NEW CONCEPTS IN THE ARCHITECTURE OF SOLIDS*

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CRYSTALS AND TRANSLATIONAL SYMMETRY

I WISH to talk to you in the next few minutes about some recent exciting developments in the field of the architecture of solids.

Some of the most beauteous forms in which Nature expresses herself are crystals. One has only to walk through the Raman Collection to become acutely aware of this. These exquisite forms arise because of the apparent propensity of molecules or ions to arrange themselves in three-dimensional arrays or lattices.

It is this periodicity or translational symmetry which is the basis of x-ray crystallography. The lattice periodicity acts like an amplifier of the intensity of x-rays scattered in particular directions by the atoms and sharpens the diffraction maxima. The geometry of the lattice defines the positions of these spots while the molecular or ionic structure affects the relative intensity. A material which does not have translational symmetry *cannot* be a crystal; such substances are hence treated as liquids or glasses and expected to produce a diffraction pattern of diffuse rings. The determination of the structure from diffuse patterns produced by solids lacking translational symmetry involves a great deal of speculation. It is only because of the existence of translational symmetry in many solids that x-ray crystallography has made immense contributions to the understanding of the structure of matter. This has resulted in many advances in the fields of inorganic chemistry, mineralogy, organic chemistry and even to the understanding of the very processes of life.

Translational symmetry imposes many severe symmetry restrictions. For example, a five-fold axis of symmetry is forbidden in crystallography. This may be illustrated simply in two dimensions. A floor can be paved with identically shaped tiles which are parallelograms, rhombuses, rectangles, squares, triangles or hexagons but not with equiangular pentagonal tiles (figure 1). Because of this and other similar restrictions some of the most elegant solid shapes are excluded from the ambit of crystallography.

The ancient Greeks, who were great aesthetes and also geometers, discovered five perfect solids, *the so-called Platonic solids. They are the tetra*hedron, the cube, the octahedron, the dodecahedron and the icosahedron. The last (figure 2) has twenty equilateral triangular faces with six five-fold axes. There may be a site symmetry in a crystal having icosahedral symmetry (as was discovered long long ago at Bangalore[1]) but it cannot survive the imposition of lattice translation.

THE PENROSE TILING

This was the state of affairs till Roger Penrose of Oxford, one of our great living geometers, (who showed that our universe must have a mathematical singularity in its history) appeared

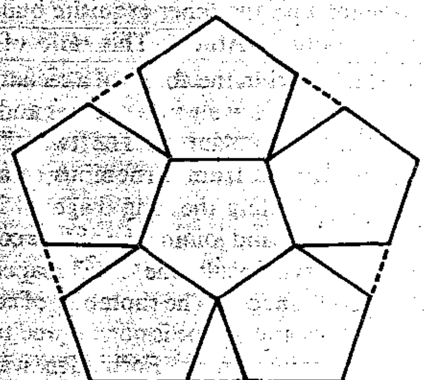

Figure 1. Impossiblity of tiling a floor using equiangular pentagonal tiles.

* From the Presidential address delivered on 6th February 1985 at the Golden Jubilee meeting of the Indian Academy of Sciences.

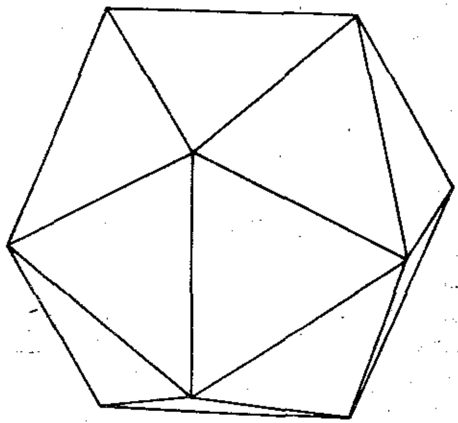

Figure 2. The icosahedron—one of the Platonic solids.

$$(1 + \sqrt{5})/2 = 1.61803398\ldots$$

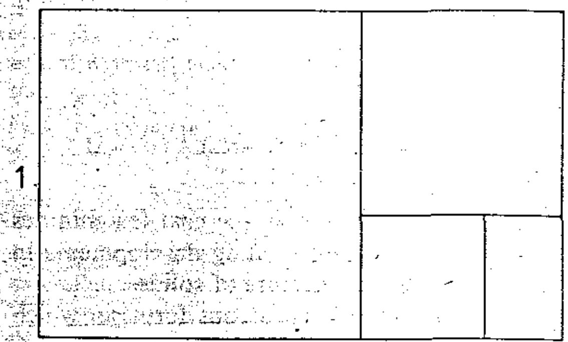

Figure 3. The golden mean of the Greeks.

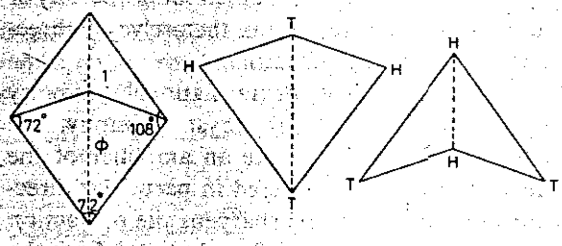

Figure 4. Two basic tiles of Penrose.

on the scene. Mathematical recreations have been his favourite hobby. Along with his father, he was the originator of the idea of the demon stairs which goes round and round without going higher and higher and which was made famous by the lithograph "Ascending and Descending" by the renowned Dutch artist Escher.

One of the basic questions Penrose[2, 3] asked himself was 'Can a floor be paved with a set of tiles having two or more *different* shapes that tile *only* non-periodically[1]. He discovered a set of two tiles that force non-periodicity. To understand this, we go back again to the Greeks who discovered the golden mean or the golden section. This ratio is said to be the one most pleasing to the eye, and is the basis of the stark beauty of the Parthenon and the other exquisite buildings on the Acropolis in Athens. This ratio of $1:(1+\sqrt{5})/2$ derives from the ability of a rectangle to be subdivided successively into squares and rectangles as shown in figure 3. The two tiles of Penrose are derived from a rhombus of angles 72° and 108°, dividing the long diagonal in the golden ratio $(1:\Phi)$ and joining the obtuse corners (figure 4). Two tiles result, one "kite" shaped and the other "dart" shaped. The rhombus, of course, tiles periodically and so one is not allowed to join the pieces in this manner. Forbidden ways of joining sides of equal length can be enforced in many ways, the simplest being to label the corners H and T (Heads and Tails) and to follow the rule that in fitting edges only corners having the same letter may meet. Using these simple principles one can tile any floor and the pattern necessarily will be non-periodical and will have no translational symmetry.

The properties of these Penrose tilings are indeed very beautiful. Figure 5 shows such different patterns. It can be proved that the number of Penrose tilings is "uncountable". There are local pentagonal symmetries—a symmetry forbidden by conventional crystallography. If one is living in a place tiled by one of the uncountable infinity of Penrose tilings, one cannot know which tiling one is on! "Suppose we have explored a circular region of diameter d and we call it a town where we live. If we ask ourselves how far are we from a region that exactly matches the streets of our hometown", the answer is a remarkable theorem of Conway which states[3]: "never greater than $2d$. If you walk in the right direction

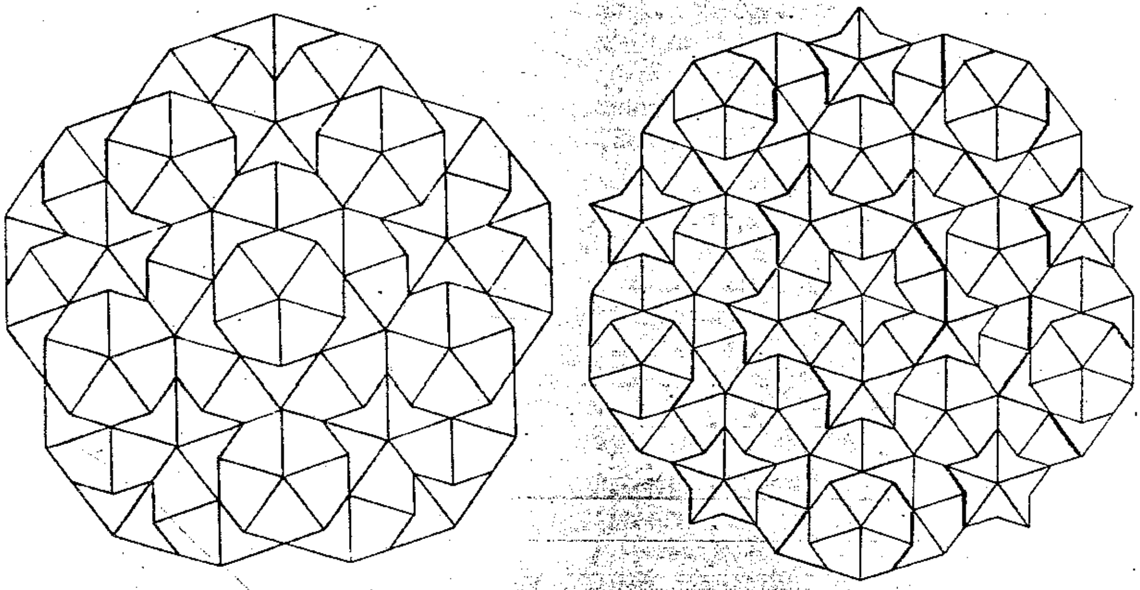

Figure 5. Two non-periodic Penrose patterns.

you need not walk more than $2d$ to find an exact copy of your home town, with the same street pattern"!

I believe that Penrose was reluctant to disclose his extraordinary findings because he wanted to apply for patents (I would like to verify this) but he did permit a popular exposition of his scheme to be written up. When Martin Gardner's article[3] in *Scientific American* appeared, I asked myself as to what the diffraction pattern of one of these non-periodic Penrose tilings would be. It is not difficult to visualise a possible atomic structure corresponding to a Penrose tiling and to calculate the diffraction pattern. One gets the most surprising result that the two-dimensional non-periodic Penrose structure shows sharp diffraction spots. These are arranged broadly on circular regions giving an appearance of a "diffuse" x-ray powder pattern composed of a large number of discrete sharp spots. The optical transform of one of the Penrose-tiling structures (after Mackay[4] who made so many pioneering contributions to this field) is shown in figure 6. We shall not discuss here why a non-periodic structure gives sharp diffraction spots instead of a diffuse pattern.

The next logical question is to ask whether there can be a Penrose non-periodic tiling in three dimensions. The person who answered this first was again A. L. Mackay of Birkbeck College, London. He generalised the two-dimensional Penrose tiling to three dimensions using two rhombohedra, one acute and the other obtuse using simple recursion relationships (figure 7). These three-dimensional tilings project in two dimensions to the Penrose tiling described earlier which in turn projects into one dimension as non-periodic lattice made up of two characteristic lengths which are related by the golden ratio[4].

EXPERIMENTAL CONFIRMATION

All the above is in the realm of elegant theory and imaginative speculation. What is the experimental situation?

Crystals of gold having icosahedral symmetry[5,6] which give sharp electron diffraction spots have been observed under the electron microscope. These have been explained as due to twinning, impurity twinning or distortion. One has to examine carefully (in view of what follows) whether these explanations were not prompted

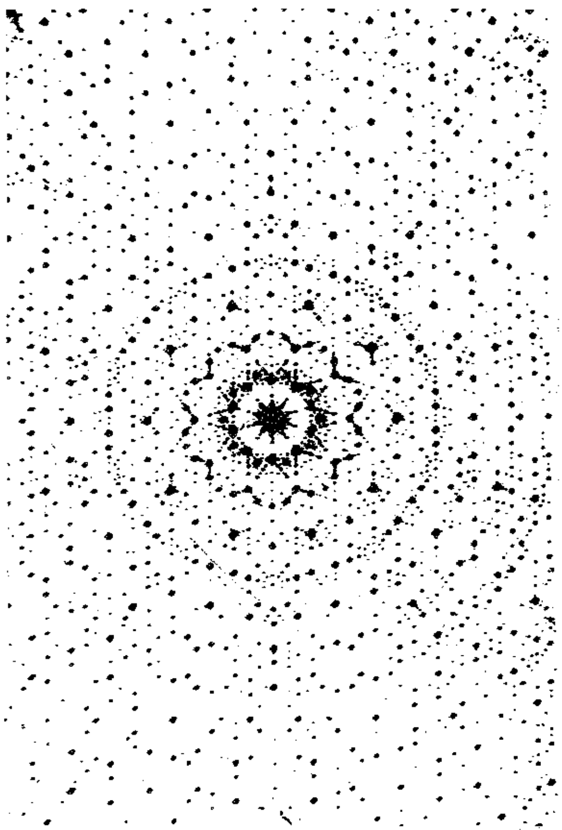

Figure 6. Optical transform of a two-dimensional Penrose tiling pattern (after Mackay[4]).

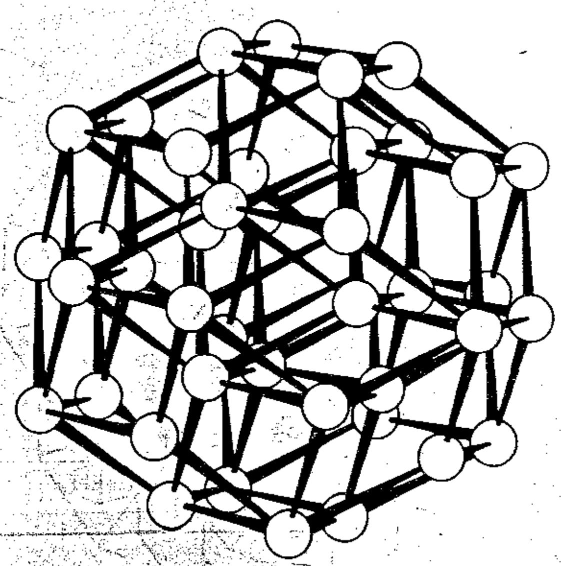

Figure 7. A three-dimensional analogue of the Penrose tiling (after Mackay[4]).

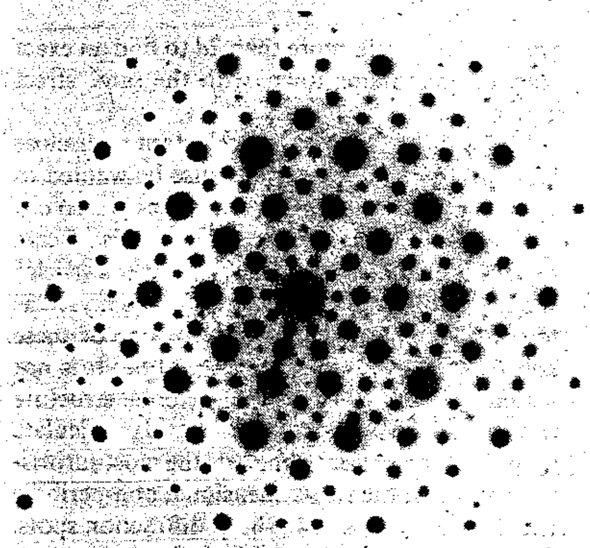

Figure 8. Electron diffraction pattern of supercooled Al-Mn alloy showing icosahedral symmetry.

by a desire to preserve the sacred dogma of crystallography.

In the November 12th (1984) issue of Physical Review Letters there appeared a paper by D. Shechtman (Israel), I. Blech (Israel), D. Gratias (France) and J. W. Cahn (USA)[7], where a metallic solid (aluminium alloyed with 14% atomic per cent manganese prepared by rapid solidification) showed very sharp electron diffraction peaks (figure 8). These diffraction peaks could not be indexed to any of the conventional Bravais lattices. What took the world of crystallography by surprise was that the sharp diffraction patterns displayed all the symmetries of the icosahedron. The diffraction geometry looks similar to the optical transform of the Penrose tiling.

The discovery is a vindication of the concept held by some of us that "the crystal does not form by the insertion of components in a three-dimensional framework of symmetry elements. It arises from a local interaction between individual atoms, and symmetry elements are a consequence"[8]. It is obvious that one has to extend our concept of crystallinity to mean the degree to which identical components of a structure are in a similar environment. It has now been shown that by pursuing recursive relationships, it is possible to produce an infinite variety of structures which are regular but "non-crystalline". There can be no doubt that a new era in solid state architecture has been opened up.

SOME IMPLICATIONS

This new type of architecture presents many challenges. The structural scientist has not only to determine the structure of the molecular or ionic conglomeration, but also the Penrose pattern—a problem more complex than that of conventional crystallography. Does a glass (or even a liquid) consist of microregions consisting of Penrose tilings distributed at random? Are there other modes of non-periodic tiling which are different from the ones discovered so far?

To the solid state physicist this non-periodic architecture presents a new class of solids with very peculiar band gaps (probably having special properties). To the organic chemist the Penrose tilings may suggest new possibilities of molecular structure in two and three dimensions.

When one looks at this new architecture one cannot but be reminded of something G. K. Chesterton said:

> "The world looks a little more regular than it is. Its exactitude is obvious, but its inexactitude is hidden. Its wildness lies in wait. There is a sort of treason in the universe."

11 March 1985

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