Chemical Geometry

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A Short History of an Elusive Yet Ubiquitous Structure in Chemistry, Materials, and Mathematics

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"Geometry...supplied God with patterns for the creation of the world."
Johannes Kepler[1]

1. Introduction

Herein we describe some properties and the occurrences of a beautiful geometric figure that is ubiquitous in chemistry and materials science, however, it is not as well-known as it should be. We call attention to the need for mathematicians to pay more attention to the richly structured natural world, and for materials scientists to learn a little more about mathematics. Our account is informal and eschews any pretence of mathematical rigor, but does start with some necessary mathematics.

Regular figures such as the five regular Platonic polyhedra are an enduring part of human culture and have been known and celebrated for thousands of years. Herein we consider them as the five regular tilings on the surface of a sphere (a two-dimensional surface of positive curvature). A *flag* of a tiling of a two-dimensional surface consists of a combination of a coincident tile, edge, and vertex. A generally accepted definition of regularity is flag transitivity, which means that all flags are related by symmetries of the tiling (i.e. there is just one kind of flag). In addition to the five Platonic solids, there are three regular tilings of the plane (a surface of zero curvature), and these are the familiar coverings of the plane by triangles, squares, or hexagons tiled edge-to-edge. The corresponding regular tilings of three-dimensional space are also well-known. Flags are now a polyhedron (tile) with a coincident face, edge, and vertex, and the regular tilings of the three-sphere are the six nonstellated regular polytopes of four dimensional space. We remark that four dimensions is the richest space in this regard; higher dimensions have only three regular polytopes (and of course three dimensions has five). However, in flat three-dimensional (Euclidean) space, the space of our day-to-day experience, there is disappointingly only one regular tiling—the familiar space filling by cubes sharing faces (face-to-face). The classic reference to these figures is Coxeter's *Regular Polytopes*, in which he remarks on the tilings of three-dimensional Euclidean space: "For the development of a general theory, it is an unhappy accident that only one honeycomb [tiling] is regular…".[2]

Unhappy indeed, because, perhaps as a consequence, the rich world of periodic graphs, which are the underlying topology of crystal structures, has been largely neglected by mathematicians. The graph associated with (carried by) the regular tiling by cubes is the set of edges and vertices. It is notably the structure of a form of elemental polonium, and chemists often refer to it as the α-Po net. Recently a system of symbols for nets has been developed and this net has the symbol **pcu**.[3] Our review is concerned with another such periodic graph, and an associated surface.

2. Nets and Tilings

Some years ago in an effort to develop a taxonomy of three-periodic nets (which are special kinds of a periodic graph), it was decided to focus on the nets, rather than the tilings that carried them.[3,4] Regular nets were defined as those for which the symmetry required the figure (vertex figure), defined by the vertices neighboring a given vertex, to be a regular polygon or polyhedron. Five such nets were identified; these have vertex figures that are an equilateral triangle, square, tetrahedron, octahedron, and cube (see Figure 1). For each of the nets there is a unique natural tiling, but the tiles are not necessarily polyhedra in the usual sense, as they may have vertices at which only two edges meet (Figure 1). We note that in the case of the regular nets, the natural tiling is the unique tiling that has the full symmetry of the net. Interestingly these five nets appear to be the only ones with natural tilings that have one kind of vertex, one kind of edge, one kind of face, and one kind of tile (*transitivity* 1111).[3] These five nets play an essential role in the geometry of crystals and periodic materials in general.

3. The srs Net and K_4

Independent of the work on regular nets, Toshikazu Sunada recently asked,

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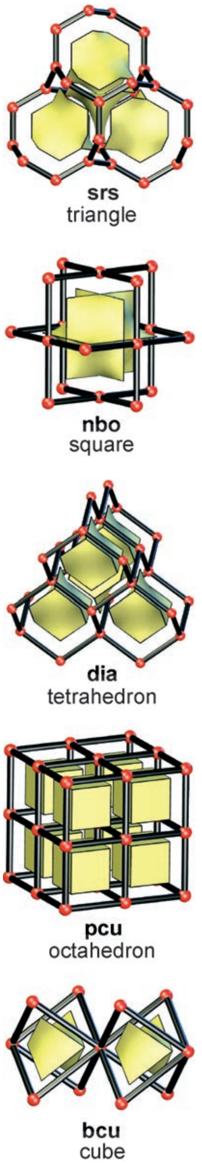

Figure 1. Fragments of the regular nets with their symbols and vertex figures. The natural tiles for the nets are shown shrunken for clarity; in reality they fill space.

in a stimulating paper, what three-periodic nets were strongly isotropic, that is, which permutation of vertices neighbouring a vertex can be realized by an operation that is a symmetry of the pattern, so that all such permutations extend to isometries of the net.[5] As the number of permutations is $n!$ for an n-coordinated vertex, the restriction of crystallographic symmetry in a three-periodic structure (in particular no symmetry elements of order 5) limits the possible coordination in a strongly isotropic net to three or four, and only two of the regular nets mentioned above are strongly isotropic. The two nets (Figure 1) have the symbols **srs** (three-coordinated) and **dia** (four-coordinated).[3] The latter is the familiar net of the diamond structure and the former is the main topic of our essay. As Sunada noticed, the quotient graph (the graph with the translations factored out) of this structure is the complete graph with four vertices, K_4, so he named it the K4 crystal.

Sunada's paper caused a considerable stir that was started by a press release from the American Mathematical Society about its "stunning beauty" under the heading "A Crystal that Nature May Have Missed", stating that "it is tempting to wonder whether it might occur in nature or could be synthesized".[6] It was described in Science, Nature Materials, and many other places in similar terms. The fact that a structure, well-known to crystallographers and crystal chemists for almost a hundred years and to materials scientists and solid state physicists for over fifty years, could be described in this way dramatically illustrates the gap that exists between much of the physical sciences and mathematics.

In its most symmetrical embedding, the **srs** net is cubic and the vertices are at fixed sites of 32 (D_3) symmetry where threefold and twofold axes intersect. This fixes the coordinates, and the structure is known to crystallographers as an invariant lattice complex. All such structures are documented in the International Tables for Crystallography (which should be required reading for mathematicians interested in periodic structures) where **srs** has the symbol Y^*.[7] It appears in a celebrated 1933 paper by Heesch and Laves, which is concerned with rare sphere packings,[8] and is also known as the Laves net. It also appears as "Net 1" [later as (10,3)-*a*] in the first of a series of pioneering papers on the geometrical basis of crystal chemistry by A. F. Wells who noted some occurrences in crystal chemistry.[9] The most conspicuous of these occurrences is the family of compounds with structures related to $SrSi_2$, where the net describes the topology of the Si substructure, hence the symbol **srs**. A recent spectacular occurrence is the high-pressure, three-coordinated form of elemental nitrogen.[10] With the resurgence of interest in coordination polymers and metal-organic frameworks in the 1990s examples having the **srs** topology were soon found,[11,12] and it is now common in this area. As Sunada remarked, it has also been considered as a possible allotrope of carbon (and predicted to be metallic).[13] To additionally appreciate the beauty and other properties of the net, illustrated in Figure 2, one should consider the symmetry. In its most symmetrical embedding the symmetry is $I4_132$, isomorphic with the combinatorial symmetry (automorphism group) of the graph. This symmetry is the most complex of the space groups with only proper symmetry operations (rotations and translations). It is relevant that there are nonintersecting fourfold axes, which are either 4_1 or 4_3 screws. There are also nonintersecting threefold axes which are either threefold rotations or 3_1 or 3_2 screws. As all the symmetry operations are proper, the structure is chiral—it comes in left- and right-handed forms. We remark that the **srs** net is the only three-coordinated, three-periodic net with threefold symmetry at the vertices, and accordingly, the only such net with equivalent edges (edge-transitive).

There is an interesting way in which the **srs** net had arisen 50 years earlier in mathematics. The regular polyhedra $\{n,3\}$ with $n = 3$, 4, or 5 have 3 n-gons meeting at each vertex (tetrahedron, cube, and dodecahedron respectively). $\{6,3\}$ is the tiling of the plane with regular hexagons and $\{n,3\}$ with $n > 6$ are tilings of the hyperbolic plane. But if, as suggested by H. S. M. Coxeter,[14] and taken up later by B. Grünbaum,[15] we allow faces to have infinitely many edges and to be skew polygons, then $\{\infty,3\}$ corresponds to a generalized polyhedron defined now as a family of polygons, such that any two polygons have in common either one vertex or one edge (two adjacent vertices) or have no vertices in common, and each edge is common to exactly two polygons.

There are in fact two such polyhedra in which the faces are helices that have trivalent vertices: $\{\infty,3\}a$ and $\{\infty,3\}b$ with faces that are threefold or fourfold helices, respectively (Figure 3) and their nets (the set of edges and vertices) are the **srs** nets in both cases. This characteristic was recognized and clearly illustrated by Grünbaum,[15] who in fact also

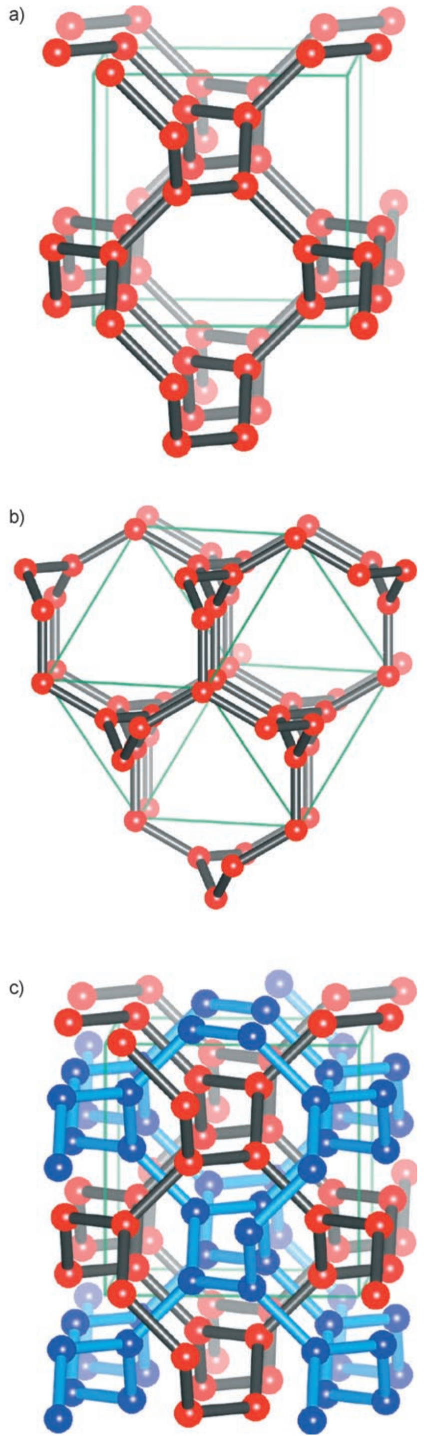

Figure 2. Aspects of the **srs** net. a) View almost along a fourfold axis. Note the 4_3 helices. b) View almost along a threefold axis. Note the 3_1 helices. c) Two **srs** nets of opposite handedness intergrown.

cites Wells'[9] paper. In his earlier work Coxeter referred to the net as "Laves' graph".[14]

In the natural tiling of the net there is just one kind of tile with three 10-sided faces (Figure 1).[3] These 10 rings

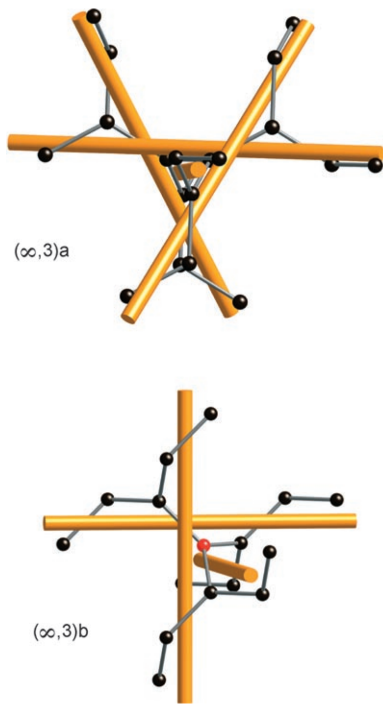

Figure 3. Fragments of the (∞,3) polyhedra. The faces shown are 3_2 and 4_1 helices with axes shown as cylinders. The net, **srs**, is the same in both cases.

are the only rings in the structure (a ring in this context is a cycle that is not the sum of smaller cycles) and 15 of these decagons meet at each vertex.

4. Interthreaded srs

For every tiling one can define a dual tiling moti obtained by putting new vertices in the middle of the old tiles and joining them by new edges through the old faces to new vertices in adjacent tiles. It should be clear that the net of the dual tiling will have a coordination number equal to the number of faces of the original tiling. In fact in the case of the **srs** net, the dual tiling is just **srs** again but now of the opposite hand. Accordingly, the two enantiomorphs can elegantly intergrow (Figure 2), as was already known to Wells,[16] and indeed subsequently observed for coordination polymers.[17] It is this intergrowth and the periodic surface dividing them that leads to the most interesting part of our story.

Wells' geometric patterns (nets) used to describe arrangements in crystals, soon appeared in a very different context: soft, atomically disordered liquid crystals. The gulf between atomic and molecular (liquid) crystallography and pure geometry was narrowing thanks to the efforts of Vittorio Luzzati and colleagues in France, who spent many years in the 1960s investigating the self-assembly of organic amphiphiles, including metallic soaps and lipids. These materials form ordered supramolecular structures, whose atomic ordering is often no different to a structureless melt, yet collectively form structures that, like atomic crystals, give rise to diffraction. Luzzati's group uncovered a rich array of phases, depending on temperature and water content, heralding a new class of condensed materials which are now collectively termed soft matter.

One of the structures, first reported by Spegt and Skoulios in 1964 for dry soaps, was later described by Luzzati and Spegt as a pair of interpenetrating nets, whose edges are composed of Sr rods, embedded in an nonpolar (hydrocarbon) continuum.[18] This pattern is the left- and right-handed pair of **srs** nets shown in Figure 2. By the late 1960's, Luzzati et al. had found this structure in a variety of soaps and lipid/water systems.[19] Remarkably, the structure was deduced on the basis of powder diffraction patterns alone (the scientists deliberately destroying large single liquid crystals), without any knowledge of prior work on those nets.

5. The Gyroid

Similar investigations into liquid crystals were also being carried out at the same time by Swedish and Finnish physical chemists, pioneered by Per Ekwall and furthered by Krister Fontell, Kåre Larsson, and colleagues in Sweden. Their own work suggested that the molecules forming these liquid crystals tend to aggregate into sheet-like structures, such as the molecular bilayers that sheath cells.[20] How then can those molecules aggregate to form the pair of chiral **srs** networks of threaded edges (re)discovered by Luzzati? The connection was not definitively made until 1984, when Larsson and co-workers recognized the link between the pair of **srs** nets and a sponge-like surface, known as the gyroid (or *G* surface).[21] This surface, discovered in the 1960's by NASA scientist Alan Schoen[22,23] (Figure 4), bisects space into a pair of interthreaded channels, whose axes coincide precisely with edges of the **srs** nets (Figure 5). So the net description by Luzzati was reconciled with the membrane description: the net described the sponge-like channels of the intricately folded membrane.

In 1992 there were two reports from a group at the Mobil Research and Development Corporation showing that ordered liquid crystal structures could serve as templates for silica-based mesoporous materials in which the glass-like inorganic material was confined to the interface and after calcination ordered empty channel systems remained.[24,25] In the cubic material, subsequently named MCM-48, the interface is the gyroid surface, and the channels are a pair of interpenetrating **srs** nets.[26]

Figure 4. Alan Schoen, on the roof of the Courant Institute in Manhattan, with his model of the gyroid. (Picture courtesy of Stefan Hildebrandt. Reproduced by permission of Springer-Verlag.)

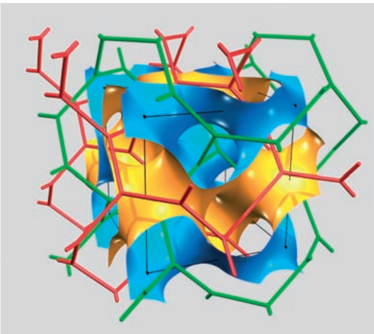

Figure 5. The gyroid, a three-periodic minimal surface discovered by Alan Schoen. The surface is illustrated together with its labyrinth graphs (red and green), which describe the channel structure. Each graph is the **srs** structure as in Figure 2c. (Picture courtesy of Gerd Schröder-Turk).

The impact of those two papers can be gauged from the fact that they have been cited over 10000 times in the 15 years since publication. Very many inorganic materials based on the MCM-48 structure have since been reported, including a recent hierarchical mesoporous inorganic material with crystalline ordering on the atomic scale; the ordering is observed simultaneously on the atomic and meso scales, thus closing the gap between atomic and liquid crystals.[27]

The gyroid is closely related to other important triply periodic minimal surfaces (surfaces with zero mean curvature everywhere). The natural tilings of the regular nets, **dia** and **pcu**, are also self-dual (the remaining pair **nbo** and **bcu** have mutually dual tilings), and for these structures pairs of nets can likewise interpenetrate. The periodic minimal surfaces separating the pairs are known as the *D* and *P* surfaces respectively. The *D* surface was parameterized by Bernhard Riemann around 1860 and published posthumously;[28] it was rediscovered shortly thereafter by Schwarz (splendid engravings of it can be found in his papers), who also introduced the *P* surface.[29] Both surfaces share identical intrinsic two-dimensional geometry and it is only their three-dimensional embedding in space that makes them different. Just as a sheet of paper can be morphed into a cylinder by simple bending, patches of the *D* and *P* surfaces are interchangeable by the *Bonnet transformation*.[30] Schoen built beautiful plastic models of the *P* and *D* surfaces that were able to bend *à la Bonnet*.[31] His mathematical and physical manipulations revealed a third triply-periodic minimal surface hidden among the aperiodic intermediates to the *D* and *P*: the gyroid. Yet the gyroid remained unknown to mathematics until Schoen's discovery—announced only in a NASA patent and accompanying report.[22,23] This discovery was a bona fide example of an important structure that had been overlooked by mathematicians for over a century! Indeed, each labyrinth of the gyroid is centered by the net that intrigued Sunada.

One wonders if this discovery might have been recognized earlier if the regular nets and their tilings had been recognized (although not all pairs of nets of dual tilings necessarily have corresponding minimal surfaces). As it is, perhaps we should rephrase Sunada's characterisation of **srs** (K_4) as the structure that "nature might miss creating" to "the structure that mathematicians missed—from Riemann on"?

The identification of the **srs** net with the gyroid, one of the most uniform foldings of a saddle-like sheet into three-dimensional euclidean space, paved the way for a host of other links between the net and materials. The gyroid structure is now known to underlie many other supramolecular "soft" materials, from lipids in cells to synthetic polymeric molecular melts.[32] It also affords an elegant description of the director field of molecules within the lowest temperature (blue phase), a class of tunable electro-optic materials of some interest in both academic and practical circles.[33,34]

The gyroid is a supreme example of a regular partition of space, and it is that regularity that explains why it is found in so many different materials.[35] One measure of its universality can be gauged from the range of crystal sizes in gyroid structures. Bicontinuous phases in amphiphiles have a lattice repeat spacing of the order of 100 Å. In larger polymeric systems, that spacing can be ten times larger, giving (liquid) crystals a period roughly one hundred times greater than the spacings in hard atomic crystals. It is remarkable that a soft, quasi-molten molecular assembly such as polymeric melts, can sustain such long-range structural ordering, typically containing 10^3–10^4 molecules within a single unit cell of the membrane.

Perhaps the most spectacular example of the **srs** structure in nature can be found in the summer fields of Europe, rather than in the labs of materials scientists. The Green Hairstreak (*Callophrys rubi*) is a splendid butterfly, readily identified by its metallic green wings. Those painted wings contain a myriad of overlapping scales, easily seen in an optical microscope. Electron microscopy reveals an extraordinary three-dimensional matrix of the hard skeletal material within many scales[36] whose morphology of which is related to the gyroid.[37] Recent structural studies have revealed that the matrix structure is accurately described by the **srs** net, where edges of the net are thickened, so that the material resembles a smooth sponge formed by filling one labyrinth of the gyroid surface (Figure 6).[38,39]

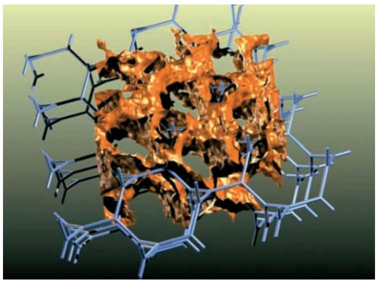

Figure 6. Chitin network in the butterfly wing scales of *Callophrys rubi*. The brown surface defines the outer form of the chitin matrix determined by electron tomography, so that the channels containing blue edges are filled. The blue **srs** net describes the chitin network to a remarkable degree of accuracy. (Image courtesy of Stuart Ramsden, Gerd Schröder-Turk).

The length of this giant **srs** material is around 3000 Å—on the same order as the wavelength of visible light. Indeed, the lovely coloring of the flapping wing in the sunshine is very likely because of the scattering of visible light within the **srs** matrix. Optical physicists are keen to exploit these materials as they may be natural three-dimensional photonic crystals that have been long sought after to advance optical computing. This material forms within the butterfly chrysalis and is a living example of supramolecular self-assembly of soft matter, composed of membrane and protein materials that form a soft matrix that templates the later formation of the hard skeleton in the emergent butterfly. The matrix forms by condensation of lipid bilayers in the smooth endoplasmic reticulum, induced by proteins, giving a foliated multilayered sponge. The homogeneity of the gyroid partition allows uniform bending and packing of the lipid membranes and the intervening proteins. Here too, the extreme regularity of the **srs**/gyroid structures explains their genesis in this complex set of chemical crucibles.

We end this progress report (for it is not the end of the story) with a plea for more awareness of the work by mathematicians and materials scientists. The beautiful and complex periodic structures found in nature would surely be fertile ground for more in-depth mathematical studies. At the same time we beg mathematicians to make their work more accessible to physical scientists (e.g. by including pictures such as the beautiful one presented by Sunada[5]).

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