

Symmetry in Crystallography

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Abstract

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

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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 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 millennia 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.

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 intermolecular 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 complementarity in packing.

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 parallelehedra, 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

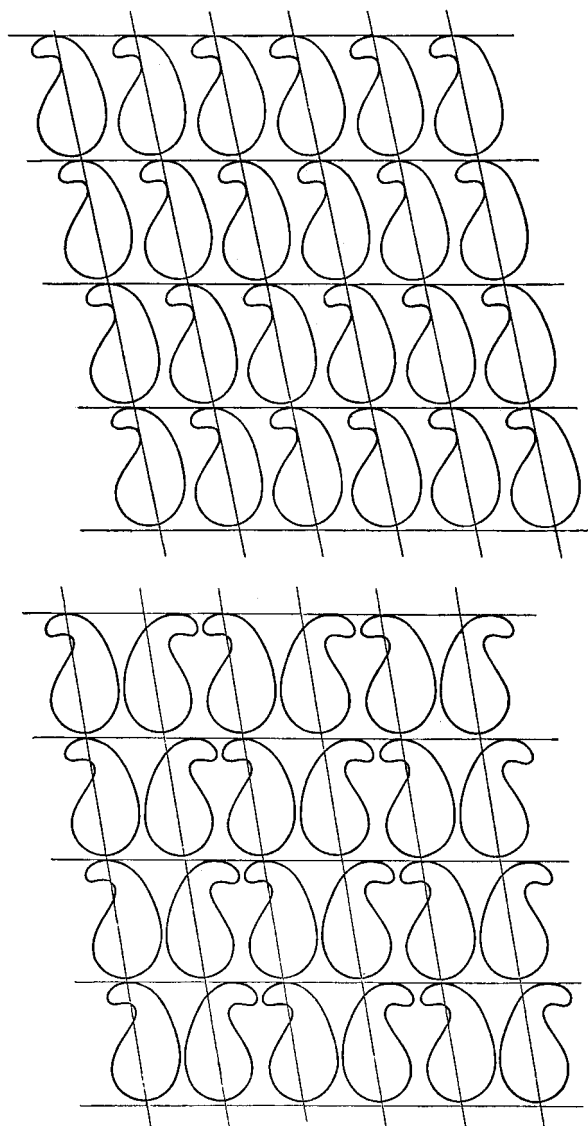


Fig. 1. Arrangements of molecular shapes by Lord Kelvin (1904).

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 determined 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).

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 Delbrück (Pauling & Delbrück, 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 interactions, hydrogen-bond formation *etc.* give stability to a system of two molecules with complementary rather than identical structures in juxtaposition. Accordingly, complementarity should be given primary consideration in discussing intermolecular interactions.

Considerations of complementarity in molecular packing culminated in the works of Kitaigorodskii (1971). His most important contribution was the prediction 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

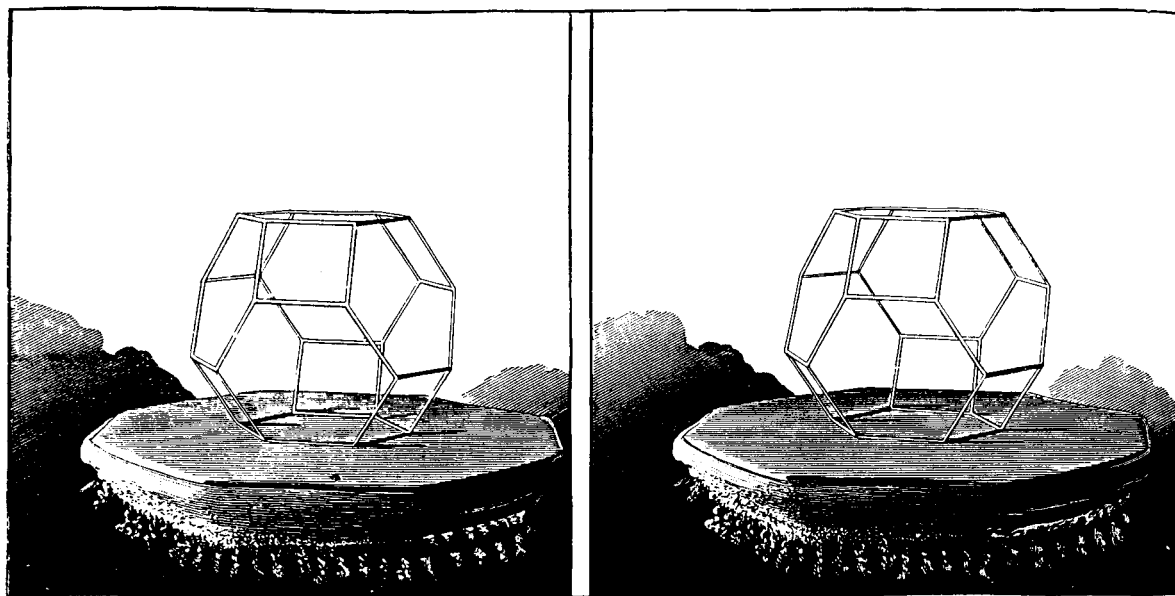


Fig. 2. Truncated octahedron by Lord Kelvin (1904).

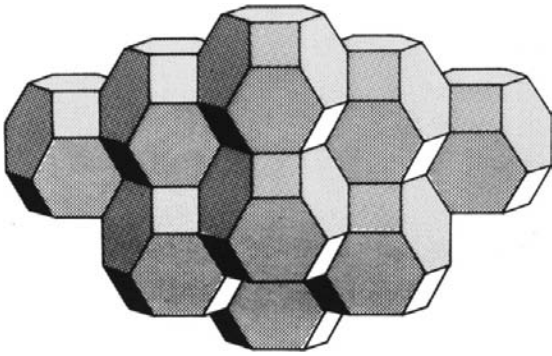


Fig. 3. Space filling by truncated octahedra by Weyl (1952). Reprinted with permission. Copyright (1946) Princeton University Press.

crystals while many of the 230 groups hardly ever occur.

3. Biological structures

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

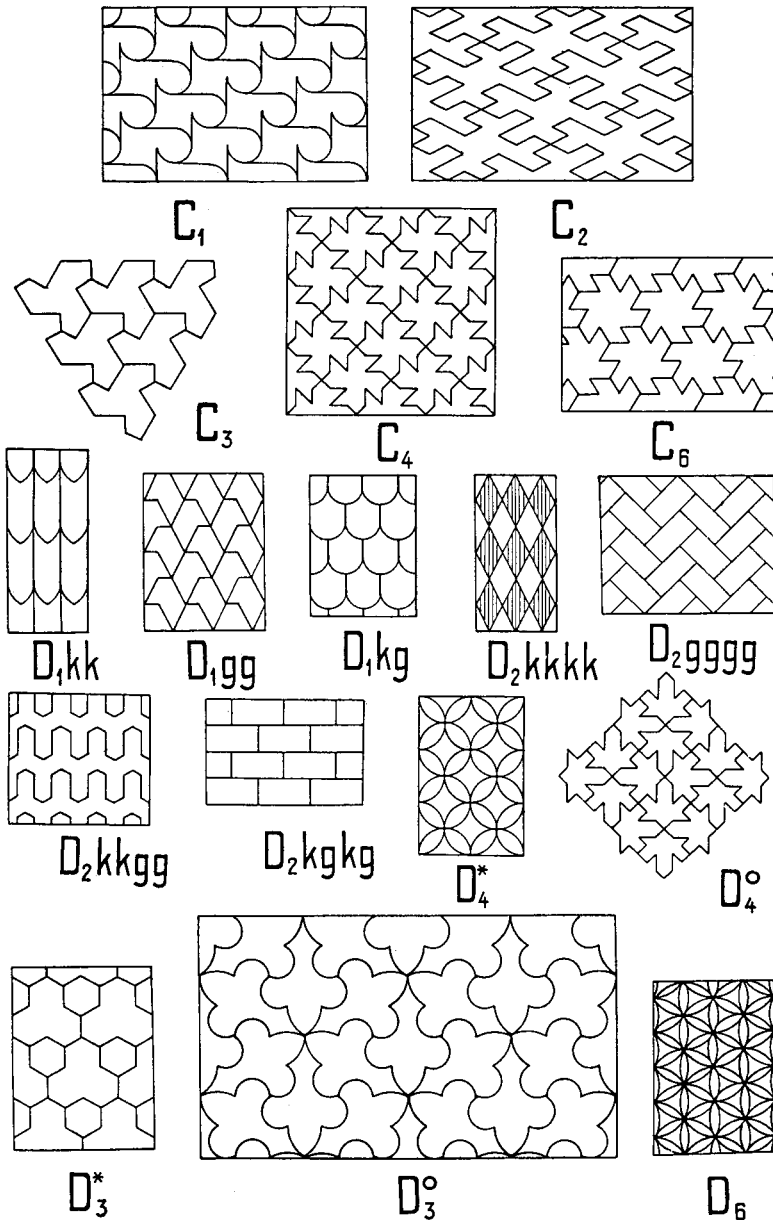


Fig. 4. The 17 two-dimensionally plane groups by Pólya (1924).

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 unstretched hair. This was interpreted as two forms of the polypeptide chain, β -keratin and α -keratin, today known as β -pleated sheet and the α -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 α -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 α -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 noninteger screw, a shift by slight coiling facilitates their best

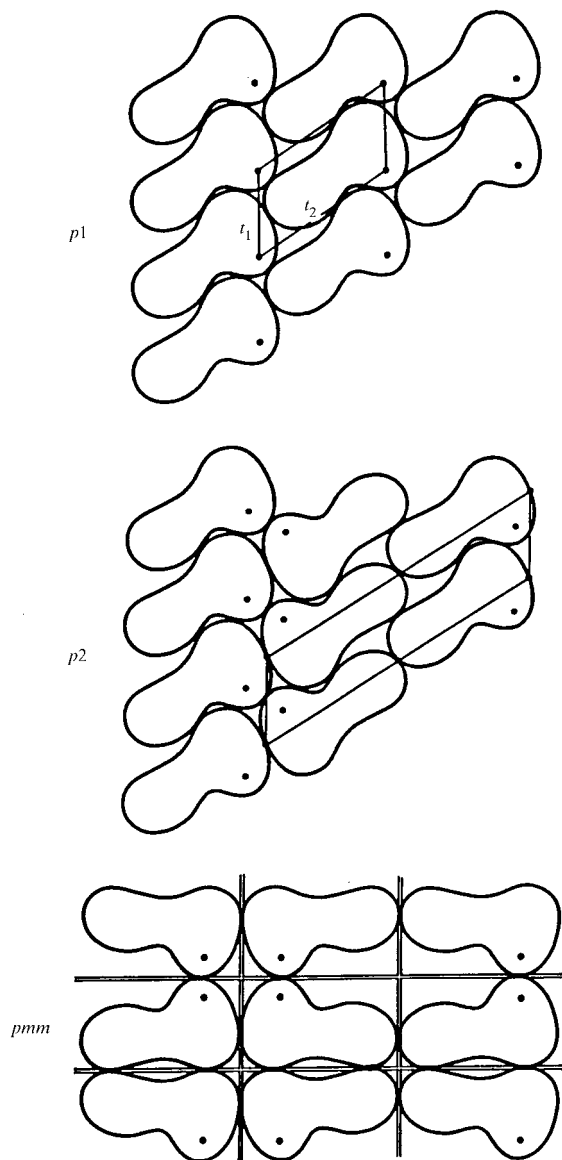


Fig. 5. Sampler of molecular packing arrangements in the plane by Kitaigorodskii (1971).

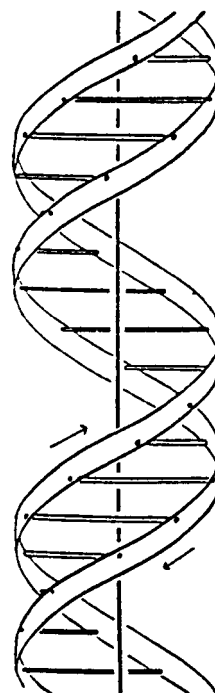


Fig. 6. Diagrammatic representation of the double helix by Watson & Crick (1953a,b). Reprinted with permission. Copyright (1953) Macmillan Magazines Ltd.

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, 1953a; Wilkins *et al.*, 1953; Franklin & Gosling, 1953).

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



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



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



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.

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 self-duplication. 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 α -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 sixfold, 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".

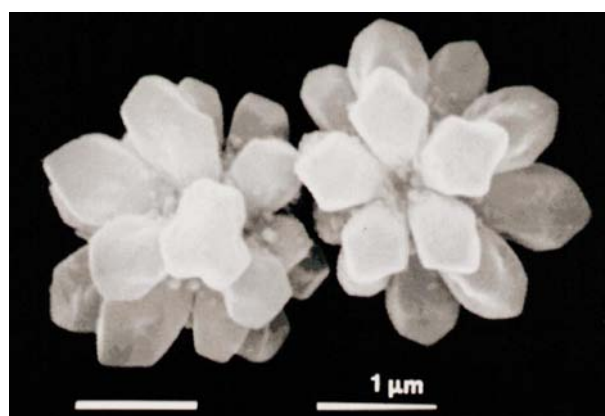


Fig. 10. Flower-like icosahedral quasicrystal in a quenched Al/Mn sample. Photograph courtesy of Dr Ágnes Csanády (Budapest).



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

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).

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 icosahedron (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.

The quasicrystal discovery *could* be described in the following *fictional* way: "For centuries excellent minds, including Johannes Kepler and Albrecht Dürer, 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 consequence 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

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 phénomène*", '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 violation of parity discovery, J. B. S. Haldane (1960) graciously returned to Pasteur's conclusion, "*L'univers est 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 crystallography 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 (MacGillivray, 1976) and sculptures resembling quasicrystals, helices and double helices in various artifacts all help crystallographers to reach outside their specialization and help noncrystallographers 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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