

WHAT IS A CRYSTAL ?

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ABSTRACT

An historical survey of our knowledge of crystal structure and of the mathematical problem of paving space with one or a few types of stones show that a crystal has not necessarily a translation lattice. The recently discovered crystals of alloys Al with 14% Mn have an icosahedral symmetry (incompatible with translation lattice). Their electron micrographs show a structure similar to a Penrose tiling. It seems that long range order characterizing crystals can be obtained from projection of a thin slab of genuine crystal in higher dimension so that crystal physical properties can be described by quasi-periodic functions (as generalizing periodic ones) or may be almost periodic functions.

1. HISTORY BEFORE 1985.

Steno (1669), Haüy (1783) began to answer this question. In the XIXth century, not only the detailed structure of some mineral compounds (as Na Cl diamond) was established, but the 7 crystallographic systems (Weiss, 1816), the 32 crystallographic point groups (Hessel, 1830), the 14 types of lattices (Bravais, 1850) and the 230 crystal symmetry classes (Schönflies, Fedorov, 1892-93) were classified. Since 1912 (Von Laue) X-ray diffraction yields an experimental verification of the previous theoretical speculations : crystals are triply periodic alignments of atoms, ions, molecules. Now we have the refined tools of the diffraction of X-ray, electron or neutron de Broglie waves, for determining crystal structure. And the last fifteen years (see A. Janner's lecture) physicists have discovered that crystals (when one forgets their symmetry defects and their finite size...) can be "modu-

lated", "incommensurate". Finally, last November the experimental observation of a completely new type of crystal was announced by Schechtman, Blech, Gratias, Cahn ¹⁾.

To illustrate my lecture it would be more agreeable for you if I showed some beautiful samples of crystals; but as an abstract theoretician whose computer can draw only in two dimensions, I show in Fig. 1, 2, 3 some idealization of crystals : each point of the figure symbolizes a fixed set of atoms - or a molecule - called the motive of the crystal.

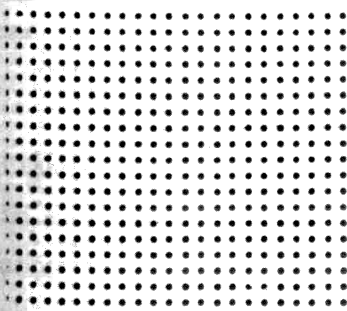


Fig.1 : p4m

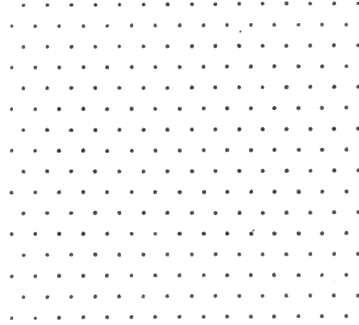


Fig.2 : p6m

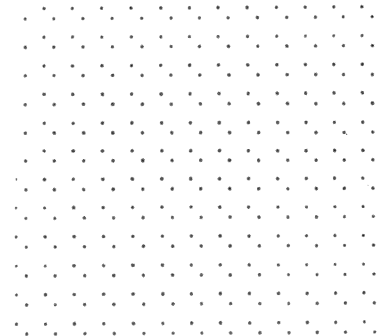


Fig.3 : cmm

(We give the international symbol for the corresponding 2-dimensional crystallographic groups).

Extrapolating from the finite size of the structure, the symmetry group is a crystallographic (space-) group G , i.e. a closed discrete subgroup of the Euclidean group $E(n)$ (here n is 2, but mathematically n can be any natural number) containing a translation lattice $\sim Z^n$. The point group

$$P = G/Z^n < O(n) \quad (1)$$

acts on the lattice, so it is a subgroup of $GL(n, Z) = \text{Aut } Z^n$. Therefore this group is finite $P < O(n) \cap GL(n, Z)$ and, since it has a faithful representation by integer matrices, it can contain only elements of order k such that the value of the Euler function $\phi(k)$

is $\leq n$.

$$\text{Number of integers } \leq k \text{ and prime with } k \equiv \phi(k) \leq n \quad (2)$$

(The function ϕ was defined by Euler : $\phi(k)$ is also the number of generators of the cyclic group Z_k). For $n = 2$ or 3 this means simply that the rotation angle $2\pi/k$ must satisfy: $2 \cos(2\pi/k)$ is integer, i.e. $k = 1, 2, 3, 4, 6$.

As soon as we give a general rule, it is good to give a counter-example: This is the case of Fig.4 : the points of Fig.4 are the vertices of Fig.5 (which is more picturesque).

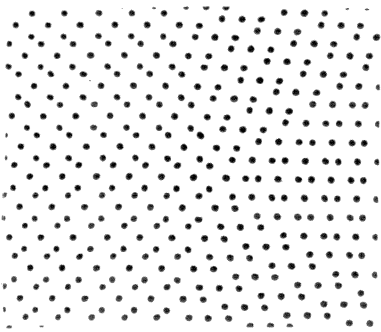


Fig.4

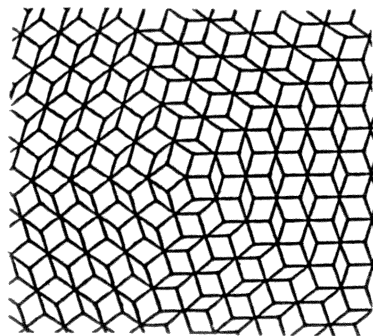


Fig.5

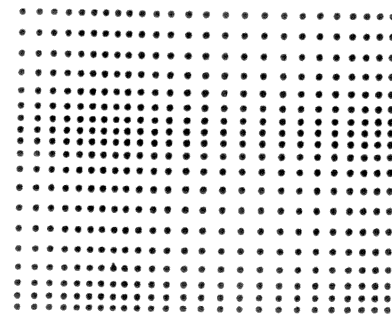


Fig.6

These drawings have a symmetry group Z_5 whose elements are the rotations by $2\pi n/5$ around a fixed center*. Hence they have no translation lattice of symmetry. They are made of five genuine crystals stucked together along natural lines of patching. Such composite crystals exist in nature mainly as "twins" (the general word is macle); quintuplets are rare but seems to have been observed.

There are many more natural crystals without translation lattice Z^3 , because the preserved translational symmetry is Z^2 , Z or trivial. This happens for instance when we superpose to the crystal periodic modulations, as in fig.6. The coordinates of the points are

* For lack of space, similar drawings with rotational symmetry of order 7 and higher were projected at the lecture but are not drawn here.

$$i = 1, 2 \quad x_i = c_i (n_i + a_i \sin(2\pi n_i / A_i)) , \quad n_i \in \mathbb{Z} \quad (3)$$

(in Fig.6 $c_1 = c_2$, $a_1 = .7$, $a_2 = .5$, $A_1 = 19,378\dots$, $A_2 = 11,154$). Of course if all A_i are rational numbers: $A_i = p_i/q_i$, there is still a translation lattice with periods q_i times larger. Many such crystals exist in Nature (e.g. CO_3Na_2): the A_i are usually continuous functions of the temperature different from the temperature-dependent dilation of the lattice. So the A_i are essentially irrational numbers and modulated crystals have no translational lattice. There also exist more complicated structures with two, or sometimes three, different crystals imbricated together, with different temperature dilation coefficients. So there are in nature crystals without lattice of translational symmetry. The beautiful lecture of A. Janner²⁾, last Monday, was devoted to this subject.

In three dimensions there exist only 7 conjugation classes of finite irreducible subgroups of $O(3)$. Five of them are point groups in the cubic crystallographic system; the largest one, $O_h \equiv \bar{m}3m$ of order 48, is the symmetry group of the cube or of its dual, the octahedron (also called crossed polytope in higher dimensions). The two others are $Y_h \equiv \bar{m}5m$, of order 120, the symmetry group of the regular icosahedron and dodecahedron (dual of each other), and its rotation subgroup $Y = Y_h \cap SO(3)$; it is simple and isomorphic to the group A_5 of even permutations of 5 objects. Y_h occurs in Nature as the group of symmetry of virus shapes, of molecules (e.g. carboranes) and small clusters of atoms (e.g. a few hundred argon atoms); such small clusters also seem to exist in some amorphous materials. This local icosahedral symmetry is entirely compatible with the absence of long range order in these materials and it will show up in a Fourier transform corresponding to a diffraction at most as average, e.g. as for crystals in small powder. On the contrary a long range correlation between the atomic positions^{*} seems to me a required property of crystals.

^{*}) To be precise, because of the thermal agitation, one should speak of mean positions of the atoms.

The second section will be a mathematical digression on :

2. PAVINGS.

Given a set S of points in the n -dimensional affine space A , the Dirichlet domain Δ_s of $s \in S$ is the closure of the set of the points $x \in A$ which are nearer to s than to any other point of S . It is convex. If S is the orbit of a translation lattice L' , the Dirichlet domains are called parallelohedras; they are all congruents, have a symmetry center with a point group P which is that of the lattice. Motivated by crystallography Fedorov (1885) studied the combinatorial type of parallelohedra for dimension $n = 2$ (4 or 6 sides) and $n = 3$ (5 types with 6,8,10,12,14 faces). They were also studied at the same period by Minkowski, motivated by number theory. He proved (1887) that the maximum number of faces of parallelohedra in n dimensions is $2(2^n - 1)$. Parallelohedra were also studied by Voronoï at the beginning of the century and later on by Delone (who determined ³⁾ their 51 types for $n = 4$). In crystallography they are called by physicists Wigner-Seitz cells and, for the dual lattice, Brillouin zone. They form a paving of space; this is a particular case of a normal (i.e. neighbour polyhedra share an entire face) regular (i.e. with a translation lattice of symmetry) of space with copies of one paving stone.

Such a normal regular paving with one prototype of stone (one says in the jargon one prototile) can be obtained as Dirichlet domains of one orbit of a crystallographic group G . An upper limit to the number of faces of the prototile has been given by Delone as $2(2^n - 1) |P|$ where $|P|$ is the order of the point group. This number can be as large as 672 for $n = 3$ but the highest number known for an actual paving is 38 (P. Engel ⁴⁾ in 1979). Such an enormous difference shows that there are still things to be proven in 3 dimensions (and this might interest an isolated scientist in Korea or elsewhere!). There are also normal regular pavings with one prototile, forming two orbits of a crystallographic group. The first example known is that of Heesch ⁵⁾ in 1935; its prototile is given in Fig.7.

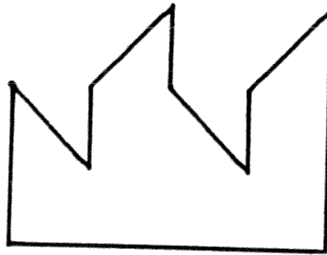


Fig.7

Given a prototile one can ask two questions : Is it possible to make with it a normal regular paving of the plane ? , is it possible to make with it a normal aperiodic one (i.e. without translation lattice symmetry) ? With regular hexagon the answers are : yes, no; with regular pentagons : no, no; with the rhombs of fig.5 : yes, yes. It is still an open problem to find a prototile with answers : no, yes. These questions were suggested by Wang (1961). He obtained in 1966 an aperiodic tiling with 20246 prototiles, number soon reduced by him to 107, by Knuth to 91, by Robinson to 32, by Hamman to 16, by Robinson to 6, by Penrose to 6 and finally in 1974 to 2 (see e.g. ⁶⁾); a detailed history will appear in ⁷⁾). Fig.8 gives such an example of Penrose tiling : he called the two pieces : kite and dart. With matching condition (or what is equivalent to the deformation of the matching sides as in a jigsaw puzzle) one can make a regular map with the kites and darts. Fig.9 represents the vertices of the tiling. De Bruijn ⁸⁾ showed the equivalence of this tiling to a tiling with two kinds of rhombs (whose angles are respectively θ and 4θ for one and 2θ and 3θ for the other, where $\theta = \pi/5$. Forgetting the matching conditions one can obtain a generalized aperiodic tiling as illustrated in Fig.10.

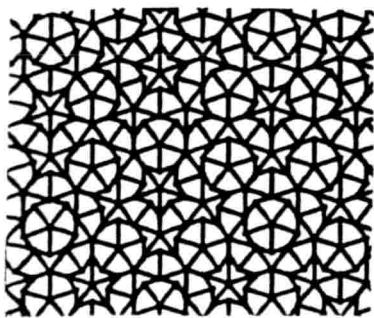


Fig. 8

Penrose patterns with
kites and darts

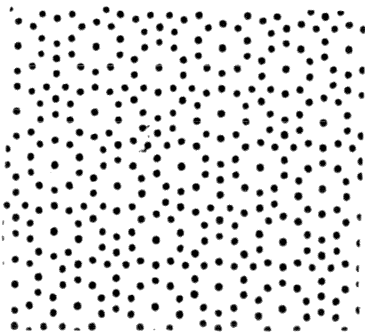


Fig. 9

Vertices of the
Penrose pattern of
Fig. 8

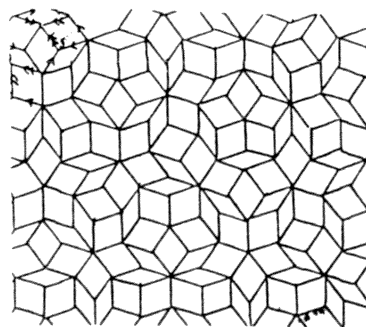


Fig. 10

Generalized Penrose
patterns made with
rhombs

If the vertices of a lattice have same intensity (as in Fig. 1, 2) the Fourier transform is the dual lattice. Fig. 11, 12, 13 show the Fourier transforms of Fig. 6, 4 and 10.

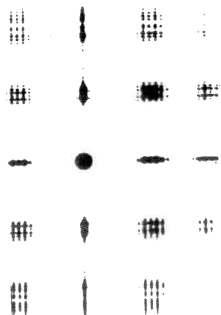


Fig. 11

Fourier transform of
the modulated crystal
of Fig. 6

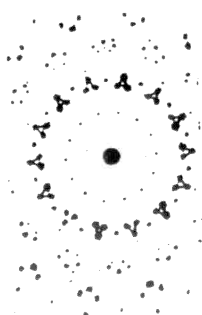


Fig. 12

Fourier transform of
the twin crystals of
Fig. 4

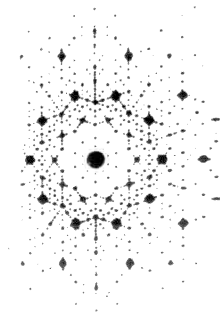


Fig. 13

Fourier transform of
Fig. 9, the vertices
of the Penrose pattern

(I thank D. Gratias for making these Fourier transforms experimentally from a laser beam passing through a diapositive of Fig. 6, 4, 9 and received in the focal plane of a lens).

The Fourier transforms of Fig. 12 and 13 are alike but with some differences; that of the twin has characteristic tails absent in that of the Penrose pattern. These Fourier transforms are completely different

from that of a 2-dimensional crystal whose motive has a five fold symmetry axis as in Fig.14. Fig. 15 is the Fourier transform of Fig.15.

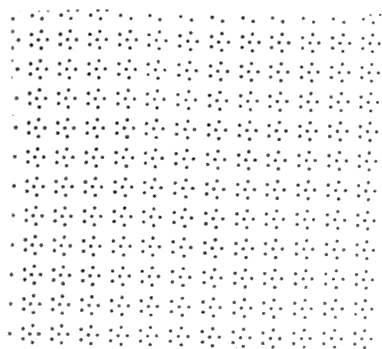


Fig.14

"crystal" with a five fold symmetry motive

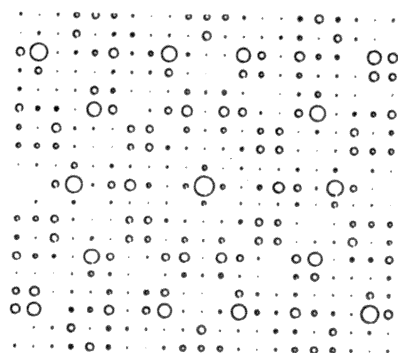


Fig.15

Fourier transform of Fig.15 (made by computer)

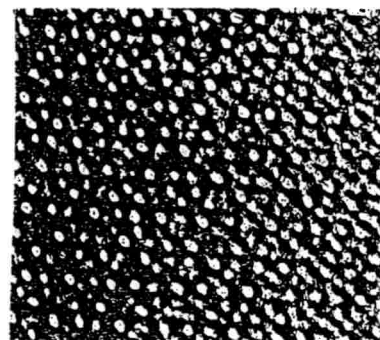


Fig.16

Electron microphotograph of an actual crystal published in ref. 13

The generalization of Penrose tilings to 3 dimensions has been made by A. Mac Kay ⁹⁾ and by P. Kramer ¹⁰⁾ (who gave a beautiful lecture on the subject last Monday). They require only two prototiles. Their Fourier transform was computed independently by Levine and Steinhart ¹¹⁾ (they do not give the one in a direction of a two fold axis) and by Duneau and Katz ¹²⁾.

3. THE EXPERIMENTAL DISCOVERY.

Reference ¹⁾, completed by ¹³⁾, was the first announcement of the existence of crystals with icosahedral symmetry. Indeed, the published electron diffraction patterns along directions forming the angles corresponding to those of the rotation axes of the group I_h are very convincing. They are definitely of the type of Fig.13; so it seems that a twin-like structure can be excluded. These crystals are formed by very fast cooling of an alloy of Al with 10 to 20 % Mn. Their thickness is of the order of the micron. They have been obtained now by several experimental groups (including one in China, led by Kuo) and industrial groups. The electron microphotograph ¹³⁾ reproduced in Fig. 16 and all those obtained elsewhere possess several properties of a

Penrose pattern : local five fold symmetry, local semi-groups of a scale invariance set of five points forming the vertices of a regular pentagon are surrounded by five vertices of a pentagone enlarged by the golden ratio $\tau = (1+\sqrt{5})/2$ and rotated by π . The Penrose patterns have also the property of local isomorphism : take any part of it and within a distance of the order of the diameter of this part, you arrive at an identical copy of this part. Alignments of points appear in the microphotographs, and in Penrose patterns, along five directions at angles multiple of $2\pi/5$. The distribution of points of these lines is that of a one-dimensional pattern. Such a pattern can be obtained as explained in Fig.17. Draw two parallel straight lines forming an angle $\theta = \tan^{-1}(\tau)$ with one of the directions of a square lattice, and whose distance is the diagonal of a square. Project on one of them the vertices which are in the band formed by the two parallels. The projected points form a suit of segments with two lengths L, S in the ratio $L/S = \tau$. The ratio of the frequency $Nb(L)/Nb(S) \rightarrow \tau$ when one extends

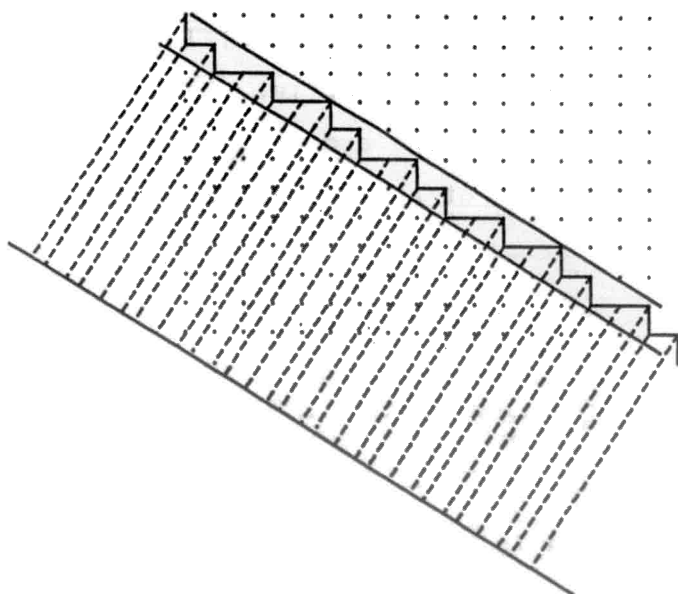


Fig. 17

Construction of a one dimensional Penrose pattern

indefinitely the pattern. Each pattern is completely fixed by the line ordinate of the band modulo one. So the set of one dimensional pattern is labelled by one continuous parameter $0 \leq X_1 < 1$. Similarly the set of Penrose tilings is described by X_1 and X_2 ; fixing two of the five one-dimensional patterns made by the parallel lines of alignments, fix the others. Two among these two parameter families of Penrose tilings have a global symmetry group Z_5 .

The equivalent description of the Penrose tiling by rhombs (see Fig.10) suggests that this pattern can be obtained, as a generalization of Fig.17, by a projection on two dimensions of a slab with well chosen director cosines in a higher dimensional cubic lattice. This is also the case for 3-dimensional Penrose-like pavings, as was proven in ¹⁰⁾ and ¹²⁾. From the Fig.17 construction, it is easy to prove (and left to the reader) that given a finite subset of the one-dimensional pattern of L's and S's, one can predict the position of some other vertices whose set goes to infinity (the density of such vertices decreasing exponentially). This is a measure of the long range order. This was extended to more than one dimension by Duneau and Katz (unpublished).

To study incommensurate and modulated crystal, Janner and Jensen (see Janner's lecture) had already considered higher dimensional regular crystal structure. This method of projecting on 3-dimensional space a slab of crystal in higher dimension seems to give more generally all the varieties of crystals that are observed up to now. Can it lead to a new definition of crystal structure? For instance, that the functions describing the physical properties of crystals are quasi-periodic functions, that is a restriction on a submanifold of their definition domain E_n of a periodic function of n (≥ 3) variables. That is what some of us believe. It can lead to a new and broader classification of crystal structures.

I will end this lecture by two remarks: there is a natural topology in the set $K(E(n))$ of closed subgroups of the Euclidean group (and more generally on $K(G)$ when G is locally compact ¹⁴⁾) and this topological space is compact. So every sequence of closed subgroups converges. It is possible (Gratias, private communication) to transform a cubic crystal by multiplying by F_n (the n^{th} Fibonacci number) the size of the generators of the translation lattice and enriching the motive of the crystal so that when $n \rightarrow \infty$ the translation symmetry disappears and the sequence of motives gets to the limit $n \rightarrow \infty$, the icosahedral symmetry (the sequence is labelled by the Fibonacci numbers); its first steps seem to correspond to known crystals. The

symmetry groups of the sequence are isomorphic $O_n^1 = Pm3m$ space groups with larger and larger translation unit cells and the limit is Y_h !

D. Ruelle ¹⁵⁾ predicted that, by modulating a crystal with more than two irrational periods (e.g. by means of external fields) one can obtain a stable state that he calls "turbulent" by analogy with turbulent states in hydrodynamics : there are still diffraction peaks, but they are fuzzy. I think that to describe this state, we need almost periodic function of H. Bohr ¹⁶⁾.

It was a great pleasure for me to give this lecture on my first visit to Korea, at the first international scientific conference held there. I congratulate the local committee for its perfect organization.

NOTE ADDED ON PROOFS

The conclusion of the first of my two remarks is wrong. The limit of the symmetry group of the sequence of crystals is $\{1\}$; it is not the symmetry group Y_h of the limit of this sequence.

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