

Cover of the February 1, 1983, issue of *Journal of Chemical Education* from I. Hargittai, "Degas' Dancers: An Illustration for Rotational Isomers." Reprinted with permission, © 1983, American Chemical Society.

## Degas' Dancers: An Illustration for Rotational Isomerism<sup>a</sup>

#### Istvan Hargittai

The representation of rotational isomerism by projection drawings is difficult for some students to grasp because of its abstract nature. Two drawings by Degas, "End of the Arabesque"<sup>1</sup> and "Seated Dancer Adjusting Her Shoes,"<sup>2</sup> provide an opportunity to introduce the concepts of staggered and eclipsed conformations of A<sub>2</sub>B-BC<sub>2</sub> molecules in a concrete, interesting (and aesthetic) way.



Figure 1. (left) Lantos' drawing after Degas' "End of the Arabesque." (right) Lantos' drawing after Degas' "Seated Dancer Adjusting Her Shoes." Full color reproductions of the originals are available in editions of Degas' work.

The two dancers are shown in Figure 1 as drawn by Lantos<sup>3</sup> after Degas. Stylized contour drawings are presented in Figure 2 in order to facilitate understanding the transition from the dancers to the chemical formulas. A staggered and an eclipsed forms of the A2B-BC2 molecule are shown by the usual projection representation in Figure 3.

<sup>&</sup>lt;sup>a</sup> Journal of Chemical Education 1983, 60:94. Reproduced with permission, © 1983 American Chemical Society



Figures 2 and 3. Contour drawings of the dancers shown in Figure 1 illustrating the preparation of the projection representation (top).

Staggered and eclipsed rotational isomers of the A2BBC2 molecule by projection representing the view along the B-B bond (bottom)

The projections represent the view along the B–B bond. The dancer's body then corresponds to this bond. The plane bisecting the B–B bond is shown by the circle, and it is represented by the dancer's skirt. The dancer's arms and legs refer to the B–A and B–C bonds, respectively. Even the bouquet in the right hand of the dancer showing the staggered conformation may have a useful function: it is viewed as a different substituent, and may help to understand more complicated rotational isomerism. My experience is that showing Degas' drawings not only enlivens a lecture on conformational problems but also facilitates the introduction of the subject.

<sup>&</sup>lt;sup>1</sup> Louvre, Musee de l'Impressionisme, Paris

<sup>&</sup>lt;sup>2</sup> The Hermitage, Leningrad

<sup>&</sup>lt;sup>3</sup> The author appreciates the kindness of the artist Mr. Ferenc Lantos, Pécs, Hungary, who prepared the drawings of Figure 1 after postcards of the pictures by Degas.



Cover of the December 1, 1984, issue of *Journal of Chemical Education*. The art is an actual needlework by one of the editors of the journal, from I. Hargittai and G. Lengyel, "The Seven One-Dimensional Space-Group Symmetries Illustrated by Hungarian Folk Needlework." Reprinted with permission, © 1984, American Chemical Society.

# The Seven One-Dimensional Space-Group Symmetries Illustrated by Hungarian Folk Needlework<sup>a</sup>

### Istvan Hargittai and Gyorgyi Lengyel

The idea of infinite translations is a crucial point in teaching crystallography and symmetry. However, for some students it is difficult to grasp because of its abstract nature. Experience shows that analogies from outside crystallography greatly facilitate the understanding of this concept.

The seven one-dimensional classes are the simplest space-group symmetries. They are illustrated here by patterns of genuine Hungarian needlework. This kind of needlework is a real "one-sided band" and is ideally suited for this purpose.

Figure 1 shows a consistent system of an asymmetric motif, a black triangle, corresponding to the seven symmetry classes of the one-dimensional space groups. In the table, the symmetry elements are enumerated together with a brief description of the corresponding needlework presented in Figure 2.



Figure 1

<sup>&</sup>lt;sup>a</sup> Journal of Chemical Education 1984, 61:1033-1034. Reproduced with permission, © 1984 American Chemical Society



Figure 2

## Symmetry Elements and Corresponding Needlework Designs

Symmetry Elements Shown in Figure 1		Needlework Designs from Figure 2	Symmetry Elements Shown in Needlework Designs Figure 1 Figure 2	Needlework Designs from Figure 2	
1. Tran tra be	Islation axis. The period of anslation is the distance etween two identical points of nsecutive black triangles	Edge decoration of table cover from Kalocsa, southern Hungary	4. Translation by transverse symmetry planes Embroidered edge dect sheet from the 18th of the deviations from the symmetry in the low	pration of bed century. Note he described ver stripes of	
2 Glid	Glide-reflection plane. The black triangle comesinto coincidence with itself after translation through half of the translation periodand reflection ina plane perpendicular to the plane of the drawing	Pillow end decoration from Tolna County, southwest Hungary	the pattern 5. Translation axis combined with a Decoration of shirt from	t from Karad	
CC			longitudinal symmetry plane southwestHungary	southwestHungary	
tra tra re pe th			6 Combination of a glide-reflection plane with transverse symmetry planes. Translation axis and two-fold rotation axes are generated	rn from Transylvania,	
3. Tran 18 pe th	nslation on rotation through 80° around an axis erpendicular to the plane of ne one-sided band	Decoration patched onto a long embroidered felt coat of Hungarian shepherds in Bihar County, eastern Hungary	7. Combination of translation axis with transverse and longitudinal symmetry planes. Two-fold rotation axes are generated Grape leaf pattern from east of the river Tisz	the territory a	

István Hargittai/Magdolna Hargittai

# Symmetry through the Eyes of a Chemist



Cover of the first edition of Symmetry through the Eyes of a Chemist. The model of the polymeric molecule is embedded in the pattern of a pillow-slip decoration with scrolling stem motif, which was much used in Hungary around the (18/19) turn of the century.

## The Seventeen Two-Dimensional Space-Group Symmetries in Hungarian Needlework<sup>a</sup>

### Istvan Hargittai and Gyorgyi Lengyel

We have recently demonstrated all seven one-dimensional space-group symmetries through examples found in Hungarian needlework [1]. The utility of these analogies is obvious in teaching crystallography and symmetry. Several colleagues have urged us to compile and communicate a similar system for the 17 two-dimensional space groups.

The two-dimensional space groups are more complex than the one-dimensional ones, but they are considerably also closer to the three-dimensional space-groups of the crystals. As is well known, there are 230 of the latter, but unfortunately no needlework analogies can be presented for them.

Seventeen Hungarian needlework are shown below together with corresponding systems of an asymmetric motif, the black triangle. Some of the most important symmetry elements are also indicated on them. More detailed descriptions can be found in books, including Buerger's classic, "Elementary Crystallography," [2] which has in some ways inspired the present work.

A brief description of the 17 pieces of needlework is given in the captions.



<sup>&</sup>lt;sup>a</sup> Journal of Chemical Education 1985, 62:35–36. Reproduced with permission © 1985 American Chemical Society





Figure in 17 parts:

p1 and p4: Patterns of indigo-dyed decorations on textiles for clothing. Sellye, Baranya County, 1899

p2: Indigo-dyed decoration with palmette motif for curtains. Currently very popular pattern

p3 and p6: Decorations with characteristic bird motifs from peasant vests. Northern Hungary

pm: Decoration with tulip motif for table-cloth. Cross-stitched needlework from the turn of the century

pmm2: Bed-sheet border decoration with pomegranate motif. Northwest Hungary, 19th century

p4mm: Pillow-slip decoration with stars. Cross-stitched needlework, Transylvania, 19th century

p6mm, p3m1, and p31m: Decorations with characteristic bird motifs from peasant vests. Northern Hungary

cm: Pillow-slip decoration with peacock tail motif. Cross-stitched needlework. Much used throughout Hungary around the turn of the century

cmm2: Bed-sheet border decoration with cockscomb motif. Cross-stitched needlework. Somogy County, 19<sup>th</sup> century

pg: From a pattern book of indigo-dyed decorations. Pápa, Veszprém County, 1856

pgg2: Children's bag decoration. Transylvania, turn of the century

pmg2: Pillow-slip decoration with scrolling stem motif. Much used throughout Hungary around the turn of the century

p4gm: Blouse-arm embroidery. Bács-Kiskun County, 19th century

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Khudu S. Mamedov (Mammadov) Azerbaijani crystallographer in Baku, 1982 (photograph by I. Hargittai). Mamedov often applied anti-symmetry in his periodic drawings and combined crystallography education and the preservation of cultural heritage.

#### Symmetry of Opposites: Antisymmetry<sup>a</sup>

#### István Hargittai and Magdolna Hargittai

Symmetry has long been identified with the properties of geometrical figures. The Russian crystallographer E. S. Fedorov, for example, gave it the following definition (quoted in [1]): "Symmetry is the property of geometrical figures of repeating their parts, or more precisely, their property of coinciding with their original position when in different positions." According to the Canadian geometer H. S. M. Coxeter [2], "when we say that a figure is 'symmetrical' we mean that there is a congruent transformation which leaves it unchanged as a whole, merely permuting its component elements."

However, it has also been recognized for a long time that symmetry, as observed in real nature, cannot be reduced entirely to this geometrical symmetry. K. Mislow and P. Bickart [3] observed in their epistemological note on chirality that "when one deals with natural phenomena, one enters 'a stage in logic in which we recognize the utility of imprecision." Material symmetry, devoid of the rigor of geometrical symmetry, has been viewed as applicable to material objects as well as abstractions with limitless implications [4]. Symmetry also connotes harmony of proportions, a rather vague notion according to Weyl [5]. Human ability to geometrize nongeometrical phenomena helps us see symmetry even in its "vague" and "fuzzy" variations [6, 7]. Thus Weyl [5] said Dürer "considered his canon of the human figure more as a standard from which to deviate than as a standard toward which to strive."

The vagueness and fuzziness of the broader interpretation of symmetry allow us to talk about degrees of symmetry. There must be a range of criteria, which may change from problem to problem, and may very well change in time as well. Today, Science is turning to the examination of the less orderly systems, yet symmetry considerations are not losing importance. On the contrary, their applications are gaining depth as well as breadth.

Chemistry [8], for example, is a science where the symmetry concept has played an increasing role, and not only in such areas as spectroscopy and crystallography but more recently even in such a seemingly nonexact field as organic synthesis. The so-called antisymmetry has become a seminal consideration in modern chemistry, for example, in the description of atomic and molecular orbitals of electronic structure and its changes and interactions during chemical reactions, and in the description of molecular vibrations.

"Operations of antisymmetry transform objects possessing two possible values of a given property from one value to the other" [9]. The simplest antisymmetry operation is color change. Let us first consider an identity operation and an antiidentity operation in Figure 1. Move on then to antireflection in Figure 2, and a few further examples of this in Figure 3. Of course, geometrical symmetries are not restricted to reflection, and Figure 4 presents examples combining color change with both reflection and rotation, after Shubnikov [1].

<sup>&</sup>lt;sup>a</sup> The Mathematical Intelligencer 1994, 16(2):60-66



Figure 1. (a) Identity operation and (b) antiidentity operation [8].



Figure 2. Reflections (1/2 and 3/4) and antireflections (1/4 and 2/3) [8].





Figure 3. Antireflections: (a) Hungarian batik design; (b) logo of Tungsram Works.

Figure 4. Antisymmetry operations after Shubnikov [1]. 2, 4, 6, antirotation axes;  $\overline{2}$ ,  $\overline{4}$ ,  $\overline{6}$ , antireflection-rotation axes;  $2 \cdot m$ ,  $\underline{4} \cdot m$ ,  $\underline{6} \cdot m$ , antirotation axes combined with ordinary reflection planes;  $1 \cdot \underline{m}$ ,  $3 \cdot \underline{m}$ , ordinary rotation axes combined with antireflection planes.



Figure 5. Pictures by Victor Vasarely (courtesy of the artist)





Figure 6. (top) Vasarely-like car decoration and (bottom) logo of sporting goods store in Boston, Massachusetts (photographs by the authors).

Figure 5 presents some op-art patterns. The first Vasarely picture, at least in this black-and-white version, illustrates simple color change between the upper and lower parts of the figure. The second Vasarely picture and the decorated car involve a change in the shape of the motifs in addition to the color change. Here we have alternative properties, color and shape, either of which can be changed into its opposite. We are also moving away from rigorous geometrical symmetry, and moving toward a wider application of the antisymmetry concept. The presence of a property turning into its opposite becomes the dominating effect; symmetry elements, such as reflection or rotation, may or may not accompany it.

Figure 6 shows the logo of a sporting goods store in Boston, Massachusetts. The antireflection plane relates winter and summer. Obviously, this store caters to both winter sports and summer sports fans. The color change in the self-serve/full-serve sign attracts attention in Figure 7, but the concepts may also be considered to have an antisymmetrical relationship.



Left: Figure 7. Self-serve versus full-serve gas station in Oahu, Hawaii (photograph by the authors). Right: Figure 8. "This is perestroika to some." An award-winning Soviet poster from 1987.

The Perestroika<sup>b</sup> poster of Figure 8 displays color change only, and the implication is ironic: Forces against reform would like to reduce the significance of Perestroika to mere color changes.

Let us interrupt our visual examples for two literary examples. The first refers to some antisymmetrical geographical relationships between, say, Western Europe and New Zealand. These locations can be connected by a straight diameter of the Earth going through its center. The noted American journalist James Reston [10] writes in his "Letter from Wellington. Search for the End of the Rainbow": "... Nothing is quite the same here. Summer is from December to March. It is warmer in the North Island and colder in the South Island. The people drive on the left rather than on the right. Even the sky is different--dark blue velvet with stars of the Southern Cross—and the fish love hooks." (He might have added, cyclones go clockwise there, as does water draining from a sink.)

The other example is taken from the Hungarian writer of the 1930s, Frigyes Karinthy, from a short story "Two diagnoses" [11]. The same person, Mr. Same, goes to see a physician at two different places on two different occasions. At the recruiting station he would obviously like to avoid getting drafted, whereas at the insurance company he

<sup>&</sup>lt;sup>b</sup> The Russian word "Perestroika," re-structuring, was a buzz word by Soviet President Mikhail Gorbachev when he tried to save the Soviet system by introducing reform.

would like to acquire the best possible terms for his policy. His answers to the identical questions of the physicians are related by antisymmetry.

At the recruiting station Mr. Same: *Broken-looking, sad, ruined human wreckage, feeble masculinity, haggard eves, unsteady movement.* 

Physician: How old are you?

Mr. Same: Old... very old, indeed.

Physician: Your I.D. says you're thirty two.

Mr. Same: *With pain.* To be old is not to be far from the cradle--but near the coffin. Physician: Are you ever dizzy?

Mr. Same: Don't mention dizziness, please, Doctor, or else I'll collapse at once. I always have to walk in the middle of the street, because if I look down from the curb, I become dizzy at once.

At the insurance company Mr. Same: *Young athlete with straightened back, flashing eyes.* 

Physician: How old are you?

Mr. Same: Coyly, Oh, my gosh, I'm almost ashamed of it... I'm so silly...

Physician: Your I.D. says you're thirty two.

Mr. Same: To be young is not to be near the cradle, but far from the coffin.

Physician: Are you ever dizzy?

Mr. Same: Quite often, sorry to say. Every time I'm aboard an airplane and it's upsidedown, and breaking to pieces. Otherwise, not...



Figure 9. Belgian holiday ad in Flemish and French from 1983 (photograph by the authors).

Returning now to visual examples, Figure 9 shows a Belgian travel ad, and the changing property is the language, Flemish/French. The horizontal antireflection is very approximate in Figure 10 on the election poster by the Alliance of Young Democrats at the time of the 1990 Hungarian elections.<sup>c</sup> The Viennese dancing school ad (Figure 11) relates an elephant's legs and a girl's by antisymmetry, obviously for the ability to dance. Figure 12 shows two military jets and a sea gull off Bodø, Norway, a military base, and they may imply the polarity of war and peace.

 $<sup>^{\</sup>rm c}$  On the poster, Leonid Brezhnev was the Soviet President and Erich Honecker the East German communist leader



Figure 10. Election poster by the (Hungarian) Alliance of Young Democrats (FIDESz), 1990. Upper half: Brezhnev and Honecker. Text in the middle: "Please, make your choice."



Left: Figure 11. Viennese dancing school ad (photograph by the authors). Right: Figure 12. Military jets and a sea gull, off Bodo, Norway, 1981 (photograph by the authors).



Left: Figure 13. E Brisse: (a) "Northwest Territories"; (b) "Canada" (From Ref. 13, reproduced by permission). Right: Figure 14. M. C. Escher: "Dogs" (From Ref. 16, reproduced by courtesy of the International Union of Crystallography).



Drawings by Kh. Mamedov, Left: Figure 15. "Girls," Right: Figure 16. "Unity" (From Ref. 17, courtesy of Professor Mamedov).

A few examples of translational antisymmetry are shown above. Apparently, the first systematic discussion of the 46 two-color two-dimensional patterns was communicated by H. J. Woods in 1936, in a work recently saved from oblivion by D. W. Crowe [12]. Woods pointedly called these two-color patterns "counterchange" patterns. The first two of our illustrations (Fig. 13) are by a Canadian crystallographer, F. Brisse [13]. In one, the polar bear is subjected to a twofold rotational antisymmetry and then translation in two directions. In the other, the two-dimensional space group of the pattern, disregarding color change, would be p4gm. This pattern has already been used by G. Po1ya [14] among his representations of the 17 two-dimensional space groups. It may also be found as a typical decoration in Islamic geometrical patterns [15]. However, in Brisse's pattern there is a two-color change during a complete revolution. There is then translation in two directions. Further simple color changes are involved in the next two figures. M. C. Escher's famous "Dogs" [16] is an excellent illustration of closest packing (Fig. 14). The color change is combined with glide lines. Reflection is also involved in generating Kh. Mamedov's "Girls" in Figure 15 [17]. The Azerbaijani crystallographer's other drawing "Unity" (Fig. 16) once again combines geometrical symmetries with a conceptual opposition: young versus old.



Figure 17. Symmetric (a, when the road chosen is parallel to the mirror) and antisymmetric (b, when we chose a road perpendicular to the mirror) consequences of reflection (drawing courtesy of architect G. Doczi [8]).

The symmetric and antisymmetric consequences of reflection for two movements are illustrated in Figure 17. Suppose we walk alongside a long wall of mirror (Fig. 17a). Our mirror image will be walking with us; the two velocities will be the same. Now walk from a distance toward the mirror, perpendicular to it (Fig. 17b). In this case, our mirror image will have a different velocity from ours. The speed will be the same again, but the direction will be the opposite. If we don't stop in time, we shall collide.

We conclude our discussion by mentioning A. Koestler's concept of bisociation. According to Koestler [18], the connection in thought association is made between thoughts on the same plane, whereas bisociation refers to connection of thoughts from different planes. Thus, bisociation may be considered to be the antisymmetric partner of thought association. Let us just quote one example from Koestler: "The Prince, travelling through his domain, noticed a man in the cheering crowd who bore a striking resemblance to himself. He beckoned him over and asked: 'Was your mother ever employed in my palace?' 'No Sire,'—the man replied.—'But my father was.'"

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Cover of the Summer 1995 issue of *The Mathematical Intelligencer* from I. Hargittai, "Fullerene Geometry under the Lion's Paw." © 1995, Springer.

## Fullerene Geometry under the Lion's Paw<sup>a</sup>

#### István Hargittai

"... the spherical is the form of all forms most perfect, having need of no articulation; and the spherical is the form of greatest volumetric capacity, best able to contain and circumscribe all else; and all the separated parts of the world—I mean the sun, the moon, and the stars--are observed to have spherical form; and all things tend to limit themselves under this form--as appears in drops of water and other liquids--whenever of themselves they tend to limit themselves. So no one may doubt that the spherical is the form of the world, the divine body."

From Copernicus, *De Revolutionibus Orbium Caelestium*, 1543. Heaven, in fact, is often depicted as a sphere in sculptures. The sphere may also be a representation of the Globe, and it is said to symbolize power as well.



Figure 1. Two lions in front of the Chamber of Deputies (*Congreso de los Diputados*), Madrid, Spain

Two lions stand guard in front of the Spanish Chamber of Deputies (*Congreso de los Diputados*). One of them has a sphere under the right paw and the other under the left paw (Figure 1). The surfaces of these spheres are smooth, without any decoration.

It has been common practice in China to have lion sculptures in front of important (and not so important) buildings. These lions also appear in pairs. The female has a baby lion under the left paw and the male has a sphere under the right paw. The female lion is apparently teasing the baby lion while the sphere under the male's paw is said to represent a ball made of strips of silk, which was a favorite toy in ancient China.

<sup>&</sup>lt;sup>a</sup> The Mathematical Intelligencer 1995, 17(3):34–36



Figure 2. Two bronze lions in front of the *Gate of Supreme Harmony* (TAIHEMEN) in the Forbidden City, Beijing, China.



Figure 3. Two gold-plated lions in front of the *Gate of Heavenly Purity* (QIANQINGMEN) in the Forbidden City, Beijing, China.

Figure 2 shows a pair of bronze lions in front of the *Gate of Supreme Harmony* (Taihemen) in the Forbidden City, Beijing. It was made during the reign of the Ming Dynasty (1368-1644). An elaborate regular hexagonal decoration of the surface of the sphere is under the male lion's paw. It is not possible, however, to cover the surface of the sphere by a regular hexagonal pattern. Indeed, considerable chunks of the sphere are hidden by the lion's paw and by the stand itself on which the lion and the sphere stand. Other lions with similar decorations of the sphere are found in many other places.

An interesting pair of lions whose male partner has a sphere under the paw with a different decoration is shown in Figure 3, with sphere in a close-up in Figure 4. This pair

is in front of the *Gate of Heavenly Purity* (Qianqingmen) in the Forbidden City and dates back to the reign of Qian Long (1736-1796) of the Qing Dynasty. The surface of this sphere is decorated by a hexagonal pattern which, however, is interspersed by pentagonal shapes. Such a pattern can indeed cover the complete surface of a sphere.



Left: Figure 4. Close-up of the sphere under the male lion's paw ; several pentagonal shapes are seen interspersed in the hexagonal pattern decorating the surface of the sphere.

Right: Figure 5. Structure [4] proposed for the super-stable  $C_{60}$  all-carbon molecule. Each vertex is occupied by a carbon atom. The single and double lines represent two different carbon-carbon linkages. This structure has been proved by a variety of physical and computational techniques (see, e.g., [5]).

Mathematicians have known, of course, that one can close an even-number of vertices with any number of hexagons (except one), provided 12 pentagons are included in the network (see, e.g., [1]). An important recent discovery in chemistry is related to such structures. When Kroto and co-workers observed [2] the great relative abundance of  $C_{60}$  molecules in their laser vaporization cluster-beam experiment, a search followed for the structure of this extraordinarily stable species. Kroto [3] describes eloquently how his previous encounters with Buckminster Fuller's work, and in particular the Geodesic Dome as the U.S. Exhibition Hall at the Montreal Expo, assisted him and his colleagues to arrive at the highly symmetrical truncated icosahedral structure (Figure 5). A visit to the Forbidden City might have been similarly instructive and beneficial.

All photographs in this Note were taken by the author in 1993. I am grateful to Miss Jing Wei, student of Peking University, for her kind assistance in gathering information about the lion sculptures in the Forbidden City.

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## System of Elements in Anagni<sup>a</sup>

## István Hargittai and Aldo Domenicano

Anagni is an ancient little town, beautifully situated on top of a hill about 60 km southeast of Rome, off the Rome–Naples motorway. Originally a Hernic settlement, it was conquered by the Romans in 306 B.C. Anagni became wealthy and important in the thirteenth century, during which it gave four popes to the Roman Catholic church.

Anagni Cathedral (Fig. 1) was built between 1072 and 1104, originally in the Romanesque style. Gothic elements were added later in the thirteenth century. A famous feature of the cathedral is its mosaic floors, created by the Cosma family in the first half of the thirteenth century.



Fig. 1 Anagni Cathedral (the transept and two apses). (Photograph taken by I. Hargittai, June 1995).

To the chemical tourist though, the most interesting feature may be some of the frescoes covering the walls and ceiling of the crypt, built in the same period as the upper church. These twelfth- and thirteenth-century frescoes are due to Benedictine painters of the Roman-Byzantine school. They blend religious topics and representations of the physical world, namely, medicine, astrology, and alchemy [1, 2]. In one of the 21 vaults, a human figure symbolizes the allegory of life in relation to the astronomical cycles. The four ages of man are presented in relation to the four seasons and *the four elements*. The fresco is thought to have been inspired by Platonic cosmology (Plato's teachings were spread in southern Italy by the Salerno medical school). Another fresco displays two physicians, Hippocrates (fourth century B.C.) and Galenus (second century A.D.), sitting together as Teacher and Disciple.

Next to the two physicians, there is a diagram of the four elements (Fig. 2), Earth, Water, Air, and Fire, and six properties, *immobile, corpulent, obtuse, mobile, subtle,* and *acute*. The straight connecting lines indicate correspondence (e.g., fire is mobile, subtle, and acute) whereas the curved lines connect opposite qualities. There are Roman

<sup>&</sup>lt;sup>a</sup> B. Hargittai and I. Hargittai (eds.), Culture of Chemistry: The Best Articles

on the Human Side of 20th-Century Chemistry from the Archives of the Chemical Intelligencer, DOI 10.1007/978-1-4899-7565-2\_13, © Springer Science+Business Media New York 2015

numerals beneath the names of the elements: for Earth,  $8 = 2^3$ ; for Fire,  $27 = 3^3$ ; for Water,  $12 = 3 \times 2^2$ ; for Air,  $18 = 2 \times 3^2$ . The equality containing these numbers, i.e., 8/12 = 18/27, unifies the whole universe in its perfection according to Platonic philosophy [3]. This relationship may be generalized as  $x^3/[(x + 1)x^2] = x(x + 1)^2/(x + 1)^3$ .



**Fig. 2** System of four elements in the crypt of Anagni Cathedral (twelfth-or thirteenth-century fresco). (a) Scheme after Ref. 1; (b) photograph (taken by I. Hargittai, June, 1995).

A detailed description of the six properties and their relationship to the four elements, corresponding closely to the Anagni diagram, was already given by Chalcidius (ca. fourth century A.D.), a Latin philosopher who translated and commentated Plato's *Timaeus* [3].

#### Acknowledgments

Alan L. Mackay (Birkbeck College, University of London) suggested that we visit Anagni Cathedral to see its mosaic floors. The Cathedral authorities graciously gave us permission to take one photograph in the crypt.

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- 3. Plato, Timaeus. XXXI-XXXII.





The central section of the Petrovsky Palace, Leningradsky Avenue 40, Moscow (photograph by I. Hargittai). A star polyhedron (in close-up, top image) decorates the top of each of the two towers at the entrance. The Petrovsky Palace was designed by the architect Matvei F. Kazakov and built in 1776–1782 at the order of Catherine II. Years before he photographed the Petrovsky Palace, Istvan discovered a star polyhedron at the top of the Sacristy of St. Peter's Basilica in Vatican City and he wrote a note about it for *The Mathematical Intelligencer*.

### Sacred Star Polyhedron<sup>a</sup>

#### István Hargittai



Figure 1. Left: The Sacristy of St. Peter's Basilica in Vatican City; right: the star polyhedron at its top.

There is a beautiful star polyhedron at the top of the Sacristy of St. Peter's Basilica in Vatican City (Fig. 1). It was built by the architect Carlo Marchionni in the years 1776–1784. It is a great stellated dodecahedron, called also Kepler's great stellated dodecahedron (Fig. 2 [1]), with 2 of its 20 triangular pyramids left out to accommodate the vertical rod serving as the stand of the cross above the polyhedron. There are many other examples of star polyhedron decorations from even earlier times, such as at the top of the obelisks in St. Peter's Square and in the Rotunda Square in Rome, and on the gate in the Square of September 20 in Bologna (Fig. 3). The star polyhedron often stands on a pile of dome-shaped stones. An octagonal star standing on top of a pile of dome-shaped stones was a characteristic motif in the coat of arms of the Chigi family of Pope Alexander VII (1655–1667). This motif is prominently displayed on the colonnades of St. Peter's Square (Fig. 4).

Giovanni Lorenzo Bernini (1598–1680) and Francesco Borromini (1599–1667) were leading architects of the Baroque period and their activities overlapped with the reign of Pope Alexander VII. The octagonal star and the coat of arms of the Chigi family are conspicuously present in many of their works. Figure 5 shows Sant Ivo's Church and three of its details by Borromini. Two of them display star polyhedra on piles of dome-shaped stones and octahedral stars. However, the decoration beneath the cross at the top of the tower is not a polyhedron but a sphere.

<sup>&</sup>lt;sup>a</sup> The Mathematical Intelligencer 1996, 18(3):52-54



Left: Figure 2. Great steUated dodecahedron. Photograph courtesy of Magnus J. Wenninger [1]. Right: Figure 4. Decoration from the top of the colonnade in St. Peter's Square, Vatican City.



Figure 3. Left: Top of the obelisk in St. Peter's Square, Vatican City; center: top of the obelisk in Rotonda Square, Rome; right: one of the two side decorations of the gate in the Square of September 20, Bologna.



Figure 5. Three details of Sant Ivo's Church.

All photographs in this article were taken by the author in 1993. I am grateful to Anna Rita Campanelli and Aldo Domenicano (Rome), Lodovico Riva di Sanseverino (Bologna), and Magnus J. Wenninger (Collegeville, Minnesota) for assistance and advice.



Mountain goats in the Budapest Zoo (photograph by Istvan Hargittai) displaying gradual size and age changes. They can be considered to be a segment of an "infinite" succession of *similarity symmetry* (see in Figure 16a in the following article).

## The Universality of the Symmetry Concept<sup>a</sup>

## István Hargittai and Magdolna Hargittai

#### Abstract

The notion of symmetry brings together beauty and usefulness, science and economy, mathematics and human relations. This presentation demonstrates the breadth and versatility of the symmetry concept. There are no symmetries specific to various disciplines, yet there are differences in emphasis in applications of the concept. The sciences, humanities and arts have gradually drifted apart; symmetry can provide a connecting link among them. The symmetry concept may be broadened to include harmony and proportion, constituents of symmetry often present in architectural composition. The symmetries considered here are point group, chiral, space group, and translational. While mathematical symmetry is exact and rigorous, the symmetry we encounter in everyday life is much more relaxed. The broad interpretation of the symmetry concept, coming close to blending fact and fantasy, may help scientists recognize trends, changes, and patterns.

#### Introduction

The notion of symmetry brings together beauty and usefulness, science and economy, mathematics and music, architecture and human relations, and much more, as has been shown recently with many examples (Hargittai 1986, 1989; Hargittai and Hargittai 1995, 1996). There is a lot of symmetry, for example, in Béla Bartók's music. It is not known, however, whether he consciously applied symmetry or was simply led intuitively to the golden ratio so often present in his music. Bartók himself always refused to discuss the technicalities of his composing and stated merely "We create after Nature." Another unanswerable question is how these symmetries contribute to the appeal of Bartók's music, and how much of this appeal originates from our innate sensitivity to symmetry. This question might be equally asked of symmetries in architectural composition.

The present chapter takes a broad view of the symmetry concept. It demonstrates its breadth and versatility. There are no distinctly different specific symmetries in various disciplines, yet there are discernible differences in emphasis of the application of this concept in different fields. This emphasis changes with time as well. For example, there is a marked emphasis on the presence of symmetry in chemistry, in contrast to physics

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where the importance of broken symmetries has been stressed during the past decades. Generally though the symmetry concept unites rather than divides the different branches of science, and even helps bridge the gap between what C.P. Snow called "two cultures." Sciences, the humanities, and the arts have all drifted apart over the years and symmetry can provide a connecting link among them. Its benefits are available to us if we free ourselves from the confinements of *geometrical symmetry*.

Everything is rigorous in geometrical symmetry. According to one definition, "symmetry is the property of geometrical figures to repeat their parts" (Shubnikov 1951). Another definition says that "a figure is symmetrical if there is a congruent transformation which leaves it unchanged as a whole, merely permuting its component elements" (Coxeter 1973). In the geometrical sense, symmetry is either present or it is absent. Any question regarding symmetry has a restricted *yes/no* alternative. For the real, material world, however, degrees of symmetry and even gradual symmetry is feasible and applicable. Beyond geometrical definitions there is another, broader meaning to symmetry—one that relates to *harmony* and *proportion*, and ultimately to *beauty*. This aspect involves feeling and subjective judgment and, as a result, is especially difficult to describe in technical terms.

Simple considerations are indispensable in classifying different kinds of symmetry. There are two large classes of symmetry, *point groups* and *space groups*. For point group symmetries there is at least one special point in the object or pattern that differs from all the others. In contrast to this, in space groups, there is no such special point. There are also some terms that are useful in the description of different types of symmetry. Thus, the action that characterizes a particular type of symmetry is called a *symmetry operation*. The tool whereby the operation is performed is called a *symmetry element*.

#### **Point Group Symmetry**

The simplest kind of point-group symmetry is *bilateral symmetry*. Bilateral symmetry is present when two halves of the whole are each other's mirror images (Fig. 40.1). This is the most common symmetry and the every-day usage of the term "symmetry" refers to this meaning. The symmetry element is a *mirror plane*, also called a *symmetry plane* or a *reflection plane*. The symmetry operation is *reflection*. Applying a mirror plane to either of the two halves of an object with bilateral symmetry recreates the whole object. Bilateral symmetry is probably the most common symmetry in architecture as well, from simple buildings to larger assemblies (Fig. 40.2a, b).



Fig. 1 The orchid has bilateral symmetry. Photo: authors



**Fig. 2** (a) The whole assembly of the Blue Mosque in Istanbul, Turkey, has bilateral symmetry. (b) The design of St. Peter's Square in Vatican City also shows bilateral symmetry. Photo: authors

Another kind of point-group symmetry is *rotational symmetry* (Fig. 40.3). It is present when, by rotating an object around its axis, it appears in the same position two or more times during a full revolution. *Rotation* is the symmetry operation and the *axis of rotation* is the symmetry element. Rotational symmetry may be twofold, threefold, fourfold, etc. It is common that reflection and rotation appear together. The presence of some symmetry elements may generate others and vice versa. If we look at the Eiffel tower from below (Fig. 40.4) we have twice two orthogonal reflection planes which generate a fourfold rotation. The cupolas of many state capitols and other important buildings have reflectional and rotational symmetry together (Fig. 40.5).


Fig. 3 This hubcap has sevenfold rotational symmetry. Photo: authors



Fig. 4 The Eiffel Tower from below. It shows both reflections and rotational symmetry. Photo: authors



Fig. 5 The cupola of the Hungarian Parliament with both reflectional and rotational symmetry. Photo: authors

The regular polygons, so basic in architectural design, also have both rotational and reflectional symmetry. Best seen when viewed from above, many buildings have outlines of a regular polygon (Fig. 40.6). The regular polyhedra, also called Platonic solids, all have equal regular polygons as their faces. As H.S.M. Coxeter, professor of mathematics at the University of Toronto, remarked, "the chief reason for studying regular polyhedra is still the same as in the times of the Pythagoreans." Namely, that their symmetrical shapes appeal to one's artistic sense. There are other highly symmetrical polyhedra, called Archimedian polyhedra, whose faces are also regular polygons but not identical ones. Buckminster Fuller's geodesic dome is composed of lightweight bars forming regular polygons. His geodesic dome at the Montreal expo (Fig. 40.7) inspired some chemists who saw that the structure of a newly discovered substance may be the truncated icosahedron. This molecule,  $C_{60}$ , called buckminsterfullerene (Fig. 40.8) is characterized, among others, by six axes of fivefold rotation (Hargittai and Hargittai 1994: 100–101). Experimentally discovered in 1985, its great relative stability was predicted already in 1970, based solely on symmetry considerations.



Fig. 6 The outline of the Pentagon in Washington, D.C. with its regular pentagonal shape. Photo: authors



Fig. 7 Buckminster Fuller's Geodesic Dome at the Montreal Expo. Photo: authors



Fig. 8 C<sub>60</sub>, the buckminsterfullerene molecule. Image: authors

## Chirality

A special kind of symmetry relationship is when two objects are related by mirror reflection and the two objects cannot be superposed. Our hands are an excellent example, and the term *chiral* derives from the Greek word for hand. Chiral objects have senses and following the hand analogy they are left-handed (L) and right-handed (D). The simplest chiral molecule is a methane derivative in which three of the four hydrogens are replaced by three different atoms, such as, for example, fluorine (F), chlorine (Cl), and bromine (Br). There may then be a left-handed C(HFClBr) and a right-handed C(HFClBr) molecule which will be each other's mirror images but won't be superposable (Fig. 40.9). A chiral object and its mirror image are called each other's *enantiomorphs*.





The two chiral molecules look the same in every detail; only their senses are different. The distinctions between the twins of a chiral pair have literally vital significance. Only 1amino acids are present in natural proteins and only d-nucleotides are present in natural nucleic acids. This happens in spite of the fact that the energy of both enantiomers is equal and their formation has equal probability in an achiral environment. However, only one of the two occurs in nature, and the particular enantiomers involved in life processes are the same in humans, animals, plants, and microorganisms. The origin of this phenomenon is a great puzzle.

Once a chiral molecule happens to be in a chiral environment, the two chiral isomers will be behaving differently. This different behaviour is manifested sometimes in very dramatic ways. In some cases one isomer is sweet, the other is bitter. In some other cases the drug molecule has an "evil twin." A tragic example was the thalidomide case in the 1950s in Europe, in which the right-handed molecule cured morning sickness and the left-handed one caused birth defects. Other examples include one enantiomer of ethambutol fighting tuberculosis with its evil twin causing blindness, and one enantiomer of naproxen reducing arthritic inflammation with its evil twin poisoning the liver. Ibuprofen is a lucky case in which the twin of the chiral form that provides the curing is converted to the beneficial version by the body.

Even when the twin is harmless, it represents waste and a potential pollutant. Thus, a lot of efforts are directed toward producing enantiomerically pure drugs and pesticides. One of the fascinating possibilities is to produce sweets from chiral sugars of the enantiomer that would not be capable of contributing to obesity yet would retain the taste of the other enantiomer.

Chiral symmetry is also frequently found in architectural design either in two- or in three dimensions, as illustrated by Fig. 40.10.



Fig. 10 Chiral rosettes on a building in Bern, Switzerland. Photo: authors

#### **Space Group Symmetry**

A different kind of symmetry can be created by simple *repetition* of a basic motif leading us to *space-group symmetries*. The most economical growth and expansion patterns are described by space-groups symmetries. There are three basic cases of space groups, depending on whether the basic motif extends periodically in one direction only, or in two, or finally, in three. These three cases are described by the so-called *onedimensional, two-dimensional*, and *three-dimensional* space groups.

Border decorations are examples of one-dimensional space groups. In border decorations a pattern can be generated simply by repeating a motif at equal intervals. This is *translational* symmetry. The symmetry element is *constant translation;* the operation is the *translation* itself. The resulting pattern shows periodicity in one direction. Repetition can be achieved by a simple shift in one direction as can be seen very often in the rows of columns of grandiose buildings (Fig. 40.11) or in the ancient aqueducts of the Romans. Fences are typical examples of one-dimensional space groups (Fig. 40.12), the ease and

economy of using the same elements repeatedly makes this obvious. Repetition can also be achieved in other ways, such as by reflection, rotation (Fig. 40.13), or *glide- reflection*. Glide-reflection is another new element that does not occur in point-group symmetries. It means the consecutive application of translation and horizontal reflection. When we walk in wet sand along a straight line we leave behind a pattern of footprints whose symmetry is described by glide-reflection. There is a total of seven possibilities for generating one-dimensional space-group symmetries.



Fig. 11 Colonnade on St. Peter's square in Vatican City. Photo: authors



Fig. 12 Repeating pattern of a fence in the Topkapi Palace in Istanbul, Turkey. Photo: authors



Fig. 13 Another illustration for one-dimensional space groups: the units turn  $90^{\circ}$  at every translation in this chain. Photo: authors

Helices and spirals have also one-dimensional space-group symmetries although their bodies may extend to three dimensions (Hargittai and Pickover 1992). *Helical symmetry* is created by a constant amount of translation accompanied by a constant amount of rotation. In *spiral symmetry*, again, translation is accompanied by rotation but the amount of translation and rotation changes gradually and regularly. An extended spiral staircase has helical symmetry. Well-ordered biological macromolecules also have helical symmetry. Helices are always three-dimensional whereas there are spirals that extend in two dimensions only. Occurrences of spirals may be as diverse as chemical waves and galaxies and snails. Spirals and helices have also been used in various ways in architecture, from ancient times to the present, as Trajan's column in the Forum Romanum (Fig. 40.14) and the spiral ramp of Frank Lloyd Wright's Guggenheim Museum in New York indicate.



Fig. 14 Spiral symmetry of Trajan's column in the Forum Romanum in ancient Rome. Photo: authors

Another beautiful example of spiral symmetry is the scattered leaf arrangement around the stems of plants, called *phyllotaxis*. Numbers of the Fibonacci series (1, 1, 2, 3, 5, 8, 13, 21, ...—each new element is the sum of the two previous elements) characterize the ratios defining the occurrence of every consecutive new leaf in scattered leaf arrangements. Thus, for example, there is a new leaf at each 3/8 parts of the

circumference of the stem as we move along the stem in one of the characteristic cases. The pineapple (Fig. 40.15) displays a pattern of spirals that can be thought of as if it were a result of compressed phyllotaxis. Such ratios when involving very large numbers approximate an important irrational number, 0.381966..., expressing the so-called *golden ratio*. The golden ratio is created by the golden section in which a given length is divided such that the ratio of the longer part to the whole is the same as the ratio of the shorter part to the longer part. If the whole is 1.00, the lengths of the longer and shorter parts will be 0.618 and 0.382, respectively. This may be the single most important proportion in architecture and in artistic expression. Its relationship to phyllotaxis may have inspired Leonardo da Vinci's description of the scattered leaf arrangement as "more beautiful, more simple, or more direct" than anything humans could devise (Leonardo da Vinci 1939).



**Fig. 15** The pineapple displays a pattern of spirals that can be thought of as if it were a result of compressed phyllotaxis. Photo: authors

Spiral symmetry can also be considered as belonging to the broad concept of *similarity symmetry*. Here pattern generation always involves an increment of a characteristic property (Fig. 40.16).



**Fig. 16** (a) Similarity symmetry, the increments being the change in size or the change in age. (b) An architectural example of similarity symmetry where the increment is the change in size of the units of the church-tower in London, England. Photo: authors

With two-dimensional space-groups, there is a total of 17 ways to generate different patterns. It is a special case when the planar network covers the plane without gaps and overlaps. Of the regular polygons, only the equilateral triangle, the square, and the regular hexagon are capable of covering the plane without gaps and overlaps. For arbitrary shapes though, there are infinite possibilities. M.C. Escher's periodic drawings and the wall decorations in the Alhambra of Granada, Spain (Fig. 40.17) are famous examples. The façades of buildings, especially those of modern skyscrapers often display symmetries in two dimensions (Fig. 40.18).



Fig. 17 Two-dimensional space group: decoration from the Alhambra Granada, Spain. Photo: authors





Space utilization by periodic arrangements seems to be the underlying principle of the occurrence of three-dimensional space-group symmetries. This is a common arrangement of the building elements in *crystals*. The packing of spheres was first considered as the key to the internal structure of crystals by Johannes Kepler. As he was looking at the exquisitely beautiful hexagonal snowflakes, he made drawings of sphere packing, similar to a pyramid of canon balls (Fig. 40.19).



Fig. 19 Random arrangement of canon balls provides much poorer space utilization than their regular arrangement. Photo: authors

There are restrictions for the regular and periodic structures, such as the nonavailability of fivefold symmetry in generating them. This can be understood easily when we find it impossible to cover the plane without gaps or overlaps with equal-size regular pentagons.

Crystals are advantageous for the determination of the structure of molecules. The great success of X-ray crystallography may have diverted attention from structures of lesser symmetry though of not necessarily lesser importance. The discovery of quasiperiodic crystals [in short, quasicrystals (Hargittai 1990)] by the Israeli scientist Dan Shechtman in 1982 has by now persuaded many scientists that their view of crystals is unnecessary narrow. David Mermin compared abandoning the traditional classification scheme of crystallography, based on periodicity, to abandoning the Ptolemaic view in astronomy, and likened changing it to a new foundation to astronomy's adopting the Copernican view (Mermin 1992).

Recently, even such descriptive fields of biology as zoology have displayed a growing activity in symmetry matters. Not surprisingly, the role of external symmetry is being recognized as decisive in mate selection. Empirical evidence supports the notion relating "animal beauty" to the symmetry of outlook. The degree of left-and-right correspondence of the wings seems to correlate with hormone and pheromone production (Angier 1994: C1).

In view of the fundamental importance of the symmetry concept, it is surprising that even very basic discoveries about it were left to be made in this century. When P.A.M. Dirac was asked about Einstein's most important contributions to physics, he singled out Einstein's "introduction of the concept that space and time are symmetrical" (Yang 1991: 11). An important step was Emmy Noether's recognition that symmetry and conservation are connected. Indeed, the idea that the great conservation laws of physics, like the conservation of energy and momentum, are related to symmetry opened up a wholly new way of thinking for scientists. Realizing that Nature included continuous symmetry in her design physicists started to look for new connections.

It was Dirac who had the prescience to write already in 1949, that "I do not believe that there is any need for physical laws to be invariant under reflections" (Dirac 1949). Yet, even most physicists were surprised by the discovery of the nonconservation of parity in 1957 that brought the Nobel prize in physics to T.D. Lee and C.N. Yang. C.P. Snow called this discovery one of the most astonishing in the whole history of science. Since then broken symmetries have been receiving increasing attention.

There seems to be a difference in approach and emphasis between physicists and chemists in viewing symmetry. It may even be related to the ancient Greek philosophers, stressing the importance of continuum by Aristotle, and of the discreet, by Lucretius and Democritos. From the point of view of continuum, even the ideal crystal may be discussed in terms of broken symmetries. On the other hand, the chemist's approach is succinctly symbolized by Democritos' statement: "Nothing exists except atoms and empty space; everything else is opinion."

Of course, the way symmetry is looked at can vary a great deal. While mathematical symmetry is exact and rigorous, the symmetry we encounter in everyday life is much more relaxed. The vague and fuzzy interpretation of the symmetry concept may also aid

scientists to recognize trends, characteristic changes, and patterns. This is getting close to blending fact and fantasy. As Arthur Koestler expressed it, "artists treat facts as stimuli for the imagination, while scientists use their imagination to coordinate facts" (Koestler 1949).

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Next to me, a waterwheel—an example of rotational symmetry—many years ago in Budapest (photograph by Istvan Hargittai).

# Symmetry and Perception: Logos of Point-Groups Induce the Feeling of Motion<sup>a</sup>

## Magdolna Hargittai and István Hargittai

In addition to being aesthetically pleasing, the symmetric design of decorations can induce the feeling of motion or the feeling of stopping motion (see the References). Polar one-dimensional space-group border decorations (frieze patterns) can direct the movement of people in underpasses or airline terminals. Two-dimensional space-group patterns of rotational symmetry only have been suggested for decorating dance halls; those containing symmetry planes have been suggested for decorating the sites of serious meetings. Glide-reflection may induce the feeling of confusion.

In this article we suggest that point-groups also have the capability of inducing a feeling of motion, and that certain symmetries in company logos may be better suited to convey the essence of company activities than others.



Figure 1. Four-bladed propeller displayed in front of the Budapest Technical Museum. (All photographs in this article are by the authors.)

First, let us consider a four-bladed propeller (Figure 1). It has four-fold rotational symmetry and no symmetry plane. Having rotational symmetry only corresponds to its function, as do the rotational symmetries of other rotating parts in machinery, such as propellers, turbine wheels, windmills, or children's pinwheels.

Logos themselves do not rotate physically, but they may best convey the essence of the company's activities if their symmetries induce consistent feelings in observers. Thus a railway company, or travel companies in general, may be best represented by a logo with rotational symmetry only, and even more specifically, by two-fold rotational symmetry. There is always motion, and the motion is back and forth: the train is taking you there and bringing you back, again and again. Our sampler of examples in Figure 2

<sup>&</sup>lt;sup>a</sup> The Mathematical Intelligencer 1997, 19:355–358

includes logos of railway companies and other transportation companies, such as subways, tourist bureaus, bus companies, and expediters.



Austrian Railways





Slovenian Railways



Spanish Railways



Seoul Subway



**City Thameslink (London)** 



Haifa Subway



Suburban trains (Vienna)

Hungarian Travel Bureau (Pécs)



Tokyo Subway



France)

Bus company (Toulouse,

Italian transportation company



Egged Tours (Israel)

Madrid municipal bus company



Figure 2. Sampler of logos of transportation companies (all of two-fold rotational symmetry)

Of course, we are not suggesting that a transportation company with a logo containing mirror planes would perform its function any worse. We are suggesting,

though, that a logo of only rotational symmetry conveys the essence of transportation companies better than a logo with mirror planes.



Osterreichische Verkehrakreditbank (Linz, Austria), Bank in Stockholm, Banco Mello (Portugal) American Service Bank



Banca Popolare di Ancona (Rome), Sicilcassa (Palermo, Italy), Chase Manhattan Bank, and a bank in Illinois







Korea Housing Bank (Seoul), Bank in Tokyo, and Frost Bank (Austin, Texas) Figure 3. Sampler of bank logos

Banks very frequently have logos of rotational symmetry only and no symmetry planes. A sampler of examples is shown in Figure 3. Here the abstraction is of even higher degree, as banks and other financial institutions do not represent or perform physical motion. Yet turning around money is characteristic of them, and this activity may be the reason, if only subconsciously, why logos with rotational symmetry come to them so naturally. By the same token, we would suggest mirror-symmetric logos for insurance companies, health care services, retirement systems, and any other organizations where mobility is less desirable. We are not suggesting any rigorous correspondence between the symmetries of logos and the activities of the companies they represent, but there seems to be some correlation.

Note also that the logos of transportation companies, displayed in Figure 2, are invariably of two-fold symmetry, yet the bank logos have no such characteristic number

and show diversity in their rotational symmetries. This again seems natural, as there is a definite two-way directionality in the activities of transportation companies but a multiplicity of possibilities in directionality of bank activities.



Reynolds Aluminum Recycling and Bottles recycling (Italy)



Recycling (Washington, DC), New Hampshire recycling, University of Toronto recycling, Recycle Hawaii Figure 4. Sampler of recycling logos

Our third and final category is recycling logos. They are, again, of only rotational symmetry, in keeping with the process of recycling--that is, turning around the wastes and producing new materials. Although three-fold rotational symmetry is the most common, there is a variety in rotational symmetries. The variety of design is less than for banks, in keeping with the international and less competitive character of recycling.

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George Pólya (1887–1985; courtesy of Gerald L. Alexanderson). Pólya was born in Budapest and became a world renowned mathematician. He did his high school studies in the Berzsenyi Gimnázium in downtown Budapest. It was one of the elite schools from which a number of internationally recognized personalities graduated, such as the Nobel laureate Denis Gabor, the computational specialist John Kemeny, the tumor biologist George Klein, the financier George Soros, and many others. Pólya attended the universities of Budapest and Vienna and did his doctoral work under Leopold Fejér. He was a mathematics professor at the Zurich Federal Institute of Technology until 1940. Then, fearing the spread of Nazism, he moved to the United States and was professor at Stanford University. In 1924, Pólya published a set of the 17 twodimensional plane groups Istvan reproduced in the following article.

# Symmetry in Crystallography<sup>1</sup>

### Istvan Hargittai

The science of crystals involves symmetry. Symmetry is also an excellent link to other fields of human endeavor. The first scientific crystallographer, Johannes Kepler, came to the idea of close packing when he was considering the symmetry of snow crystals. When Louis Pasteur observed crystal and molecular chirality, he opened a Pandora's Box of the notion of the dissymmetry of the universe. Since the start of X-ray crystallography in 1912, emphasis has been on single-crystal symmetry, and the field has moved from triumph to triumph. In the late 1920s, however, interest in less than perfect structures developed, leading to the establishment of molecular biology. Helical symmetries were found to characterize life's most important molecules. Symmetry considerations were decisive in these discoveries, which stimulated the expansion of the symmetry concept. In the mid-1980s, the belief that fivefold symmetry was a noncrystallographic symmetry crumbled, and the concept of the crystal had to be revised. Crystallography has now become the science of structures. Symmetry has helped crystallography to influence the arts. This tends to unify our culture—a side effect of the enormous work of uncovering the secrets of matter for the betterment of human life.

#### **1. Introduction**

With the appearance of combinatorial chemistry, we have lost count of the number of new substances produced in the laboratory. Does this mean that we are losing sight of the structure of matter because its variations are too numerous? We should not fear this because there are patterns in the structures, appearing as symmetry, and the search for pattern is the most characteristic scientific approach in uncovering the secrets of nature. The patterns of elementary particles and those of the chemical elements are well established yet patterns are becoming discernible only in outline for the structures of substances. With about a quarter of a million crystal structures determined so far, the prediction of the crystal structure of a new substance is still elusive.

Eugene Wigner (1967) made a brief speech at the Stockholm City Hall in December 1963 on the occasion of the presentation of his Nobel Prize in Physics. This is what he said, when he talked about the inspiration received from his teacher, Michael Polanyi: 'He taught me, among other things, that science begins when a body of phenomena is available which shows some coherence and regularities, that science consists in assimilating these regularities and in creating concepts which permit

<sup>&</sup>lt;sup>1</sup> Acta Crystallographica 1998, A54:697–706 and in: H. Schenk (ed.), Crystallography across the Sciences: A Celebration of 50 Years of Acta Crystallographica and the IUCr. (International Union of Crystallography 1998), pp. 697–706.

expressing these regularities in a natural way. He also taught me that it is this method of science rather than the concepts themselves (such as energy) which should be applied to other fields of learning'. What Polanyi taught Wigner was to recognize patterns, and the main tool was the symmetry concept.

The determination of structure by X-ray diffraction is based on symmetry, which exists in the internal arrangement of the building elements of the structure. Thus, there are two aspects of symmetry underlying much of recent structural research. One is the symmetry of the building element of the structure and the other is the limited number of rules needed to generate all structures.

Crystallography had initially evolved as a science of crystals. Then the application of X-ray diffraction gave a tremendous emphasis to the structure of individual molecules. These molecules are embedded in a matrix of other molecules in the closest proximity. Yet the fascination with their structures and the emerging regularities among them had, for a while, pushed back the interest in the interactions between the molecules themselves. The appearance of supramolecular chemistry in general and the recognition that the molecular crystal is a supermolecule *par excellence* (Dunitz, 1996), in particular, has brought back the interest in crystal chemistry and, more generally, in materials crystallography.

Focusing on molecular structures and their variations has also provided enormous benefits. Murray-Rust (1992) estimated that Linus Pauling (1939), at the time of the first edition of *The Nature of the Chemical Bond*, possessed one hundredth of one per cent of the structural chemistry information that was available 50 years later, yet his observations and generalizations have been found to apply to almost all the rest.

The present article illustrates the role of the symmetry concept in the science of structures and the contribution of crystallography to the enhancement of the symmetry concept as a research tool. This concept has been a bridging tool between the most diverse fields of human endeavor (Hargittai, 1986, 1989; Hargittai & Hargittai, 1994). As a set of examples, packing, biological structures, the recent discoveries related to fivefold symmetry, and chirality are chosen. We comment on the role of the symmetry concept in countering the effects of narrow specialization and in bringing science into human proximity for a broader audience. Materials of a forthcoming book have aided the preparation of the present article (Hargittai & Hargittai, 1999).

#### 2. Packing

The importance of symmetry in structure does not mean that the highest symmetry is the most advantageous. Lucretius (Dunitz, 1996) proclaimed about two millenia ago in his *De Rerum Natura* that 'Things whose textures have a mutual correspondence, that cavities fit solids, the cavities of the first the solids of the second, the cavities of the second the solids of the first, form the closest union'. In modern science, Kepler (1611) recognized that the origin of the shape and symmetry of snowflakes is the internal arrangement of the building elements of water. This observation may be considered as the start of scientific crystallography. Lord Kelvin's (William Thomson's) mostly forgotten geometry (Kelvin, 1904) was a return to Lucretius's fundamental observation.



Fig. 1. Arrangements of molecular shapes by Lord Kelvin (1904).

As Lord Kelvin was building up the arrangement of molecular shapes, he examined two fundamental variations (Fig. 1). In one, the molecules are all oriented in the same way, while, in the other, the rows of molecules are alternately oriented in two different ways. Kelvin considered the puzzle of the boundary of each molecule as a purely geometrical problem. This is the point where his successors introduced considerations for inter- molecular interactions and, ultimately, Aleksandr I. Kitaigorodskii 'dressed the molecules in the fur-coat of van der Waals domains'.

Lord Kelvin was using nearly rectilinear shapes for partitioning the plane but he did not let his molecules quite touch one another. Otherwise, he created a modern representation of molecular packing in the plane, including the recognition of complementariness in packing.



Fig. 2. Truncated octahedron by Lord Kelvin (1904).



Fig. 3. Space filling by truncated octahedra by Weyl (1952). Reprinted with permission. Copyright (1946) Princeton University Press.

Then he came to extending the division of continuous two-dimensional space into the third dimension. He restricted his examinations to polyhedra and found one of the five space-filling parallelohedra, which were discovered by E. S. Fedorov as capable of filling the space in parallel orientation without gaps or overlaps (Fig. 2). The Fedorov polyhedra are the cube, the hexagonal prism, the rhombic dodecahedron, an elongated rhombic dodecahedron with eight rhombic and four hexagonal faces, and the truncated octahedron. Fig. 3 shows the truncated octahedron filling space (after Weyl, 1952).

Fedorov was one of the three scientists who deter- mined the number (230) of three-dimensional space groups. The other two were Arthur Schoenflies and the amateur William Barlow. Barlow considered oriented motifs, and 'his method was hanging pairs of gloves on a rack to make space-group models'. It was a truly empirical approach. "He bought gloves by the gross, so the story goes, mystifying the sales lady by answering 'I don't care' to her question, 'What size, sir?'" (Senechal, 1990).



Fig. 4. The 17 two-dimensional plane groups by Polya (1924).

Fedorov also derived the 17 two-dimensional plane groups but their best known presentation is by George Pólya (1924) who illustrated them with patterns that completely fill the surface without gaps or overlaps (Fig. 4). Today we would call them Escher-like patterns (Schattschneider, 1990).

An important contribution appeared in 1940 from the structural chemist Linus Pauling and the physicist- turned-biologist Max Delbruck (Pauling & Delbruck, 1940), dealing with the nature of intermolecular forces in biological processes. They suggested precedence for interaction between complementary parts, rather than the importance of interaction between identical parts. They argued that the intermolecular interactions of van der Waals attraction and repulsion, electrostatic inter- actions, hydrogen-bond formation *etc.* give stability to a system of two molecules with complementary rather than identical structures in juxtaposition. Accordingly, complementariness should be given primary consideration in discussing intermolecular interactions.



Fig. 5. Sampler of molecular packing arrangements in the plane by Kitaigorodskii (1971).

Considerations of complementarity in molecular packing culminated in the works of Kitaigorodskii (1971). His most important contribution was the pre- diction that three-dimensional space groups of lower symmetry should be much more frequent than those of higher symmetry among crystal structures. This was a prediction at a time when few crystal structures had been determined experimentally.

Kitaigorodskii's realisation of the complementary packing of molecules was not intuition; he arrived at this principle by empirical investigation. Today his findings appear simple, almost self-evident, a sure sign of a truly fundamental contribution.

When Kitaigorodskii finally came to the idea of using identical but arbitrary shapes, he started by probing into the best possible arrangements in the plane. Fig. 5 presents a sampler of the arrangements considered by Kitaigorodskii (1971). He established the symmetry of two-dimensional layers that allow a coordination number of six at an arbitrary tilt angle of the molecules with respect to the tilt axes of the layer unit cell. He found that such an arrangement will always be among those that have the densest packing. In the general case for molecules of *arbitrary* shape, there are only two kinds of such layers. One has inversion centers and is associated with a nonorthogonal lattice. The other has a rectangular net, from which the associated lattice is formed by translations, plus a second-order screw axis parallel to the translation. The next task was to select the space groups for which such layers are possible. This was of great interest since it answered the question as to why there is a high occurrence of a few space groups among the crystals while many of the 230 groups hardly ever occur.

#### **3. Biological structures**



Fig. 6. Diagrammatic representation of the double helix by Watson & Crick (1953*a,b*). Reprinted with permission. Copyright (1953) Macmillan Magazines Ltd.

Fig. 7. Sculpture of the double helix by the sculptor Bror Marklund. Photograph by the author.

While single-crystal studies were still on the climb and most modern techniques of structure elucidation were still in the making, research on biologically important macromolecules had also begun. In the early 1920s, Polanyi found (*cf.* Morawetz, 1994) that the X-ray diffraction from cellulose fibers indicated the presence of crystallites oriented in the direction of the fiber axis. The first proteins subjected to X-ray diffraction were protein fibers. In the early 1930s, W. T. Astbury and his co-workers published a series of papers on the X-ray studies of hair, wool and related fibers (Astbury & Street, 1932; Astbury & Woods, 1934; Astbury & Sisson, 1935). They observed that stretched moist hair showed a drastic change in its X-ray diffraction pattern, compared with dry un-stretched hair. This was interpreted as two forms of the polypeptide chain,  $\beta$ -keratin and  $\alpha$ -keratin, today known as  $\beta$  -pleated sheet and the  $\alpha$ -helix. One of Astbury's co-workers, H. J. Woods, studied extensively the symmetry properties of textile decorations (Crowe, 1986).

Linus Pauling (1996) decided to determine the atomic arrangement of  $\alpha$  -keratin, using his knowledge of structural chemistry in addition to Astbury's X-ray diffraction patterns. The effort cost about 15 years and led to the discovery of the  $\alpha$ -helix. It was a spectacular example of pattern recognition and modeling. In the course of this work, Pauling utilized the structural information on small molecules determined by gas-phase electron diffraction and the resonance theory, and deduced the planarity of peptide bonding. He also disregarded nonessential features, such as the differences in the side chains of the various amino acids and the discrepancy between the 5.1 Å repeat distance along the axis measured from Astbury's patterns and the 5.4 Å repeat distance that came out of his own modeling. Finally, he remembered a mathematical theorem that the most general operation relating an asymmetric object to another copy is a rotation-translation equivalent to a helix when repeated. Thus, helical symmetry made its entry into the description of biological systems (Pauling & Corey, 1950; Pauling et al., 1951) although it was not for the first time that it was used to describe assemblies of identical units. Eventually, Cochran et al. (1952) worked out the theory of diffraction of the polypeptide helix. Astbury's observation of the 5.1 Å repeat distance was correct and, eventually, Pauling and Francis Crick explained (Crick, 1988), independently, this discrepancy by a slight additional coiling of the helices. Because of the non-integer screw, a shift by slight coiling facilitates their best packing, providing a nice example of symmetry breaking by a weak interaction. Shortly before Pauling's discovery, Bragg et al. (1950) proposed about 20 polypeptide structures, none of them correct, and not only because they rigorously adhered to the 5.1 Å repeat distance but also because they did not observe the planarity of peptide bonding (Perutz, 1997).

Although crystallographic work on biological macromolecules had begun in the 1920s, the great debate about colloids *versus* polymers in biological systems raged on for some time. It was only in 1953 that H. Staudinger was awarded the Nobel Prize in Chemistry for his fundamental studies of macromolecules. The Nobel Prize for 1954 went to Linus Pauling, stressing his contribution to the understanding the nature of the chemical bond. By then, he had published a triple helix for DNA, which proved to be a wrong structure. The correct double-helix structure of DNA was communicated by groups of Cambridge and London scientists (Watson & Crick, 1953*a*; Wilkins *et al.*, 1953; Franklin & Gosling, 1953).



Fig. 8. The double helix on a medal of the Pontifical Academy and on a Swedish stamp.

The double-helix structure had important novel features. One was that it had two helical chains, each coiling around the same axis but having opposite direction. The two helices going in opposite directions, and thus complementing each other, is a simple consequence of the twofold symmetry with the twofold axis being perpendicular to the axis of the double helix. The other novel feature was the manner in which the two chains are held together by the purine and pyrimidine bases. 'They are joined in pairs, as a single base from one chain being hydrogen-bonded to a single base from the other chain, so that the two lie side by side with identical *z*-coordinates. One of the pair must be a purine and the other a pyrimidine for bonding to occur'. A little later, Watson & Crick (1953a) add that 'if the sequence of bases on one chain is given, then the sequence on the other chain is automatically determined'. Thus, symmetry and complementarity appear most beautifully in this model but the paper culminates in a final remark which sounds like a symmetry description of a simple rule to generate a pattern, 'It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material'. This is a far from casual remark; on the contrary, a lot of consideration had been distilled into this sentence (Watson, 1994). Watson & Crick (1953a) illustrated their brief note with a purely diagrammatic figure (Fig. 6) of elegant simplicity, showing the two chains related by a twofold axis of rotation perpendicular to the axis of the helices. The structure since has been immortalized in sculptures (see the one, for example, in Fig. 7), on medals and stamps (examples are shown in Fig. 8), and by other means.

There are four different nucleotides in the DNA double helix but even four building elements can permute in virtually infinite possibilities if the chain is long enough, and the DNA molecules are very long. Thus it seemed likely to Watson & Crick (1953b) that the precise sequence of the bases is the code carrying the genetic information. The double-helix structure offers a simple visually appealing way of selfduplication. Once the hydrogen bonds are broken, each of the chains may reassemble a new partner chain from among the nucleotides available in their surroundings. Basically, this is the mechanism that has been accepted ever since and utilized with outstanding results in various applications such as, for example, the polymerase chain reaction invented by Kary Mullis (Mullis & Faloona, 1987).

#### 4. Pentagonal synergy

To some extent, the success of X-ray diffraction in single-crystal structure determination has hindered research in areas of less-ordered materials. However, some of the best scientists have paid a lot of attention to these both in materials science and in biological structures. J. D. Bernal was one of the pioneers in both areas. His interest in liquid structures was expressed by Nikolai Belov (1991) as: 'His last enthusiasm was for the laws of lawlessness'.

There was a curious absence of integer number residues in the a-helix structure, in the unit cell along the fiber direction, which was a sign of formal crystallography breaking down. Bernal (Olby, 1994) commented upon this in the following way: "We

clung to the rules of crystallography, constancy of angles and so forth, the limitation of symmetry rotations of two-, three-, four-, and six-fold, which gave us the 230 space groups, as long as we could. Bragg hung onto them, and I'm not sure whether Perutz didn't too, up to a point, and it needed Pauling to break with them with his irrational helix".

In view of Bernal's interest in generalized crystallography, it is curious that at one point in his career he actually refrained from studying less-ordered rather than more-ordered systems. He and W. T. Astbury apparently divided crystallographic areas between themselves. In the words of Bernal (1968): "A strategic mistake may be as bad as a factual error. So it turned out to be with me. Faithful to my gentleman's agreement with Astbury, I turned from the study of the amorphous nucleic acids to their crystalline components, the nucleosides".

Nonetheless, Bernal had great influence in extending traditional crystallography into the science of structures. A sure sign of the expansion has been the gaining importance of fivefold symmetry in it. It is remarkable that two outstanding discoveries of the mid-1980s in materials, the fullerenes and the icosahedral quasicrystals, are both related to fivefold symmetry (Hargittai, 1990).



Fig. 9. Truncated icosahedron sticking out of the wall above the entrance into the 'Hall with the Fountain' at the Topkapi Saray in Istanbul. Photograph by the author.

The stability of the truncated icosahedral  $C_{60}$  molecule was initially predicted by Eiji Osawa (1970) on the basis of purely symmetry considerations. When the conspicuous relative stability of  $C_{60}$  was observed, Kroto *et al.* (1985), not knowing of Osawa's prediction, were looking for a highly symmetrical structure. Although they eventually 'rediscovered' the truncated icosahe- dron (an artistic representation is shown in Fig. 9), they also reached out to R. B. Fuller's geodesic dome and thereby established a most valuable linkage between structural chemistry and design science. This was not the first time Fuller's ideas had facilitated structural research. Caspar & Klug (1962) also acknowledged the inspiration received from Fuller's physical geometry in their discovery of the icosahedral virus structures.



Fig. 10. Flower-like icosahedral quasicrystal in a quenched Al/Mn sample. Photograph courtesy of Dr Ågnes Csanady (Budapest).

The quasicrystal discovery *could* be described in the following *fictional* way: "For centuries excellent minds, including Johannes Kepler and Albrecht Durer, have tried to employ regular pentagons for covering the extended surface with a pattern of repetitive fivefold symmetry without gaps or overlaps. In the early 1970s, Roger Penrose (Gardner, 1977) came up with such a pattern. Alan Mackay (1982) extended this pattern into the third dimension, and has urged experimentalists to be on the lookout for such solids in their experiments. Taking up Mackay's challenge, Dan Shechtman *et al.* (1984) made such an observation. He used metal alloys of various compositions in rapid solidification and anticipated that this rapid solidification of the alloys would produce the predicted structures. Shechtman's experimental observations were published promptly and were embraced instantly by the leading scientists of structure. Fig. 10 shows a quasicrystal. Shechtman's experimental observations were also interpreted right away by Dov Levine & Paul Steinhardt (1984) and many others with various theoretical models. As a result of these *concerted* activities, the science of structures has fast expanded".

Alas, this is not the way it happened. In reality, the story of the quasicrystal discovery (Hargittai, 1997) illustrates a development when many different threads of far-away origins come together for a unique moment of great importance, only to diverge again in many different directions. The moment may be an experiment or a sudden realisation of the significance of data or it may be a longer period in time. In the quasicrystal discovery, it was the period from Dan Shechtman's original observation in April 1982 to the end of 1984 when the wider world of science learned about the discovery and took over. It is noted though that the observation of incommensurately modulated structures (de Wolff & van Aalst 1972; Janner & Janssen, 1979) had already challenged the periodicity paradigm. It was, however, salvaged by bringing these disturbing experiments into line, as if following a prescription by Kuhn (1970) in *The Structure of Scientific Revolutions* (see Cahn, 1995).

The discovery of quasicrystals has led to a paradigm change in crystallography, expressed even in a proposal for a new definition of what is a crystal by one of the IUCr's commissions: 'any substance is a crystal if it has a diffraction pattern with Bragg spots'.

Mackay (see Hargittai, 1997) has called attention to the rather careless original definition of crystallinity which needlessly excluded substances such as what we call

today quasicrystals. In this sense, the discovery was a kind of legalistic discovery. This happens when the human classification system is more restrictive than the laws of nature and discoveries appear to break the laws that had been artificially constructed in the first place.

Pejorative words, such as deviation, imperfect, distortion, deformation, disordered *etc.*, may be a con- sequence of such human imperfection, rather than nature's. This also applies to the various degrading and upgrading adjectives of symmetry in pseudosymmetry, subsymmetry, supersymmetry and such-like. Molecules and atoms do not follow human-made rules of symmetry in their arrangements; rather, our symmetry rules reflect our observations.

#### 5. Dissymmetry



Fig. 11. Louis Pasteur's chiral models of enantiomeric crystals in the Pasteur Institute, Paris. Photograph by the author.

Louis Pasteur's 1848 discovery of molecular and crystal chirality (Fig. 11) was a rich starting point for many branches which grew from a common root. The specific chirality of biological molecules has puzzled scientists and philosophers alike ever since. This is the question that Vladimir Prelog (1976) called 'molecular theology'. It was a great achievement of crystallography when Bijvoet, Peerdeman & van Bommel (1951) determined the sense of chirality of molecules. Originally, Emil Fischer (1894) had arbitrarily assigned an absolute configuration to sugars, with a 50% chance of being correct and, luckily, indeed it proved correct. By now the absolute configuration has been established for relatively simple as well as for large biological molecules.

Pasteur (1897) was aware of the possible implications of chirality; in his words, 'Is it not necessary and sufficient to admit that at the moment of the elaboration of the primary principles in the vegetable organism, [a dissymmetric) force is present? ... Do these [dissymmetric) actions, possibly placed under cosmic influences, reside in light, in electricity, in magnetism, or in heat? Can they be related to the motion of the earth, or to the electric currents by which physicists explain the terrestrial magnetic poles?' The most general symmetry statement, by Pierre Curie (1894), must have relied a great

deal on Pasteur's observations: "*c'est la dissymétrie qui crée le phénoméne*", 'dissymmetry creates the phenomenon'.

When Lee & Yang (1956) predicted the nonconservation of parity in certain interactions of fundamental particles, and it was immediately confirmed by a series of experiments, the notion of the 'asymmetric universe' received general acceptance. In the wake of the viola- tion of parity discovery, J. B. S. Haldane (1960) graciously returned to Pasteur's conclusion, "*L'universest dissymétrique*". Almost as a follow-up, such diverse areas of science as particle physics and astrophysics are being joined today in the search for fundamental forces in nature.

There are practical consequences of understanding the mechanism of chiral discrimination in organisms. Accumulated knowledge has included some tragic experiences. By now, research, characterization, manufacturing and marketing of enantiomers as potential drugs are rigorously legislated (Richards & McCague, 1997).

#### 6. Appeal

The examples selected above have demonstrated various applications of the symmetry concept in crystallography. The fruitful interplay between them has also contributed to the development of the concept. The examples have also demonstrated the connecting ability of symmetry. Packing considerations are of importance not only to crystallography but to mathematics as well. Helical symmetry is a link between crystallography and molecular biology, fivefold symmetry between crystal- lography and materials science, chirality between crystallography and both medicine and physics, and examples relating to chemistry also abound (Hargittai & Hargittai, 1995).

There is yet another important area of human endeavor, the arts, where the symmetry concept provides a link for crystallography. Escher's periodic drawings (MacGillavry, 1976) and sculptures resembling quasicrystals, helices and double helices in various artifacts all help crystallographers to reach outside their specialization and help non-crystallographers grasp the discoveries of the science of structures. Perhaps, however, nowhere so much as in education (Hargittai & Hargittai, 1998) does the symmetry concept help understand and appreciate our material world from the smallest molecule to the largest biological system and draw the most thrilling intellectual experience from it.

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# Symmetry by Numbers<sup>1</sup>

# Mario Livio, The Equation that Couldn't be Solved: How Mathematical Genius Discovered the Language of Symmetry Simon & Schuster 2005, 368 pp

#### Istvan Hargittai

The equation in the title is the quintic equation, the mathematical genius is Évariste Galois (1811–32), and the language of symmetry he discovered is group theory. Symmetry combines both beauty and science, and can easily be seen in the world around us. But before he could use it in science, Galois had to create the necessary mathematical tools. The world was slow to listen, and it took almost a hundred years for the practical value of group theory to be truly appreciated. Galois, meanwhile, was killed in a duel at an early age. In *The Equation that Couldn't be Solved*, Mario Livio follows his brief existence like a sleuth.

Born into a scholarly family in a Paris suburb in Napoleonic France, Galois was educated at home before being sent to a boarding school in Paris that rivaled the English schools of the time for austerity and rigid discipline. He was not a great success at school, but soon found satisfaction in mathematics, which became his sole occupation by the time he was 16. Having failed to gain entrance to a more prestigious college, he continued his studies in a high school.

Galois was still only 17 when he continued work started by the Norwegian mathematician Niels Henrik Abel, showing in general terms whether an equation is solvable by a formula or not. For this he introduced the seminal concept of a group, and created a new branch of algebra now known as Galois theory. His first publication appeared in 1829, but a combination of neglect and egotism prevented senior mathematicians of the day from giving him the exposure he deserved. When the work was finally introduced to the French Academy of Sciences, it was hardly appreciated.

Nonetheless, Galois continued his creative work, against all the odds. He failed another entrance examination as people greatly inferior to him could not appreciate his work, and lost his adored father, a Republican, who was driven to suicide by his royalist political opponents. Young Galois also had a passion for Republican revolution and served a prison term for his political activities. He fell in love with an undeserving girl and was killed in a duel that was related to this unfortunate entanglement. During the night before the tragedy, Galois hurriedly wrote a profound description of his group theory, remarking in the margin: "I have no time."

The Equation that Couldn't be Solved covers a remarkable number of different topics, including biographies of scientists and mathematicians. It also covers the Rubik cube and other puzzles; string theory; supersymmetry; the origin of creativity; the

<sup>&</sup>lt;sup>1</sup> Nature 2005, 437:34

relationship between the external symmetry of the human face and body, and mate selection and sex life; and much more. Livio examines the contributions of others that led up to Galois' discovery, and gives a panoramic view of the direct, as well as quite remote, applications of group theory.

Very little escapes Livio's attention, especially in twentieth-century physics. But one omission is the contribution to the story of Eugene Wigner. He applied group theory to quantum mechanics in the 1920s, when most of his contemporaries were yet to value it: Wolfgang Pauli called it "die Gruppenpest" — roughly translated as "that pesky group business". Wigner was awarded a Nobel Prize in 1963 for this work.

Another omission from the book is that, in discussing crystallography, Livio stops at the classical notions of symmetry and defines crystallography as "the science studying the structures and properties of assemblies made of very large numbers of identical units". This idea supposes regularity and periodicity, and was largely a result of the tremendous success of X-ray diffraction in the twentieth century. Recently, however, the field has embraced other structures, such as the newly discovered quasicrystallographer Alan Mackay that the rules describing 'crystal' structures be relaxed—and they have been. They now include structures that fall beyond the 230 space groups, and the new rules do not necessarily form groups.

Overextending the inferences from symmetry can be restrictive. As the historian of mathematics E. T. Bell said: "The cowboys have a way of trussing up a steer or a pugnacious bronco, which fixes the brute so that it can neither move nor think. This is the hogtie and it is what Euclid did to geometry."

The book seems a little biased in places when it emphasizes the omnipresence of symmetry, but it nevertheless makes a lively and fascinating read for a broad audience.


Vladimir Prelog in 1995 in his office at the Zurich Federal Institute of Technology (photograph by Istvan Hargittai). Prelog is holding a gold-plated model of the backbone of tRNA (transfer ribonucleic acid) molecule According to private communications from Alex Rich and Jack Dunitz to Istvan Hargittai in 1998, when Prelog was given this model, he exclaimed, "God's signature!"

## Prelog Centennial: Vladimir Prelog (1906– 1998)<sup>a</sup>

### István Hargittai and Balazs Hargittai



Vladimir Prelog in his office at ETH Zurich in 1995 (photo by I. Hargittai).

<sup>&</sup>lt;sup>a</sup> Structural Chemistry 2006, 17, 1–2



Prelog's familiar ex libris by Hans Erni with an inscription to one of the authors.

Vladimir Prelog was "the founder of modern stereochemistry, it was he who initiated and intellectually invigorated the current renaissance of this field …" So wrote Kurt Mislow [1] in 1998, the first recipient of the Vladimir Prelog Medal and the first Prelog lecturer at the Swiss Federal Institute of Technology (ETH Zürich) in 1986. Among his many achievements we mention here only a few following Mislow [1]. Prelog was the first who employed conformational analysis to rationalize the physical and chemical properties of medium-size-ring compounds. He made generalized observations concerning the steric effects in Grignard reactions. Together with Robert Cahn and Christopher Ingold, he proposed a terminology to specify the configuration of stereoisomers (the CIP system), and, together with William Klyne, a terminology to describe steric relations across single bonds. He did fundamental work on novel types of stereoisomers.

Prelog's innovations in nomenclature became popular and he often worked them out in unison with other luminaries of organic chemistry. At the end of 1953, beginning of 1954, an identical Note appeared in *Nature* and in *Science* concerning the nomenclature of bonds in cyclohexane [2]. Of the four authors of the Note—Barton, Hassel, Pitzer, and Prelog—three would eventually win the Nobel Prize in Chemistry. Prelog's Nobel Prize came in 1975 and it was shared with John Cornforth. Prelog's citation said, "for his research into the stereochemistry of organic molecules and reactions."

According to Cornforth [3], Prelog "stood out from among his contemporaries ... because he asked better questions and analyzed problems with greater clarity." Cornforth also noted that "Stereochemistry was the love of his life: he pursued it in many guises, devised rules for it, illuminated every aspect of it that he touched."

As Mislow noted [1], natural products chemistry was Prelog's first love and he remained true to it to the end of his days. However, his interest did not include proteins

and nucleic acids. This is why one of his most brilliant disciples, Albert Eschenmoser [4] gently provoked him by saying, "Vlado, every year during which we did not work on DNA was a wasted year." Prelog did not rush to give an answer, but when he did, he put it in writing because he realized its importance for science history:

Zurich, October 3, 1995

Dear Albert

For some time you have prodded me to tell you, why the great Leopold [Ruzicka] and I did not recognize, in a timely fashion, that the nucleic acids are the most important natural products, and why did we waste our time on such worthless substances as the polyterpenes, steroids, alkaloids, etc.

My light-headed answer was that we considered the nucleic acids as dirty mixtures that we could not and should not investigate with our techniques. Further developments were, at least in part, to justify us.

As a matter of fact, for personal and pragmatic reasons, we never considered working on nucleic acids.

Yours Vlado

In 1995, one of us recorded a conversation with Vladimir Prelog [5], in which he talked about his family background, youth, studies, about his interests, and sprinkled his narrative with anecdotes about which he was famous. His room was full of memorabilia of stereochemistry and chirality in particular. The most conspicuous was a series of Hans Erni's drawings, one of which became Prelog's *ex libris*. A peculiar feature of this drawing is that the two hands of the youth appear as if they were turned around, inverted. In a version of Erni's drawings, however, the two hands appeared to be non-inverted, being parallel. In the familiar version, the two hands can be imagined as a result of the two arms being crossed.

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EDITORIAL

### Graphene 2010

István Hargittai

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**Abstract** The first production of graphene was awarded the 2010 Nobel Prize in Physics. This discovery has implications for chemistry and within it for structural chemistry as well.

**Keywords** Graphene · Andre Geim · Konstantin Novoselov · Diamagnetic levitation · Fullerenes

"Science does not need to be boring to be good." Andre Geim in 2006 [1]

On October 5, 2010, the Royal Swedish Academy of Sciences in Stockholm awarded the 2010 Nobel Prize in Physics jointly to Andre Geim and Konstantin Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene" [2]. By happy coincidence, earlier on the same day, our editorial office had accepted a manuscript for publication, "Remarkable diversity of carbon–carbon bonds: Structures and properties of fullerenes, carbon nanotubes, and graphene," in which T. C. Dinadayalane and Jerzy Leszczynski reviewed, among others, the results of computational studies on graphene [3]. The manuscript had been submitted in July, however, due to the summer vacations, its reviewing process took a little longer than it normally would have.

The Nobel Prize in Physics in 2010 was among those rather rare cases when the Nobel recognition followed relatively quickly the discovery. Geim and his co-authors

I. Hargittai (🖂)



Andre Geim (courtesy of Andre Geim)



Konstantin Novoselov (courtesy of Konstantin Novoselov)

communicated the production of graphene in 2004 for the first time. Graphene is a single sheet of carbon atoms. It was a fortunate circumstance that they gave the easy and appealing name of graphene to the new material. Coining a

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Fig. 1 "Graphene model" as a window fence at Topkapi Sarayi in Istanbul (photograph and © by the author)

name—and an easy and attractive one at that—is arguably one of the most important, if not the most important component of a scientific discovery [4]. The new material is extremely strong along with many other favorable properties promising a plethora of applications. It may well be that the speedy Nobel recognition was a consequence of the anticipation of an avalanche of studies in the foreseeable future in this area of research after which it might be more difficult to single out up to three awardees. Here graphene is symbolized by an obviously strong window fence in the Topkapi Sarayi, Istanbul, which could be taken as a model of graphene (Fig. 1).

The principal discoverer, Andre Geim was born in 1958 in Sochi, Russia, which is on the Eastern shore of the Black Sea. When he was six years old, the family moved to Nalchik, further East, on the Northern slopes of the Caucasian Mountains, approximately midway between the Black Sea and The Caspian Sea. There he graduated from a high school specializing in the English language. He continued his studies in Moscow and did his Diploma work (Master's degree equivalent) in 1982 at Moscow Institute of Physics and Technology. He earned his Candidate's degree (PhD equivalent) in 1987 at the Institute of Solid State Physics of the Soviet Academy of Sciences (now Russian Academy of Sciences). Geim came from a family of Jewish-German origin and as being Jewish was considered to be a nationality his identity documents carried this designation causing barriers in his receiving higher education. He always felt he had to outperform others to survive in the Soviet system. Following his doctorate, Geim did research at the Institute of Microelectronics Technology of the Soviet (then, Russian) Academy of Sciences in Chernogolovka, near Moscow. With the crumbling and then collapse of the Soviet Union, travel became easier and Geim continued as postdoctoral fellow at the University of Nottingham, University of Bath, and University of Copenhagen. Finally, he got his appointment as associate professor at the Radboud University in Nijmegen, Holland. In 2001, he became Langworthy Professor of Physics at the University of Manchester and he has directed its Center for Mesoscience and Nanotechnology. He is now a Dutch citizen.

Konstantin S. Novoselov was born in 1974 in Nizhny Tagil, Russia, in the Southern region of the Ural Mountains. He did his Diploma work at the Moscow Institute of Physics and Technology and in the early 1990s he moved to Nijmegen where he started his PhD work with Geim as his mentor. Novoselov moved to Manchester along with Geim in 2001. He holds both Russian and British citizenships.

Geim (while still in Nijmegen) and his colleagues communicated a photograph in April 1997 displaying a levitating frog [5]. It was taken as an April Fool's joke. In reality, however, Geim and his colleagues suspended the frog, among many other similar experiments with nonmagnetic objects, by creating an upward magnetic force from a powerful magnet and thus they succeeded in compensating for the effect of gravity. Soon a British scientist Michael Berry developed a theory to interpret the phenomenon. When it was realized that Geim's experiment was not meant to be a joke; rather, the frog was truly levitated in Geim's experiment, this piece of research was deemed so outrageous that he and Berry were awarded the 2000 Ig Nobel Prize "for using magnets to levitate a frog."

The Ig Nobel Prize is a joke-taken seriously-which had been created to recognize scientific contributions that should not have been made. Ridiculing the experiment of frog levitation was a severe misunderstanding on the part of the organizers of the very popular Ig Nobel award. Apparently, they did not realize that using a frog was merely a device to attract attention, but the science behind it was serious pioneering achievement. The initiation of the Ig Nobel Prize was a sign of a great sense of humor and it was ironic that the awarders of the Ig Nobel Prize did not recognize humor when others practiced it. Thus, Geim has become the only scientist so far who has received both an Ig Nobel and a real Nobel Prize. Incidentally, the Ig Nobel Prize did not diminish Geim's affinity for joking. The following year he published another serious result, this time about the detection of earth rotation using a diamagnetically levitating gyroscope, and he listed as his co-author H. A. M. S. ter Tisha, which is supposed to be his favorite hamster by the name of Tisha [6].

The discovery of graphene and the award for it make one think about the history of the fullerene discovery. The surprise in Geim's and Novoselov's discovery in 2004 was that they were able to isolate and stabilize a single-atom-sheet carbon [7]. Prior to their report, many believed that such a two-dimensional atomic crystal simply could not exist. In contrast, back in 1966, David Jones wondered about the possibility of graphite sheets curling up and forming huge balls [8]. When Eiji Osawa described the  $C_{60}$  molecule of truncated-icosahedron shape in his Japanese-language publication, he based his suggestion on symmetry consideration and did not follow it up neither by computation nor by experiment [9]. This was followed by a computationbased prediction of the stability of truncated icosahedronshaped C<sub>60</sub> molecule by DA Bochvar and EG Galpern [10]. This work was not followed up either. Both these reports disappeared in oblivion to be discovered again only after the actual observation and production of buckminsterfullerene in 1985 [11] and 1990 [12], respectively.

The experimental observation of  $C_{60}$  was eventually awarded a chemistry Nobel Prize in 1996 to Robert Curl, Harold Kroto, and Richard Smalley. Two physicists pioneered the production of  $C_{60}$ , Donald Huffman and Wolfgang Krätschmer, and they might have been recognized by a similar distinction, but they were not. Graphene could be considered at least in principle to be the initial material of all carbon nanotubes and fullerenes. The nanotubes are represented here by a detail of the decorations of the Bangkok Royal Palace (Fig. 2) and the fullerenes by a



Fig. 2 "Nanotube model" as detail of a decoration at the Royal Palace in Bangkok (photograph and by the author)

slightly irregular model under the paw of a dragon in the Forbidden City outside Beijing (Fig. 3) and a buckminsterfullerene shape from the Topkapi Sarayi in Istanbul (Fig. 4).

Geim's and Novoselov's discovery and their Nobel Prize in Physics might also be viewed as the closing act of this beautiful round of discoveries and their ultimate recognition. By this it is not meant that the discoveries might also end; on the contrary, these latest events will undoubtedly contribute to further invigoration of the field and its researchers.

**Dedication:** The present Editorial is dedicated to the memory of a late friend, David Shoenberg (1911–2004) who was a pioneer in the application of strong magnetic



Fig. 3 "Slightly irregular fullerene model" under the paw of a dragon at Forbidden City outside Beijing (photograph and © by the author)



Fig. 4 "Buckminsterfullerene model" as an entrance decoration at Topkapi Sarayi in Istanbul (photograph and © by the author)

fields, including levitation of type I superconductors [13, 14].

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EDITORIAL

### Geometry and models in chemistry

#### István Hargittai

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Abstract Geometry is an important ingredient in the chemical sciences and especially in structural chemistry. It is closely related to modeling, which is a favorite epistemological tool in chemistry. In the history of chemistry, simple geometrical models have often preceded sound experimental elucidation of structures. A series of examples are presented that include gas-phase electron diffraction; the origin of molecular mechanics; estimation of experimental error in quantum chemical computations; qualitative models of molecular structures; symmetry-lowering effects; biological macromolecules; and chirality.

**Keywords** Geometry · Modeling · Molecular mechanics · Experimental error in computation · Precision and accuracy · Molecular packing · Biomolecular structures · Enantiomers

#### Ubi material, ibi geometria.

Johannes Kepler (1571–1630)

I. Hargittai (🖂)

#### Geometry is the daughter of property.

Bernard Le Bouyer (Bovier) (1657–1757), Conversations on the Plurality of Worlds (1686, translated by H. A. Hargreaves, 1990)

#### We could present spatially an atomic fact which contradicted the laws of physics, but not one which contradicted the laws of geometry.

Ludwig Wittgenstein (1889–1951), Tractatus Logico–Philosophicus 1961 (London: Routledge & Kegan Paul)

I have been influenced by Eugene P. Wigner's characterization of scientific research. He expressed it eloquently in his Nobel lecture when he quoted his teacher, Michael Polanyi in that "...science begins when a body of phenomena is available which shows some coherence and regularities, [that] science consists in assimilating these regularities and in creating concepts which permit expressing these regularities in a natural way." Wigner (and Polanyi) saw in this the real transferability of the scientific approach, and more so than in transferring concepts, such as energy, for example, "to other fields of learning" [1].

The beginning of my interactions with Wigner dated back to 1964 when he wrote me a long letter in response to an article I had published in a Hungarian literary magazine in reference to his essay on the limits of science. This article was my first ever publication and it was in my senior year of university studies. Our interactions culminated in our meeting in person and extended conversations in 1969 at the University of Texas at Austin (Fig. 1). On this occasion, he introduced me to the intricacies and broad applications of the symmetry concept [2]. We then remained in on-and-off correspondence throughout the years. The utilization of the symmetry concept has become

This editorial is based on an invited talk by the author for the seminar series "Mathematical Modeling" of the Mathematical Institute, Budapest University of Technology and Economics, on November 9, 2010.

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Fig. 1 Eugene P Wigner and the author on the campus of the University of Texas at Austin in 1969 (by unknown photographer, © I Hargittai)

an all-embracing feature of our work in structural chemistry throughout the decades [3].

#### Gas-phase electron diffraction

Of the uses of models in my research in structural chemistry, my first example is the electron diffraction determination of molecular structure [4, 5]. It is amazing how much information may be extracted from the diffraction pattern of a gaseous sample—a set of diffuse concentric rings (Fig. 2). However, the primary information obtainable from an electron diffraction pattern is scarce; it may be just about the magnitude of the principal internuclear distances in the molecule and about the relative rigidity of the molecule. The same is true for the visual inspection of the intensity distribution that comes directly from the



Fig. 2 Gas-phase electron diffraction pattern of adamantane recorded by Kenneth Hedberg and the author in 1969 in Corvallis, Oregon

experimental pattern. In contrast, the sine Fourier transform of the intensity distribution is related to the probability density distribution of the internuclear distances in the molecule (called the radial distribution—a misnomer), and thus it provides a considerable amount of information graphically, in a visually perceivable way. However, since the radial distribution is obtained via certain mathematical manipulations, it is used for general orientation rather than for quantitative elucidation of parameters.

It is the intensity distribution, referred to above, that is subjected to rigorous analysis and is the primary source of the reliable quantitative structural information. More often than not, the analysis utilizes a least-squares procedure for the refinement of parameters. Such a procedure, howeverit being based on a non-linear relationship-necessitates suitable initial sets of parameters for best results. Here is where model building comes into the structure analysis for which the sources include already existing structural information, intuition, and information directly read off from the Fourier transform of the intensity data. A poor initial model may result in reaching a local minimum in the structure refinement yielding a false structure for which there have been plenty of examples in the literature. The situation may be remedied by careful compilation of the model, by testing the results against all other available evidence, and by employing more than one technique simultaneously in the structure determination that would complement each other.

#### **Roots of molecular mechanics**

Concerning modeling in the computational determination of molecular structure, a pioneering step was made in the 1940s by Frank Westheimer [6] who initiated a new technique, molecular mechanics. He had participated in the American defense efforts and, when the war had ended, he had returned to the University of Chicago to resume his teaching and research. He had to start anew and had time to think about basic problems. This is how half a century later he described the birth of molecular mechanics [7]:

I thought through the idea of calculating the energy of steric effects from first principles and classical physics, relying on known values of force constants for bond stretching and bending, and known values of van der Waals constants for interatomic repulsion. I applied this idea to the calculation of the energy of activation for the racemization of optically active biphenyls. Minimizing the energy of a model for the transition state leads to a set of n equations in n unknowns, one for each stretch or bend of a bond in the molecule. It seemed to me that, to solve these

equations, one needed to solve a huge  $n \times n$  determinant. Fortunately for me, Joe Mayer came to the University of Chicago at the end of WWII. Joe was an outstanding physical chemist; he and his wife Maria [Goeppert Mayer] wrote the outstanding text in statistical mechanics. During the war, he had been working at Aberdeen, Maryland, using the world's first digital computer to calculate artillery trajectories. Perhaps Joe could have access to that computer, and could show me how to solve my determinant on it. So I went to him and asked him to help me. He didn't know about optically active biphenyls, so I made some molecular models and explained the stereochemistry to him, and showed him my mathematical development, up to the determinant. Then, in something like half an hour, he found a mathematical trick that we used to solve my equations without needing the determinant. That's how the solution of real problems in molecular mechanics got started. It has become big business since. Furthermore, it turns out that my instinct for computerizing was correct, since that is the way in which the field has since been developed.

The history of molecular mechanics must include—in fact perhaps begins with—a publication by Terrell Hill that presented the same general method I had invented for expressing the energy of molecules in terms of bond stretching, bond bending, and van der Waals interactions, and then minimizing that energy. Hill published the method [8], but with no application, no "reduction to practice." I hadn't known that we had a competitor, or that one could publish a bare research idea. After Hill published, I immediately wrote up the work that Mayer and I had already done, theory *and* successful application to determining the activation energy for the racemization of an optically active biphenyl, and submitted it for publication [9].

### "Experimental errors" in quantum chemical calculations

Tremendous progress has been made in computational chemistry and in particular in ab initio determination of molecular structures. This is another area where modeling has fundamental role, but here only one aspect is singled out, viz., the consideration of "experimental error," in quantum chemical computational work. One of the pioneers of the field, John Pople described the estimation of "experimental error" [10]:

The way I like to do this is to set up a theoretical model. You apply one theoretical model essentially to

all molecules. This model is one level of approximation. Then you apply this one level of calculation to a very large number of different molecules. In fact, one level of approximation is applied to all molecules, giving you an entire chemistry corresponding to that approximation. That chemistry, of course, would not be the same as real chemistry but it would approach that chemistry and if it is a good model, it will approach real chemistry well. What I try to do is to take a given model and then to use that model to try to reproduce a lot of well-known facts of experimental chemistry. For example you try to reproduce the bond lengths in a large number of simple organic molecules, or the heats of formation for that set of molecules, in a situation where the experiment is beyond question. Then you can actually do statistics and say that this theory reproduces all known heats of formation to the root-mean-square accuracy of 2 kcal/mol. When you've done that you build some confidence in the level of theory. If you then apply the same theory in a situation where experiment may not exist, you know the level of confidence of your calculations.

#### Qualitative models

Even in today's world of sophisticated quantum chemical calculations, qualitative models continue to play an important role in chemical research. As is known, successful models select one or a few of the properties of the system or systems they intend to describe and ignore the rest. A model is successful if it can be used for predictions of properties of systems not yet studied and, on occasion, not yet even existing. The systems used for testing the model should be within the scope of applicability of the model. One of the most successful qualitative models in predicting molecular shapes, geometries, and even structural variations in series of substances has been the Valence Shell Electron Pair Repulsion (VSEPR) Model [11]. It assumes that the valence shell of the central atom in the molecule is spherically symmetrical and the interactions among the electron pairs in this valence shell-taking into account all electron pairs regardless whether they are bonding pairs or lone pairs-are described by the potential energy expression  $V_{ii} = k/r_{ii}^n$ . Here, k is a constant,  $r_{ij}$  is the distance between the points *i* and *j*, and the exponent *n* is large for strong and small for weak repulsions, but they are generally stronger than simple electrostatic coulomb interactions.

The task is to look for the molecular shape for which the potential energy reaches its minimum. The exponent n is not known, but this is not an impediment to the application of the

model, because as soon as it is larger than three, the results become insensitive to the choice of n. This insensitivity of the results to *n* is the secret of the wide applicability of the model. The resulting shapes of the arrangements of the electron pairs for two, three, four, five and six electron pairs in the valence shell will be linear, equilateral triangular, tetrahedral, trigonal bipyramidal, and octahedral, respectively. A set of sub-rules extends the model toward more subtle variations of molecular geometry. The applicability of the model has limits, of course. Thus, for example, it is gradually less applicable with increasing ligand sizes relative to the size of the central atom, because for such structures non-bonded repulsions become gradually the dominating interactions [12]. The popularity of the VSEPR model has been greatly enhanced by its successful application for predicting and explaining structures that initially appeared to be counter-intuitive. A rich collection of examples discussed in a systematic way has appeared [13].

#### Precision and accuracy

An important feature of any model aiming at a realistic representation of structures is the inclusion of motion. The low-frequency, large-amplitude, so-called deformation motions may lead to some of the experimental techniques yielding lower symmetry molecular shapes than the equilibrium structure that would correspond to the minimum position of the potential energy function [14, 15]. The relationship between average structures and the equilibrium structure has become a cornerstone consideration with increasing precision of the experimental determination of molecular geometry and the enhanced sophistication of quantum chemical calculations. Beyond certain precisions, for example, the computed bond lengths and their experimentally determined counterparts cannot be the same, and any demanding comparison of such information and their meaningful discussion requires considerations of the accuracy of structural information [16]. The experimental results also depend on the way averaging over molecular motion takes place in the interactions any given technique utilizes in the experiments [17]. The impact of motion, however, may only be one of the possible origins of changes in molecular symmetry. Various other effects have been uncovered and taken into account with the expanding scope of reliable structure determinations, including the Jahn–Teller effect [18], and other effects [19].

#### Molecular packing

When molecules aggregate and build crystal structures, their geometries undergo changes to smaller or larger extents. Again, with improving precision, such changes have come increasingly to the attention of structural chemists. First of all, the symmetries of extended structures can be described by space groups and this approach also points to certain limitations in the classification of crystal structures within classical crystallography. Even within the framework of classical crystallography, the interesting question arises whether or not some of the modes of molecular packing are more advantageous than others. Both questions will be touched upon briefly in our following discussion.

Starting with the second question, as early as two millennia ago, already Lucretius noted that "Things whose fabrics show opposites that match, one concave where the other is convex, and vice versa, will form the closest union" [20]. With this statement Lucretius annunciated a fundamental principle of the best packing arrangement for arbitrary shapes. Packing considerations can be studied in a simplified way using two-dimensional space group patterns,



Fig. 3 George Polya's two-dimensional space group patterns in which the basic motives cover the surface without gaps or overlaps [21]

as was done by the mathematician George Polya [21]. His 17 groups were distinguished by the property that the repeating motives covered the surface without gaps or overlaps (Fig. 3). His conceptual approach was well augmented by Aleksandr I. Kitaigorodskii's (Fig. 4) empirical approach in which he designed a rudimentary structure-seeker (Fig. 5). With this device, he tested virtually all 230 threedimensional space group possibilities on arbitrary-shaped wooden molecular models for most efficient packing.



Fig. 4 Aleksandr I Kitaigorodskii in the 1960s in Moscow (courtesy of Laszlo Breier, Budapest)



Fig. 5 Kitaigorodskii's "structure-seeker" with wooden molecular models



Fig. 6 Packing of the same arbitrary shapes with twofold symmetry (*top*) and mirror planes (*bottom*) after Ref. [3]

Kitaigorodskii showed the preeminence of twofold symmetry and the disadvantage of mirror symmetry for most efficient space utilization (Fig. 6). For a more detailed discussion, see, e.g., Ref. [3].

As to the first question, the importance of modeling appeared conspicuously in two recent discoveries of new materials, quasicrystals [22] and fullerenes [23], but they are not discussed here at any lengths.

#### **Biomolecules**

Modeling was also decisive in the discovery of the alphahelix structure of proteins by Linus Pauling [24] as well as in the discovery of the double-helix structure of nucleic acids by James D Watson and Francis Crick. In addition to physical modeling, Watson and Crick utilized Rosalind Franklin's X-ray diffraction information and Erwin Chargaff's data on the quantitative equivalence of purine and pyrimidine bases in the DNAs of diverse organisms along with other sources of knowledge.

In this connection, and with the benefit of hindsight, the reverse question might also be asked concerning modeling, viz., Why did not Franklin and Chargaff use modeling in their respective investigations? In case of Franklin, this would have been most straightforward, given the similarity of her research and those of Linus Pauling, on the one hand, and Watson's and Crick's, on the other. It has been suggested that Franklin was close to the solution, but, lacking modeling, the results of her DNA structure would have emerged in steps rather than in one big splash as did Watson's and Crick's.

The situation with Chargaff's research is fuzzier. His careful measurements established not only that the molar ratio of total purines to total pyrimidines was close to one, but also that the molar ratios of adenine to thymine and of guanine to cytosine, respectively, were not far from one [25]. This was the kind of regularity that Wigner and Polanyi considered to be the gist of science. The data Chargaff collected scattered quite a bit, and the pattern did not emerge unambiguously as we think of it today. Yet Chargaff did notice it and was brave enough to annunciate it. Alas, he stopped short of asking the crucial question of Why? If the regularity was a real phenomenon, there must have been a reason for it; it must have occurred as a consequence of something. Today we know that it was basepairing between the two strands in DNA, and Chargaff might or might not have arrived at the concept of the double helix had he attempted to model what he had observed. The sad truth is, he never tried. His missing this may have been the reason for his ubiquitous bitterness to the end of his long life in connection with the whole field of molecular biology.

An interesting example of helical structure is shown by the tobacco mosaic virus (TMV) as depicted in Fig. 7. It has a simple rod shape with a regular helical array of proteins and there is a single-stranded ribonucleic acid molecule embedded within this protein coat. When this structure was to be modeled for the Brussels world exhibition in 1958, the builders of the large-scale model ran into the problem of identifying the initial point in building this model. The structure had been worked out originally by Rosalind Franklin and Aaron Klug with the participation of Kenneth Holmes and John Finch at Birkbeck College in London. By the time of the preparation of the physical model, Franklin had become ill and died in March 1958. It fell on Klug to recognize that to build the structure physically, there must be an initial point-in nature, it is a specific nucleation event. This realization led Klug to formulate the "difference between ordinary polymers and biological macromolecules. The key to biological specificity is a set of weak interactions. A polymer chemist could start building the model in the middle or at any other point. But for us, it was important to find the special sequence for initiating nucleation" [26].

At this point it is perhaps prudent to issue a caveat that not all model-building leads to the solution of all problems, especially if it is done remotely from experiment. Watson's and Crick's triumph in their quest for the DNA structure could easily mislead some who thought otherwise, because Watson and Crick did not carry out experiments. That did not mean though to rely on model building alone; on the



**Fig. 7** Aaron Klug with the tobacco mosaic virus model at the Laboratory of Molecular Biology of the Medical Research Council in Cambridge, UK, in 2000 (photograph and © by the author)



Fig. 8 Classification of chemical isomerism after Ref. [13]





Fig. 9 Two sets of Louis Pasteur's models demonstrating enantiomers at the Institut Pasteur in Paris (photographs and © by the author)

contrary, they relied on experiment and the best one at that, except that it was not their own experiment. Even then, Watson's and Crick's initial model necessitated a large amount of experimental work in Maurice Wilkins's laboratory before the original model could be considered established unambiguously. Quite a few other proposed structures for fibrous polynucleotide systems that were based on model building did not survive the test of eventual experimental studies [27].

#### Isomers

An important historical example of modeling involved the classification of isomers in chemistry as illustrated in Fig. 8. Of the kinds of isomerisms, the enantiomers-not superimposable mirror images-stand out in that they have no differences in distance geometry, i.e., in the interatomic distances, between the isomers. Yet even for relatively simple molecules the enantiomers may be vastly different in biological function. This isomerism may be described as differing in handedness, hence the name often used for the phenomenon-chirality. Louis Pasteur was the first who suggested that molecules may be chiral and he made macroscopic models of chiral objects to improve their perception. He may have been motivated to make these large-scale models because he wanted to demonstrate them to Jean Baptiste Biot, the discoverer of optical activity, and by the time of Pasteur's discovery, Biot's vision had considerably deteriorated. Pasteur's models have been preserved at Institut Pasteur in Paris (Fig. 9).

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### **Ambiguity of Symmetry**

Istvan Hargittai\*<sup>[a]</sup>

**Abstract**: Beyond the universality of the symmetry concept, there are different emphases on its application in different branches of science. Chemistry, being between particle physics and astrophysics, represents a bridge in, and a utilitarian approach to, the application of the symmetry concept, which has proved immensely fruitful in twentieth-century science. Some pivotal discoveries, especially in structural chemistry, molecular biology, and materials science, emerged by relaxing some of the stipulations of the classical teachings about symmetry. This highly personal presentation relies on ideas expressed by a number of notable individuals in recent science, among them J. Desmond Bernal, Francis Crick, Ronald J. Gillespie, Aleksandr I. Kitaigorodskii, Alan L. Mackay, George A. Olah, Linus Pauling, Roger Penrose, Dan Shechtman, James D. Watson, Steven Weinberg, and Eugene P. Wigner.

Keywords: Ambiguity · chirality · history of science · scientific discovery · symmetry

### 1. Introduction

Five years ago, I published another essay in the *Israel Journal of Chemistry, Dan Shechtman's Quasicrystal Discovery in Perspective*, and I concluded my presentation by mentioning my encounter with Eugene P. Wigner (Figure 1).<sup>[1]</sup> That I am starting the present essay with mentioning Wigner, signifies a pleasant continuity.

Wigner's contributions were fundamental to the understanding of the importance of the symmetry concept for science. In his terminology, symmetries and invariances were interchangeable. According to Wigner, the invariances make it possible to formulate the laws of nature. He underlines that "the first and perhaps the most important theorem of invariance in physics" is that "absolute time and position are never essential initial conditions."<sup>[2]</sup> In everyday language, this means that the validity of the physical laws of nature are independent of the location where and the point in time when we are considering them.

Wigner formulated the consecutiveness of invariances, laws of nature, and the events we observe and experience; that is, the physical phenomena:

The concept of initial conditions has utmost importance, even for dividing the sciences into disciplines in a meaningful way. Wigner says: "Other sciences which deal with what we physicists consider to be initial conditions, are, among others, geography and descriptive astronomy."<sup>[3]</sup> These examples explain what initial conditions mean. Events described by geography and descriptive astronomy depend on the place and time – initial conditions – hence, they are not governed by the laws of nature.

True laws of nature do not depend on the initial conditions. Sciences such as geography and descriptive astronomy "tell us only facts." Physics and mathematics are concerned with regularities. These are the two extremes. There are then sciences that are in between the two extremes, such as, for example, botany, zoology, and the medical sciences - according to Wigner. By geography, he means descriptive geography. As we move from descriptive geography toward physical geography, likewise, from descriptive geology to physical geology, and so on, we move from sciences solely concerned with initial conditions toward sciences concerned with regularities, that is, the laws of nature. "Physics does not endeavor to explain nature. In fact, the great success of physics is due to a restriction of its objectives: it only endeavors to explain the regularities in the behavior of objects. ... The regularities in the phenomena which physical science endeavors to uncover are called the laws of nature."<sup>[4]</sup> This formulation reflects Wigner's modesty, and his modesty may have helped him to recognize this profound limitation of the natural sciences.

Before Wigner (Figure 2), physicists used to use symmetry considerations for solving particular issues, whereas Wigner applied them in a most general way. One of the most profound messages Wigner conveyed to me was about the universality of the symmetry concept; that its validity cuts across the disciplines. We need to keep this in mind in the discussion following here, because there will be peculiarities assigned here to various disciplines

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**Figure 1.** Eugene P. Wigner with the author in 1969 at the University of Texas at Austin.

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modeling of molecular structures. He is the Editor-in-Chief of the international Springer journal Structural Chemistry. His recent books include Wisdom of the Martians (with B. Hargittai), Budapest Scientific (with M. Hargittai), Great Minds (with B. Hargittai and M. Hargittai), Buried Glory, Drive and Curiosity, Judging Edward Teller, Martians of Science, The Road to Stockholm, and Symmetry through the Eyes of a Chemist (with M. Hargittai). His most recent edited books are, both with Balazs Hargittai, Culture of Chemistry and Science of Crystal Structures.



Figure 2. Eugene P. Wigner in the late 1960s (courtesy of the late Martha Wigner Upton).

for an easier understanding and more efficient utilization of the symmetry principle.

Broken symmetry may be as important as symmetry itself. Such broken symmetries appear, for example, under the conditions above certain temperatures, and this has special significance for chemistry. As Steven Weinberg (Figure 3) explains:<sup>[5]</sup>

"The laws that govern atoms are completely symmetrical with respect to direction. There's nothing in nature that says that one direction in the laboratory, whether it's east and west or up and down, is any different from any other direction. On the other hand, when atoms join to form a molecule, for example, when three oxygen atoms join to form an ozone molecule, that's a triangle that points in a definite direction. It breaks the rotational invariance of the laws of chemical attraction by forming a particular object that has not the full rotational symmetry but a smaller symmetry, just rotations by multiples of sixty degrees. If you had a more complicated molecule, there'd be no symmetry left, yet the underlying laws are perfectly symmetrical. Those molecules only exist below a certain temperature. You



Figure 3. Steven Weinberg in 1998 at the physics department, University of Texas at Austin (photograph by I. Hargittai).

can always restore the symmetry by heating them sufficiently so the molecules break up into a gas. If you have a gas of monoatomic oxygen, without worrying about the walls, it is symmetrical; all directions are the same."

When the monoatomic gas has a distribution equivalent in all directions, perfect disorder emerges; thus, we equate this perfect disorder with symmetry. Further, according to Weinberg:<sup>[6]</sup>

"Perfect disorder is symmetry. To have order, for example in a crystal, you break the symmetry. You only have symmetry by finite rotations. A crystal of salt is invariant when you change your point of view by rotation of 90 degrees around various axes. It's a cubic crystal. But if you have molten sodium chloride, then there's no preferred direction at all. You've created complete disorder, as far as the directions are concerned. People in condensed matter physics very often use the terms order and disorder rather than broken symmetry and restored symmetry although they are very closely related.

"The symmetries that we talk about in elementary particle physics are not broken because of any particular object has formed. The physical state that breaks the symmetry is not a molecule or a crystal. It is empty space. The vacuum, although it's perfectly symmetrical with regard to rotations in space, or translations in space, is not invariant with respect to changes in your point of view about which particles are viewed. It's the vacuum that distinguishes the neutrino from the electron, or the weak interactions from the electromagnetic interactions. The reason that the photon is massless whereas the other particles on the same symmetry multiplet, the W and the Z particles, are very heavy, is because of the way they propagate through the vacuum."

At this point, I have to refer to my long conversation with Yuval Ne'eman in 2000 in Stockholm. In the course of that conversation, he told me that on the basis of symmetry considerations, he had predicted the mass of the Higgs particle, which at that time had not yet been observed. Ne'eman said, "If and when the Higgs [particle] will be found and its mass measured, I would now like to advertise my theory and people to know that I had predicted it."<sup>[7]</sup> As Ne'eman died before the actual observation of the Higgs particle, I find it important to mention his prediction here.

Weinberg stressed the importance of the symmetry of the laws of nature, but the symmetry of objects is also important, and in chemistry, and in molecular biology, they play a distinct role:<sup>[6]</sup>

"It is important that the sugars in living things are right-handed and the amino acids are left-handed, but it's not the most fundamental about them. On the other hand, the symmetries of nature are the deepest things we know about nature. It's much easier to learn about the symmetries of a set of laws than about the laws themselves. For example, long before there was any clear understanding of the nuclear forces, it was clear that there was a symmetry that the nuclear forces obeyed that related neutrons and protons and it said that they behaved the same way with regard to the strong forces."

We shall mention the issue of chirality later in our discussion. At this point, we once again bring up the relationship of crystals and symmetry to illustrate how different interpretations may there be depending on the kind of question we are asking about them. In chemistry, when crystallization occurs, there is translational symmetry on the inside, in addition to other symmetries, let alone the symmetry of the external shape. On a deeper level, as we speak about the external shape of a crystal, it already points to the breaking of translational symmetry, because translational symmetry does not include an ending of such symmetry; it should extend to infinity. In reality, although the crystal is finite, it is usually large enough to consider it infinite (from the point of view of a diffraction experiment, for example).

If we take the point of view in physics, there is a different approach, and this is what Weinberg emphasizes: "When you have a crystal, condensed from a liquid, the crystal breaks translational invariance. The crystal is in one location and if you translate the crystal by an infinitesimal amount, you have a different crystal, the atoms are clearly moved, the crystal has a definite location, it's here, not there. That means that translational invariance is a broken symmetry."<sup>[8]</sup>

In the examples that follow, mostly chemical structures will figure, and a utilitarian approach to symmetry. Emphasis will be on the application of the symmetry concept in a variety of discoveries in chemistry. The limits of the applicability or the utility of this concept will be indicated at places. We will mention examples in the complementarity in crystal structures; structure elucidation of large, biologically important molecules; determination and prediction of the molecular geometries and structural variations of simple molecules, among them, the intriguing carbocations; the discovery of fullerenes and quasicrystals; and chirality.

### 2. Complementarity in Crystal Structures

For our discussion, the main interest of complementarity in crystal structures is in that the most symmetrical arrangements are by far not the most frequent among crystal structures. By now, with hundreds of thousands of crystal structures available in databases, the preeminence of complementarity is a well-established fact. The Soviet-



Figure 4. Aleksandr I. Kitaigorodskii lecturing (courtesy of Irena Akhrem).

Russian crystallographer, Aleksandr I. Kitaigorodskii (Figure 4),<sup>[9]</sup> predicted the relative frequencies of symmetry occurrences of all the 230 kinds of symmetry in crystal structures. He made his predictions long before hundreds of thousands of structures had become available. His initial goal was even more ambitious: it was finding regularities in how molecules build up crystals, and on such a basis predicting crystal structures as soon as the composition of a new substance would become available. This goal has so far proved elusive.

In the late 1930s, the German physicist Pascual Jordan suggested that interactions between identical or nearly identical parts of molecules represent the advantageous mode of building up stable systems (Zur Frage einer spezifischen Anziehung zwischen Genmolekülen; To the question of a specific attraction between gene-molecules).<sup>[10]</sup> In contrast, Linus Pauling and the physicistturned-biologist Max Delbrück argued for precedence for interactions between complementary parts, rather than identical ones.<sup>[11]</sup> The title of their short communication was The Nature of the Intermolecular Forces Operative in Biological Processes. It is unlikely, especially under the war-time conditions, that Kitaigorodskii (Figure 5) could have been familiar with the Pauling-Delbrück paper. Yet Kitaigorodskii, independently, declared a research program, "The close packing of molecules in crystals of organic compounds" in the then still-existing English-language Soviet physics journal.<sup>[12]</sup> The program was based on his views on the preeminence of attractive interactions between complementary molecular shapes. He predicted that "the mutual location of molecules is determined by the requirements of the most close-packing."

Kitaigorodskii used his own so-called structure-finder, a simple stand to which he fastened wooden models of molecules of the same arbitrary shape and examined the densest packing of virtually all 230 symmetry variations.



Figure 5. "Complementary Kitaigorodskii" (drawing by and courtesy of lstván Orosz).

He found that the highest frequency occurrence of molecular packing should be that characterized by two-fold rotational symmetry (Figure 6). This is what corresponds to the complementary arrangement of molecules in which



**Figure 6.** Densest packing with space groups (top) p1 and (bottom) p2. After Ref. [15].

protrusions of one molecule meet with cavities of the other molecule. This is spatial complementarity. Molecular packing characterized with symmetry planes is not impossible, but it is rather disadvantageous for densest packing (Figure 7). In other words, "lower symmetry packs better."<sup>[13]</sup> Today's wealth of data on hundreds of thousands of crystal structures has proved Kitaigorodskii's predictions, demonstrating the correctness of his far-sighted vision of the interactions directing crystal architecture.<sup>[14]</sup>

### 3. Alpha-helix and Double-helix Structures

During the first half of the twentieth century, the existence of biological macromolecules was not yet generally accepted, but the efforts to establish the nature of biolog-

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**Figure 7.** The presence of symmetry planes in the space groups (top) pm and (bottom) pmm hinder densest packing. After Ref. [15].

ical substances and to uncover their structures were going on. Michael Polanyi and Herman F. Mark subjected fibrous materials to X-ray diffraction in the 1920s, at the Kaiser Wilhelm Institute in Berlin. The experiments on cellulose indicated the presence of crystallites in cellulose that were oriented in the direction of the fiber axis. Furthermore, Polanyi and Mark observed characteristic changes when they stretched the cellulose fibers. X-ray crystallography was becoming the preeminent tool for the structure determination of biopolymers.

Linus Pauling (Figure 8) joined early the quest for uncovering the structure of biopolymers. He had been the foremost structural chemist accumulating information about the structure and bonding of small molecules, including amino acids, the building blocks of proteins. Hemoglobin was the first protein that attracted Pauling's interest. As is well known, hemoglobin carries the oxygen in our organism. There was also a British group in Cambridge working on the structure of hemoglobin that had



Figure 8. Linus Pauling's autographed photograph (courtesy of the late Linus Pauling).

chosen this protein for their inquiry, independent of Pauling's interest.

There were two types of proteins known; for example, hair, horn, porcupine quill, and fingernail belonged to one, and silk to the other. Hair in its normal state and in its wet state showed differences in their X-ray diffraction patterns, according to the experiments by William T. Astbury. He called one alpha keratin, and the other beta keratin. The beta keratin was the stretched form and the Xray pattern of the beta keratin state of hair was similar to the X-ray pattern of silk. Pauling decided to start his studies with alpha keratin. He launched a complex investigation in which he used all his accumulated knowledge of the structure of small molecules and all his knowledge about the correlation of geometrical features and bonding peculiarities of molecular structure. Understanding chemical bonding was as important as collecting X-ray diffraction data. Thus, knowing about the double-bond character of the peptide bond meant a drastic reduction of possible protein structures, because the bond configuration about such a bond had to be planar or nearly planar. This piece of information helped Pauling to drastically reduce the number of possible models. Nonetheless, at the time this was during the second half of the 1930s - Pauling still did not have enough information about the details of the protein structures to be able to propose a model that would be in agreement with all the X-ray diffraction evidence he possessed. Among the unknown factors, it was not known how the diversity among the building blocks that is, among the amino acid units of the proteins would influence the overall structure of the protein molecule.

About a decade later, Pauling continued his quest for the protein structures. At this time - this was in 1948 - he decided to ignore the fact that the building block amino acids were different from each other, and assumed them to be equivalent. This was a huge simplification; in a way, it was the introduction of translational symmetry in the protein chain, where, rigorously considering it, it did not exist. His subsequent results justified this simplification. Once he could consider the protein chain more uniform than it was, he could apply to it a mathematical theorem according to which an asymmetric object can be converted into an equivalent asymmetric object by the application of rotation-translation. Subsequent and repeated application of this operation - and this is also prescribed by the mathematical theorem - produces a helix. This was a breakthrough and one of the factors that permitted Pauling to reach it was his bravely overlooking the absence of rigorous symmetries among the building blocks of the protein chain.

Pauling realized the fruitfulness of building models. He prepared a rudimentary drawing of the protein chain (Figure 9) – using uniform amino acids – and determined the possible models emerging from folding the drawing in such a way that satisfied the possibility of hydrogen-bond



**Figure 9.** Linus Pauling's sketch of the polypeptide chain in 1948. Pauling folded the paper along the creases and arrived at the alpha helix (courtesy of the late Dorothy Munro, Linus Pauling's long-time personal assistant).<sup>[16]</sup>

formation that he had also found to be present in the desired structure.<sup>[16]</sup> The result showed one problem that did not seem to be surmountable, viz., the turn about the chain did not correspond to an integer number of amino acids. This, again, lowered the degree of symmetry of the emerging structure. In a bold move, Pauling decided to ignore this deficiency of his model, as there really was no stipulation that such a symmetry requirement should be fulfilled. Once he went ahead, two models appeared satisfactory, of which one could be discarded readily and the other was the model he called alpha helix. The Cambridge (UK) group that was working on the protein structures simultaneously with Pauling came up with numerous models, none of which turned out to be acceptable. Pauling's competitors did not apply the simplifications that Pauling did with such success.

There was at least one general lesson from Pauling's achievement in producing the alpha-helix structure of proteins: "Pauling's approach to solving this complex problem was exemplary in focusing on what was essential and ignoring what had little consequence. When it turned out that the turn about the chain did not correspond to an integer number of amino acids, hinting at less than perfect symmetry, he did not let himself bothered by this. He thus expanded the realm of crystallography toward structures that were not part of classical crystallography yet included literally vital substances."<sup>[17]</sup>

Francis Crick (Figure 10) and James D. Watson (Figure 11) published their suggestion for the structure of deoxyribose nucleic acid (DNA) in April 1953 (Figure 12). They wrote that their "structure has two helical chains each coiled round the same axis. ... The two chains (but not their bases) are related by a *dyad* [two-fold axis] *perpendicular to the fibre axis.* Both chains follow right-handed helices, but owing to the dyad the sequences of the atoms in the two chains run in opposite directions"<sup>[18]</sup> (emphasis by me). It may be argued that the



Figure 10. Francis Crick in 2004 in La Jolla (photograph by I. Hargittai).



Figure 11. James D. Watson in 2000 in the author's home in Budapest (photograph by I. Hargittai).

mention of dyad here is equivalent to a two-fold axis of rotation ( $C_2$  symmetry), but one wonders why Watson and Crick were not more explicit about this feature of the structure. There was some ambiguity about how Watson and Crick, each of them separately, handled the presence of symmetry in the DNA structure.<sup>[19]</sup> The impression has formed "that for Watson, the  $C_2$  symmetry of the structure was not as revealing as it was for Crick. Back in 1951, he [Watson] wrote to Delbrück, 'Our method is to completely ignore the X-ray evidence.<sup>[20]</sup> In February 2004, Crick noted that Watson did not understand the significance of  $C_2$  symmetry of the DNA structure.<sup>[21]</sup>

In his book, *What Mad Pursuit*, Crick was more selfcritical with respect of the difficulties in recognizing the importance of  $C_2$  symmetry and its implication for the DNA structure. He notes that discovering base-pairing was more the result of serendipity than logical thinking. It would have been more elegant to come to the right conclusion by logical thinking: "first to assume Chargaff's

**Figure 12.** Artist's rendition of the double helix of DNA; Bror Marklund's sculpture in front of the Biomedical Center of Uppsala University (photograph by I. Hargittai in 1997).<sup>[a]</sup>

rules were correct and thus consider only the pairs suggested by these rules, and second, to look for the dyadic symmetry suggested by the C2 space group shown by the fiber patterns."<sup>[22]</sup>

At this point, it is of interest to mention that Watson's apparent indifference to the  $C_2$  symmetry of the DNA structure was not characteristic of his general demeanor towards symmetry. When the work on the DNA structure was temporarily halted in Cambridge, and he joined the investigation of tobacco mosaic virus, he did consider its symmetry. Donald Caspar described the story:<sup>[23]</sup>

"It was Jim Watson who recognized the helical symmetry in tobacco mosaic virus (TMV). This had grown out of the work on the DNA structure. [W. L.] Bragg was the director of the Cambridge laboratory where Watson and Crick were working on DNA, and he [Bragg] found out in 1952 that DNA research was also going on in Randall's lab at King's College in London. Bragg called Crick and Watson into his office and ordered a moratorium on the DNA work in his lab. At that time it was considered ungentlemanly in Great Britain to work on the same problem as your colleagues and to compete with them. That's when Watson switched temporarily to the TMV problem. He recognized that TMV was a helix and applied to it the theory of diffraction by helical structures that Crick had worked out. The helical symmetry that Watson had

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inferred had turned out to be incorrect and Rosalind Franklin had got it right a few years later. But in 1952, DNA was more exciting than TMV, and when Bragg learned about the ongoing work on DNA by Linus Pauling in Pasadena, he lifted the moratorium and gave Watson and Crick full support to resume their DNA work."

The structure of TMV did have helical symmetry, though different from the initial suggestion. It has a rod shape and the proteins envelop, with a helical array, a single-stranded RNA molecule (Figure 13). At first sight, biological macromolecules and other polymeric structures appear very similar. There is, though, an important difference. To build a model for a biological macromolecule, the starting point should correspond to a nucleation event. According to Aaron Klug (Figure 14), "The key to biological specificity is a set of weak interactions. A polymer chemist could start building the model in the



Figure 13. The model of TMV (courtesy of Aaron Klug).



**Figure 14.** Aaron Klug with the TMV model in 2000 at the laboratory of Molecular Biology in Cambridge (photograph by I. Hargittai).

<sup>[</sup>a] The area surrounding the sculpture has been built in since the time the snapshot was taken.

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middle or at any other point." In contrast, for building the models of biological macromolecules, it is "important to find the special sequence for initiating nucleation."<sup>[24]</sup> Incidentally, preparing a model of TMV was a task for the world exhibition in Brussels in 1958. Rosalind Franklin was a major contributor to elucidating the TMV structure. By the time her group was preparing for the Brussels exhibition, she was already gravely ill and died in the same year as the world exhibition took place.

The terms helix and spiral are rigorously distinguishable, but everyday language often, and even scientists sometimes, use them interchangeably. Helical symmetry is when a constant amount of translation is accompanied by a constant amount of rotation. For spiral symmetry, both the amounts of translation and accompanying rotation change gradually and regularly (Figure 15). The biological molecules have helical, rather than spiral, symmetry, whereas oscillating reactions, accompanied by color changes, may form beautiful spiral patterns (Figure 16).<sup>[25]</sup>

The two-fold rotational symmetry of the DNA doublehelix structure is in beautiful correlation with the function of this biological macromolecule. Symmetry does not appear in such a directly visible way for many other bio-



**Figure 15.** Artist's rendition of a true double spiral, detail of "The Inner Light" by Gidon Graetz, in the garden of the Weizmann Institute in Rehovot (photograph by I. Hargittai).



Figure 16. Enhancing spiral pattern in a reacting Belousov-Zhabotinsky system (drawing by and courtesy of the late Endre Kőrös).



**Figure 17.** The structure of the photosynthetic reaction center with approximate  $C_2$  symmetry (courtesy of Johann Deisenhofer).

logical systems. Sometimes it does, but the function is still not correlated in any perceivable way with it. An example is the attractive two-fold symmetry of the photosynthesis reaction center, yet what, if anything, it means for the process of photosynthesis remains a puzzle (Figure 17). Johann Deisenhofer described the moment of the discovery as follows:<sup>[26]</sup>

"It was extremely exciting to localize these features and build models for them. When I stepped back to see the arrangement, the unexpected observation about it was symmetric. There was symmetry in the arrangement of the chlorophyll that nobody had anticipated. Nobody, to this day, completely understands the purpose of this symmetry. I think it can be understood only on the basis of evolution. I think that the photosynthetic reaction started out as a totally symmetric molecule. Then it turned out to be preferable to disturb its symmetry, sticking to an approximate symmetry but changing subtly the two halves of the molecule. Because of the difference in properties of the two halves, the conclusion had been, before the structure came out, that there cannot be symmetry; that it has to be an asymmetric molecule. Now, when people looked at the structure, it looked totally symmetric to the naked eye. That realization was the high point I will never forget."

### 4. Structural Complications for Simple Molecules

Ronald J. Gillespie's (Figure 18) valence shell electron pair repulsion (VSEPR) model or theory predicts the geometry of the molecule on the basis of the number of electron domains (bonding pairs, lone pairs, multiple bonds) in the valence shell of its central atom.<sup>[27]</sup> The predicted shapes and symmetries depend not only on the general number of electron domains, but to various ex-

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Figure 18. Ronald J. Gillespie in 1998 in Austin, Texas (photograph by I. Hargittai).

tents, also on the nature of those domains, whether they are single bonds, lone pairs, or multiple bonds.

In all VSEPR considerations, spherical symmetry of the valence shell of the central atom is assumed, and that all electron domains are at equal distances from the nucleus of the central atom (Figure 19). The geometries may be determined as the ones assigned to the minimum of the potential energy. Its terms can be expressed as  $V_{ij} = k/r_{ij}^{n}$ , where k is a constant,  $r_{ij}$  is the distance between the points *i* and *j* in the spherical valence shell, and the exponent *n* is large for strong and small for weak repulsions. The value of *n* is generally much larger than what it would be for merely electrostatic interactions, but it is not known. The great advantage of the model is that it



Figure 19. A variety of VSEPR geometries.

Early on, the determination of the structure of xenon hexafluoride was a conspicuous success for the model. As soon as the substance was produced, some rudimentary molecular calculations predicted that the molecule has the highly symmetrical  $(O_h)$  regular octahedral shape. However, according to the VSEPR model, XeF<sub>6</sub> should be described as an  $AB_6E$  system, where A is the central atom, the ligands B are linked to it by an electron pair each, and there is also a lone pair of electrons, E, in the valence shell of xenon. Hence, the molecule cannot have a regular octahedral shape. When Gillespie predicted a distorted geometry for  $XeF_6$ , the subsequent experimental studies suggested C<sub>3v</sub> symmetry, or even C<sub>2v</sub> symmetry, for the molecule could be derived from the O<sub>h</sub> structure by small distortions. Further work, however, vielded less unambiguous results. The suggestion was that it all depended on the stereochemical activity of the lone pair of electrons. In the case of a stereochemically active lone pair, the molecule is expected to display fluxional behavior, i.e., rapidly interconverting series of configurations. In the case of stereochemical nonactivity, a rather rigid structure should be present. The case of XeF<sub>6</sub>, which was such a convincing case for the utility of the VSEPR model, has become an example of its limitations.<sup>[28]</sup>

Rigorously applying the VSEPR arguments in cases where they should work impeccably, it is interesting to note that it is not always the highest symmetries that emerge in molecular structures. Thus, the seemingly analogous molecules OPF<sub>3</sub> and OClF<sub>3</sub> should be described in VSEPR formulation as CAB<sub>3</sub> and C(E)AB<sub>3</sub>, respectively, where A is the central atom, C and B are ligands, and E is a lone pair of electrons in the valence shell of the chlorine atom. The bond configuration of OPF<sub>3</sub> has a distorted tetrahedral shape of  $C_{3v}$  symmetry, whereas OClF<sub>3</sub> has a trigonal bipyramidal arrangement of the five electron domains and a bond configuration of C<sub>s</sub> symmetry (Figure 20). The electron domains, whether they represent a single bonding pair, a multiple bond, or a lone pair, have different spatial requirements, and accordingly, repulsion strengths, in the valence shell. They are, in decreasing order: lone pair, multiple bond, and single bond.



**Figure 20.** OPF<sub>3</sub> is of  $C_{3v}$  symmetry and OCIF<sub>3</sub> is of  $C_s$  symmetry.

Further refinement of the model is necessary when, for example, single bonds connect ligands of different electronegativities. An example is the comparison of the molecular symmetries of  $F_3PCl_2$  and  $F_2PCl_3$  (Figure 21). Both



**Figure 21.** In both trigonal bipyramidal structures of  $PF_3Cl_2$  and  $PF_2Cl_3$ , the fluorine atoms occupy axial positions and the chlorine atoms occupy equatorial positions.  $PF_3Cl_2$  is of  $C_{2\nu}$  and  $PF_2Cl_3$  is of  $D_{3h}$  symmetry.

structures have  $C_3AB_2/C_2AB_3$  descriptions, and accordingly, trigonal bipyramidal bond configurations. However, the bonds leading to more electronegative ligands (fluorine) have smaller space requirements in the valence shell of the central atom than the bonds leading to less electronegative ligands (chlorine). Further, in the trigonal bipyramidal configuration, not all positions are equivalent in their space requirements. The surroundings of the axial positions are more crowded than those of the equatorial positions. Hence, the bonds to fluorine are expected to be in axial positions, and the bonds to chlorine in equatorial positions. The corresponding symmetries are, indeed,  $C_{2v}$ for  $F_3PCl_2$ , and  $D_{3h}$  for  $F_2PCl_3$ .

In the examples mentioned above, we focused on the variations of molecular symmetry. Changing the nature of the ligands may also cause characteristic changes in the bond lengths and bond angles in a series of substituted derivatives without changes in the molecular symmetry. Sometimes, it is fruitful to look at the variations in the distances between atoms not connected by chemical bonding, especially when the ligand atoms are large with respect to the central atom. Generally speaking, the VSEPR rules may work best for small ligands relative to the central atom. The relative weight of the nonbonded interactions in shaping the geometry of the molecule increases with increasing ligand size with respect to the central atom.

Thus, for example, retaining the constancy of such nonbonded distances may be looked at as the primary factor in the realization of certain structures. Here, we single out the remarkable constancy of the O...O nonbonded distances of the sulfone groups in a series of substituted sulfone molecules,  $O_2SXY$  (Figure 22). The O...O distance hardly changes from being 2.48 Å in a series of free sulfone molecules, while the lengths of the S=O bonds vary up to 0.05 Å, and the O=S=O bond angles vary up to 5 degrees, depending on the nature of the X and Y ligands.<sup>[29]</sup> The variations in the sulfone series could be visualized by a tetrahedron of the two oxygen atoms and



Figure 22. Tetrahedral sulfur configurations. From the left: sulfones; sulfuric acid; and alkali sulfates.

the X and Y ligands about the central sulfur atom, with the two oxygen atoms firmly taking the positions of two of the vertices of the tetrahedron. Depending on the nature of the X and Y ligands, the central sulfur atom would be sliding along the bisector of the OSO angle, changing the SO bond lengths and OSO bond angles, but keeping the O...O distances unchanged. The recognition of the constancy of the O...O distances in an extended series of sulfone molecules enhanced the possibilities of the combined application of electron diffraction and microwave spectroscopy in the accurate determination of related molecular structures.

Even systems as simple as metal dihalides may have complications in their molecular symmetry. The free molecules of dihalides of alkaline earth metals used to be considered linear, of  $D_{\infty h}$  symmetry. We have learned, however, that this holds only for the dihalides of lighter metals, viz., beryllium and magnesium. Toward the dihalides of heavier metals, especially when combined with smaller halogens, the molecules are bent, as of C<sub>2v</sub> symmetry. There are a few structures in between that are called quasilinear. They are characterized with a small energy barrier on the bending potential energy distribution at the position of the linear configuration, but this energy barrier may even be below the ground-state energy level. A broad and flat minimum of the bending potential energy curve is typical for quasilinear molecules. They are floppy and very little energy input suffices to bend or straighten such molecules (Figure 23).

The symmetry descriptions  $D_{\infty h}$  and  $C_{2v}$ , as well as quasilinearity, refer to the minimum positions on the bending potential-energy curve. There is a related, but rigorously distinguishable, case when a molecule that is strictly linear in the minimum energy position appears nonetheless as bent from certain experimental structure elucidations. This happens most conspicuously when the bending vibrations of a metal dihalide appear as low-frequency, large-amplitude motion. Any experimental technique that determines the time-averaged structure and for which the interaction time is longer than the bending motion of the molecule, will yield a bent geometry, even when the molecule is linear in the minimum energy position. In terms of the halogen-halogen nonbonded distance, in the linear configuration, this will be exactly twice the bond length; in any bent position of the molecule, the halogen-halogen



**Figure 23.** Bending motions and a sampler of potential energy functions. Top: bending vibrations of a linear triatomic molecule, where *r* is the instantaneous distance between the end atoms and  $r_e$  is the equilibrium distance of the linear configuration ( $r < r^e$ ). Bottom: Comparison of bending potential functions for linear and bent models of symmetric triatomic molecules.

distance will be shorter than twice the bond length. However, this is only an apparent deviation from linearity. Such a difference between molecular shapes and symmetries of the minimum position structure (called also equilibrium structure) and the average structure is characteristic not only of the triatomic  $AB_2$  molecules, but any polyatomic molecule. Again, the higher the probability of low-frequency, large-amplitude deformation motion, the larger the difference expected between the equilibrium and average structures.

Generally speaking, fluxional molecular behavior decreases the probability of unambiguous determination and description of molecular shape and symmetry. Permutational isomerism is an example of fluxional behavior. R. Stephen Berry discovered it for trigonal bipyramidal structures, and it is called Berry pseudorotation (Figure 24).<sup>[30]</sup> Permutational isomerism is when different structures with different symmetries of the same molecule interconvert. Identical atoms permute among nonequivalent sites in these processes. The VSEPR model suggests only a slight energy preference for the trigonal bipyramidal model (D<sub>3h</sub>) over the square pyramidal one (C<sub>4v</sub>) and they easily interconvert.

Above, we have already considered, in passing, the important relationship of the interaction time required by the physical phenomena on which the experimental technique is based, and the lifetime of the structure being measured. The interaction times are relatively long for



**Figure 24.** Berry-pseudorotation of PF5-type molecules, with a potential energy function; and R. Stephen Berry in 2001 in Erice, Italy (photograph by I. Hargittai).

the techniques of NMR spectroscopy, and very short for the diffraction techniques. Vibrational spectroscopy is somewhere in between. Thus, for example, for the rapidly interconverting  $AB_5$  trigonal bipyramidal geometries, NMR spectroscopy may yield information only about the average A–B bond, whereas electron diffraction may distinguish the axial and the equatorial A–B bonds.

Berry-pseudorotation introduces a great deal of ambiguity into the description of structures analogous to PF<sub>5</sub>. It plays an important role in the chemistry of large, biologically important molecules, as well as in the physicalphilosophical considerations of the concept of molecular structure. Frank Westheimer found far-reaching implications of Berry-pseudorotation when he and his students investigated the hydrolysis of phosphate ester. In this process, the four-coordinate phosphorus becomes five-coordinate as it goes into its transition state, then becomes fivecoordinate through pseudorotation, and then returns to four-coordinate. The driving force of this process is in the difference in bond strengths. In the five-coordinate situation, the bonds are weaker in the axial positions than in the equatorial positions. The formation of a weaker axial bond precedes its rearrangement into a stronger equatorial bond, while another equatorial bond becomes a weaker axial bond and breaks off. This is a pivotal event for important biochemical processes.[31]

The philosophical implication of Berry-pseudorotation may be formulated in this way: it appears to be a paradox that in the process of pseudorotation, identical nuclei occupy observably nonequivalent sites. Quantum mechanics prescribes that identical particles, electrons, for example, but not only electrons, have to be indistinguishable,

and the wavefunction for identical particles reflects this indistinguishability. In contrast, in chemistry, we operate with the distinguishability of different sites in molecules. The considerations of the time scales, interaction time versus the lifetime of a structure, resolve this apparent paradox.

Above, we have considered the appearance of a bent average geometry for a linear molecule, as a result of averaging over all configurations during bending vibrations. We have also mentioned that the interaction time in NMR spectroscopy may be too long to distinguish between axial and equatorial bonds in trigonal bipyramidal systems. It is possible, however, to conduct a series of NMR experiments with a changing relationship of the two time scales, demonstrating, for example, the coalescence of NMR lines, which in a fast experiment correspond to different chemical shifts, and in a slow experiment correspond to the average.<sup>[32]</sup>

Symmetry-lowering may happen due to the Jahn–Teller effect. A nonlinear, symmetrical nuclear configuration in a degenerate electronic state is unstable and gets distorted – this is how it removes the electronic degeneracy until it achieves a nondegenerate state, according to the formulation of the Jahn–Teller effect.<sup>[33]</sup> A typical case of Jahn–Teller distortion is the structure of crystalline manganese trifluoride. The six fluoride ions surround the manganese ion in six-coordination in its structure. In a regular octahedral arrangement, the six manganese-fluoride distances would be uniform, but this is not the case. Rather than having  $O_h$  symmetry, there is the lower  $D_{4h}$  symmetry with two different manganese-fluorine distances.

Recently, the Jahn–Teller effect of a free molecule in gaseous manganese trifluoride was demonstrated with reliable geometrical parameters.<sup>[34]</sup> For this molecule, the highest possible symmetry would be  $D_{3h}$ , but the Jahn–Teller effect lowers it to  $C_{2v}$  symmetry. Rather than having three 120 degree bond angles, there are two of 106 and one of 148 degrees; also, one of the Mn–F bonds is shorter than the other two. The distortion stabilizes the molecule. These are not apparent, but real geometrical changes that are present in the minimum position of the potential energy distribution and characterize the corresponding equilibrium structure.

The complexity of the  $CH_5^+$  structure rivals that of the XeF<sub>6</sub> molecule. This carbocation has had special significance in organic chemistry, as its discovery was related to the beginning of a whole new direction in the discipline.<sup>[35]</sup> This new direction has transformed hydrocarbon chemistry from a rather inert kind of domain into the source of exceptional wealth of new substances. It became possible by the application of superacids that stabilized the otherwise short-lived carbocations and enabled the otherwise unreactive covalent carbon-carbon and carbon-hydrogen bonds to become reactive. The discoverer, George A. Olah (Figure 25), could rightly con-



**Figure 25.** George A. Olah in 1995 at the Budapest University of Technology and Economics (photograph by I. Hargittai).

clude: "The realization of the electron donor ability of shared electron pairs could one day rank equal in importance with G. N. Lewis' realization of the electron donor unshared pairs."<sup>[36]</sup>

The carbocation  $CH_5^+$  contains a five-coordinated carbon – note, however, that it is not a hypervalent carbon, only hypercoordinated. Thus, it could be viewed as containing five electron domains such that each is somewhat poorer in electrons than a two-electron covalent bond. In that case, the five-coordination and five-electron domain carbocation could have a trigonal bipyramidal arrangement of  $D_{3h}$  symmetry, according to the predictions of the VSEPR model. This turned out to be not the case.

Early quantum chemical computations predicted a C<sub>s</sub> symmetry structure for CH<sub>5</sub><sup>+</sup>, which would correspond in Olah's description to the presence of three two-electron two-center bonds and one two-electron three-center bond.<sup>[37]</sup> This may be a structure of either having a high degree of localization, or having a fluxional character by exchanging the positions of the two-electron two-center bonds and the two-electron three-center bond. Provided that the C<sub>s</sub> symmetry structure is in a sufficiently deep energy minimum, it could be observable in experiments if the lifetime of this structure is long enough, as compared with the interaction time of the experimental technique employed. There had been attempts to apply the concept of pseudorotation to the highly fluxional CH<sub>5</sub><sup>+</sup>, however, if the CH<sub>3</sub><sup>+</sup> plus H<sub>2</sub> description holds, pseudorotation would not be the right approach to its description.

Recent high-resolution spectroscopic experiments on  $CH_5^+$  have suggested the presence of structures corresponding to Olah's description (Figure 26).<sup>[38]</sup> We have to keep in mind, however, that all the spectroscopic evidence are also consistent with a highly fluxional character of  $CH_5^+$ : "the five proton swarm around the central



Figure 26. Two-electron two-center bonds and two-electron threecenter bonds in protonated alkanes.<sup>[40]</sup>

carbon".<sup>[39]</sup> Olah's model of three two-electron covalent bonds and one two-electron three-center bond may thus be only one of the models that can be singled out from among a multitude of models. They, in their totality as an average, may be considered as a more realistic representation of this carbocation that Oka called the "enfant terrible" of structural chemistry.<sup>[39]</sup>

Although the VSEPR model could not predict unambiguously the geometry of  $CH_5^+$ , some analogous structures appear consistent with VSEPR predictions. The geometry of mono-positively charged carbocation  $\{[(C_6H_5)_3PAu]_5C\}^+$  containing five-coordinate carbon is trigonal bipyramidal (Figure 27). According to Olah, this



Figure 27. The trigonal bipyramidal mono-positively charged carbocation  $\{[(C_6H_5)_3PAu]_5C\}^+$  and the octahedral di-positively charged carbocation  $\{[(C_6H_5)_3PAu]_6C]^{2+}.^{[40]}$ 

gold complex is an isolobal analog of  $\text{CH}_5^+$ , hence the isolobal analogy would suggest a trigonal bipyramidal geometry for  $\text{CH}_5^+$ , which is not the case (see above). A similar discussion could apply to the  $\text{CH}_6^{2+}$  carbocation and the {[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PAu]<sub>6</sub>C]<sup>2+</sup> carbocation. Six equivalent electron domains would favor a regular octahedral geometry of O<sub>h</sub> symmetry and the six bonding directions point to the vertices of a regular octahedron in the gold complex. In contrast, the computations have suggested the presence of two two-electron covalent bonds and two two-electron three-center bonds for the  $\text{CH}_6^{2+}$  carbocation. There is then the  $\text{CH}_7^{3+}$  carbocation, for which one two-electron covalent bond and three two-electron threecenter bonds would apply by analogy.

### 5. Five-fold Symmetry in Extended Structures

Five-fold symmetry is just as common in the world of molecules as any other symmetry. This is not the case, however, in extended structures. Five-fold symmetry was an excluded symmetry in classical crystallography. Two important discoveries in the 1980s, both in materials science – one in the world of molecules and the other in extended structures – were related to five-fold symmetry. Each of the two discoveries was eventually awarded a chemistry Nobel Prize.

The discovery of buckminsterfullerene (first of its existence,<sup>[41]</sup> then, its production<sup>[42]</sup>) made waves due to the beauty of its structure and the fact that it was a heretofore unknown modification of carbon. The  $C_{60}$  molecule is of truncated icosahedral shape. There is a presence of fullerene-type structures and their fragments in nanotubes. Considering today's importance of nanoscience and nanotechnology, even a symbolic impact by the buckminsterfullerene discovery in this development is noteworthy.

The icosahedral arrangement of atoms has interested researchers because they considered it as containing some of the clues of the puzzle of the progression from isolated molecules to extended systems. The icosahedral arrangement caught J. Desmond Bernal's (Figure 28) eye early on. He was interested in the structure of liquid water and the icosahedral arrangement was viewed as the one preventing the crystallization of water. Linus Pauling also showed distinct interest in icosahedral structures.



Figure 28. J. Desmond Bernal giving a speech (photograph by and courtesy of Alan L. Mackay).

Alan L. Mackay (Figure 29) enveloped a sphere with an icosahedral shell consisting of 12 spheres and enveloped this structure by another shell, and the second shell was arranged over the first so that the spheres were in contact along five-fold axes. When he added a third shell, the structure already contained 147 spheres, and this is what has been known as the Mackay icosahedron or Mackay polyhedron.<sup>[43]</sup> When icosahedra are packed together, like in the Mackay polyhedron, they gradually curve up to form a closed system. In addition to the Mackay polyhedron, another example is the icosahedral polyoma virus (Figure 30).<sup>[44]</sup>



**Figure 29.** Alan L. Mackay in 1982 in Budapest (photograph by I. Hargittai).



Figure 30. Icosahedral polyoma virus drawn after Adolph et al.[44]

In a parallel development, Roger Penrose (Figure 31) invented a two-dimensional pattern of hierarchic tessellation of the plane, which was regular, that is, it was constructed by well-defined rules, but it was not periodic.<sup>[45]</sup>



Figure 31. Roger Penrose in 2000 in Oxford, UK (photograph by I. Hargittai).

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Penrose had seen a logo of a pentagon surrounded by same-size pentagons, and Penrose started iterating it and augmented the gaps of the pattern by parts obtained by cutting up additional pentagons. Penrose, when he was still a graduate student, had had some interactions with Bernal in the mid-1950s; the story borders the mysterious as Penrose remembered decades later: "He [Bernal] came to see me completely out of the blue, just because he was looking for people who might have ideas, to do with these pentagons, and so on."<sup>[46]</sup>

Mackay took Penrose's effort one step further and produced a simulated electron diffraction pattern of a threedimensional Penrose pattern.<sup>[47]</sup> Mackay warned that if we exclude the possibility of extended structures with five-fold symmetry, we may experience it, yet ignore it.<sup>[48]</sup> Fortunately, this is not how it played out, although it could have.

In 1982, at the then National Bureau of Standards, Dan Shechtman (Figure 32), a visiting scientist from the Technion, was experimenting with electron diffraction of a great variety of manganese-aluminum alloys. He obtained a diffraction pattern that could be interpreted as an extended structure of ten-fold symmetry – clearly "in violation" of the rules of classical crystallography.<sup>[49]</sup> When the experimental observation was properly documented, it turned out that there was instant theoretical interpretation and even a catchy name for this new state of matter.<sup>[50]</sup> Shechtman's perseverance brought this discovery to triumph, but not before he had to face the dis-



**Figure 32.** In 1984, at NBS, from left to right: Dan Shechtman; Frank Biancaniello; Denis Gratias; John Cahn; Leonid Bendersky; and Robert Schaefer. Photograph by H. Mark Helfer/NIST; courtesy of NIST. Biancaniello prepared the alloy samples and created a broad range of allowed compositions. John Cahn and Dennis Gratias were two of Shechtman's three co-authors on his seminal paper reporting the discovery.

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belief, and even ridicule, of establishment scientists. The story has been well documented by several authors, including the present one.<sup>[51]</sup>

In this case, it was not the ambiguity of a concept, but the ambiguity of the scope and definition of classical crystallography that was what had to be sorted out. It was not trivial though. We have seen above how innovative Linus Pauling could be in breaking down previous dogmas in his quest for the alpha helix. Decades later, he could not accept Shechtman's breaking down some other dogmas. Planck's words come to mind about the new ideas that keep appearing in science and that even great old scientists find unable to accept: "An important scientific innovation rarely makes its way by gradually winning over and converting its opponents: it rarely happens that Saul becomes Paul. What does happen is that its opponents gradually die out, and that the growing generation is familiarized with the ideas from the beginning."<sup>[52]</sup>

### 6. Chirality

This contribution is for a special issue in the Israel Journal of Chemistry honoring the fiftieth anniversary of the first successful chiral column separation of racemic amino acids by the late Emanuel Gil-Av of the Weizmann Institute. Chirality plays a fundamental role in many chemical events, while, according to Weinberg, "chiral symmetries ... are not fundamental symmetries underlying the laws of nature."<sup>[53]</sup> For the importance of differences in the properties of chiral pairs of molecular substances, suffice it to mention the thalidomide story. It had many more tragic consequences in Western Europe in the 1950s than in the United States. The difference was primarily due to an officer at the Food and Drug Administration, Frances O. Kelsey (Figure 33), who was not satisfied with the knowledge about the substance enough to give it the green light to the US market. As it turned out, in the enantiomeric mixture of thalidomide, one enantiomer was teratogenic, the other was not (but even that transformed into the teratogenic isomer in the organism). For some time now, legislation has mandated that only enantiomerically pure pharmaceuticals can be marketed.

Yet another scientist to mention here is Vladimir Prelog, one of the founders of modern stereochemistry. His office at the Eidgenössische Technische Hochschule Zürich (Swiss Federal Institute of Technology in Zurich) was full of memorabilia of stereochemistry and chirality, in particular. His *ex libris* was a drawing by Hans Erni, which has become well known all over the world (Figure 34). Prelog chose this drawing, because it represented all the paraphernalia that describe chirality: human intelligence, a left and a right hand, and two enantiomorphous tetrahedra. Erni prepared more than one version of this drawing, but the one Prelog chose for his books was peculiar. The two hands appear as if they are



**Figure 33.** Frances O. Kelsey in 2000 in her office at the Food and Drug Administration in Rockville, MD (photograph by and courtesy of Magdolna Hargittai).



**Figure 34.** Vladimir Prelog's *ex libris* plate by Hans Erni with Prelog's dedication to the author (courtesy of the late Vladimir Prelog).

turned around, inverted, as can be imagined as a consequence of the two arms being crossed.<sup>[54]</sup> Other versions of Erni's drawing were displayed in Prelog's office with the two hands being non-inverted, parallel. Further examples of pairs of hands appear in Figures 35 and 36.

Chirality may not be a fundamental property underlying the laws of nature, yet it has vital consequences for our lives and for life in general. It intrigued Lewis Carroll's *Alice* when she asked a question deep-rooted in chirality (Figure 37). In the book, *Through the Looking Glass*, comparison of an image and its mirror reflection makes Alice wonder, "Perhaps Looking-glass milk is not good to drink ..."<sup>[55]</sup> Some time ago, in a brief paper titled *Eternal dissymmetry*, we summarized some examples that illustrate how "the teachings of Louis Pasteur about chirality continue to instruct and inspire."<sup>[56]</sup>



**Figure 35.** Heterochiral pair of hands in the old Jewish cemetery in Prague (photograph by I. Hargittai).



**Figure 36.** Homochiral pair of hands, "The Cathedral," by Auguste Rodin in the Rodin Museum in Paris (photograph by and courtesy of Magdolna Hargittai).

### 7. Conclusion

Ambiguity of symmetry impacts the validity of the symmetry concept and its applicability. Take, for example, molecular structure. Information about its symmetry is always interesting, often useful, and sometimes crucial. The reliability of the determination of molecular symmetry increases with increasing molecular rigidity and fluxional behavior enhances its ambiguity. Ambiguity may also exist in our various definitions, as it turned out, for example, for the one used to define what a crystal is. The old definition had to be replaced by a more inclusive one following the discovery of quasicrystals. The more comprehensive definition has rendered the label quasicrystal a misnomer or at least superfluous; nonetheless, its usage has continued without causing any misunderstanding.

Another aspect of ambiguity is when perfect symmetry is damaged – is symmetry still there? The expression per-



**Figure 37.** Sculptural group "'Curiouser and curiouser!' cried Alice" (by Jose de Creeft, 1959) in Central Park, near the Conservatory Lake (76<sup>th</sup> Street and Fifth Avenue), New York City, 2015 (photograph by I. Hargittai).

fect symmetry does not make sense in a rigorously geometrical sense. There is symmetry or there is not. However, in real systems, this is not the way we handle symmetry, and in real systems, the ambiguity may develop into arbitrariness. In other words, it depends on our tolerance – some times on our goodwill – whether we continue to consider something symmetrical, whereas it no longer is, according to stronger criteria.

Take, for example, the sphere whose simple figure possesses an infinite number of symmetries and about which Copernicus wrote: "... the spherical is the form of all forms most perfect, having need of no articulation; and the spherical is the form of greatest volumetric capacity, best able to contain and circumscribe all else; and all the separated parts of the world – I mean the sun, the moon, and the stars – are observed to have spherical form; and all things tend to limit themselves under this form – as appears in drops of water and other liquids – whenever of themselves they tend to limit themselves. So no one may doubt that the spherical is the form of the world, the divine body."<sup>[57]</sup>

For thirty years, Fritz Koenig's 7.6-meter metallic sculpture "The Sphere" graced the plaza at the World Trade Center (Figure 38). It was not a perfect sphere in the geometrical sense, and it did not have all the symmetry elements of the sphere in the rigorous geometrical sense, yet nobody doubted its being a sphere. It symbolized world peace through world trade. The terror attack on September 11, 2001, badly damaged this sculpture. Defiance and resilience reconstructed the sculpture from its salvaged remains, and now it honors the victims of the terror attack. In this disfigured version, "The Sphere" has lost none of its grace and nobody has any problem in identifying it as being a sphere. Its sculptor noted its transforma-







**Figure 39.** The sculpture-turned-monument in Battery Park, Manhattan, Fall 2014 (photograph by I. Hargittai).

tion from being a sculpture to becoming a monument (Figure 39).<sup>[58]</sup>

There is a steady extension of our knowledge of materials, including systems under extreme conditions (created on our planet or existing in space), many of them disordered or partially disordered. Many others may yet emerge. Structural variations of the building blocks of living organisms have also expanded the scope of science about structures. We have learned to live with ambiguities and we are learning to value ambiguities in symmetry and elsewhere.

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I have drawn on the generous assistance of many in creating my views on, and knowledge about, symmetry over the years. I cannot list all the names of the individuals who have enriched my thinking about this topic (some, though by far not all, appear in the text above). I thank Steven Weinberg for having looked at my manuscript and for giving me permission to quote extensively from our 1998 conversation. I appreciate Robert Glaser's kindness of inviting me to participate in this special issue, and Bob Weintraub's comments on the manuscript. I remember with gratitude the inspiring interactions with the late Yuval Ne'eman. Magdolna Hargittai's partnership, artistic talent, and scientific rigor have shaped the directions I have taken in this, as in all my endeavors.

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### Essay

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EDITORIAL

### From an electron micrograph to a postage stamp

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**Abstract** Soon following Dan Shechtman's discovery of quasicrystals, Ágnes Csanády and her associates started producing beautiful quasicrystals of flowerlike morphology. The image of one of their specimen appeared on the Israeli postage stamp honoring Shechtman's discovery, his Nobel Prize, and the International Year of Crystallography.

**Keywords** Dan Shechtman · Ágnes Csanády · Quasicrystals · Flowerlike morphology · Electron micrographs · Symmetry · Postage stamps

Dan Shechtman was conducting experiments with alloys in the spring of 1982 at the National Bureau of Standards (NBS, as it was then) in Washington, DC. Shechtman had developed a technique for studying metallic powders by transmission electron microscopy at the Technion—Israel Institute of Technology. At NBS, he collaborated with associates of the metallurgy group in producing and analyzing rapidly solidified aluminum-iron and other aluminum alloys, including aluminum-manganese alloys. Frank Biancaniello was Shechtman's enthusiastic colleague in preparing alloys of a great variety of composition. Of the aluminum-manganese alloys, the practically useful ones contained only a few percent of manganese.

⊠ Istvan Hargittai istvan.hargittai@gmail.com However, it seemed that alloys much beyond the practically useful manganese content might be also of interest to study. As they put an alloy with 25 percent manganese content into the electron microscope, Shechtman made a most unexpected observation. The electron diffraction diagram showed ten-fold symmetry. This happened on April 8, 1982, and it was for the first time that someone observed and recorded symmetry in the condensed state that classical crystallography deemed impossible in crystals.

Shechtman had a hard time getting his interpretation of his observation accepted by the crystallographic community and the broader scientific community. However, when he published his experiment in 1984 [1], an avalanche of studies and papers appeared, and many laboratories worldwide produced the new substance for which the name quasicrystals had been coined—short for quasiperiodic crystals. The story has been well documented (see, for example, [2–6]). From early on following Shechtman's discovery, I found that Ágnes Csanády and her colleagues produced the most beautiful quasicrystals at the development center of the Hungarian Aluminum Industry (Fig. 1).

Csanády and her group conducted extensive studies of the morphology of quasicrystals and the phase transformation of quasicrystals to crystals [7]. Some of the specimen selected for such investigation were quasicrystals of flowerlike morphology that Csanády and her colleagues started describing in 1987. They followed the phase transformation directly and observed that the nucleation of crystallization started on the surface of the icosahedral phase. As the new phase grew, the icosahedral phase kept shrinking. Here one has to be careful with semantics. At the time indeed they had to speak about phase transformation from the quasicrystal phase to the crystalline phase. Today, such a usage of terminology appears obsolete as the current

In memoriam Oleg Shishkin in acknowledgment for his contributions to the science of structural chemistry and for his dedicated work for our journal Structural Chemistry.

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Fig. 1 Electron micrograph of flowerlike quasicrystals of a quenched aluminum-manganese alloy. The length of the full horizontal bar corresponds to 1µm (courtesy of Ágnes Csanády)

definition of what a crystal is includes quasicrystals; then, this was not yet the case.

Above, I made reference to Csanády et al.'s paper in the periodical Symmetry [7]. This was a curious publication that did not survive its charter issue, but it was quite an issue. As I am mentioning this attempt for a uniquely interdisciplinary journal, Symmetry, it was exactly 25 years ago that its only issue appeared. It happened so that some of the communications in this issue were quite relevant to those interested in quasicrystals. I mention here a few only. Alan L. Mackay, major player in the quasicrystal story, wrote a thought-provoking essay, "Lucretius: Atoms and Opinion" [8]. Arthur Loeb and his coauthors discussed the icosahedron, pentagonal dodecahedron, and the rhombic triacontahedron [9]. Magnus J. Wenninger wrote about polyhedra and the golden number [10]. I single out a few additional contributions that were of a broader scope, from Erwin Chargaff [11], Herbert A. Hauptman [12], Jerome Karle [13], and Ernő Lendvai [14].

In May 1995, we organized an international school/conference on quasicrystals in the resort place at Lake Balaton, Balatonfüred, Hungary. There, in an unhurried atmosphere, we could learn, exchange ideas, and enjoy being part—at least as onlookers—of a fast emerging field. It was on this occasion when Ágnes Csanády could demonstrate personally her flowerlike quasicrystals to Dan Shechtman and everybody else (Fig. 2).

Shechtman discovered the quasicrystals on April 8, 1982. His report with co-authors appeared in November 1984 [1]. The Royal Swedish Academy of Sciences announced Shechtman's Nobel Prize in October 2011. The discovery was straightforward, but the scientific community, especially those deeply rooted in the teachings of classical crystallography, were slow in accepting it. By the time the International Year of Crystallography came about



Fig. 2 Ágnes Csanády and Dan Shechtman in 1995 in Balatonfüred (photo by I. Hargittai)



Fig. 3 Israeli postage stamp (2013) honoring Dan Shechtman's discovery of quasicrystals and his Nobel Prize of 2011 as well as the International Year of Crystallography of 2014. The original image of the quasicrystals displayed on this postage stamp is that in Fig. 1

in 2014, the discovery of quasicrystals were among the stellar achievements of recent science.

When toward the end of 2013, the Israel Postal Company decided to issue a postage stamp to commemorate Dan Shechtman's Nobel Prize for the quasicrystal discovery and to honor the International Year of Crystallography (2014) they associated Csanády's appealing flowerlike quasicrystals with Shechtman's electron diffraction pattern. The Israel Postal Company made an excellent decision to put quasicrystals on a postage stamp and they chose one of the most beautiful representatives of such substance for display. The result was a scientifically sound and aesthetically pleasing image (Fig. 3).

Csanády's quasicrystals and Shechtman's electron diffraction pattern were immortalized. Science has gained a tool for popularization in an unobtrusive and straightforward manner.

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EDITORIAL

### Generalizing crystallography: a tribute to Alan L. Mackay at 90

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Abstract Alan L. Mackay, one of the rare generalists of our time, was a disciple and follower of J. Desmond Bernal. Mackay has contributed decisively to the development of the science of structures and taught generations to look at the broader picture when determining crystal and molecular structures. He was constantly seeking coherence and regularities in observations and in thought experiments and was aiming at creating concepts on the basis of those regularities. His inquiries prompted him to predict the existence of regular but not periodic crystal structures that are known today as quasicrystals.

**Keywords** Alan L. Mackay · J. Desmond Bernal · Generalized crystallography · Quasicrystals · Mackay icosahedron · Birkbeck College

In our preoccupation with finding out how atoms are arranged in space, we are in danger of losing sight of the whole picture.

Alan L. Mackay [1]

Crystallography is not just a scientific specialty, but is a way of life. Alan L. Mackay [2]

#### Introduction

My first encounters with Alan L. Mackay (Fig. 1) were in the scientific literature. We met in person for the first time in 1981 in Ottawa during the Congress of the International Union of Crystallography. It was not a glorious

⊠ Istvan Hargittai istvan.hargittai@gmail.com occasion: I went up to him, introduced myself, we exchanged a few words; he then turned and left. I was surprised when a few weeks later I received a gracious letter from him that he was happy having made my acquaintance and urged me to visit him whenever I had an opportunity. A great interaction developed, including weeks of stays in each other's homes in Budapest and in London. We organized his first visit to Budapest in September 1982 and he gave three lectures on that occasion at the University of Budapest, including two on various aspects of five-fold symmetry. He said, among other things, that we should be aware of the possibility of extended structures of five-fold symmetry, although these were forbidden by the rules of classical crystallography. If we thought them impossible, they might go by us unnoticed and unrecognized.

By the time Mackay was delivering his talks on five-fold symmetry and issuing his warning about extended structures of five-fold symmetry, and without Mackay knowing about it, Dan Shechtman had already observed the first such extended structures—soon they became known as quasicrystals. Mackay did not merely think and speak about such structures, but he had published papers discussing them, complete with a simulated electron diffraction pattern. When I was listening to Mackay speaking about five-fold symmetry in September 1982, and, increasingly, in hindsight, I felt as if I were present at creation.

The universal importance of five-fold symmetry should not be exaggerated at the expense of other symmetries. However, because classical crystallography exiled it from its considerations as non-crystallographic symmetry, its come-back was all the more spectacular. It was remarkable that two outstanding discoveries in the mid-1980s, both in the science of materials, were related to five-fold

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Fig. 1 Alan L. Mackay in 1982 in Budapest (photograph by I. Hargittai)

symmetry. These were the fullerenes and the quasicrystals. Quoting Mackay [3]:

The main significance of five-fold symmetry for science is that it furnishes us with an explicit example of frustration, which has proved a most fertile concept in the physics of condensed matter. ... Neither we nor nature can have everything simultaneously—not all things are possible ... We have only the freedom of necessity. 'Nature must obey necessity' as Shakespeare (*Julius Caesar IV:iii*), Democritus, Monod, Bernal, and many others have also recognized. Science probes the limits of necessity and, in the case of five-fold symmetry, has found a corridor that leads us to a new territory.

#### The beginning

Alan Lindsay Mackay was born on September 6, 1926, in Wolverhampton, England. Both his parents were born in Glasgow. They were physicians, and lived in Wolverhampton in the English Midlands. Alan's father served as an infantry officer in World War I before he became a doctor and as a second in charge of a military field hospital in the Middle East in World War II. Alan's parents ran their own practice in the late 1920s and 1930s, which they sold in 1938. They then became consultants and, especially Alan's mother, served the community in various other capacities dictated by her social conscience. There was always professional talk at their table during their meals, which Alan found exciting. It was also understood that what he heard there could not be retailed outside their home. There were brothers and sisters who eventually dispersed to Australia and America.

Alan started his formal education in a small private school at the age of five, continuing at the Wolverhampton Grammar School from 1935 to 1940. He had to pass an entrance examination at the age of eight to get into this school. His school years overlapped with the Second World War. At the age of thirteen, he was a messenger in the Auxiliary Fire Service. From 1940, he was sent to a boarding school—Oundle School—after he passed another entrance examination. There was talk of a possible German invasion. Alan stayed at Oundle until 1944 and received there an excellent science education. There were difficulties in life during the war, but not in education. His teachers had first class degrees in science and mathematicsteaching was a sought-after profession during and after the Depression. Just to characterize the level of instruction, his chemistry teacher one day demonstrated periodic chemical reactions, today called oscillating or Belousov-Zhabotinsky oscillating reactions. The concentrations of reactants and products undergo periodic changes in such a reaction and they offer a spectacular view if the participants have colors. No such reactions could occur under equilibrium conditions, but they can occur far from the equilibrium. Even twenty years later, Belousov found it difficult to get his manuscript describing such reactions accepted for publication.

School instruction included many demonstrations of experiments and an emphasis on practical applications of knowledge. Alan was a good student and was awarded various scholarships, which eased the financial burden on his parents. But there was never any doubt that he should study regardless of whether or not there were scholarships available. Alan developed an independent mind from an early age and he refers to this as that he was becoming an "internal immigrant."

Early on Alan had acquired a skeptical attitude and later he himself thought about the influences that must have moved him in this direction. He did remember one incident, when he was about five or six, and he told a girl of the same age that her parents had been lying to her over the nature of Father Christmas. In Alan's words, "I was very surprised to find how annoyed people were. It was like Gandhi's or H.G. Wells' experiments with truth. I discovered that you should not believe everything that grownups tell you nor say what you actually think. ... The tradition of my ancestors was to listen to what authority said and keep their doubts to themselves" [4].

This intellectual disposition of being an internal immigrant was probably strengthened by a predicament of gradually increased difficulty of hearing, which started becoming noticeable from 1955. On the other hand, Alan developed exceptional reading skills in at least half a dozen languages—he has been a voracious reader. He travelled a great deal, especially in Eastern Europe and from 1961, in Asia, including Japan, China, and Korea as well as India.

#### Start of a profession

Alan L. Mackay (Fig. 2) had earned excellent credentials and in October 1944, he went to Cambridge with a scholarship for the famed Trinity College. He focused on physics and chemistry and studied also electronics, mineralogy, and mathematics. Sir Lawrence Bragg was one of his professors along with other famous scientists, such as the physical chemist and later Nobel laureate R.G. W. Norrish, the physical chemist Frederick Dainton, the inorganic chemist H.J. Emeleus, and others. He won the Percy Pemberton Prize and graduated in 1947.

In the summer of 1947, Alan went with a group of students to Yugoslavia to help build a railway and he has been actively interested in politics ever since. After graduation, in the years 1947–1949, Alan worked in the crystallography laboratory of Philips Electrical Ltd., and, while working for Philips, he earned his BSc degree in physics in 1948 as an external student. He decided to study for his PhD and he joined Birkbeck College of London University, and he has stayed at Birkbeck for the rest of his professional life. First he was there part-time, from 1949, in the crystallography laboratory of J. Desmond Bernal (1901–1971), later moving to full time. He defended his PhD thesis and was awarded the degree in 1951.

Mackay learned Russian in summer school, and there, he met Sheila, his future wife (Fig. 3). They married in 1951 and by 1961 they had three children, two boys and a girl, and moved to their home in North London where they stayed ever since.

Already by then, Alan's interests were broad and he published more broadly than would someone with a narrow specialization. This did not help his promotion in the university ranks. In this he followed his mentor's example although he learned also from Bernal that for his career broad interests counted as a disadvantage. Alan would be awarded his DSc degree in crystallography and studies of science in 1986. He was appointed Professor of Crystallography in the same year and became Professor Emeritus in 1991. In 1988, he was elected Fellow of the Royal Society (FRS).

Bernal's example was an inspiration for Alan ever since he had chosen Bernal's book, The Social Function of Science, as his prize for winning a competition in Cambridge. It would be difficult to imagine an environment more conducive to developing a generalist approach to science, and, in fact, to life, than Bernal's circle. Bernal was nicknamed "Sage" for he was supposed to know everything worth knowing. In the 1930s, Bernal was a member of the Club for Theoretical Biology, along with Joseph Needham, C. H. Waddington, and others. They dealt with such questions as the application of X-ray crystallography and other physical techniques to solving problems in biology. Already in the mid-1930s, Bernal had shone X-rays onto protein molecules and the fact that he could record interference patterns led him to believe that the structures of such large biological systems could be solved on the atomic level. Bernal was good in delegating tasks and he delegated the structure determination of large biological molecules to such disciples as the future Nobel laureates Dorothy Hodgkin, Max Perutz, and Aaron Klug. Bernal served as science advisor at the highest level during World



Fig. 2 The young Alan L. Mackay (courtesy of Robert H. Mackay)



Fig. 3 Alan and Sheila Mackay around 2000 in front of their home in London (photograph by I. Hargittai)

War II. After the war, his communist politics and friendship with the Soviet Union were a serious impediment to his obtaining support for building up a research center that would have been adequate for implementing his farreaching research ideas.

J. Desmond Bernal (Fig. 4) collected around him an excellent group of scientists in mathematics and computing, in the theory and experiment of X-ray crystallography, physical chemistry, both inorganic and organic structures, and his laboratory ran a skilled workshop. A stream of international visitors complemented his staff. Scientists like Norbert Wiener, Linus Pauling, André Lwoff, and H.S.M. Coxeter came and so did representatives of world culture, like Picasso and Paul Robeson. Bernal's associates felt they were "living in the center of the universe" [2]. Mackay realized from the start how privileged it was to be part of Bernal's circle of his closest associates. The combination of scientific, social, and political activities appealed to Mackay's own inclinations.

In 1956, Bernal invited Mackay to accompany him to Moscow. Bernal gave lectures on the origin of life at Aleksander I. Oparin's institute. Mackay had the opportunity to meet such giants of Soviet science as Petr L. Kapitza, Lev D. Landau, Igor E. Tamm and Vladimir A. Fock (of Hartree-Fock fame). Bernal and Mackay visited the Institute of Crystallography of the Soviet Academy of Sciences and met its director, Alexey V. Shubnikov and Shubnikov's co-workers, among them Boris K. Vainshtein and Zinovii G. Pinsker (Fig. 5). Mackay had already begun building up an international network of friends, especially with crystallographers at international meetings, and his interactions with the Moscow crystallographers were especially active. In 1962, he spent five months at the Institute of Crystallography in Moscow. Scientifically it was not a very fruitful stay, but for getting to know many colleagues and Soviet life, in a more realistic way than from propaganda materials, it was.

#### Research

Mackay's first research project was the structure analysis of a particular modification of solid calcium phosphate used in fluorescent tubes, which was of interest to Philips. The company had an array of various projects involving X-ray crystallography related to practical applications. When Mackay moved to Birkbeck College, he continued doing research on inorganic materials. He joined the section whose major concern was the properties of cement. When Bernal was at a committee of the Ministry of Works, he volunteered that he could find out why cement sets, and a whole research project developed from this assertion.

Icosahedral structures became the focus of Mackay's interest rather early. He had already met with the structure of beta-tungsten at Philips. Then, he found some interesting old papers at Birkbeck, evidence that there had been interest in these structures at the College before Mackay. Bernal also considered the icosahedral arrangement rather early, because it would prevent crystallization, and he thought that icosahedral coordination might give some clues to understanding the structure of liquids. Mackay was also aware of Pauling's interest in icosahedral structures. When Bernal was to go to Budapest to give a talk at the meeting honoring Zoltan Gyulai's 70<sup>th</sup> birthday, he asked Mackay to draw the figures. Bernal's talk was about the



Fig. 4 J. Desmond Bernal about 1960 in London (photograph by and courtesy of Alan L. Mackay)



Fig. 5 Alan L. Mackay (in the middle) in the company of Boris K. Vainshtein (left) and Zinovii G. Pinsker (right) in 1962 in Moscow (courtesy of Alan L. Mackay)

symmetry in solids and liquids. It was a most comprehensive presentation [5].

The icosahedral arrangement of atoms is interesting because it could also be a step in the progression from the isolated molecule to an extended structure. When a second icosahedral shell surrounds an icosahedron of 12 spheres about a sphere in the center, the size of this second shell is exactly twice the size of the first shell [6]. This second shell contains 42 spheres and lies over the first so that spheres are in contact along the five-fold axis. Further layers can be added in the same fashion.

The third layer is shown in the Figure and this is known as the Mackay polyhedron (Fig. 6) or Mackay icosahedron-an example of icosahedral packing of equal spheres. The layers of spheres succeed each other in cubic close packing sequence on each triangular face. Each sphere which is not on an edge or vertex touches only six neighbors, three above and three below. Each such sphere is separated by a distance of 5% of its radius from its neighbors in the plane of the face of the icosahedron. The whole assembly can be distorted to cubic close packing in the form of a cuboctahedron. The Mackay icosahedron has "made tremendous impact on particle, cluster, intermetallics, and quasicrystal researchers...," [7] according to the late K.H. Kuo, the doyen of Chinese crystallographers. Kuo identified two basic concepts in Mackay's paper. One was the icosahedral shell structure consisting of concentric icosahedra displaying five-fold rotational symmetry. This structure occurs frequently and not only in various clusters, but also in intermetallic compounds and quasicrystals. The other concept, according to Kuo, was the hierarchic icosahedral structures due to the presence of a stacking



**Fig. 6** The "Mackay polyhedron" emerging from the icosahedral packing of equal spheres. Only the third shell is visible (courtesy of Alan L. Mackay [6])

fault in the face-centered-cubic packing of the successive triangular faces in the icosahedral shell structure.

Mackay questioned dogmas wherever and whenever he met them. This was especially so in the case of crystallography where the classical rules had worked so well but eventually proved increasingly to be limiting the scope of structures the subject embraced. Those rules limited the inclusion of novel kinds of structures that kept emerging as well as structures that had been abandoned by crystallographers; but the need arose to include them in a broader system. There was an obvious deficiency when the theoretical constraints of crystal symmetry were confronted with real crystals in that crystals are not infinite. The approach to discussing crystal symmetry used to be to think of the formation of a crystal through insertion of individual atoms or groups of atoms into the three-dimensional framework of symmetry elements, whereas in reality-as Mackay liked to point out-the symmetry elements emerge as a consequence of the structure being formed through the local interactions between individual atoms or other building elements. The concept of crystal symmetry itself became a target of Mackay's inquiry and he creatively deepened and expanded its meaning. When I asked him if he would like to select one of his papers for inclusion in the current special collection of articles, he chose the one titled "Crystal Symmetry" [8] reproduced in the "Appendix".

Mackay compiled a list of concepts in two versions, showing the transition from the classical to the modern (Table 1). He has refined his list over the years, but the 1981 one demonstrates from a 35-year perspective how forward-looking his ideas were.

This list appeared in a paper, which Mackay titled *De nive quinquangula* (on the pentagonal snowflake), which was a direct reference to Johannes Kepler's treatise on the six-cornered snowflake [10].

There were several threads in Alan's career that were rapidly coming together. In his words [11]:

I used to do science abstracts—for ten years I abstracted all the Russian papers on crystallography—and I remember abstracting a paper on the incommensurate arrangements of spins in iron oxides, in hematite. The period of the helical magnetic spin is not the same as the crystallographic period. So incommensurate structures were current before that time. Even much longer before that I thought of a simple thing about printing wall paper. Suppose your wall paper is simply printed from a roller. But suppose you are printing two motifs from two rollers of different diameter. Then you get a non-repeating pattern. I wasn't able to think of producing an aperiodic two-dimensional pattern in this way. I was only aware of the possibility of one-

Table 1 Mackay's compilation of classical versus modern concepts in 1981 (courtesy of Alan L. Mackay [9])

Classical concepts	Modern concepts
Absolute identity of components	Substitution and nonstoichiometry
Absolute identity of the environment of each unit	Quasi-identity and quasiequivalence
Operations of infinite range	Local elements of symmetry of finite range
"Euclidean" space elements (Plane sheets, straight lines)	Curved space elements. Membranes, micelles, helices. Higher structures by curvature of lower structures
Unique dominant minimum in free energy configuration space	One of many quasi-equivalent states; metastability recording arbitrary information (pathway); progressive segregation and specialization of information structure
Infinite number of units. Crystals	Finite numbers of units. Clusters; "crystalloids"
Assembly by incremental growth (one unit at a time)	Assembly by intervention of other components ("crystallise" enzyme). Information-controlled assembly. Hierarchic assembly
Single level of organization (with large span of level)	Hierarchy of levels of organization. Small span of each level
Repetition according to symmetry operations	Repetition according to program. Cellular automata
Crystallographic symmetry operations	General symmetry operations (equal "program statements")
Assembly by a single pathway in configuration space	Assembly by branched lines in configuration space. Bifurcations guided by "information", i.e., low-energy events of the hierarchy below

dimensional incommensurate patterns. I was really interested in hierarchic patterns and not in aperiodicity as such. It came directly from Bernal's suggestions and the polio virus project. I produced a hierarchic pattern, a hierarchic packing of pentagons. Then in 1974 I was getting some help in computing from Judith Daniels at the University College Computing Centre and, incidentally, showed her these patterns. She said that Roger Penrose had



Fig. 7 Roger Penrose and Alan L. Mackay (courtesy of Alan L. Mackay)

something like them. So I made an appointment with Roger Penrose [(Fig.7)] and Robert, my son, and I went to see Penrose in Oxford, and he showed us the jigsaw puzzle, with the kits and darts and so on. Basically his concern was with forcing aperiodicity, and my concern was with hierarchic structures. It turned out to be very similar.

In the paper about the pentagonal snowflake, Mackay, à la Penrose, built up a regular, but non-periodic (he called it then "noncrystalline") structure from regular pentagons in a plane (Fig. 8).

It starts with a regular pentagon of given size, which we may call the zeroth-order pentagon. Six of these pentagons are combined to form a larger regular pentagon, the first-order pentagon. There are triangular gaps in this pentagon and Mackay filled these gaps with pieces from cutting up a seventh zeroth-order pentagon. This cutting up yielded five triangles and a smaller regular pentagon as left-over, which is the pentagon of the order of -1. This design is repeated on an ever increasing scale.

After the meeting with Penrose, Alan's son Robert went back to his university at York where he was studying computer science and plotted a tiling on his pen-plotter (Fig. 9). We could call what he plotted a Mackay tiling as it was different from the standard Penrose kites and darts. Robert (Fig. 10) started from



Fig. 8 Tiling with regular pentagons (courtesy of Alan L. Mackay [9])

pentagons of a certain size and as he kept going to larger and larger pentagons, he built up a pentagonal snowflake. Mackay included Robert's design in his paper on pentagonal snowflakes to give his considerations added emphasis.

Mackay was getting ready to make significant predictions concerning the possibilities of real three-dimensional structures with five-fold symmetry. At one point, he got the idea of producing a simulated diffraction pattern of the Penrose tiling [11]:

First I just drew the Penrose type pattern and sent it to George Harburn in Cardiff who was a colleague of Charles Taylor who had a good optical diffractometer. I had stuck it into a laser beam here but you need a precise adjustment. You can do many beautiful things with the optical diffractometer that you can't see in the computer, with very fine detail; it is amazing. Then George Harburn made a second version which instead of consisting of lines, had dots; thus the diffraction pattern was not dominated by the streaks from the lines ([11], p 154)

Mackay wrote up and published his paper in which he communicated a simulated diffraction pattern (Fig. 11) [12].

It is remarkable, how, once again in a broader context, he was considering the characteristics of the pattern and the diffraction it generated [11]:



**Fig. 9** Robert H. Mackay's computer drawing of the formation of a "pentagonal snowflake" in 1975 [9] autographed by Roger Penrose in 2005 (courtesy of Robert H. Mackay)



Fig. 10 Alan L. Mackay and Robert H. Mackay in April 2016 in London (photograph by and courtesy of Magdolna Hargittai)



Fig. 11 Mackay's simulated "electron diffraction" pattern of a threedimensional Penrose tiling (courtesy of Alan L. Mackay) [12]

I had also a theory about collagen, and had some patterns bearing on that. The theory was that collagen fibers are connected with the Fibonacci spiral. If you draw a Fibonacci spiral of circles along the spiral, then locally the pattern keeps changing between square packing and hexagonal close packing. This corresponds closely to the diffraction you infer from collagen fibers. Richard Welberry in Canberra, Australia, had a still better optical diffractometer and took some very good diffraction pictures from the Fibonacci spiral. Then [the botanist] Eriksson in Philadelphia showed that the diffraction pattern of the Fibonacci spiral was self-similar to the Fibonacci spiral itself. ... This may point to a connection between phyllotaxis-the scattered leaf arrangement about stems-and internal structure on the atomic level" ([11], p 155).

Alan's story is a brilliant example of the importance of pursuing a lot of lines in research and look for their possible convergence. In this, Mackay followed Bernal's philosophy of asking a thousand questions rather than just one, because this way the probability of finding answers is greatly enhanced. Along the way, Mackay documented his findings. This was useful, because after the publication of Shechtman's experimental observation of quasicrystals in November 1984 [13], theoretical/modeling papers followed in rapid succession [14]. It could have been easy to distort the real succession of events related to the circumstances of the discovery. Indeed, one-sided reports did appear. For example, an account in one of the January issues of The New York Times stressed the priority of theoretical work, but failed to mention Mackay's modeling and simulation studies and even downplayed the experimental discovery itself. This prompted me to send in a "Letter to the Editor"

in which I described Mackay's contributions, explicitly citing his two publications (*Physica* 1982, 114A:609–613 and *Soviet Physics Crystallography* 1981, 26:517–522). As far as I know the letter was not printed but it is well documented ([11], pp 171–172).

Mackay recognized the potential practical applications of quasicrystals early on. He thought that Shechtman's discovery may very well be more important than it had been believed. He recognized that the low thermal conductivity of quasicrystals may be utilized for nonstick frying pans, turbine blades, in internal combustion engines, and so on. A suitable technology might be able to create quasicrystal surfaces by glazing metal with a laser. He foresaw great economic potential in the discovery.

Alan told me about this when I asked him about Shechtman's possible Nobel Prize, back in 1994. He had an interesting line of thought about the different kinds of Nobel Prize as he saw them. He characterized Shechtman's discovery as when someone turns over a stone and finds something truly important, maybe like superconductivity or the scanning tunneling microscope or the Mössbauer effect. There isn't an enormous amount of work but someone was in the right place at the right time, and recognized what he's found. In 1994, Mackay thought that Shechtman's Nobel Prize would come in this category.

The only reservation Mackay had in evaluating the importance of the discovery of quasicrystals was that it may have appeared more significant than it really was. He thought that the too restrictive definitions of classical crystallography lent a pivotal character to the discovery. Had the definitions of classical crystallography been broader and more inclusive, there would have been no need to bring about a paradigm change. However, as it happened, the discovery of quasicrystals did prove to be pivotal and it did bring a paradigm change about.

Mackay had truly predicted the existence of regular but non-periodic structures that Dan Shechtman (Fig. 12) then observed in his experiments. It would have been a wonderful sequence of events had Shechtman and others known about Mackay's prediction and have embarked on looking for such structures and found them. The search for extended structures with five-fold symmetry had been going on for centuries and involved excellent minds, such as Johannes Kepler and Albrecht Dürer. Roger Penrose came up with such a pattern in two dimensions and Mackay crucially extended it to the third dimension, and urged experimentalists to be on the lookout for such structures. Nobody took up his challenge and when Shechtman made his observations, he was not aware of Mackay's predictions. Eventually though all these lines came together. In 2010, the American Physical Society awarded the Oliver Buckley Prize to Alan Mackay, jointly with Dov Levine and Paul Steinhardt for their contributions to the



Fig. 12 Alan Mackay and Dan Shechtman in 1995 in the author's home in Budapest (photograph by I. Hargittai)

quasicrystal discovery. The next year Shechtman received the Nobel Prize in Chemistry.

#### Summing up

Alan does not mind the adjective once applied to him by a colleague, "the well-known eclectic," and chose this word for the title of a selection of his writings, *Eclectica*, self-published for personal use in a handsome volume in 2009 (Fig. 13) [15]. In it, he reproduces many of his published papers and communicates a number of unpublished works as well. The volume is a rich source of information and ideas and here we will merely dip into it for a few selected entries to illustrate its scope and depth.

Appropriately the volume begins with a discussion of copyright—one of Mackay's pet projects. He has been an advocate of protecting the rights of scientist authors to their own intellectual productions versus the publishing companies. One of the solutions he found promising was for professional societies to start their own electronic journals with open access that would be supported by authors' fees. Currently the open access approach is gaining ground rapidly, but there may be a great divide between authors who can and those who cannot afford the often hefty fees for having their manuscript published in open access venues.



Fig. 13 The cover of Mackay's *Eclectica*. The art is a computercreation by Alan L. Mackay, one in a long series of images inspired by his studies of minimal surfaces (courtesy of Alan L. Mackay [15])

As we have seen above, the discovery of the Mackay polyhedron and his prediction of the structures today called quasicrystals, did not happen in isolation. Mackay had long been interested in structures that fell beyond the rigorous and confined system of classical crystallography. He has published at least three reviews under the title "Generalized Crystallography," the latest in 2002 [16]. He defined the aim of generalized crystallography as "to understand the properties of matter, inert and living, at our human scale, in terms of the arrangement and operation of atoms." He recognized the pioneering role of X-ray crystal structure analysis in this quest, but noted that as the array of techniques has become vast, it might be advisable to replace the term crystallography by structural chemistry. He also realized though that terms that had been embedded long in scientific literature would be hard to displace. This may be so unless the new term is glued to a fad as, for example, in the case of nanoscience and nanotechnology.

Concerning the pioneering role of X-ray crystallography, Mackay has written about the phenomenon of when a pioneering field becomes a brake on further progress. This happened with classical crystallography whose rigid system hindered the recognition of those structures that fall beyond this classical system. In short, its success became a barrier to progress. Of course, for this, blame should not be assigned to those who originally worked out the system, but it is our task to overcome the barriers that have been erected by the developments since. This kind of success turning into a brake is not unique to classical crystallography. When insulin was discovered for treating diabetes it was a great triumph of the biomedical sciences. It has then been gradually recognized that the availability of this successful treatment, which is not a cure, might have diverted efforts and resources from continuing a quest for the cure of diabetes. Another example from the science of structures was the resistance to recognizing other techniques against the background of the enormously successful X-ray diffraction making it harder for electron crystallography and for neutron crystallography to become accepted and spread [17]. However, Mackay's teachings on generalized crystallography fell onto fertile ground; suffice it to mention a couple of additional contributions to the volume of Structural Chemistry dedicated to his 75th anniversary [18, 19].

Mackay's impact on the structural science community is hard to measure, but the impression is that it will be long lasting. He has impacted us through his writing and through personal interactions. In this connection it is notable that he adapted himself easily to local conditions on the occasion of his many visits. When he spent a longer period at the Institute of Crystallography in Moscow, he developed the habit of carrying a shopping bag with him. This was not only because the shops did not give out such bags to carry away their goods; but even more because one never knew what purchase might suddenly become available. After his return to London, he did not find it easy to give up the habit of having his shopping bag at readiness. Although his stay at the Institute of Crystallography in Moscow did not produce scientific results, his interactions with the Azerbaijani crystallographer Khudu Mamedov (1927-1988) greatly helped Mamedov to become well known in the West. Mamedov prepared periodic drawings that were reminiscent of Escher's patterns, but he used historical/cultural motifs from his region. Thus he created a unique interrelationship between art and science. Mamedov, perhaps in Mackay's style, used the term "crystallographic" in a broad sense. Mackay dedicated a talk to Mamedov's memory in 1991, "Form and pattern in Azerbaijani civilization," and its text is reproduced in Eclectica.

Mackay (Fig. 14) and Bernal co-authored a presentation entitled "Towards a science of science" for the 11<sup>th</sup> International Congress for the History of Science in Warsaw in 1965. They outlined what Science of Science was, why it was needed and the methods of their inquiry. Their program included practical recommendations, such as the establishment of departments of the history of science and the need for looking at science as a whole rather than always taking up merely its specificities. Further, they called for establishing the profession of science critic similarly to that of literary critic, and called for



Fig. 14 Alan L. Mackay in 2011 in his study among many of his computer-generated drawings (photograph by I. Hargittai)

international cooperation as recognition of science as a world-wide activity. They also suggested experimental work in order to find the best means of science training and the like. They emphasized the importance of learning about non-European cultures where emphases were different from European cultures as illustrated, for example, by a lower priority for written records, but a higher one for master-pupil relationships. This joint Mackay-Bernal presentation has been reproduced in a number of publications and in a number of languages, yet it is not easily accessible. Hence, it is very useful to have it in *Eclectica*. Mackay coedited a volume on this topic and the idea of science of science permeated his activities throughout his entire career [20].

In the early 1980s Mackay ran a column called "Anecdotal evidence" in the journal *The Sciences* and the entries are reproduced in *Eclectica*. It suited him eminently, bringing together seemingly disparate ideas and facts. Even the titles reveal some aspects of his approach, such as "Science and Travel," "Rhyme and Reason," "How to write a best seller," "Mackay's *Michelin*," "Molecules and Moores" (referring to Henry Moore), "Message in a Bottle," and suchlike. The column served the readers of this unusual periodical well, but its editors liked to smooth over his often unorthodox style of writing; apparently the flavor of Mackay's writing was a little too much for them.

The *Eclectica* volume is concluded by a list of Mackay's work, including scientific publications (176 entries), miscellaneous publications (130), and book reviews (46). There is then a list of 30 unpublished papers, and 10 entries which he calls "indirect material," and those publications

by others in which he figures, including the special issue in *Structural Chemistry* in 2002 dedicated to him [21].

#### Legacy

The full story of the quasicrystal discovery has yet to be written. At this point, I am offering my thoughts concerning only a tiny aspect of this story, viz. the demeanor of its principal protagonists with respect to the loneliness of the scientific discoverer. With justifiable simplification, there were three protagonists in this story. Alan L. Mackay predicted the existence of quasicrystals. Dan Shechtman discovered them in his experiments. Dov Levine (a graduate student, then) and Paul J. Steinhardt (Levine's professor) coined the name quasicrystals and offered a theoretical interpretation of the structure of this new kind of matter. I have had opportunities of discussing the circumstances of their discoveries in person with Mackay, Shechtman, and Levine. I interacted with Steinhardt only via e-mail exchanges.

Alan L. Mackay's (Fig. 15) demeanor has been such that he was looking consciously for dismantling dogmas and scientific taboos. In doing so, he realized the indefensibility of the dogma of classical crystallography with respect to the prohibition of five-fold symmetry in extended structures. Once he recognized this, he voiced it in his publications and in his presentations. He did not have second thoughts about making a stand and risking his reputation. He did this at a time when there was a reduction of personnel at British universities and he could have been retired prematurely. In 1982, he was 56 years old, had been a Reader in Crystallography at Birkbeck College for quite



Fig. 15 Alan L. Mackay and Istvan Hargittai in April 2016 in London (photograph by and courtesy of Magdolna Hargittai)

some time. It would only be in 1986 that he was awarded a personal chair as Professor of Crystallography and was elected FRS in 1988. It seems that the loneliness of the scientific discoverer was his natural mode of existence.

In contrast, Dan Shechtman was not looking to do anything revolutionary. His interest in alloys was in finding compositions for improved practical applications. However, he possessed a good deal of curiosity and this was his driving force at his pre-discovery stage. This curiosity made him embark on testing metal compositions that could have not been expected to offer improved, or any, applications. Once he made the discovery and realized that it was revolutionary, he grew to the challenge and his stubborn nature helped him to see it through to general acceptance. In doing so, he invited the disapproval, even wrath, of the powers that be in science, for example that of the greatest chemist of his time. Shechtman conducted himself with dignified determination in his loneliness, but he was not enjoying it and welcomed any easing of this loneliness. He felt relief and gratitude when Ilan Blech joined him in co-authoring the first paper in which Shechtman-half-heartedly and half-buried among other materials-mentioned his discovery. When he was finally preparing the manuscript that reported unambiguously his discovery, he was happy and grateful that he found three co-authors who helped him formulate what he wanted to say and who eased his loneliness of the scientific discoverer.

Levine and Steinhardt were ready to publish their interpretation of the quasicrystal structure as soon as they had learned about the paper reporting its experimental observation. At this point, they did not have to face the loneliness of the scientific discoverer, because that burden had already fallen onto Shechtman, let alone Mackay. Had Levine and Steinhardt come out with their theoretical model before the experimental discovery, they might have felt the most acute loneliness, possibly even ridicule. From the immediacy of their publication following Shechtman's, we may suppose that they might have made their theoretical discovery some time before. Levine might have written a good thesis even on the basis of a failed model, but for Steinhardt, the risk would have been considerable and possibly sufficient to damage his reputation. He was a Professor of Physics at the University of Philadelphia, then; later on, at Princeton University. Steinhardt (not Levine) had the choice of taking the risk and face the loneliness of the discoverer or wait and see whether there might be a safer opportunity to strike out.

All this is my supposition only, but I see consistency with it in how things played out during those years in the second half of the 1980s. The adjectives "consistent" and "rational" are among the many characterizing Alan L. Mackay, and they shine through the poem he composed recently that sounds like a parting gift:

Atoms and our Vision of the World There are no gods. We are alone. I am thus two-fold alone but I have the second sight of science. As my eyes grow dim, my mind sees the future. I see a hand writing on the wall the wall surrounds a giant alembic built to win gas from coal. The Chinese hand wrote large the character which stands for entropy. It questions the solid state of Earth. Asking my computer, I find the words "disordered hyperuniformity" - today's myopic Vision of the World glimpsed in the microcosm of atoms. Death came to my wife of more than sixty years Her flame went out. Her body was cremated -Atoms to atoms - Lucretius saw truth. But where is past history now? Information increases locally from time to time but Entropy will win. A.L.M. 30 August 2015 [22]

This was not the first time Mackay had expressed his views and sentiments through poetry. His published poems often express topics in crystallography and the science of structures [23]. He titled his collection of poems published in 1980 the Floating World after the works of Japanese artists who lived in the latter half of the 18<sup>th</sup> century and the first half of the 19<sup>th</sup>.

According to Mackay, "Scientists inhabit a kind of Floating World of their own, a kind of Global Village, in which they have friends, or friends of friends, everywhere. Rather, like members of a religious order, they can go to any laboratory dealing with their field of study and be hospitably received" [24]. Alan and Sheila Mackay certainly practiced this very hospitable attitude toward many members of the international scientific community.

Mackay has been much concerned with the ways to expand the science of structures to embrace systems with varying degrees of regularity. Here intentions and desires that cannot be formulated yet with exactitude can be expressed as a poem [25]:

We cruise through the hydrosphere Our world is of water, like the sea, But the molecules more sparsely spread, Not independent, not touching But somewhere in between, Clustering, crystallizing, dispersing In the delicate balance of radiation And the adiabatic lapse rate.

Even when he is composing prose, it sometimes sounds like poetry. Consider this example: "Amorphous materials may be shapeless, but they are not without order. Order, like beauty, is in the eyes of the beholder. If you look only with X-ray diffraction eyes, then all you see is translational order, to wit crystals. ... [T]here is a wide range of structures, between those of crystals and those of gases, ... Other structures need not be failed crystals but are *sui generis*"[26]. (Italics in the original)

Contemplating Alan Mackay's legacy, it is often said that scientific discoveries, however important, are sooner or later overshadowed by new developments in science. So it is happening with Mackay's contributions to crystallography and the science of structures. However, his demeanor as a researcher and scientific discoverer will serve as inspiration for a long time.

**Acknowledgments** I thank John L. Finney, Magdolna Hargittai, Alan L. Mackay, and Robert H. Mackay for their kind assistance in the preparation of this manuscript.

#### Appendix

Alan L. Mackay, Crystal Symmetry, *Physics Bulletin* November 1976, published by the Institute of Physics. © IOP Publishing. Reproduced with permission. All rights reserved.

# A L MACKAY

# **CRYSTAL SYMMETRY**

How can we develop a unified way of dealing with structures covering the range from diamond, naphthalene and iron to living objects? Dr Mackay suggests that 'cellular automata', which show aspects of reproduction, growth and evolution, may provide the answer

E T Bell, the historian of mathematics, has castigated the formalism of Euclidean geometry by saying: 'The cowboys have a way of trussing up a steer or a pugnacious bronco which fixes the brute so that it can neither move nor think. This is the hog-tie and it is what Euclid did to geometry'. The formalism of the International Tables of Crystallography is similarly restrictive. The 230 space groups characterize exhaustively all the symmetries possible for infinite lattice structures. However, crystals are not infinite and there are some which do not have regular three-dimensional lattices. The lattice results from the relationships between the parts of the crystal and not vice versa.

The crystal does not form by the insertion of components into a three-dimensional framework of symmetry elements. It arises from the local interactions between individual atoms and the symmetry elements are a consequence. We must observe that the traditional formalism of crystallography handles occurrences of pseudosymmetry and local symmetry elements rather inadequately. Our argument is that a regular structure should mean one generated by simple rules and that the list of rules regarded as simple and 'permissible' should be enlarged. These rules will not necessarily form groups.

With the recent immense progress in examining biomolecules by crystallographic and other imaging methods, the desirability of developing a unified way of dealing with spatial structures (and their changes, growth, evolution and transformations) which will cover the range from diamond, naphthalene and iron, to recognizably living objects (such as bacteriophages) steadily increases. It is argued here that concepts of cellular automata, having their origins in computer theory, and now being elaborated for the purposes of developmental biology, provide a suggestive ideology for recasting crystallo-

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graphic ideas so that they can be carried forward.

#### Cellular automata

Cellular automata are known by a variety of names, not exactly synonymous, such as local programme, tessellation automata, abstract computational devices, transition rules, formal languages, etc. They derive from the Turing machine, formulated first in 1936, which was a conceptual device which notionally could read and write binary digits on a paper tape. Turing investigated the conditions under which a finite part of an infinite sequence could be generated by the machine when it was provided with a finite set of instructions in the same form. This led to von Neumann's theory of selfreproducing automata, which was later seen to be realized in the genetic code.

In cellular automata a coordinate system is assumed and the programme is executed at every cell in it simultaneously, and not sequentially as in the single arithmetic unit of the typical computer. The best-known example is J H Conway's game 'Life' where a configuration of crosses is marked in the cells of an infinite chessboard. Transition rules then specify the configuration for the next interval of time. These rules are applied simultaneously to all cells. Picturesquely stated, these rules are: (i) each cell has eight neighbouring cells, (ii) if a cross has more than three neighbouring crosses it dies of overcrowding, (iii) if it has two or three neighbouring crosses it survives for the next generation, (iv) if it has less than two neighbours it dies of loneliness and (v) if an empty cell has exactly three neighbouring crosses then a cross is born there.

Cellular automata, such as Conway's game, show an immense variety of behaviour, suggesting aspects of reproduction, growth and evolution which are encountered in systems of real cells. They stress the kinematic and configurational, rather than the dynamic or energetic features of a system, and deal with information rather than energy. They are thus more apt for the modelling of very complex systems, with large numbers of local minima in the free energy landscape, where the system cannot easily 'find' the lowest minimum. Metastability is enough.

The cellular automaton consists of (i) a space, (ii) an initial configuration, (iii) an alphabet of components, (iv) a grammar of syntactic rules, and (v) a transition scheme for applying these rules. Given the state at one instant, the state at the next can readily be found and thus, by repeated induction, the behaviour of the system in time (or space). The rules may depend only on the state of the one cell to which they are being applied or they may involve the states of other cells in more complex ways. They may be snatches of programme containing, for example, conditional or probabilistic statements.

Even a simple rule can give quite interesting consequences. For example, we can take a linear cellular automaton consisting of a sequence of binary digits. These will be zeros or ones, but could have some physical representation as, for

Figure 1 The icosahedral packing of equal spheres. In all the particle contains 147 spheres, but only the third shell is visible



example, the sequence of layers in some a polytype such as silicon carbide. Starting with an initial sequence of four digits, the next digit is generated by comparing the previous digit with the digit three spaces earlier (i.e. skipping over two). If these digits are the same, then the next digit is a zero; if they are different, then the next digit is to be a one. This rule results in a structure of period 15. The same sequence results whatever the seed (the initial four digits). Thus, from the seed 1111 we get 1111/010110010001111/010110010001111/ . . etc. If we jump over four digits instead of two, and compare the previous digit with the one five spaces earlier, we get a structure of period 63. This application of a simple transition rule shows how long range structure may arise from short range atomic interactions.

We could apply this approach to the description of polytypes, for example, the hexagonal ferrites such as the compound Ba70Zn66Fe444O802 which has a period of 1455 Å and where the atomic interactions are still of only the normal range. The unit cell of this compound contains more than 4100 atoms and the structure was solved by identifying the stacking sequence of subunits by electron microscopy. In such cases the high degree of pseudosymmetry makes the conventional spacegroup characterization an uninformative description, 'uninformative' meaning 'of low information content'. In fact, M and Y blocks are recognizable and these are stacked in the sequence  $MY_6MY_{10}MY_7$  $MY_{33}$  which gives the very long period. M is a five-layer block BaFe<sub>12</sub>O<sub>19</sub> and Y is a six-layer block Ba<sub>2</sub>Me<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub>. Each layer contains four oxygen atoms or three oxygen atoms plus one barium atom per hexagonal cell.

How can we describe the traditional perfect crystal in terms of this model? The asymmetric unit is repeated by the unit cell operations to give a block which is repeated by translations to give a crystal. The order in which the operations are applied is not significant since they form a group. The most general relationship between two identical asymmetric units consists of a rotation followed by a translation. This requires six variables for its description. The relationship is equivalent to a rotation by a particular angle along a helical path. If a series of units are related in the same way then they will all lie on the same helix. The 230 space groups include only those rational helices (2, 3, 4, 6, 2<sub>1</sub>,  $3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5$ ) which are compatible with three-dimensional lattices. All other helices are excluded, although these can occur in structures finite in one or more dimensions. The same form of generative rule, a helical displacement from one unit to the next, can be used to generate either the regular 230 groups or other structures such as the helical rod of TMV or the icosahedral 532 group of certain viruses. We should note that the rules for making a TMV rod include a statement that construction must be stopped when a specified length of RNA has been incorporated.

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Figure 2 a Real snowflakes (from: W A Bentley and W J Humphreys 1962 Snow Crystals London: Dover). b The asymmetric unit from a two-dimensional pattern produced by S Ulam (Burks A W (ed) 1970 Essays on Cellular Automata University of Illinois p223) by simple rules of growth. c The asymmetric unit from a three-dimensional pattern produced by R G Schrandt and S Ulam (Burks 1970 p234)

#### The snowflake

The rules describing the morphology of growing crystals are more like those of the 'Life' game. For example, new molecules may bombard the surface of a growing crystal. If a molecule finds itself alone on the surface, it re-evaporates. If it lands in a corner or in a re-entrant angle then it sticks. If it arrives in the angle of a step, then it moves along until it reaches a reentrant corner, and so on. Recast in this form there is an evident analogy, but the Struct Chem (2017) 28:1-16

significance is that a set of simple rules (a little more elaborate than those of the crystallographic symmetry operations) can produce a complex structure. It would seem possible to devise a set which would generate a convincing snowflake. Figure 2 compares a real snowflake with two- and three-dimensional patterns generated by S Ulam, one of the main promoters of the cellular automaton, using a few simple transition rules. These define how one molecule adds on to those which arrived earlier. In deciding whether an arriving molecule sticks or re-evaporates, consideration must be given to the neighbourhood and the notional 'vapour pressure' which it represents in a real ice crystal. (The pressure is higher over convex surfaces.)

#### Diffraction patterns

We can see how systematic or even local departures from 'perfect' crystallinity can be made implicit in the cellular automata which describe them. We need a way of applying this technique to evidence for such irregularities which has hitherto been overlooked.

Crystals are important for the determination of the structure of molecules because they provide an amplifier which multiplies the scattering of x-rays from a single molecule by the number of molecules in the array, perhaps 1015, and resistance to the damage of single molecules by the viewing radiation. Both emphasize the spots in the diffraction pattern and neglect the background. Molecules which are damaged transfer their scattering contribution to the background as do those which are not repeated with the regular lattice periodicity. It follows that even systematic departures from the regular lattice are likely to be missed or neglected in current techniques of structure analysis. It is, for example, probable that the icosahedral particles of gold, discussed below, have been observed earlier as minor features in diffraction patterns.

In recent years high resolution electron microscopy, most prominently by J M Cowley and his school, has shown the detailed nature of many of the defect structures which may appear in 'nonstoichiometric' compounds (such as niobium oxides). Such defects may in fact be an essential part of the structure but are liable to be neglected because they do not contribute much to the integral spots in the diffraction patterns. It seems likely that there may well be a continuum of structural types connecting the classical crystal structures, through twins, multiple or polysynthetic twins, 'heavily dislocated' structures, and various other disorders, to the definitely noncrystalline but nevertheless 'regular' structures of liquids and glasses.

The aim is to have a notation which carries right across this spectrum, and this may be done by a system of transition rules, some of which may be probabilistic. To extend the definition of crystallinity to mean 'the degree to which identical components in a structure are in similar environments' demands the construction of

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appropriate quantitative indices of 'simi- 3a alarity of environment'.

#### Crystalloids

This new approach to crystals, which consists in regarding them as the product of a series of programmed growth steps, could lead to a new classification of imperfect or incomplete crystals.

Consider the very small particles of gold which can be seen with an electron microscope in an evaporated film. Gold is facecentred cubic, but these particles do not have that structure. They are actually icosahedral shells (figure 1). This structure is in no way a distortion or a twin, although formally it could be derived from the FCC structure by either of these descriptions. It has been shown, both experimentally and theoretically to be the most stable configuration for 55 or 147 atoms of gold. Only after growing for several more layers according to this icosahedral rule, does the usual FCC structure become the more stable. Now icosahedral symmetry is not treated in the International Tables and crystals are really only defined for infinite repetition. Yet every crystal must be defective, even if the only defect is the surface. However, if a crystal is only ten unit cells cube, about half of the unit cells lie in the surface and thus have environments very different from those of the other half. The physical observation is that very small aggregates need not be crystalline, although they may nevertheless be perfectly structured. It is proposed that the word *crystalloid* should be applied to them. (The word formerly occurred in chemistry but is now in disuse.) Accordingly, we may have revised definitions of the words crystalloid, crystal and crystallite:

*Crystalloid:* a configuration of atoms (or other identical components) finite in one or more dimensions, in a true free energy minimum, where the units are not related to each other by three lattice operations. It may be possible to describe the arrangement as approximately that of a twinned or dislocated lattice. Under the conditions prevailing, the configuration is more stable than a crystallite with the same components. A crystalloid may be characteristic of a certain number of components and the question of what happens when more are added is not considered.

*Crystal:* a unit cell consisting of one or more atoms or other components is repeated a large number of times by three noncoplanar translations. Corresponding atoms in each unit cell have almost identical surroundings. The fraction of atoms near the surface is small and the effects of the surface can be neglected.

*Crystallite:* a small crystal where the only defect is the existence of an external surface. The lattice may be deemed to be distorted but it is not dislocated. Crystallites may be further associated into a mosaic block.

*Crystallinity* is the degree to which corresponding components in a structure are in identical surroundings. **Recursive rules** 

It is possible to use recursive rules to pro-

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Figure 3 a The dissection of a pentagon into five triangles plus a smaller pentagon. b The assembly of six pentagons plus five triangles to give a larger pentagon

Figure 4 The hierarchic packing of pentagons

**Figure 5** The *A* and *B* units which can be combined to give an infinite nonperiodic hierarchic packing of pentagons

duce interesting structures which are 'regular' but noncrystalline. Two examples concerned with the packing of pentagons in a plane demonstrate some of the possibilities.

They exhibit two different ways of relaxing the rules of symmetry to comply with the demand to tile a plane with regular pentagons. (There are, of course, a number of ways in which a plane can be tiled with identical, nonregular pentagons.) The first way allows the pentagons to be dissected as shown in figure 3a.

We are given a large supply of pentagonal tiles of order O and asked to cover a plane. This is done hierarchically by combining six zero-order pentagons to make a larger, first-order pentagon (figure 3b) and proceeding recursively. Unfortunately there are five triangular gaps. These are filled by cutting up a seventh pentagon which provides five triangles plus a pentagon of order -1. These constructions are then repeated on an ever-increasing scale (figure 4). The ratio of the linear dimensions of pentagons of successive order dure embodies the identities:  $\varphi^1 + \varphi^{-4} = 7$ ,  $\varphi^8 + \varphi^{-8} = 47$ ,  $\varphi^{12} + \varphi^{-12} = 322$ , etc. It is continued until the desired area, however large, is covered and the small residual pentagon almost disappears. This procedure is, of course, unlikely to be encountered in nature, since atoms, from which structures must be built, are indivisible.

A similar hierarchic packing of pentagons can, however, be realized without requiring a variety of sizes of components, by using pieces of only two types (A and B of figure 5). These can be combined together to five pentagons of order O and can also be packed to give the isosceles triangles of all orders which are required for filling in the gaps. We then obtain a tiling of A and B units which will cover the whole plane. It has many interesting properties, among which are: (i) the composition tends to  $A_{\phi}B$ ; (ii) there is a unique centre and rules can be given for finding a path to it; (iii) the pattern is an example of a hierarchic structure which looks almost the same at a number of scales if the boundaries of the pentagons are emphasized; (iv) although there is only one centre of true five-fold symmetry, there is an infinite number of centres of local pentagonal symmetry. Relatively short range centres are more densely distributed and longer range centres are more sparsely distributed; (v) circles can be inscribed in the pentagons and in certain interstices, to give a packing of finite density (the density does not tend to zero at an infinite distance from the start). R Penrose has independently produced a very similar pattern.

Hierarchy represents a natural way in which Wilson and Fisher's theory of phase transitions can appear. In this theory the region of interaction increases exponentially until, at the critical point, it comprises the whole specimen.

Attempts to find a three-dimensional analogy of these packings have not been successful, although it has earlier been shown that the packing of 13 icosahedra, each made of 13 spheres, is related to the icosahedral shell packing assumed by gold particles. A three-dimensional packing might be based on the identity  $\varphi^3 - \varphi^{-3} = 4$ , etc, but none has been found, the conditions being much more stringent than in two dimensions.

We must ask, as many have asked since Kepler, what the rules which lead to the formation of a snowflake are. We are just beginning to see how the rules for the growth of a tree are written in the genetic code. Is there really any resemblance between these two extremes of complexity? Does it make any sense to look back and ask where the programme for growing a snowflake may be stored?

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## **Art Remembering Science**

**DIFFERENT KINDS OF INTERACTIONS** exist between Art and Science. Artistic creations have inspired scientists to make discoveries. Scientists enlist artistic creations to make abstract scientific concepts accessible to a broader audience. The 50-year-old *Leonardo* has contributed much and significantly to fostering these interactions. In this editorial, I mention yet another aspect—when art assists science and the public in remembering scientists and scientific discoveries.

I find there is a fundamental difference when credit is assigned for artistic and scientific creations. Every artistic creation is unique; it could not have been made by anybody else, and its author's name remains assigned to this creation forever. In contrast, except in a very small number of examples, the names of discoverers disappear soon following their scientific contributions. Usually a scientist makes a discovery as the time becomes ripe for it; if one scientist does not succeed, another will sooner or later. The fate of discoveries is that they tend to become bricks in the edifice of science: the layers build onto others' work, and the names of the bricklayers tend to disappear in oblivion. As time goes on, remembering the names of great and even lesser scientists not only gives tribute to them but also helps future generations value and know the past. Art plays a great role in erecting proper memorials that serve a purpose and are visually appealing.

With Magdolna Hargittai, I have surveyed and photographed the memorials of scientists in Budapest [1], New York [2] and Moscow [3] (Fig. 1) and have embarked on similar projects for London and Washington, DC. In fact, the project involves far more than cataloging memorials. The memorials have their own stories, as obviously do the scientists and the discoveries they commemorate. Each city lends its own flavor to its scientist memorials. Budapest has been the venue of numerous scientific achievements and the cradle of the many scientists born in this city and who gained world renown both here and, even more notably, elsewhere. New York, known as a world center of many areas of human endeavor, is less known as a world center of science—which it is. Many more milestone discoveries have occurred in New York than there exist memorials of scientists that, incidentally, may have worked in New York or elsewhere in the U.S. No city in the world has had such a concentration of science as Moscow, and Moscow has many more memorials of scientists than any other city in the world.

Many factors play a role in who is commemorated and who is not. These factors may include politics, the efforts of devoted pupils or family members, financial considerations and suchlike. Thus, no reliable science history could be compiled on the basis of the memorials. Nonetheless, having awareness of the existing memorials and visiting them enhances our outlook about science and may even call attention to the *absence* of memorials that we might judge should also exist. Scientists, no less than politicians and military leaders, deserve to be part of our collective memory, and this can be accomplished through artistic creations.

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Figure 1. (left) Alajos Stróbl, 1906: statue of obstetrician lanác Semmelweis (1818-1865), "the Savior of Mothers," who introduced disinfection following autopsy before examining patients, in front of St. Roch Hospital, Budapest. (middle) Detail of the Hall of Fame of Great Americans in the Bronx; of 99 busts, 42 depict explorers, conservationists, scientists, innovators, educators and medical scientists. (right) I.M. Rukavishnikov, 1971: monumental head statue of Igor V. Kurchatov (1903–1960), the Soviet "atomic tsar," Kurchatov Square, Moscow. (Photos © Istvan and Magdolna Hargittai)







# Memorials of Mathematicians in Moscow

# Magdolna Hargittai & Istvan Hargittai

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# Memorials of Mathematicians in Moscow

#### Magdolna Hargittai and Istvan Hargittai

Does your bometown have any mathematical tourist attractions such as statues, plaques, graves, the café where the famous conjecture was made, the desk where the famous initials are scratched, birthplaces, houses, or memorials? Have you encountered a mathematical sight on your travels? If so, we invite you to submit an essay to this column. Be sure to include a picture, a description of its mathematical significance, and either a map or directions so that others may follow in your tracks.

Submissions should be uploaded to http://tmin.edmgr.com or sent directly to Ma. Louise Antonette N. De Las Peñas, mathtourist I@gmail.com. ur recent book *Science in Moscow*<sup>1</sup> stated boldly that the capital of Russia may have more memorials to scientists—statues, busts, reliefs, and memorial tablets—than any other city in the world. London may be a competitor, where the magnificent network of blue plaques and plaques of other colors considerably enhances the number of scientists remembered. The special interest distinguishing the Moscow memorials from those in London and other cities in the Western world is explained by the often secretive world of Soviet/Russian science. Here we introduce the reader to a sampler of the memorials to mathematicians and computer scientists in Moscow.

The well-known tower of the Lomonosov Moscow State University (MSU), at 1 Lenin Hills, is by itself a memorial to science and learning. We will refer to it simply as Moscow University (or MSU), because it is not the only institution of higher learning bearing Lomonosov's name, even in Moscow, let alone in Russia. The address also warrants clarification. The hills overlooking Moscow used to be called the Vorobyovy Gori (Sparrow Hills), and then in Soviet times, the Lenin Hills. Today, they are again the Sparrow Hills. However, names and addresses that did not exist in pre-Soviet times retained their earlier designations.<sup>2</sup>

The Lenin Hills campus of MSU opened in 1953. It and its surroundings were carefully planned to radiate grandeur, including a number of memorials to the greats of Russian science. To this we may add a caveat. There used to be claims ascribing many more discoveries and innovations to Russian scientists than the rest of the world was prepared to accept. In contrast, some unsubstantiated claims then caused disbelief and hesitation when genuine Russian contributions should have been recognized, even though there have been many of these. Furthermore, many Russian geniuses in the history of science remained unrecognized due to isolation and lack of international communication. There are examples of Russian and Soviet scientists who should have been inscribed in the roster of Nobel laureates. The very Soviet authorities that complained about anti-Soviet bias in the Nobel Prize institution hindered their scientists and their discoveries from entering the international scene.

Ivan G. Petrovsky (1901–1973) has a rather peculiar memorial plaque on the façade of the tower building (Figure 1, left). Petrovsky studied mathematics at MSU, but graduated rather late, in 1927, since what would have been his student years coincided with the period of the Russian Civil War. He remained at his alma mater and was already a professor at the age of 32. He was appointed head of the

<sup>1</sup>I. Hargittai and M. Hargittai. Science in Moscow: Memorials of a Research Empire. World Scientific, 2019.

<sup>&</sup>lt;sup>2</sup>The best-known example is Leningrad, which is again called Saint Petersburg, except that Saint Petersburg continues to be located in the province (oblast) of Leningrad.

department of differential equations in 1951, and in the same year also rector of MSU. He served in both these positions to the end of his life. He is buried at the Novodeviche Cemetery (Figure 1, right), where many of the most famous politicians, military leaders, artists, technologists, and scientists are buried.

There is some hierarchy among burial places in Moscow. The Lenin Mausoleum is iconic, of course, and for a few years, it was Stalin's resting place as well. When his crimes came out in the open, he was taken out of the mausoleum and reinterred in an exclusive plot between the mausoleum and the Kremlin wall. A dozen such exclusive plots are there for Soviet political leaders, and their tombstones are marked by their busts, Stalin's included. The next most prestigious burial place is the Kremlin wall itself. From among the scientists figuring in this compilation, only Mstislav V. Keldysh was so honored, and not for his science, but for his leadership in the Soviet space program. The Novodeviche Cemetery is the most prestigious among all Moscow cemeteries. This relatively small cemetery has been closed, and no new burials can take place there except for close family members of those who are already buried there. The Novodeviche Cemetery came closest in the ostensibly classless Soviet society to having a Socialist nobility. Other cemeteries of high prestige in Moscow where great scientists and other contributors to world and Russian culture rest include the Donskoye, Kuntsevskoye, Kuzminskoye, Mitinskoye, Pyatnitskoye, Troyekurovskoye, Vagankovskoye, Vostryakovskoye, and Vvedenskoye Cemeteries.

The tower of MSU has a big Ceremonial Hall whose entrance lobbies display scores of mosaic portraits of Russian and international scientists, among them mathematicians; see Figure 2. Higher in the tower, the Faculty of Mechanics and Mathematics occupies floors 12– 16. It is an internationally renowned institution whose graduates have become professors in many colleges and universities and leading specialists of the nuclear weapons and space programs. During the Soviet regime it practiced



**Figure 1.** Left: Bust of Ivan G. Petrovsky (by I.M. Rukavishnikov) on the façade at the students' club entrance to the university tower. Right: Ivan G. Petrovsky's tombstone at the Novodeviche Cemetery. Photographs by the authors.

anti-Semitic discrimination and accepted hardly any Jewish students.

Nikolai N. Luzin (1883-1950) was one of the most famous mathematicians of MSU until he lost his job; see Figure 3. Today a modest memorial plaque marks the lecture hall named after him. He built up a strong school, and the circle around him was named "Luzitania." He was a member of the Academy of Sciences, an academician-the highest designation a scientist could achieve. He was also a representative of the old intelligentsia. In 1936, he was about to fall victim to Stalin's Great Terror, endangering not only his employment but his life-as many others had perished in the mid-1930s. Among other "crimes," newspaper accounts accused Luzin of publishing his best papers in international, rather than Soviet, periodicals. The Academy of Sciences endorsed the anti-Luzin attacks in the newspapers, though it did not terminate his membership. Some of Luzin's former students-famous mathematicians-turned against their mentor, among them Pavel Aleksandrov and Andrei N. Kolmogorov. Other luminaries of science, such as the chemist Nikolai S. Kurnakov, the geologist Vladimir I. Vernadsky, and the physicist Petr L. Kapitsa, defended Luzin. Kapitsa sent a letter to Vyacheslav Molotov, chairman of the Council of People's Commissars of the Soviet Union, explaining that it was in the national interest that scientists publish their best papers in international journals. Nonetheless, the Soviet authorities continued to prevent international publication. As for Luzin, he was among the lucky victims; although he lost his university professorship, he was otherwise left alone. The resolution of the Academy of Sciences condemning him was annulled only in 2012, finally putting an end to the infamous "Luzin affair."

There are two memorial plaques with reliefs on the façade of the professorial residential quarters of MSU, Pavel S. Aleksandrov and Andrei N. Kolmogorov, two outstanding and trendsetting mathematicians; see Figure 4. Pavel S. Aleksandrov (1896-1982) studied mathematics at MSU. Following graduation, he visited Germany in the early 1920s. There, he developed fruitful interactions with several of the great German mathematicians, including David Hilbert, Richard Courant, and Emmy Noether. He and Heinz Hopf wrote a very successful book on topology, Topologie I. It was published in 1935 by Springer, and its latest edition appeared in 2011. Aleksandrov founded the Department of Geometry and Topology at MSU in 1933 and chaired it for the rest of his life. Concomitantly, between 1935 and 1950, he was in charge of the Division of Topology at the Steklov Institute of Mathematics of the Academy of Sciences. He was recognized by memberships in international learned societies, among them the U.S. National Academy of Sciences.

Andrei N. Kolmogorov (1903–1987) graduated from MSU and in 1930 went on a study trip to Germany, where he visited David Hilbert and Richard Courant. In 1931, he was named full professor at MSU and kept that position for the rest of his life. He was a pioneer of mathematical linguistics in the Soviet Union and founded the Department of Probability at MSU. Much later, he founded the Department of Mathematical Statistics. He interrupted his fundamental



Figure 2. Top row: René Descartes, Leonhard Euler, Carl Friedrich Gauss. Bottom row: Isaac Newton, Nikolai Ivanovich Lobachevsky, Johannes Kepler. Photographs by the authors.



**Figure 3.** Left: Luzin's portrait displayed in the gallery of renowned former institute members on the ninth floor of the Steklov Mathematical Institute of the Academy of Sciences. Right: Luzin's tombstone at the Vvedenskoye Cemetery, 1 Nalichnaya Street. Photograph by and courtesy of Nikolai Andreev.

research for the duration of World War II, devoting his efforts to assisting the artillery. Later in his career, he helped to reform the teaching of high-school mathematics. After the collapse of the Soviet Union, many of his disciples became professors of mathematics in leading Western universities.

When one walks from the university tower in the direction of downtown Moscow, one sees a reflecting pool between the tower and Universitetsky Prospekt (University Avenue). There are two rows of busts of scientists, one on each side of the pool. One of the busts on the west side is



**Figure 4.** Memorial plaques of academicians Pavel S. Aleksandrov (left) and Andrei N. Kolmogorov (right) on the façade of one of the smaller residential towers adjacent to the central tower of MSU. Both individuals, as we learn from the plaques, lived here from 1953, i.e., from the inauguration of the building, until the end of their lives. Both photographs by and courtesy of Olga Dorofeeva.

of Lobachevsky, and one on the east side is of Chebyshev (Figure 5).

Nikolai I. Lobachevsky (1792–1856) graduated in 1811 in physics and mathematics from Kazan University, where he remained, rising to a full professorship in 1822 and appointed rector in 1827. Kazan University dismissed him in 1846, and he died blind and in poverty in 1856. Lobachevsky was a pioneer of non-Euclidean geometry, independently of the Hungarian mathematician János Bolyai (1802–1860). Lobachevsky's non-Euclidean



**Figure 5.** Left: Bust of Nikolai I. Lobachevsky by N.V. Dydykin, west of the reflecting pool in front of the MSU tower. Right: Bust of Pafnuty L. Chebyshev by I.A. Rabinovich, east of the reflecting pool in front of the MSU tower. Photographs by the authors.

geometry is often referred to as Lobachevskian geometry or hyperbolic geometry.

Pafnuty L. Chebyshev (1821–1894) graduated in 1841 from Moscow University. From 1847 he was a member of the professorial staff of St. Petersburg University. He was interested in mechanical devices, and this interest was further enhanced during his visit to Western Europe in 1852. The principal areas of his research were the theory of numbers, the theory of probability, and mechanics. He is considered one of the greatest mathematicians of the nineteenth century; he was elected a member of 25 academies of sciences.

Andrei N. Tikhonov (1906–1993) studied at Moscow University, where he majored in mathematics (Figure 6). Upon graduation, he remained at his alma mater in the Faculty of Physics and Mathematics, which in 1933 was divided into the Faculty of Mechanics and Mathematics and the Faculty of Physics. Tikhonov moved with the Faculty of Physics, where he worked at its Department of Mathematics, serving as its chair between 1938 and 1970. At the

same time, he held leading positions at three research institutes of the Academy of Sciences. In 1970, at Tikhonov's initiation, Moscow University established the Faculty of Computational Mathematics and Cybernetics and appointed him as its dean. A stain on his vita is that he was one of four academicians who in 1983 signed a letter of condemnation of Andrei D. Sakharov's activities. It accused Sakharov of having lost his honor and conscience and of treason. Besides Tikhonov, the other signatories were Anatoly A. Dorodnitsyn (see below), the Nobel laureate physicist Aleksandr M. Prokhorov, and the microbiologist and long-time powerful permanent secretary of the Academy of Sciences Georgy K. Skryabin. At the time of this public letter, Sakharov was living in internal exile under severe conditions. The Soviet authorities liked to have letters published as part of the persecution of their perceived enemies in order to lend credence to the idea that they were acting in concert with broad public opinion. Usually, such letters carried many signatures, and no one knew whether they were all genuine. Sometimes, some of the signatories discovered that they had supposedly signed such a letter only when they read about it in a newspaper. In this case, however, because the letter had only four signatures, there was no doubt that the four academicians had expressed their own opinions by signing this letter.

Lev S. Pontryagin (1908–1988) experienced a childhood tragedy. When he was 14 years old, an oil stove exploded near him. His face was badly burned, and he lost his eye-sight. From that point on, his mother became his eyes. He graduated from Moscow University in 1929, where he remained, being named professor of mathematics in 1935. He was also a leading associate at the Steklov Institute of Mathematics; see Figure 6. He was very successful in the applications of mathematics to practical problems. The dark side of his career and personality was his rabid anti-Semitism. He was successful in preventing even the most outstanding Jewish mathematicians from attending



**Figure 6.** Memorial plaques on the façade of the Faculty of Computational Mathematics and Cybernetics of MSU. Left: Andrei N. Tikhonov. Right: Lev S. Pontryagin. Photographs by the authors.



**Figure 7.** Left: Memorial to Ivan M. Vinogradov at the Steklov Institute of Mathematics of the Academy of Sciences, 8 Gubkin Street. Right: His tombstone at the Novodeviche Cemetery. Photographs by the authors.

international gatherings and being elected to the Academy of Sciences. He was helped in this by his high administrative positions and the active cooperation of Ivan M. Vinogradov, the long-time director of the Steklov Institute. In the background, of course, were the general anti-Semitic policies of the Soviet state and the Communist Party.

Ivan M. Vinogradov (1891–1983) was the director of the Steklov Institute for half a century (Figure 7). The Institute was originally established in Leningrad, but in 1934, it moved to Moscow. Vinogradov's directorship achieved international notoriety for its anti-Semitism, which manifested itself in his rigorously discriminative hiring practices. The Soviet authorities practiced ill-masked anti-Semitism, especially in hiring, but Vinogradov went even further than what was expected of him. Nonetheless, the Steklov Institute was always very strong professionally, and at least two other academic institutes formed from it as spinoffs.

In 1966, a new institute was spun off from the Steklov Institute, which is now the Keldysh Institute of Applied Mathematics. Its origins reach back to 1953, when the need arose to assist ongoing government programs including the nuclear project, the conquest of space, missile defense, and fusion research. More recently, computational biology and robotics have been added to its profile. Mstislav V. Keldysh (1911-1978) graduated in 1931 from Moscow University, where Nikolai N. Luzin was his mentor; see Figure 8. Keldysh began his research career in aerohydrodynamics. From 1934, he worked at the Steklov Institute of Mathematics under the mentorship of his long-time friend Mikhail Lavrentiev. From 1953 to the end of his life, he directed what is now the Keldysh Institute of Applied Mathematics. He had an important but not very publicized role in the Soviet space program. He was also a professor at Moscow University and a scientific organizer, serving as president of the Academy of Sciences from 1961 to 1975.

Sergei L. Sobolev (1908-1989; see Figure 9, left) lost his father early in his childhood. His mother, a teacher and physician, was determined to provide the best possible education for the boy, who appeared to be very gifted. He had a meteoric career in mathematics, graduating from Leningrad University in 1929, where internationally renowned mathematicians were among his professors. After graduation, he worked in mathematical physics, and in 1934, he joined the Steklov Institute. Sobolev worked for the nuclear project from 1945. Parallel to this work, he completed his principal monograph on the fundamentals of mathematical physics. In 1952, he was appointed to a professorship at the recently organized Department of Computational Mathematics of MSU. Eventually, the computational center of the university developed from this department. He was among the initiators of the Siberian Branch of the Academy of Sciences, and from 1957 to 1983, he directed the Institute of Mathematics in Novosibirsk. His activities promoting computational technology were the more remarkable because in the 1950s, cybernetics, that is, computational technology, along with genetics, was considered pseudoscience and ideologically alien in the Soviet Union. Already in the mid-1950s, he fought for reversing this approach and for the recognition of the importance of computational technology. In the mid-1960s, he defended Leonid V. Kantorovich when the latter was being attacked for applying mathematics to economics, which was declared contrary to Marxism-Leninism.

The Dorodnitsyn Computing Center grew out of applied mathematics and can be considered a spinoff of the Keldysh Institute, which itself was a spinoff of the Steklov Institute. Its founding director, Anatoly A. Dorodnitsyn (1910–1994; Figure 9, right), worked at the center, now bearing his name, between 1955 and 1994.

Israel M. Gelfand (1913–2009; Figure 10, left) had a brilliant career in mathematics despite the barriers put up by the Soviet regime and the fact that his anti-Semitic peers prevented his professional advancement and foreign travel. He organized a famous biological seminar for the application of mathematics to biology and served in a professorial appointment at the Belozersky Institute of Physical-Chemical Biology of MSU between 1965 and 1991. He had other jobs simultaneously at the Keldysh Institute of Applied Mathematics and at Moscow State University, where he taught mathematics beginning in 1935. He was one of the great mathematicians of the twentieth century, with broad international recognition long before he was



**Figure 8.** Left: Statue of Mstislav V. Keldysh by Yuri L. Chernov next to the monument "Explorers of Space" in Ostankino Park. Right: Memorial to Mstislav V. Keldysh in front of the Keldysh Institute of Applied Mathematics, 4 Miusskaya Square. Photographs by the authors.



**Figure 9.** Left: Tombstone of Sergei L. Sobolev at the Novodeviche Cemetery. Right: Memorial tablet to Anatoly A. Dorodnitsyn on the façade of the Dorodnitsyn Computing Center, 40 Vavilov Street. Photographs by the authors.



**Figure 10.** Left: memorial plaque to Israel M. Gelfand at the Belozersky Institute of Physical-Chemical Biology of MSU. Right: tombstone of Vladimir I. Arnold at the Novodeviche Cemetery. Photographs by the authors.

properly recognized in his own country. By the time he was elected a full member of the Soviet Academy of Sciences in 1984, he had already become a foreign member of the U.S. National Academy of Sciences (1970), the Royal Swedish Academy of Sciences (1974), the French Academy of Sciences (1976), and the Royal Society (London, 1977), and he had received the first Wolf Prize in Mathematics (1978). When he was finally allowed to travel, in 1989, the 76-year-old Gelfand moved to the United States and built up a strong research program at Rutgers University, in New Jersey.

Even among the conspicuous gravestones in the Novodeviche Cemetery, Vladimir I. Arnold's stands out with its many mathematical formulas and expressions carved into it (Figure 10, right). Here is a rough translation of the text beneath his portrait relief:

Being a mathematician, I always have to rely on sensations, guesses, and hypotheses rather than on proofs, moving from one fact to another, relying on the special illumination that makes me consider common aspects of phenomena under study. To a bystander, these aspects may not even appear connected to each other.

Arnold studied at Moscow University, where Kolmogorov was his mentor, and continued at the university following graduation. Because of the anti-Semitic policies of the director of the Steklov Institute, Arnold did not join the institute until the mid-1980s. His best-known achievements are in the area of catastrophe theory. During the last decade or so of his life, he commuted between Paris and Moscow.

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#### **EDITORIAL**



### 2020 Physics Nobel laureate Roger Penrose and the Penrose pattern as a forerunner of generalized crystallography

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#### **Nobel recognition**

Three physicists shared the Nobel Prize in Physics for 2020. Roger Penrose (1931, Fig. 1) received half of the prize "for the discovery that black hole formation is a robust prediction of the general theory of relativity." The other half was divided between Reinhard Genzel (1952) and Andrea Ghez (1965) "for the discovery of a supermassive compact object at the center of our galaxy." Penrose's discovery was the result of mathematical research into the general theory of relativity, whereas Genzel and Ghez utilized the most up-to-date technological advances in astronomy to make their observations. Some of the formulations of the Penrose discovery read as if the black hole had predicted the general theory of relativity, and some others, as if the formation of black holes was a consequence of the theory. In any case, Penrose uncovered the relationship between the black holes and the general theory of relativity. The black holes are super heavy formations and they swallow everything; even light cannot escape from them. Albert Einstein did not consider the kind of relationship Penrose discovered and did not even believe in the existence of black holes. Penrose discussed the nature of the black holes within a decade following Einstein's death. Penrose described the singularity occurring in the depth of black holes where the known laws of nature lose their validity. We don't know that kind of laws may apply at that point. Penrose discussed the

Dedicated to Alan L. Mackay for his 95th birthday

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details of his discovery both in research papers and in bestselling semi-popular books [1-5].

Alfred Nobel initiated his prizes to award great discoverers, not just great scientists. The two do not always coincide although at the early stages of the prize most awardees were both great discoverers and great scientists. Nowadays, it does not happen so often that the awardees are not only great discoverers but also great scientists. Roger Penrose is both and this makes even a cursory acquaintance with his oeuvre and personality especially rewarding.

#### Background

We recorded a long conversation with Roger Penrose twenty years ago, in 2000, at Oxford University, and we published it in 2005, in the fifth volume of our *Candid Science* book series [6]. In each of the six-volume *Candid Science* book series, there were at least 36 conversations of which at least 18 were with Nobel laureates [7]. In the fifth volume, there were 19 Nobel laureates when the book appeared in 2005, and there are 21 today. One of the two additions was Dan Shechtman (conversation in 1995) who received the Nobel Prize in 2011 for the discovery of quasicrystals. The other addition is Roger Penrose.

There was no interaction between Shechtman and Penrose, except for a chance meeting, and their Nobel distinctions were awarded for discoveries in faraway domains of science. However, their interests strongly overlapped in the area of the symmetry features of extended structures. This will be in the focus of the next segment, but first a little more about Roger Penrose.

Roger Penrose was born in Colchester, Essex, in Eastern England. The Penroses were a well-known intellectual family. His father, Lionel Penrose (1898–1972), was interested in genetics and the inheritance of mental illness. He considered Francis Galton an important scientist, but opposed eugenics. When Lionel Penrose was appointed to the Galton Chair of Fig. 1 Roger Penrose in 2000 in Oxford (photo by Istvan Hargittai)



Eugenics at University College London, he wanted to change the name of the chair from the start, and it was eventually renamed to Galton Chair of Human Genetics. Also, he managed to change the name of the journal *Eugenics* to *Human Genetics*. He loved science and he loved mathematical puzzles and similar entertainment and he drew no sharp line between serious science and fun. Neither does Roger, who was very close to his father. They used to take long walks together. They looked at the plants and were amazed by the scattered leaf arrangements around the stem, recognizing the underlying Fibonacci numbers in them. Roger has three siblings, one is a geneticist, another is a physicist, and one is a psychologist and a ten times British chess champion. Chess was a big deal in the family; the father solved chess puzzles and constructed others; but Roger was not interested in chess.

Roger liked to doodle, especially during boring meetings. Many people do this, but for Roger, it was often connected to solving mathematical puzzles. Both Lionel and Roger liked MC Escher's unusual graphics and Roger even visited the Dutch artist. He shared some of his own and his father's drawings of mathematical puzzles with the artist who then developed his graphics from them. Some have become well known, but most people are not aware of the origin of those drawings.

Beyond his father's influence, mentors and professors at Cambridge University helped Roger's development. Roger was initially dedicated to pure mathematics. Dennis Sciama (1926–1999) inculcated in him an intense interest in physics and enhanced his knowledge of physics. They became friends and used to go to Stratford together to watch Shakespeare plays. They talked about physics during the car rides. In Cambridge, Roger attended many courses regardless of whether or not they were directly connected with his principal studies. He attended Paul Dirac's quantum mechanics, Hermann Bondy's course on the theory of relativity, and S.W.P. Steen's mathematical logic. In Steen's course, he learned about Turing machines and Gödel's theorem. Roger read everything Schrödinger had written on the semi-popular level. Penrose spent his post-doctoral studies at Princeton where he associated mostly with John Arhibald Wheeler. Roger was fascinated by Wheeler's interest to bring much geometry into physics, as he meant to incorporate all of physics into geometry. He benefited from Wheeler's deep knowledge of the theory of relativity, and from getting to know a broad circle of Wheeler's colleagues active in this field. Wheeler liked to say that Roger's stint at Princeton was due to the efforts by NATO to catch up with the Soviet Union.

The debates between Penrose and Stephen Hawking (1942-2018) received great publicity and some compared them even to the Einstein-Bohr debates. Penrose and Hawking wrote papers together on the ideas of singularities. Penrose thought that he influenced Hawking's direction of research in this area. In their joint papers, they used topological arguments to show that gravitational collapse leads to a singular state producing the Big Bang. What people may refer to as their debate was a book in which they communicated their series of lectures, alternating one after the other. This was not a debate though. The disagreement could perhaps be expressed in the way the two considered quantum mechanics. Penrose looked at it as something still evolving, but Hawking could not accept a view about a changing quantum mechanics. This issue occupied Penrose for a long time. He even thought out a large-scale experiment of astronomical enormity, which could be carried out at huge expense.

#### Collapse of a dogma in crystallography

Giants in the history of science, such as Albrecht Dürer, Johannes Kepler, and J. Desmond Bernal, were engaged at one time or another in investigating the properties of the pentagon, the pentagonal dodecahedron, and the impossibility of fivefold symmetry in extended structures—at least, this was a powerful dogma in classical crystallography.

Penrose does not believe in any clear line between doodling and serious research. Indeed, what his doodling was initially would eventually lead to the Penrose patterns. These patterns were to prove instrumental in bringing down the dogma of classical crystallography about the impossibility of fivefold symmetry in the world of crystals. This began when he noticed a pentagonal logo in a letterhead of one of his correspondents. There was a pentagon in its center, surrounded by five same-size pentagons making a larger pentagon. The contour of this scheme left five triangles uncovered in this larger pentagon. Penrose was looking for ways to cover these triangles in this larger pentagon. He cut up a seventh same-size pentagon, which yielded the needed triangles, and left a smaller-size pentagon unused. This scheme is illustrated in Fig. 2, resulting in the simplest Penrose pattern. This happened about 1972, and it was still more doodling than serious science.

He thought of it more as a mathematical curiosity and published an article about it in a rather obscure mathematical periodical [8]. The article itself was based on his lecture at a meeting focusing on aesthetics in mathematics. From the start, the question about the possible applications of the Penrose pattern in crystallography arose. Still, the Penrose pattern might have disappeared in oblivion. This did not happen due primarily to two individuals. One was Martin Gardner, a philosopher by training, who edited a column of mathematical curiosities in Scientific American. In contrast to the obscure mathematical journal, it was well known and most popular. Gardner had an excellent ability to recognize what was important and interesting and put the Penrose pattern onto the cover of a 1977 issue. The artistic representation of the cover illustration was prepared by no less a mathematician than John Conway. Gardner's article was based on his discussion with Conway [9]. This article made the Penrose pattern famous.

The British crystallographer, Alan L. Mackay, was the other individual who recognized the extraordinary potentials of Penrose patterns in crystallography. He had a simulated light diffraction pattern produced from a Penrose pattern. He published it in 1982 [10], and this diffraction pattern displayed symmetry forbidden by the rules of classical crystallography. Mackay issued a warning that if we assume the validity of the dogma about forbidden symmetries, we might ignore them even if we would observe them. At about the same time, the Israeli materials engineer of the TECHNION, Dan Shechtman, visiting at the US National Bureau of Standards (as it was then), did observe forbidden symmetry in the electron diffraction pattern of an aluminum/manganese alloy. Although he was not familiar with Mackay's warning, he did not ignore it just because the classical dogma had taught him to do so. He documented his observation meticulously in 1982, but could publish it only in 1984 [11]. Shechtman immediately recognized the extraordinary significance of his observation, but it took much effort to convince others about its validity [12].

Crystals, according to classical crystallography, have regular and periodic structures. Amorphous materials are nonregular and non-periodic. The Penrose patterns implied and Mackay's simulation experiments suggested that there could exist extended structures that were regular, but non-periodic. Today, these structures, called quasicrystals, belong to the domain of crystallography, meaning that the definition of crystals has expanded. This was a significant step for crystallography to become—using Mackay's terminology generalized crystallography, a more general science of structures. This development was due primarily to the activities and discoveries of Penrose, Mackay, and Shechtman. The contribution of the theoretical physicists Paul Steinhardt and Dov Levine is also to be mentioned. They coined the term



Fig. 2 Developing the simplest Penrose pattern of regular pentagons with changing sizes; courtesy of Alan L. Mackay

quasicrystal and had worked out a theoretical model to describe regular and non-periodic structures. Alas, it appears that the dogma of classical crystallography forbidding fivefold symmetry was overwhelming for them, and they kept their model in their drawer. They published it only in the wake of the publication of Shechtman's observation [13]. This only emphasizes Mackay's courage and integrity.<sup>1</sup> The discovery brought about a paradigm change in broader domain of science than just crystallography—in chemistry, physics, and materials science. It has appeared in artistic creations as well.

Looking back to the origin of Penrose's interest in covering the surface with regular pentagonal shapes, he himself was keen to understand it. He was not aware initially of Kepler's attempts, but had seen Dürer's picture at some stage; it did not pique his interest though. Then, Penrose saw Kepler's drawings in a book [14] and they touched him, perhaps even psychologically. This still did not prompt Penrose to action, but he developed a friendly attitude towards them. Gradually, he became curious as to what one might do with pentagons in terms of tiling. When he produced what became known as the Penrose patterns, he found them quite close to Kepler's attempts.

Johannes Kepler published a small book in 1611, *De nive hexangula* [15]. Kepler admired the shape and symmetry of the six-cornered snowflakes. The book was a milestone in the history of science because for the first time it was enunciated that the external shape of crystals forms as a consequence of internal structure. Today it is obvious that the hexagonal shape

and symmetry of the beautiful snowflakes is a consequence of the hexagonal three-dimensional arrangements of the water molecules in the snow crystal. In 1975, Alan Mackay and Roger Penrose met, and Mackay informed Penrose about the simulated light diffraction experiment of the Penrose pattern. At the time. Penrose was experimenting with an extended pentagonal network that could be considered to be a pentagonal snow crystal. Mackay's son, Robert, was also present and Penrose gave him a copy of his hand-drawn pattern. Robert was a student at York at the time and when he returned to his computer, he automated Penrose's drawing. The computer ran out of time at some point hence the snow crystal pattern remained incomplete. This incomplete pattern had the advantage of showing many different parts of its generation, and it is more informative about how it came about than a complete pattern would have been. This computer generated pattern is shown in Fig. 3. Penrose and the Mackays thought this to be a theoretical exercise and years later they were astonished when Shechtman turned up the real thing. Thirty years later, Robert asked Penrose to autograph the drawing (Fig. 3).

It was an interesting process from the doodling by Penrose to his pattern, known as Penrose pattern. The best known among them is depicted in Fig. 4. It is a good example of how a discovery may happen when there is no such aim initially. The discovery of quasicrystals could have developed in the Penrose-Mackay-Shechtman succession, but this remains a thought experiment. An experimental scientist, like Shechtman, could have embarked on a search of what had become known as quasicrystals. This is not how it happened though. Shechtman was not aware of the Penrose pattern, neither of the Mackay simulated experiment nor his warning. That he did not brush off the "forbidden" symmetry in the electron diffraction pattern when it appeared on his screen, was due to his researcher's acumen. That he stood by it for years in spite of criticism, even ridicule, was due to his stubbornness and perseverance [16].

<sup>&</sup>lt;sup>1</sup> When Shechtman's Nobel Prize for the quasicrystal discovery was announced in October 2011, Penrose wrote a letter to Mackay in which he stressed: "If anyone had been clear in the prediction that quasi-symmetric 5-fold/10-fold patterns might underlie a completely new area of crystallography—where the very way that such materials might indeed be identified through their characteristic diffraction patterns—it was clearly you." (Private communication from Robert H. Mackay to the authors, by e-mail on October 9, 2020.)



Fig. 3 Computer-automated drawing of "Pentagonal snow crystal" by Robert H. Mackay in 1975. This was originally hand-drawn by Roger Penrose, and he autographed it in 2005 (courtesy of Robert H. Mackay)



Fig. 4 The best known Penrose pattern from [6]

#### **Heroes and views**

Archimedes, Galileo, the mathematician Bernhard Riemann, and Newton are among Penrose's heroes. In his youth, Galileo was his principal source of inspiration for Galileo's courage of being against the prevailing thought. If some consider Roger Penrose (Fig. 5) a maverick, it is because of his work that is related to consciousness. Many of his contemporaries like to divide people in two clear-cut groups. Either you are just a computer, as if operating according to an algorithm, or you are



Fig. 5 Roger Penrose in 2000 in his office at Oxford University (photo by Istvan Hargittai)

mystical, religious, and should be regarded as unscientific. Penrose emphasizes that to him conscious phenomena are real things. If there is a real phenomenon, it is part of the real world. We may not be able to explain it today, but we will be some day. The important thing is not whether or not there is yet an explanation for it; the important thing is that it be true. He knows there are people to whom quantum mechanics remains inexplicable and they interpret this by declaring quantum mechanics to be part of divine reality. Penrose realizes that there is fuzziness in the boundaries. He is not religious and it means that he does not believe any religious doctrine. However, he does not think there is nothing more than what is described by a purely reductionist view of the world. We are still learning, and even the term reductionist is not defined unambiguously. Sometimes it is meant to be scientific, which is alright. However, it is insufficient if it means that one can explain the behavior of large things in terms of the behavior of small things. Such an approach only manifests our insufficient understanding of the world. In this, we may refer to what we know and what we do not know about the black holes, in particular, when the need arises for a new physics. Some label Penrose a maverick. They dislike that he stresses our insufficient knowledge and understanding of the world. Beside the black holes, another good example is the workings of the brain. Many imagine it as if they were like the processes in a supercomputer. To Penrose, there is something more to it, and this is also why some think he is a maverick.

It is not easy to define Penrose. Like his father, he does not strictly draw a line between serious research and entertainment. He likes to understand things. He does not draw a line between his interests in mathematics and in physics. He appreciates that in British academia one is not forced to draw such lines rigorously. In the company of mathematicians, he is thought to be a physicist and in the company of physicists he is thought to be a mathematician. He does not care, but he is certain that he is not a businessman.<sup>2</sup> More characteristic is that in his semi-popular books he deals with universal questions; his area of interest and expertise is the Universe itself. Some of his books, even those not too easy to read, are bestsellers. However, the number of books sold does not necessarily express the number of books read. To many, his books represent a higher level of general education. To others, keeping his books on the shelve is a status symbol.

#### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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<sup>&</sup>lt;sup>2</sup> There may have been a reason for Penrose to stress that he was no businessman, because, maybe, he was, even if only to a very small extent. Many years ago there was a lawsuit because of an unauthorized use of the Penrose pattern on a toilet paper. A company, called Pentaplex, had been operating, making things based on Penrose's designs and another company encroached on it without agreement. Not much has transpired about lawsuit, because there was an out-of-court settlement. The Penrose pattern still appeared on the toilet paper following the settlement, but, by then, it did so with an agreement. The issue was not whether the pattern on the toilet paper was produced by some mathematical formula, which is public property, as mathematics is public property. The question was whether a certain pattern had been directly copied. This is an important distinction. A piece of mathematics could not be judged as being private property or public property, because it could only be judged as public property.