückel criteria for aromaticity favors cycles containing $4k + 2$ rather than $4k$ π-electrons where k is an integer. Pentalene units have 8 π-electrons which is an unstable »$4k$-type« number.

(2) Topological and geometrical considerations suggest that hexagonal faces favor flat surfaces (*e.g.*, graphite) whereas pentagonal faces form curved surfaces (*e.g.*, the regular dodecahedron). Thus pentagonal faces lead to positive curvature whereas hexagonal faces favor zero curvature. Fusing two pentagonal faces by sharing an edge concentrates much of the curvature of the polyhedral surface into a limited region leading to unnecessary strain in the corresponding fullerene.

Klein[19,20] has proven the following theorem concerning the IPR:

IPR Fullerene Theorem: For every even vertex count $v \geq 70$ there exists at least one fullerene satisfying the IPR and the smallest fullerene satisfying the IPR is the truncated icosahedron with $v = 60$.

Experimental observations are in excellent agreement with this theorem since the smallest isolable fullerene has been found to be C_{60} and the next higher isolable fullerene is C_{70}.

Analogous ideas can be used to limit the number of possible carbon or boron nitride structures containing hexagons and other polygons, which can generically be called »non-hexagons.« This leads to the *isolated non-hexagon rule* (INHR) stating that non-hexagonal faces in trigonal carbon or boron nitride networks must be sufficiently isolated from each other so that no pair of non-hexagons shares any edges. Thus for schwarzites based on the D surface decorated only with hexagons and heptagons, the minimum number of atoms in the unit cell of a structure satisfying the INHR (the »isolated heptagon rule« in this case) is the 168 atoms of the D168 structure proposed by Vanderbilt and Tersoff.[5] At least in this sense this D168 structure is the schwarzite »analogue« of the known C_{60} fullerene.

The Leapfrog Transformation

The truncated icosahedron of the C_{60} structure can be generated from the regular dodecahedron by omnicapping (stellating) followed by dualization. Such a process is called a *leapfrog transformation*, and the resulting network is called the *leapfrog* of the original network. A leapfrog transformation of a network with all degree 3 vertices and only non-hexagonal faces triples the number of vertices and assures that the non-hexagonal faces will

TABLE I

Comparison of several leapfrog transformations

Polygon combination	Squares + Hexagons		Pentagons + Hexagons		Heptagons + Hexagons		Octagons + Hexagons	
leapfrog process	$(BN)_4 \xrightarrow{\text{leapfrog}} (BN)_{12}$		$C_{20} \xrightarrow{\text{leapfrog}} C_{60}$		D56 $\xrightarrow{\text{leapfrog}}$ D168		D32 $\xrightarrow{\text{leapfrog}}$ D96	
original figure	O_h cube		I_h dodecahedron		Klein figure		Dyck figure	
vertices	8	24	20	60	56	168	32	96
edges	12	36	30	90	84	252	48	144
faces	6	14	12	32	24	80	12	44
$f_{\neq 6}$	6	6	12	12	24	24	12	12
f_6	0	8	0	20	0	56	0	32
$f_{\neq 6} + f_{\neq 6}$ edges	12	0	30	0	84	0	48	0
$f_{\neq 6} + f_6$ edges	0	24	0	60	0	168	0	96
$f_6 + f_6$ edges	0	12	0	30	0	84	0	48

be »diluted« by enough hexagonal faces such that the INHR is satisfied. In 1996 the author[8] showed how the D168 structure[5] can be generated by an analogous leapfrog transformation starting with a genus 3 figure containing 24 heptagons and 56 vertices first described by Klein[21] in 1879.

Table I compares the four leapfrog transformations of interest in the context of this paper. In each case the leapfrog transformation expands a highly symmetrical »seed« structure containing exclusively the regular non-hexagons of interest and only trivalent vertices to a structure with the following properties:

(1) The number of vertices in the leapfrog is triple the number of vertices in the original seed structure;

(2) The permutational symmetry (*i.e.*, the point group symmetry in the case of the genus zero polyhedra) of the seed structure is retained in the leapfrog;

(3) The minimum number of hexagons is introduced to give a structure satisfying the INHR.

In the case of the cage polyhedra the leapfrog transformation (Figure 4) converts a regular trivalent polyhedron (*i.e.*, the cube or the dodecahedron) into its truncated dual (*i.e.*, the truncated octahedron in the case of the cube and the truncated icosahedron in the case of the dodecahedron). The underlying permutational symmetry is the same as that of the corresponding polyhedral point group, *i.e.*, O_h in the case of the cube and I_h in the case of the dodecahedron. The underlying permutational symmetry of the seeds containing 24 heptagons (*i.e.*, the Klein figure) and 12 octagons (*i.e.*, the Dyck figure) is more unusual. The relevant group theory will be examined in the remainder of this paper. More details on the symmetry of the Klein figure as described by the heptakisoctahedral group are presented elsewhere.[9]

Permutation Group Theory

The most familiar applications of group theory in chemistry use symmetry point groups, which describe the symmetry of molecules.[22] The elements of symmetry point groups can include only the standard symmetry operations in three-dimensional space, namely the identity (E), proper rotations (C_n), reflections (σ), inversion (i), and improper rotations (S_n). However, the concepts of group theory can also be applied to more abstract sets such as the permutations of a set X of n objects. A set of permutations of n objects (including the identity »permutation«) with the structure of a group is called a *permutation group* of *degree n* and the number of permutations in the set is called the *order* of the group.[23] The standard symmetry operations in symmetry point groups (*e.g.*, E, C_n, σ, i, S_n) can be considered to be special

types of permutations when applied to discrete sets of points or lines such as the vertices or edges of polyhedra.[24] In such situations, symmetry point groups can be regarded as special cases of permutation groups.

Let G be a permutation group acting on the set X and let g be any operation in G and x be any object in set X. The subset of X obtained by the action of all operations in G on x is called the *orbit* of x. A *transitive* permutation group has only one orbit containing all objects of the set X. Sites permuted by a transitive permutation group are thus equivalent. Transitive permutation groups represent permutation groups of the »highest symmetry« and thus play a special role in permutation group theory.

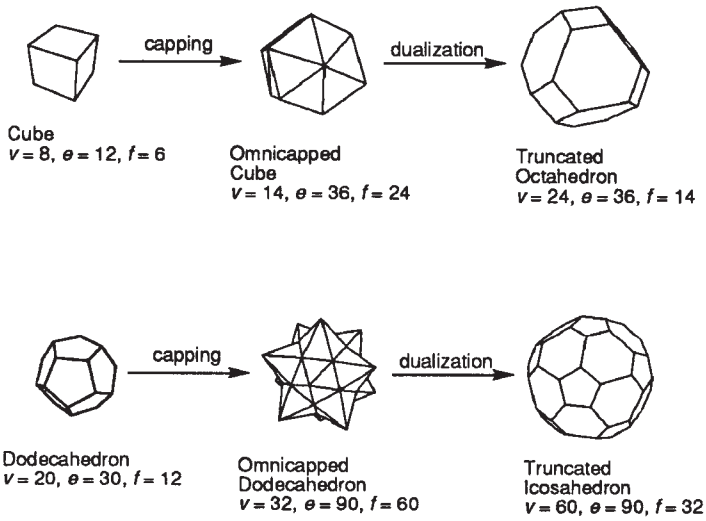


Figure 4. Applications of the leapfrog transformation to the cube and the regular dodecahedron.

Let A and X be two elements in a group. Then $X^{-1}AX = B$ is equal to some element in the group. The element B is called the *similarity transform* of A by X and A and B are said to be *conjugate*. A complete set of elements of a group which are conjugate to one another is called a *class* (or more specifically a *conjugacy class*) of the group. The number of elements in a conjugacy class is called its *order*; the orders of all conjugacy classes must be integral factors of the order of the group.

A group G in which every element commutes with every other element (*i.e.*, $xy = yx$ for all x, y in G) is called a *commutative* group or an *Abelian* group. In an Abelian group every element is in a conjugacy class by itself,

i.e., all conjugacy classes are of order one. A *normal subgroup N* of *G*, written $N \triangleleft G$, is a subgroup which consists only of *entire* conjugacy classes of *G*.[25] A *normal chain* of a group *G* is a sequence of normal subgroups $C_1 \triangleleft N_{a_1} \triangleleft N_{a_2} \triangleleft N_{a_3} \triangleleft \cdots \triangleleft N_{a_s} \triangleleft G$, in which *s* is the number of normal subgroups (besides C_1 and *G*) in the normal chain (*i.e.*, the length of the chain). A *simple* group is a group having no *normal* subgroups other than the identity group C_1. Simple groups correspond to the transitive groups of »highest symmetry« and are particularly important in the theory of finite groups.[26,27] The only non-trivial simple group found as a symmetry point group is the icosahedral pure rotation group, *I*, of order 60.

The permutation groups involved in the structures of carbon and boron nitride allotropes based on finite polyhedra necessarily correspond to familiar polyhedral point groups. Thus the truncated icosahedral structure of the fullerene C_{60} is derived from the leapfrog transformation of the regular dodecahedron (Figure 4). During this transformation the icosahedral symmetry I_h is preserved. Similarly the truncated octahedral structure of the boron nitride $B_{12}N_{12}$ is derived from the leapfrog transformation of the cube during which the octahedral symmetry O_h is preserved. The remainder of this paper discusses the interesting permutation groups which arise when analogous leapfrog transformations are used to generate the most symmetrical negative curvature structures containing only hexagons and either heptagons or octagons.

THE PERMUTATION GROUPS OF SYMMETRICAL POLYGONAL NETWORKS ON CUBIC INFINITE PERIODIC MINIMAL SURFACES

Schwarzite Structures Containing Hexagons and Heptagons

The above analysis suggests that the unit cell of the D168 schwarzite structure can be generated by decorating the unit cell of a D surface of genus 3 with 24 heptagons followed by a leapfrog transformation similar to the generation of the C_{60} fullerene structure by decorating a sphere with 12 pentagons to give the regular dodecahedron followed by an analogous leapfrog transformation (Figure 4). The D surface decorated with 24 heptagons can be obtained from a figure described by the famous 19th century German mathematician Felix Klein in an 1879 paper.[21] Figure 5, which is adapted from a figure in the 1879 Klein paper, depicts schematically the Klein figure, which is an open network consisting only of full heptagons or portions thereof which can be folded to decorate a genus 3 negative curvature surface, such as a unit cell of the D surface, in the most symmetrical manner with 24 heptagons. The seven-fold symmetry (*i.e.*, a C_7 axis) of the unfolded Klein figure (Figure 5) is clearly evident in a »central« heptagon (heptagon

1) surrounded by seven additional heptagons (heptagons 2 through 8). An »outer group« of an additional seven heptagons (heptagons 9 through 15) preserves the seven-fold symmetry of this open network.

The open network of heptagons as depicted in Figure 5 contains 14 outer arcs, which appear as sets of four edges or portions thereof because of the negative curvature of the surface. These outer arcs are labeled in pairs by the letters A through G. Joining the seven pairs of outer arcs labeled by the same letters generates the genus 3 surface which is topologically homeomorphic to a unit cell of the D surface and completes the remaining nine of the total of 24 heptagons by joining their pieces found in regions which are separated in the original open network (Figure 5). Thus, heptagons 16 though 22 are generated by joining their halves whereas heptagons 23 and 24 (not labeled in Figure 5) are each obtained by joining seven of the pieces which are the 14 »points« of the open network in Figure 5 not allocated to heptagons (heptagons 1 to 15) or heptagon halves (heptagons 16 to 22). Converting the open network in Figure 5 to a genus 3 surface by joining the pairs of outer arcs AA through GG destroys the seven-fold rotation axis in the symmetry point group of the resulting surface but in the most symmetrical presentation preserves the proper rotations (*i.e.*, O but not O_h symmetry) of the cubic unit cell of the D surface.

Klein in his 1879 paper[21] also considers the most symmetrical form of the genus 3 figure of 24 heptagons. A cubic unit cell of the D surface can be decomposed into eight octants as discussed above so that each octant contains 24/8 = 3 of the 24 heptagons with the vertices common to the eight triplets of heptagons corresponding to the eight vertices of the underlying cube. One of these triplets of heptagons is depicted in Figure 6a. This decoration of a unit cell of the D surface with 24 heptagons has (7)(24)/2 = 84

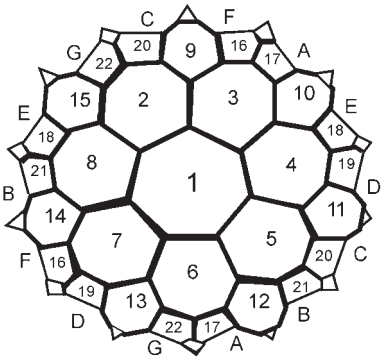


Figure 5. The Klein figure of 24 heptagons. Pairs of outer arcs to be joined to form a genus 3 surface are indicated by letters A through G.

edges and (7)(24)/3 = 56 vertices and thus has an Euler characteristic (equation (9)) of 56 – 84 + 24 = –4 corresponding to genus 3. A hypothetical carbon allotrope based on this structure is conveniently called a D56 protoschwarzite since it has a C_{56} unit cell on the D surface.

This D56 protoschwarzite structure is unfavorable for at least the following reasons analogous to the reasons why a C_{20} fullerene based on the regular dodecahedron is also unfavorable:

(1) The curvature of an sp^2 carbon vertex common to three heptagons leads to excessive angular strain;

(2) A pair of sp^2 carbon heptagons sharing an edge (*i.e.*, a »heptalene unit«) has 12 (= $4k$ rather than $4k + 2$) local π-electrons and is unfavorable in schwarzite structures for the same reasons that a pair of pentagons sharing an edge (*i.e.*, a »pentalene unit« with 8 local π-electrons) is unfavorable for fullerene structures.

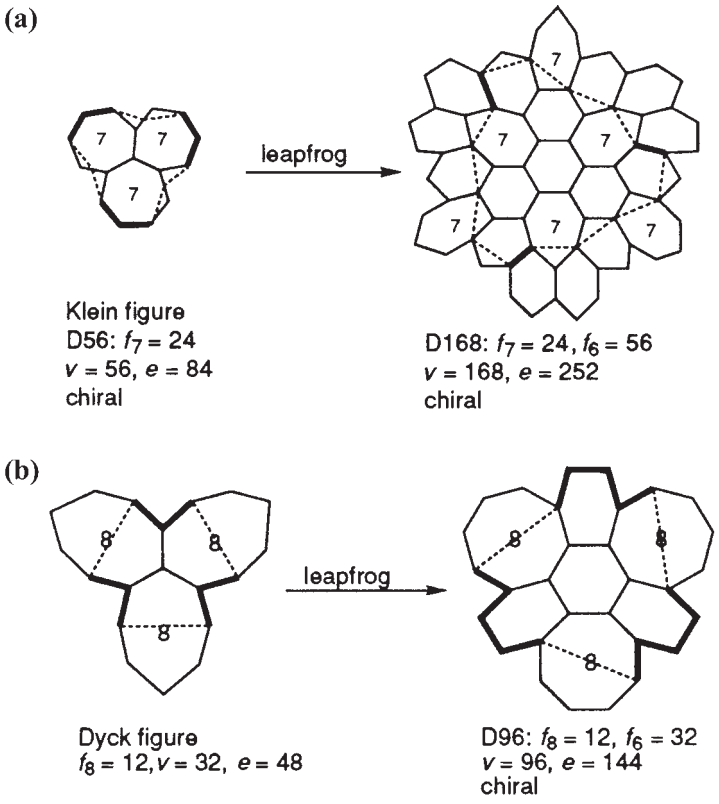


Figure 6. Leapfrog transformations on octants of the (a) Klein and (b) Dyck figures.

These unfavorable features of the D56 protoschwarzite structure can be removed by subjecting it to a leapfrog transformation which has the following effects:

(1) The number of vertices is increased by a factor of three giving $3 \times 56 = 168$ vertices in the unit cell leading to the D168 structure;

(2) The carbon heptagons are separated by the minimum number of hexagons so that no two carbon heptagons share an edge thereby eliminating unfavorable heptalene units;

(3) The symmetry and the genus of the surface are preserved.

The effect of such a leapfrog transformation on an individual octant of the Klein figure is depicted in Figure 6a.

Table I compares the effects of the leapfrog transformation on the dodecahedral C_{20} fullerene and on the D56 protoschwarzite. The products of both leapfrog transformations, namely the C_{60} fullerene and the D168 schwarzite, have the following features in common:

(1) The numbers of vertices and edges belonging to non-hexagonal faces ($f_{\neq 6} + f_6$ edges in Table I) are equal (60 in the case of C_{60} and 168 in the case of D168);

(2) The numbers of edges belonging to non-hexagonal faces ($f_{\neq 6} + f_6$ edges in Table I) are twice the numbers of edges belonging exclusively to hexagonal faces ($f_6 + f_6$ edges in Table I).

These features suggest that the C_{60} and D168 structures both represent the minimum »dilutions« of non-hexagons with hexagons so that no pair of non-hexagons has any edges in common. For this reason C_{60} is the smallest stable fullerene. Similarly, D168 has the smallest schwarzite unit cell containing only hexagons and heptagons with no pair of heptagons having an edge in common.

Now let us consider the permutational symmetry of the D56 protoschwarzite structure based on the Klein figure. First consider an alternative definition of the icosahedral pure rotation group, which can be extended to larger simple permutation groups which do not occur as symmetry point groups.[28] In this connection consider a prime number p and let F_p denote the finite field of p elements which can be represented by the p integers 0,…, $p - 1$; larger integers can be converted to an element in this finite field by dividing by p and taking the remainder (*i.e.*, the number is taken »mod p«). For example, the finite field F_5 contains the five elements represented by the integers 0, 1, 2, 3, and 4 and other integers are converted to one of these five integers by dividing by 5 and taking the remainder, *e.g.*, $7 \rightarrow 2$ in F_5 (written frequently as »$7 \equiv 2 \bmod 5$«). The group SL(2,p) is defined to be the

group of all 2×2 matrices with entries in F_p having determinant 1 and its subgroup PSL(2,p) for odd p is defined to be the quotient group of SL(2,p) modulo its center, where the center of a group is the largest normal subgroup that is Abelian. In the case of the groups SL(2,p) where $p \geq 5$, the center has only two elements and the quotient group PSL(2,p) is a simple group. The group PSL(2,5) contains 60 elements and is isomorphic to the icosahedral pure rotation group I.

An important property of the PSL(2,p) permutation groups for $p = 5$, 7, and 11 (Table II) is that they can function as *transitive* permutation groups on sets of either p or $p + 1$ objects. In the case of the group PSL(2,5), these transitive permutation groups on 5 and 6 objects can be visualized as permutations of parts of an icosahedron since PSL(2,5) is isomorphic to the icosahedral pure rotation group. Thus the PSL(2,5) group acts as a transitive permutation group on the six diameters of a regular icosahedron, where a diameter of an icosahedron is defined as a line drawn between a pair of antipodal vertices. In order to obtain in an icosahedron a set of *five* objects that is permuted transitively by the PSL(2,5) group, the 30 edges of an icosahedron are partitioned into five sets of six edges each by the following method:[29]

(1) A straight line is drawn from the midpoint of each edge through the center of the icosahedron to the midpoint of the opposite edge.

(2) The resulting 15 straight lines are divided into five sets of three mutually perpendicular straight lines.

Each of these five sets of three mutually perpendicular straight lines resembles a set of Cartesian coordinates and defines a regular octahedron. The PSL(2,5) permutation group as manifested in its isomorphic I symmetry point group functions as a transitive permutation group on these five sets of three mutually perpendicular straight lines. In fact the PSL(2,5) permutation group is also isomorphic with the so-called *alternating permutation group* on five objects,[30] namely A_5, where an alternating permutation group on n objects is the set of all possible *even* permutations and is of order $n!/2$.

The PSL(2,p) ($p = 5$, 7, 11) groups are simple groups and thus have no non-trivial *normal* subgroups. However, they contain two different sets of n smaller non-normal subgroups corresponding to pure rotation groups of regular polyhedra; these regular polyhedral rotation groups are subgroups of index p of the groups PSL(2,p). However, the PSL(2,11) group has been proven to the largest group of the general type PSL(2,p) with p a prime which has a subgroup of index p.[31] A corollary derived from this theorem is that if $p > 11$, the PSL(2,p) group cannot be a transitive permutation group for a set with fewer than p +1 elements in contrast to the PSL(2,p) ($p = 5$, 7, 11)

groups which can be transitive permutation groups for sets of p elements, namely 5, 7, and 11 respectively (Table II). Since the PSL(2,p) (p = 5, 7, 11) groups contain polyhedral point groups as subgroups they are conveniently designated as pollakispolyhedral groups.[9] Thus the PSL(2,5), PSL(2,7) and PSL(2,11) groups can be called the pentakistetrahedral, heptakisoctahedral, and undecakisicosahedral groups, respectively, and designated as ${}^5T$, ${}^7O$, and ${}^{11}I$, respectively.

The simplest example of the polyhedral subgroups of index p in the pollakispolyhedral groups occurs in the pentakistetrahedral group, ${}^5T$, which is equivalent to the icosahedral rotation group. Thus, ${}^5T$ can be decomposed into two different sets of five tetrahedra corresponding to the conjugacy classes $12C_5$ and $12C_5{}^2$. This is related to the partitioning of the 20 vertices of a regular dodecahedron into five sets of four vertices each corresponding to a regular tetrahedron. The permutations of the group PSL(2,5) act as the icosahedral pure rotation group I on the regular dodecahedron partitioned in this manner and correspondingly as the alternating group A_5 on the five subtetrahedra.

The next higher pollakispolyhedral group, namely the heptakisoctahedral group ${}^7O$ of order 168, is highly relevant to understanding the structure and symmetry of the schwarzite D168. This group can be decomposed into two sets of seven octahedral subgroups.[8,9] This relates to the embedding of the open network (*i.e.*, the Klein figure),[21,31] of 24 heptagons (Figure 5) into the unit cell of a D surface of genus 3 having a unit cell of octahedral symmetry such as the »plumber's nightmare« (Figure 2). The automorphism group of the Klein figure (Figure 5) is ${}^7O$, which thus remains the *automorphism* group of its embedding into the D surface in D168. The symmetry group of the pure rotations of the D168 unit cell is the octahedral rotation group O, which, as noted above, is a subgroup of index 7 in ${}^7O$. Thus the D168 schwarzite structure can be seen to have seven-fold (C_7) *hidden symmetry.*

TABLE II

Properties of the pollakispolyhedral groups derived from the PSL(2,p) groups (p = 5, 7, 11)

Group	Order	Conjugacy Classes	Polyhedral Subgroup
${}^5T \approx$ PSL(2,5)	60	$E + 12C_5 + 12C_5{}^2 + 20C_3 + 15C_2$	T
${}^7O \approx$ PSL(2,7)	168	$E + 24C_7 + 24C_7{}^3 + 56C_3 + 21C_2 + 42C_4$	O
${}^{11}I \approx$ PSL(2,11)	660	$E + 60C_{11} + 60C_{11}{}^2 + 110C_3 + 55C_2 + 132C_5 + 132C_5{}^2 + 110C_4$	I

Another question of interest is the relationship of the operations of the heptakisoctahedral group to permutations in the Klein figure (Figure 5). In this connection the 168 operations of ^7O can be divided into the following conjugacy classes:

(1) The identity operation E.

(2) Permutations of period 7 (C_7), each of which leave three heptagons invariant so that the cycle index on the set of 24 hexagons is $x_1^3x_7^3$. There are eight distinct »C_7 axes,« each of which passes through the midpoints of three heptagons. The resulting 48 operations can be partitioned into two conjugacy classes of 24 operations each, corresponding to C_7 and C_7^3 rotations.

(3) Permutations of period 3 (C_3), each of which leave two vertices invariant so that the 56 vertices of the Klein figure are partitioned into 28 »C_3 axes.« There are 56 operations in the C_3 class.

(4) Permutations of period 2 (C_2), each of which leave four edges invariant so that the 84 edges of the Klein figure are partitioned into 21 »C_2 axes.« There are thus a total of 21 operations in the C_2 class. The C_2 operations can be generated by combination of a C_7 and C_3 operation, *i.e.*, $C_2 = C_7 \times C_3$.

(5) Permutations of period 4 (C_4), which partition the 24 heptagons into six groups of 4. The C_4 operations are related to the other operations by the relationships $C_4 = C_7^4 \times C_3$ and $(C_4)^2 = C_2$. Because of the latter relationship there are a total of $21 \times 2 = 42$ operations in the C_4 class realizing that »C_4« and »C_4^3« will be in the same conjugacy class.

Thus permutations of these five types can be seen to lead to all 168 permutations and the six conjugacy classes of the heptakisoctahedral group listed in Table II.

The permutational symmetry of the Klein figure provides a simple explanation why the D surface rather than the more symmetrical P surface (Figure 3) is required for the Klein figure. The high symmetry of the P surface (*e.g.*, Figures 2 and 3) requires the full achiral octahedral group O_h, which however cannot be a subgroup of the ^7O since the order of O_h, namely 48, does not divide the order of ^7O, namely 168. For this reason the Klein figure cannot be embedded onto the P surface without reducing its symmetry to that of the D surface. Alternatively, it can be seen that an individual octant of the Klein figure (Figure 6a) is chiral whereas the P surface requires achiral octants.

Cubic IPMS Boron Nitride Structures Containing Only Hexagons and Octagons

The generalized Euler's theorem (equations (9) and (10)) indicates that a genus 3 structure containing only hexagons and octagons of alternating trigonal boron and nitrogen atoms has exactly 12 octagons in the unit cell or $1\ ^1/_2$ octagons per octant. The simple configuration of 12 octagons in the unit cell of a genus 3 surface leading to 32 vertices and 48 edges was studied by Dyck[32] in 1880 and is conveniently called the Dyck figure (Figure 7). In the Dyck figure a central octagon (octagon 1) can be seen to be surrounded by eight other octagons (octagons 2 through 9 in Figure 7). Octagons 10 and 11 are divided into quarters by the boundaries whereas the final octagon (not labeled in Figure 7) is obtained by joining the unlabeled 8 »points« of the open network in Figure 7. The leapfrog of the Dyck figure (Figure 6b and Table I) has 96 vertices, 144 edges, and 32 hexagons in its unit cell and is conveniently called the D96 structure.

The permutational symmetry of the Dyck figure was already recognized by Dyck[32] to be described by a group of 96 permutations which can be described as follows:

(1) The identity permutation.

(2) Permutations of period 4, each of which leaves four octagons invariant. There are thus three distinct »C_4 axes,« each of which passes through the midpoints of four octagons. Since »C_4«, and »C_4^3« are in the same conjugacy class, there are a total of $3 \times 2 = 6$ permutations in this class and these may be regarded as analogues of proper rotations C_4.

(3) Permutations of period 2, using the same three »C_4 axes« as the C_4 permutations mentioned above and thus corresponding to C_4^2. There are obviously three of these permutations.

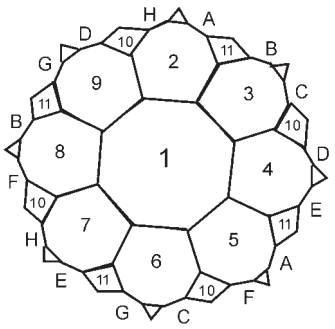


Figure 7. The Dyck figure of 12 octagons. Pairs of outer arcs to be joined to form a genus 3 surface are indicated by letters A through H.

(4) Permutations of period 8, each of which leave two octagons invariant. These operations are analogous to an improper rotation S_8 rather than a proper rotation C_8 since although S_8 leaves only two octagons invariant, $S_8^2 = C_4$ leaves four octagons invariant. Furthermore, the number of »S_8 axes« is double the number of »C_4 axes« since for each of the three »C_4 axes« passing through the midpoints of four octagons, there are two ways of choosing the pair of octagons that is permuted and the pair of octagons that remains fixed when an S_8 operation is applied. Since »S_8«, »S_8^3«, »S_8^5«, and »S_8^7«, are in the same conjugacy class, there are a total of $6 \times 4 = 24$ operations in this class.

(5) Permutations of period 3, each of which pass through 2 of the 32 vertices of the D32 structure. Since there are 16 distinct pairs of such vertices and since »C_3« and »C_3^2« are in the same conjugacy class, there are a total of $16 \times 2 = 32$ operations in this class.

(6) Permutations of period 2 (C_2), each of which pass through the midpoints of 4 of the 48 edges so that there are 12 operations in this class.

(7) Permutations of period 4, which are not derived by squaring permutations of period 8. These may be regarded as analogues of improper rotations S_4 and there are 18 operations in this class.

These seven classes add up to the 96 operations in the permutation group of the Dyck figure as $E + 24S_8 + 6C_4 + 3C_4^2 + 32C_3 + 12C_2 + 18S_4$. The pure octahedral rotation group, O, is a subgroup of index 4 in this group so that this group of order 96 can be described as the tetrakisoctahedral group and designated as ${}^4O$. However, the octahedral rotation group O is not a *normal* subgroup of the tetrakisoctahedral group since it cannot be constructed from entire conjugacy classes of ${}^4O$. Nevertheless, the tetrakisoctahedral group is not a simple group since other subgroups of ${}^4O$, albeit ones unfamiliar in chemistry or as symmetry point groups, can be constructed from entire classes of ${}^4O$. Thus ${}^4O$ has a normal subgroup of order 48 and index 2 that can be obtained by deleting the entire classes of permutations of periods 8 and 4 leaving only the permutations with periods 2 and 3 to give $E + 3C_4^2 + 32C_3 + 12C_2$ designated as $G[3,3,4]$ by adapting terminology already used by Dyck. The group $G[3,3,4]$ is clearly different from the full octahedral group O_h, which has elements of periods 4 and 6 and the very different conjugacy class structure $E + 8C_3 + 6C_2 + 6C_4 + 3C_4^2 + i + 6S_4 + 8S_6 + + 3\sigma_h + 6\sigma_d$.

The group $G[3,3,4]$ is also not a simple group since deletions of its entire class of permutations of period 3 gives a subgroup of order 16 and index 3 with only the identity and 15 permutations of period 2, namely $E + 3C_4^2 + + 12C_2$, which can be designated as $G[4,4,4]$, again adapting terminology

used by Dyck.[32] This leads to the following normal subgroup chain for the tetrakisoctahedral group ${}^4O$:

$$\begin{array}{lccccccc} & {}^4O & \overset{+2}{\rightarrow} & G[3,3,4] & \overset{+3}{\rightarrow} & G[4,4,4] & \overset{+2}{\rightarrow} & D_{2h} \overset{+2}{\rightarrow} D_2 \overset{+2}{\rightarrow} C_2 \overset{+2}{\rightarrow} C_1 \\ \text{Order:} & 96 & & 48 & & 16 & & 8 \quad 4 \quad 2 \quad 1 \end{array}$$

The normal subgroup chain of the tetrakisoctahedral group ${}^4O$ can be depicted by representing ${}^4O$ and its normal subgroups as tessellations (Figure 8), where a tessellation of a surface is an embedding of a network of polygons into a surface.[33] Such tessellations can be described in terms of their *flags*, where a *flag* is a triple (*V,E,F*) consisting of a vertex *V*, and edge *E*, and a face *F* which are mutually incident. A tessellation *T* is considered to be *regular* if its symmetry group *G*(*T*) is transitive on the flags of *T*. A permutation group can be depicted as a regular tessellation on whose flags it acts transitively.

The tetrakisoctahedral group, ${}^4O$, of the Dyck figure can be described by a tessellation with 96 white triangles and 96 black triangles so that the 96 operations of ${}^4O$ act transitively on the triangles of a given color (Figure 8). Such a tessellation can be described as {2,3,8} indicating that two white (or black) triangles meet at the midpoints of each edge of an octagon of the Dyck figure, three triangles of the same color meet at each vertex of such an octagon, and eight triangles of the same color meet at the center of each such octagon. Halving the number of triangles in this tessellation by combining adjacent triangles in a symmetrical manner gives a figure with 48 triangles of each color corresponding to the normal subgroup *G*[3,3,4] of order 48 and index 2 in ${}^4O$ (Figure 8). The designation {3,3,4} for this tessellation relates to the points at the vertices of the original octagons where three triangles of a given color meet and the points at the centers of the original octagons where four triangles of a given color meet. Taking the 96 triangles

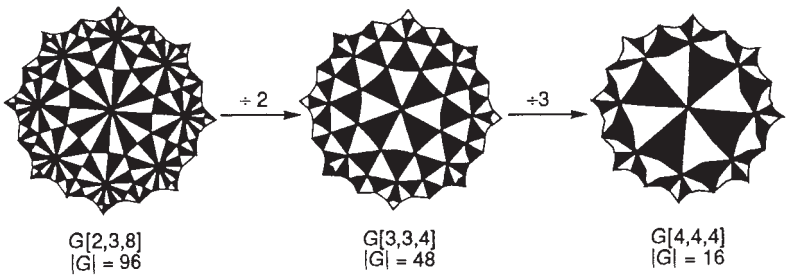


Figure 8. Tessellations showing the normal subgroup structure of the group *G*[2,3,8] ($\approx {}^4O$) of the Dyck figure.

of both colors in the tessellation {3,3,4} and recoloring them in alternate colors so that six triangles in the original {2,3,8} tessellation have a single color leads to a regular tessellation with only 16 triangles of each color corresponding to the normal subgroup $G[4,4,4]$ of index 3 in $G[3,3,4]$. The designation {4,4,4} for this tessellation relates to the fact that exactly four triangles of a given color meet at each vertex. Note that in order to show the relationship of the {4,4,4} tessellation to its »parent« {2,3,8} some of the so-called edges of its »triangles« are actually bent rather than straight lines in Figure 8.

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SAŽETAK

Neuobičajene grupe permutacija u ugljikovim i borovim nitridnim strukturama s negativnom zakrivljenošću

R. Bruce King

Pojam grupe simetrije točke za pravilne poliedre dade se poopćiti na posebne grupe permutacija koje mogu opisati mnogokutne mreže s negativnom zakrivljenošću. Primjenom transformacije »leapfrog« (kojom se utrostručuje broj čvorova) te se mreže mogu proširiti tako da opisuju moguće ugljikove i borove nitridne strukture (negativne zakrivljenosti). Pokazano je da se primjenom ove transformacije na Kleinov graf (od 24 sedmerokuta) dobiva tzv. D-površina sa 24 sedmerokuta i 56 šesterokuta u jediničnoj ćeliji. Permutacijska simetrija Kleinova grafa može se opisati jednostavnom grupom PSL(2,7) čiji je red 168, a struktura klasa konjugiranih elemenata dana je sa: $E + 24C_7 + 24C_7^3 + 56C_3 + 21C_2 + 42C_4$. Slično se primjenom transformacije »leapfrog« na Dyckov graf (od 12 osmerokuta) dobiva površina s 12 osmerokuta i 32 šesterokuta. Permutacijska simetrija Dyckova grafa može se opisati grupom čiji je red 96, a struktura klasa konjugiranih elemenata dana je sa: $E + 24S_8 + 6C_4 + 3C_4^2 + 32C_3 + 12C_2 + 18S_4$. Ta grupa nije jednostavna, jer posjeduje lanac normalnih podgrupa koji završava na trivijalnoj grupi C_1 a ide preko podgrupa (reda 48 i 16) različitih od grupe oktaedra i tetraedra.