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QUASICRYSTALS

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Résumé: On introduit le concept de quasicristaux et on discute leurs clichés de diffraction. On avance l'idée que isomorphisme local a un sens physique.

Abstract: We introduce the concept of quasicrystals and discuss their diffraction patterns. The idea of local isomorphism is argued to be a physically meaningful one.

1 INTRODUCTION

A long-established belief in crystallography is that solid matter can only exist in one of two states: crystalline and glassy. Crystals are highly ordered arrays of atoms; they have long range periodic translational order, long range bond orientational order, and point group rotational symmetry. These last are strongly constrained by the requirement of periodicity of the lattice, and this is the reason that there are so few Bravais lattices possible. Indeed, in two dimensions the unit cell of a periodic lattice must have one of only five possible symmetries, and just fourteen Bravais lattices are possible in three dimensions. By contrast, a glassy structure does not have any of the long range order present in a crystal.

One of the methods used to ascertain the nature and the extent of the order is scattering (electrons, X-rays, neutrons) off the sample. The diffraction pattern of a crystal is vastly different from that of a glass. A crystal diffraction pattern consists of a periodic array of sharp Bragg peaks, and has a rotational symmetry reflecting the crystal's bond orientational order, or equivalently, its point symmetry. The diffraction pattern expected for a glass is diffuse, consisting of rings. Since the orientational order of a crystal can only be one of a restricted class, it would come as a great surprise if a diffraction pattern was comprised of Bragg peaks but had a "disallowed" rotation symmetry.

Recently, we introduced the concept of quasicrystals, a novel state of solid matter possessing some of the characteristics of both a crystal and a glass. Like a crystal, a quasicrystal possesses long range translational order, but this order is not periodic, but rather *quasiperiodic* [1], a very general type of order which includes periodicity as a special case. The relaxation of the demand that the translational order be periodic has the consequence that there is a much richer class of "Bravais lattices" possible for quasicrystal structures than may exist for ordinary crystals. In particular, while it is a theorem that no *crystal* may possess axes of fivefold rotation, this is not necessarily so for quasicrystals, as we shall discuss presently. Quasicrystals also possess the long range bond orientational order present in crystals, but have no point group rotational symmetry.

A quasicrystal's bond orientational order and quasiperiodic translational order combine to produce one of the quasicrystal's most distinctive and striking features, a diffraction pattern consisting of delta function Bragg peaks in an array possessing crystallographically "disallowed" rotation symmetry [2]. The fact that the quasicrystal has sharp diffraction peaks is directly related to its quasiperiodic translational order, and the rotation symmetry of the pattern is a reflection of its bond orientational order. It appears that the recently reported "icosahedral phase" of aluminum and manganese (I- AlMn) [3] [4] may in fact be an example of a quasicrystal [2]. It has an electron diffraction pattern which consists of sharp peaks, but the overall rotation symmetry of the pattern is *icosahedral*, which is incompatible with periodic space filling.

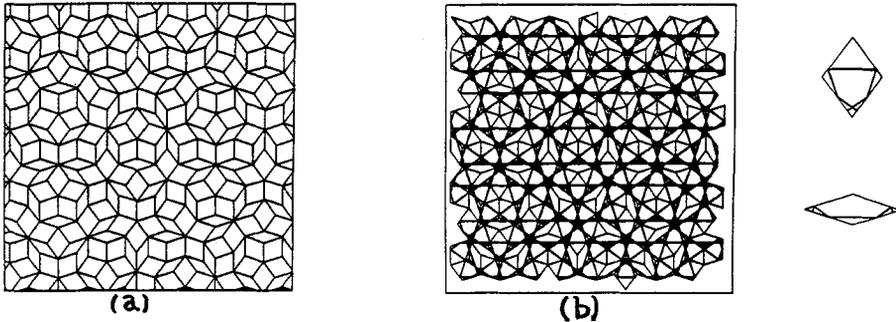


Fig (1): (a) Portion of a Penrose tiling.

(b) The tiles in (a) are decorated as shown and the resulting Ammann quasilattice is depicted.

A prototype quasicrystal, which in fact motivated our study, is the Penrose tilings of the plane [5] [6], a portion of which is shown in Figure 1(a). As may be seen, the Penrose tilings employ two rhombic unit cells (here the meaning of "unit cell" has been corrupted to include more than one shape which repeat throughout the structure, but not necessarily periodically) which fill space in a very well ordered fashion. This order is based on the pentagon, a symmetry which is not allowed for two dimensional crystals. However, the Penrose tilings satisfy all the criteria for being a pentagonal quasicrystal: (1) they have perfect pentagonal bond orientational order – all the near-neighbor bonds are aligned along the axes of a regular pentagon, (2) their lattice sites are separated by some minimal distance, (3) they have quasiperiodic translational order as can be seen in Figure 1(b) in which each of the two unit cells has been decorated with line segments as indicated to the right of the figure. In the actual *tiling* these segments join to form five sets of parallel lines oriented normal to the five axes of a regular pentagon and spaced according to the Fibonacci sequence

$$x_N = N + \alpha + \frac{1}{\tau} \left\lfloor \frac{N}{\tau} + \beta \right\rfloor \quad (1)$$

where $\tau = \text{golden ratio} = (1 + \sqrt{5})/2$; α and β are arbitrary real numbers and where $\lfloor \rfloor$'s represent the greatest integer function. This sequence is itself quasiperiodic, and the intersections of these sets of lines is called the Ammann quasilattice after R. Ammann [7] who was the first to recognize its significance in connection with the Penrose tilings. It should be noted that the Ammann quasilattice itself fulfills all of the above requirements of a quasicrystal, in particular there is a minimal separation between any two quasilattice points. This is, of course, essential if we are to be able to consider the Penrose tilings as decorations of the Ammann quasilattices. Indeed, the decoration of the individual tiles by line segments in the Ammann fashion constitutes one realization of *matching rules* for the tiles, conditions which ensure that no periodic arrangement is possible using these tiles. We demand that if two tiles are to lie adjacent to one another, their Ammann line segments must join to form longer segments and, in the limit of large tilings, unbroken lines.

An additional property that the Penrose tilings possess is self-similarity in the sense that a subset of its vertices may be erased in a process called *deflation*, leaving another Penrose tiling. Self similarity is a consequence of the high degree of symmetry of the pentagon upon which the Penrose tilings are based, and is also a property of the icosahedral quasicrystal [8]. However, quasicrystals with arbitrary orientational symmetry may be constructed, for example by the Generalized Dual Method (GDM) [9], (an extension of a technique of de Bruijn [10]) and such quasicrystals will, in general, not be self-similar.

The Penrose tilings of two dimensions suggest an analog in three dimensions which is based on the icosahedron. The unit cells for the icosahedral quasicrystal packing may be taken to be two rhombohedra, first introduced in this context by R. Ammann [11]. An icosahedral packing more closely akin to the Penrose tilings, in that it possesses simple matching and deflation rules, employs four zonohedral unit cells [12] [13], each of which may be decomposed into the rhombohedra. Elegant methods involving projection from a six-dimensional hypercubic lattice have also produced icosahedral quasicrystal packings by the two rhombohedra mentioned above [10] [14] [15] [16] [17].

The aforementioned projection methods generate only one class of icosahedral quasicrystals in the sense of *local isomorphism* (which we shall return to in Section 3), whereas the GDM appears

to generate the widest set of tilings in this sense. Two tilings are said to be locally isomorphic if any bounded region which appears in one appears in the other, and vice versa. This property is an equivalence relation, and thereby allows for a partition of quasicrystals into local isomorphism (LI) classes. As will be argued presently, the concept of local isomorphism is a physically meaningful one, and tilings belonging to different local isomorphism classes may in fact have distinct physical properties.

2 DIFFRACTION PATTERN

The diffraction pattern of the icosahedral quasicrystal consists of a set of Bragg peaks that densely fill reciprocal space in an array with icosahedral symmetry. To explain this result, we will first consider the case of a one-dimensional quasicrystal with atomic positions given by Eq. (1). This particular example is central to the study of the pentagonal and icosahedral quasilattices. The atomic positions of the 1D (Fibonacci) quasicrystal described by Eq. (1) may be re-expressed as:

$$x_n = n \left(1 + \frac{1}{\tau^2} \right) + \beta\sqrt{5} + \left[-\frac{1}{\tau} \left\{ \frac{n(1 + \frac{1}{\tau^2}) + \beta\sqrt{5}}{\sqrt{5}} \right\} - \beta\tau + \alpha \right] \quad (2)$$

where the “{ }” brackets signify the fractional part (or mod 1) function and we have used the fact that $\tau(1 + \frac{1}{\tau^2}) = \sqrt{5}$. (An identity is $x = [x] + \{x\}$. The function $\{x\}$ is periodic in x with period 1.) This expression is of the general form:

$$x_n = n a + \phi + F(n a + \phi) \quad (3)$$

where $F(x)$ is periodic in x with period b and a/b is irrational. Expressions of this variety arise in the study of the Frenkel-Kontorova model [18], which describes a 1D incommensurate crystal. The Fourier transform of such a set of atomic positions consists of Bragg peaks at positions $k = \frac{2\pi M}{a} + \frac{2\pi N}{b}$, where M and N are integers. This result may be obtained by expanding the exponential $\exp(ikF(na + \phi))$ appearing in the expression for the transform in a Fourier series of its own and employing the completeness relation for complex exponentials. For our case, this means that there will be peaks at

$$k_{pq} \equiv \frac{2\pi}{1 + \frac{1}{\tau^2}} \left(p + \frac{q}{\tau} \right), \quad (4)$$

where p and q are integers.

With this in mind, we will compute the diffraction pattern (i.e. Fourier transform) of the 1D quasicrystal of Eq. (2):

$$f_1(k) = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_n \exp(ikx_n) \quad (5)$$

where we are summing over the N atomic positions in the chain. First, consider $f_1(k)$ for k of the form, $k = k_{pq}$, as defined in Eq. (4); noting the identity $\tau(1 + \frac{1}{\tau^2}) = \sqrt{5}$, the exponent in Eq. (5) is given by:

$$\begin{aligned} ik_{pq}x_n &= 2\pi i \left(p n + q \frac{n}{\tau} \right) + k_{pq} \left(\frac{\beta}{\tau} + \alpha - \frac{1}{\tau} \left\{ \frac{n}{\tau} + \beta \right\} \right) \\ &= 2\pi i \left(p n + q \left[\frac{n}{\tau} + \beta \right] \right) + i \left(2\pi q - \frac{k_{pq}}{\tau} \right) \left\{ \frac{n}{\tau} + \beta \right\} \\ &\quad + ik_{pq}\alpha - i \left(2\pi q - \frac{k_{pq}}{\tau} \right) \beta. \end{aligned} \quad (6)$$

The first term in the final expression is an integer times $2\pi i$, and therefore only yields a factor of unity upon exponentiation. The last two terms are independent of n , and so only contribute an overall phase factor to $f_1(k)$. The second term, however, is n -dependent and contributes to the sum in an important fashion. Since $0 \leq \left\{ \frac{n}{\tau} + \beta \right\} \leq 1$, the second term lies between zero and iX , where $X \equiv 2\pi q - \frac{k_{pq}}{\tau}$. Since τ is an irrational number, the value of the second term is *uniformly and densely* distributed in the interval $(0, X)$, enabling us to approximate the sum in Eq. (5) by an integral:

$$f_1(k) = \frac{e^{i\psi}}{X} \int_0^X \exp(iy) dy = \frac{\sin(X/2)}{X/2} \exp(i\gamma) \quad (7)$$

where $\psi \equiv k_{pq}\alpha - \left(2\pi q - \frac{k_{pq}}{\tau} \right) \beta$ and $\gamma \equiv \psi + \frac{X}{2}$.

Eq. (7) is the value of $f_1(k)$ for the special values $k = k_{pq}$, which, we argued, correspond to the positions of Bragg peaks. Thus, we conclude that

$$f_1(k) = \sum_{pq} \left(\frac{\sin(X/2)}{X/2} e^{i\gamma} \right) \delta(k - k_{pq}). \tag{8}$$

Those familiar with the computation of the Fourier transform of the 1D quasicrystal via projection methods [15] [19] (which appeared subsequent to Ref. 2) will recognize that the two methods agree exactly.

The brightest spots occur for those $k = k_{pq}$ where X is small. This occurs when $\frac{q}{p}$ is close to τ . It is well known that the best rational approximants to τ occur when q and p are successive Fibonacci numbers, F_n . This means that the sequence of most intense peaks corresponds to $(p, q) = (F_{n+1}, F_n)$.

The diffraction pattern of the 3D quasicrystal is simply related to the Fourier transform of the 1D quasicrystal, just as the 3D crystal diffraction pattern is simply expressed in terms of the transform of a 1D crystal. In Ref. 2, we presented the diffraction pattern for the quasilattice underlying the icosahedral packing. This pattern has the quasiperiodicity and orientational symmetry of the packing itself since the unit cells can be viewed as a *decoration* of the quasilattice. Also, the diffraction pattern of the quasilattice should have Bragg peaks in the same places as the icosahedral packing except for possible extinctions (as found in going from sc, say, to fcc crystal lattices). Thus, the diffraction pattern of the quasilattice embodies all of the essential features of the diffraction pattern for the packing.

The quasilattice for a three-dimensional tiling is composed from sets of quasiperiodically spaced parallel planes. There are five models with icosahedral orientational order [20] [21] [12]. The model which appears to correspond most closely to the Al-Mn alloy is called the vertex model; its quasilattice is constructed out of six sets of planes oriented normal to the six axes \mathbf{e}_i of an icosahedron, each set spaced according to Eq. (1). The 3D Fourier transform of the quasilattice breaks up into a product of 1D transforms and can be written:

$$F_3(\mathbf{k}) = \sum_{i>j>k} f_1(\mathbf{k} \cdot \mathbf{u}_{ijk}) f_1(\mathbf{k} \cdot \mathbf{u}_{jki}) f_1(\mathbf{k} \cdot \mathbf{u}_{kij}). \tag{9}$$

where $\mathbf{u}_{ijk} \equiv \mathbf{e}_j \times \mathbf{e}_k / \{\mathbf{e}_i \cdot (\mathbf{e}_j \times \mathbf{e}_k)\}$.

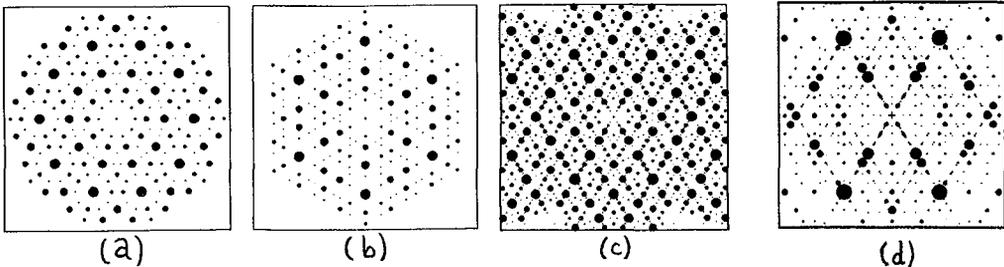


Fig (2): (a-c) The computed diffraction pattern of the Ammann quasilattice normal to the fivefold, threefold, and 2x2-fold symmetry axes of an icosahedron. (d) The computed diffraction pattern of the modified quasilattice normal to the 2x2-fold axis of an icosahedron.

Our computation of the diffraction pattern for the *quasilattice* is shown in Fig. 2(a-c); that is, the Figure shows the diffraction pattern for an ideal model in which identical atoms are placed at each point of the quasilattice. The agreement with the observations reported by Shechtman, et al [3] is remarkable; every diffraction spot observed experimentally appears in our computation. For the five-fold and three-fold symmetry axes the agreement is perfect. For the 2x2-fold pattern, there are extra spots in the quasilattice diffraction pattern that do not appear for I-AlMn. By decorating the quasilattice (similar to going from sc to fcc lattices), the unwanted quasilattice spots can be extinguished. As it turns out, the simplest decoration that extinguishes the unwanted spots is to put identical atoms at the vertices of the rhombohedral packing that decorates the quasilattice [15] [16] [17].

It is interesting to note that the extinction of the unwanted spots can also be obtained by a simple modification of the quasilattice; for example, consider planes spaced by

$$x_n = n + \frac{2}{\tau} \left[\frac{n}{2\tau} + \beta \right] + \alpha. \quad (10)$$

The diffraction patterns of the the rhombohedral packing and this modified quasilattice will have Bragg peaks at precisely the same points. The intensities of the two patterns will differ, but since neither corresponds to a realistic atomic model (e.g., both have identical point scatterers) there is no need to be very concerned about such quantitative differences. In Fig. 2(d) we show a picture of the diffraction pattern for this modified quasilattice, which it can be seen, incorporates the relevant extinctions.

3 LOCAL ISOMORPHISM

Two quasicrystals are locally isomorphic if and only if every finite configuration of vertices that appears in each quasicrystal appears in the other. A quasicrystal in one LI class will have configurations of vertices that do not appear in a quasicrystal in a different LI class.

Local isomorphism has physical significance. In particular, two quasicrystals have identical diffraction patterns if and only if they are locally isomorphic. Two quasicrystals in distinct LI classes have diffraction patterns with Bragg peaks in the same locations, but the peak intensities differ. Intuitively, one expects two locally isomorphic quasicrystals to have the same diffraction pattern because they are locally equivalent. Any finite bounded region which occurs in one also occurs in the other, and hence no local measurement can distinguish the two structures. There are some shifts in the (α_i, β_i) , though, that leave the Bragg peak intensities unchanged. These changes correspond either to translations of the quasilattice, or to shifts from one quasilattice to another in the same LI class.

The shifts that leave the intensities unchanged are of the form $(\alpha_i, \beta_i) \rightarrow (\alpha'_i, \beta'_i)$ where

$$\alpha'_i = \alpha_i + \mathbf{z} \cdot \mathbf{e}_i \quad (11)$$

$$\beta'_i = \beta_i + \mathbf{z}' \cdot \mathbf{e}_{(i)} \quad (12)$$

for all i , where \mathbf{z} and \mathbf{z}' are independent arbitrary 3-vectors. The " $\langle \rangle$ " brackets represent an operation such that $\mathbf{e}_{(n)} = \mathbf{e}_{(3n, \text{mod } 5)}$ if $n = 0, \dots, 4$, and $\mathbf{e}_{(n)} = -\mathbf{e}_n$ if $n = 5$. The vectors \mathbf{e}_i and $\mathbf{e}_{(i)}$ are related to the two different 3D representations of the icosahedral group.

Shifts of α_i of the form shown in Eq. (11) correspond to *translations* of the quasilattice. The shift of the β_i in Eq. (12) corresponds to a more subtle transformation of the lattice. In general, *the shift produces a new quasilattice that is locally isomorphic to the original*. One may show that the shifts in α_i and β_i given above represent the most general shifts which do not affect the intensities of the spots in the diffraction pattern.

In general, there are infinitely many distinct LI classes (corresponding, for example, to shifts in the (α_i, β_i) which are not of the form shown in Eqs. (11) and (12)). No such issue arises for the case of periodic crystals where there is a unique configuration of cells — a single LI class containing one element. As stated above, two quasicrystals have diffraction patterns with identical intensities if and only if they are locally isomorphic. This suggests some further physical consequences:

- Whereas modulations in the Bragg peak intensities for ideal crystals can be used to directly probe the atomic decorations of the unit cell, for quasicrystals the situation is more complicated. Modulations in intensity can be obtained not only by changing the atomic decorations of the (two or more) unit cells, but also by changing from one LI class of unit cell packings to another.
- The density wave description is in terms of the Fourier components of the density and the expression for the Landau mean free energy is expressed in terms of these components. In general, the free energy depends on both the phases and magnitudes of the components. Since two quasilattices in the same LI class have the same Fourier transform (except for an overall phase shift), their free energy must be the same, but two quasilattices in different LI classes may have different free energies, unless there is some accidental degeneracy. As support for this conclusion, note that in Ref. 22 it was shown that the density wave expansion for the Landau mean free energy of the icosahedral quasicrystal is invariant under phase shifts in the density waves (Fourier components) that correspond precisely to Eqs. (11) and (12).

- Given this conjecture, if the ground state of a some physical system is a quasicrystal state, as determined by minimizing the Landau mean free energy, then it is degenerate and corresponds to a set of configurations in a *single LI class* (neglecting the possibility of accidental degeneracy). This fact must be considered in entropy estimates to avoid vast overcounting.

Only experiment can ultimately determine whether a physical system is indeed in a quasicrystalline state. Whatever the case for I-ALMn, it is apparent that a whole class of new atomic structures for solids is possible, corresponding to a new phase of matter with unique symmetries and physical properties. Traditional concepts, such as the impossibility of five-fold symmetry, must be abandoned. We are hopeful that nature will take frequent advantage of such an intriguing possibility.

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