Science on Form: Proceedings of the First International Symposium for Science on Form,
General Editor: S. Ishizaka, Editors: Y. Kato, R. Takaki, and J. Toriwaki, 615–620.

Generalised Crystallography

Alan L. Mackay

Department of Crystallography, Birkbeck College, (University of London), Malet Street, London WC1E 7HX, U.K.

Keywords: Generalised crystallography, Curvature, Periodic minimal surfaces, Icosahedral symmetry, Quasi-crystal, Quasi-lattice, Nematics, Incommensurate structures, Pyrite

Classical crystals are not the only kind of ordered assemblies formed by atoms and molecules. Recently a body of observations and of theory has arisen with the discovery of quasi-crystals, highly ordered textures, some with icosahedral symmetry impossible for a crystal. Non-Euclidean crystallography where atoms are arranged in curved manifolds has also been extended from helices, through periodic minimal surfaces, to packings in curved 3-dimensional space. Still further generalisations will be considered.

INTRODUCTION

Classical crystallography has expanded to include the analysis of all kinds of ordered arrangements of atoms.

Because of the simplicity of their Fourier transforms, which the Bragg diffraction experiment samples, regular crystals have predominated. But even glasses are not totally random, although their regularities are difficult to quantify, being statistical in nature. The positions of large numbers of atoms, in both crystals and glasses, may be described by very few parameters. Most generally, a crystal might be defined as an arrangement of atoms, the description of which is much smaller than the assembly itself.

Local interactions determine long range order so that ideas of cellular automata are relevant. The classical 230 space groups should not be regarded as picture frames of symmetry elements which, in the current usage of solid state physics, are "decorated" with atoms, but as resulting from the local interactions of atoms which shake down into an accessible minimum energy configuration.

DIMENSIONALITY

Since the everyday world has three dimensions, it is easy to assemble and to edit structures (such as this text) which are linear sequences, since there are two other dimensions available for manipulation. Characteristically, informational structures are linear. Their primary structure, the sequence of units, means that units have a coordination number of 2. Secondary and tertiary structure may thus arise on folding in three dimensions.

In two dimensional manifolds there is less mobility, although there is one more dimension into which the manifold may be curved.

A major line of development was initiated by asking how regular pentagons may be packed in two dimensions. There are, of course, spaces between the pentagons and two strategies may be adopted for filling these in. The first is to curve the space, making a regular dodecahedron. The second is to give systematic rules for filling in the spaces so that we construct in the plane a hierarchic figure with five-fold symmetry. The latter strategy leads to the Penrose tiling and to a considerable body of theory which has since developed.

In three-dimensional manifolds editing is difficult and therefore structures tend to remain locked in a metastable configuration. However, the same two strategies may be pursued. Curving space leads to a four-dimensional figure which must be "decurved" back into the normal space of three dimensions. Inserting material in the spaces between regular dodecahedra (which are the three-dimensional analogues of pentagons) leads to the three- dimensional Penrose tilings.

PERIODIC MINIMAL SURFACES

We examine first two-dimensional crystallography upon two dimensional manifolds. In the plane the average coordination number (CN) of a point in a triangulated network is six. The perimeter of a circle increases as 2 pi r and the area as pi r^2 However, if the local mean coordination number of a point is less than six, then the manifold becomes curved with positive Gaussian curvature (spherical). The Gauss-Bonnet theorem indicates that the integral of the curvature over an area is equal to the spherical excess of the angles. The spherical excess may be provided by disclinations from some standard configuration (such as a hexagonal lattice). As is well known, when a hexagonal net is mapped round a sphere then there must be 12 vertices with CN=5 instead of 6, making a total disclination strength of 12*pi/3. Such structures are found for example, for the spherical viruses.

If the mean coordination number is greater than six, then the Gaussian curvature is negative and the corresponding surface is hyperbolic or saddle-shaped. It was recently realised that such surfaces can appear in crystal structures on various scales and the work of H.A.Schwarz and E.R.Neovius in the 1870s has become topical. More recently, A.H.Schoen (1970) has extended this work and has shown that there are at least 18 periodic minimal surfaces. These are based on taking the fundamental region of a space group, the region which is repeated by the symmetry elements of a space group to fill space, and hanging a soap film across it so that the film has a minimum surface and is repeated without discontinuities of first or second derivative. Such surfaces are minimal and have zero mean curvature, the two principal curvatures being equal and opposite so that their product, the Gaussian curvature, is everywhere negative (or zero). These surfaces are geometrical absolutes, like the polyhedra.

Given such surfaces, points can be arranged on them and the surface can be tessellated into Voronoi regions and in general the normal operations of geometry can be carried out. Tilings of the Penrose type, discussed below, can be constructed. There is a relationship between the fundamental regions in such surfaces and the arrangement of similar regions in the hyperbolic plane, a space of constant negative Gaussian curvature.

As regards physical systems, periodic minimal surfaces (or at least surfaces very similar in topology) can be seen in the structures of lipid films in lyotropic liquid crystals, in silicate cage frameworks, as Fermi surfaces, in mineralised biological tissues such as the spines of certain sea-urchins and as zero-equipotential surfaces in ionic crystals. As structures of soap-films they are not mechanically stable and further forces are necessary, just as no stable arrangement of charges can be stable under electrostatic forces alone (Earnshaw's theorem).

THREE-DIMENSIONAL MANIFOLDS

Attempts were made (Mackay, 1980) to extend this idea to three dimensions by examining the packing of points in R3, that is, on the three-dimensional space which is the surface of a four-dimensional hypersphere. The ideas was that the curvature would render unfavourable the normal coordination number of 12 to be found in for example, face-centred-cubic metals, and provide a space in which an amorphous structure could be modelled. Since the space was finite, there would be no need for cyclic boundary value conditions normally used in computer simulations of a liquid. This line has been much developed by Sadoc, Mosseri and others. The space here is positively curved (and consequently volume increases less rapidly than $(4/3)\pi r^3$.

ICOSAHEDRAL "CRYSTALS"

The world of crystallography was startled by the announcement, in November 1984, by Shechtman, Blech, Gratias and Cahn (1984) of the experimental observation of electron diffraction patterns from an Al/Mn alloy which showed full three-dimensional icosahderal point symmetry. Every crystal belongs to one or other of the 230 space groups. Each of these space groups gives rise to diffraction patterns which have the point symmetry of one or other of the 32 crystallographic point groups. The icosahedral group m35 is not one of these. Thus, the material cannot be a normal crystal. The controversy over the structure has continued for the past year, being much enlivened by a contribution from Linus Pauling who asserts that the material is a twinned crystal (for which he proposes a structure).

Such materials have now been categorised as quasi-crystals. The word quasi-lattice was first defined in 1981 (Mackay, 1981) with reference to the Penrose tiling but the definition has been appropriated, without acknowledgement, by Levine and Steinhardt (1984), who altered the emphasis of the definition. However, both aspects are implicit. Each quasi-lattice point in an N-dimensional space can be assigned

integer indices with respect to integer steps on more than N vectors forming a star. The use of four axes for the hexagonal system of crystals is a familiar example. Having redundant axes means that vectors in a particular direction can be described in more than one way and that integer dispolacements along two or more axes can produce incommensurate steps along a partiular direction. It is this latter aspect which Levine and Steinhardt's definition emphasises.

NEMATIC ASPECTS

In fact the physical material appears to be a kind of texture, not with visible grains oriented in different directions, but on the finest possible scale, where the units are local coordination polyhedra rather than assemblies of recognisable unit cells. The Penrose tiling, which is, in three-dimensions a packing of acute and obtuse rhombohdra (where all edges are the same and the interedge angle is arctan(2) and its supplement). Each tile has three pairs of parallel faces and it is possible to envisage a thread passing in at each face and out at the opposite face. The crossover in the middle may happen in various ways, but can be defined. This means that the whole tiling would be covered three times by 15 threads which are in the directions of the two fold axes of the icocashedron which represents the overall symmetry. The tiling can also be seen to be composed of crinkly layers of tiles with edges perpendicular to their mean plane. These six layers are perpendicular to the five-fold axes and their projections comprise the two-dimensional Penrose tiling. In the plane five threads cross each tile twice so that the mean spacing of the threads is 5/2 times the cell edge. Defining one crossover can lead to a consistent definintion of all others. An example has been constructed by A-M. Honeger of this laboratory. The six layers cover the pattern three times so that their mean spacing is twice the cell edge. This fabric gives literally a very fine texture. The unit cell dimensions have been estimated (for the Al/Mn alloy) at 4.6 A and together with the measured density this allows abbut five atoms per acute unit cell. These are essentially the minimum needed to define thread directions. It is not intended that this nematic model should be taken very literally but only as a way in which the topology of the system may be constructed. It has been shown first by Kramer that starting from an arbitrary star of vectors tesselations of space by paralellepipeds can be constructed with a wide variety of symmetries. The case of icosahedral symmetry where there are only two different rhombohedra is only the simplest and other tilings require more than two different tiles. As a byproduct, it follows that all such tilings can generate thread patterns which represent very complex weaves. If it were possible to execute these weaves in fibreglass or carbon fibre then we would have the basis of a new class of composite materials with nearly isotropic symmetry.

It is clear that the physical basis of the icosahedral alloys is the production of local icosahedral coordination polyhedra and the mutual adjustment of such polyhedra to have a common orientation. The Penrose tiling, in so far as it is a description of the physical structure, must result from the atomic

arrangement and not vice versa. The local rules would try to produce clusters of 20 acute rhombohedra with their vertices meeting at a point (rather than packing by translation as in a regyular crystal) and, while this can be done locally, the packing cannot continue. To a considerable extent the obtuse rhombohedra amy be seen simply as vacancies or dislocations in a tangle of acute rhombohedra packed parallel to definite directions which result in the icosahdral symmetry. Where two obtuse rhombohedra meet there will be room for more atoms which may turn out to be lying in the shared faces of the obtuse rhombohedra. At present progress awaits good methods of calculating the structure factors expected for various configurations.

INCOMMENSURABLE STRUCTURES

Alternatively, working downwards from the observed long-range order, the structure can be seen to involve incommensurable structures. This is a field of crystallography of growing importance where regular crystal structures are modulated in amplitude or frequency. In this case we may explain the situation by reference to the structure of pyrite (FeS_2).

Pyrite (which is a cubic mineral with the space group Pa3) can be seen to be a packing of the same acute and obtuse rhombohedra which occur in the three-dimensional Penrose tiling but insead of occurring in the irrational ratio of tau (1.618...) they are in the ratio of 1:1. The acute tile would contain one S-S dumbell and the obtuse rhombohedron one Fe ion. These tiles are arranged in alternation as in the structure of NaCl. (V.Elser has predicted, as a consequenxce of his projection method of generating the Penrose tiling, a series of cubic structures which would have ratios of tiles corresponding to every third Fibonacci ratio. This is the first, with the ratio 1:1 and the alloy $Mg_{32}(Al,Zn)_{49}$ is close to the next with the ratio of 5:3).
In pyrite the faces of the form (210) are very prominent. If we take the pair of faces with indices 120 and -1 2 0, then they intercept the y-axis at regular intervals. Correspondingly, the pair of faces 012 and 0 1 -2 define spacings of twice this value on the y-axis. In cubes of pyrite the faces of the form 100 can be seen to be made up of fine striations due to the intersection of the face of the form 210. The form 210 is a dodecahedron but not quite a regular one. The regular dodecahedron would have faces of the form (tau, 1, 0) and here two incommensurate periods along the cube axes would be prescribed. We believe that this incommensurablity can be seen in the corresponding directions in the the beautiful electron micrographs taken by Hiraga and the group in Sendai, and by Knowles, Saxton, Stubbs and Greer in Cambridge.

REFERENCES

Bernal, J.D., (1958). "The importance of symmetry in solids and liquids". Acta Physica Hung., 8, 269-276. Bernal, J.D., (1968). "The range of generalized crystallography". Krist., 13, 927-951 and Sov. Phys. Cryst., 13, 811-831, 1969.

Levine, D. and Steinhardt, P.J., (1984). "Quasi-crystals: a new class of ordered structures". Phys. Rev. Letters, 53, 2477-2480.

Mackay, A.L., (1975). "Generalised crystallography". Izv. Jugoslav. Centr. za Krist., 10, 15-36.

Mackay, A.L., (1981). "De nive quinquangula: On the pentagonal snowflake". Krist., 26, 910-919 and Sov. Phys. Cryst., 26, 517-522.

Mackay, A.L., (1985). "Periodic minimal surfaces". Physica, 131B, 300-305.

Schwarz, H.A., (1890). "Gesammelte Abhandlungen". Springer, Berlin.

Schoen, A.H., (1970). "Infinite periodic minimal surfaces without self-intersection". NASA Technical Note D-5541.

Shechtman, D., Blech, I., Gratias, D. and Cahn, J.W., (1984). "Metallic phase with long-range orientational order and no translational symmetry". Phys. Rev. Letters, 53, 1951-1953.

13-6
Q: Do you think that there exists n-fold symmetric non-periodic pattern for every integral n? Can you show the algorithm to generate the pattern? (T. Soma)

A: Yes. Steinhardt & Levine & others have shown that any star of > N vectors can generate a tiling in N-dimensional space.