Quasicrystals: A New Class of Ordered Structures

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A quasicrystal is the natural extension of the notion of a crystal to structures with *quasiperiodic,* rather than periodic, translational order. We classify two- and three-dimensional quasicrystals by their symmetry under rotation and show that many disallowed crystal symmetries are allowed quasicrystal symmetries. We analytically compute the diffraction pattern of an ideal quasicrystal and show that the recently observed electron-diffraction pattern of an Al-Mn alloy is closely related to that of an icosahedral quasicrystal.

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Recently, extended icosahedral near-neighbor bond orientational order (BOO) has been observed in computer simulations of simple supercooled liquids and metallic glasses at temperatures about ten percent below the equilibrium melting point.[1] This observation suggested the possibility of a three-dimensional (3D) state with long-range icosahedral BOO[1] but only short-range translational order: the analog of the hexatic phase[2] that has been studied in two dimensions. The Landau expansion for the icosahedral BOO parameter was shown to imply a first-order phase transition (neglecting fluctuation effects) from an isotropic to an icosahedrally oriented state.[1] Nevertheless, given that icosahedra are not space filling (i.e., the icosahedral group is not an allowed crystal point group), it appeared unlikely that a state with infinite-range icosahedral BOO could exist. Nelson[3] later argued that icosahedral BOO in flat space requires disclination defects that can disrupt the orientational order and he computed the maximum range of BOO for a random arrangement of defects with the minimum allowed density.

The 2D Penrose tiling[4,5] offers a tantalizing counterexample to these arguments. We find that the vertices of a Penrose tiling form a nonperiodic lattice with perfect long-range decagonal BOO even though the decagonal group is not an allowed 2D crystal point group. The lattice has a high density of disclination defects that might disrupt the orientational order, except that the defects are spatially ordered such that the long-range BOO persists. The lattice contrasts with the conventional (crystalline) Frank-Kasper phases[6] in which there is a low density of defects and a limited range to the icosahedral BOO. Nelson[3] has suggested that the glass transition occurs as a supercooled liquid approaches a Frank-Kasper phase. As a result of entanglement of the defects, the liquid falls out of equilibrium and forms a glassy state. In this sense, the Frank-Kasper phase serves as a template for the "ideal" (metallic) glass state. However, if a 3D icosahedral BOO state analogous to the Penrose lattice exists, it would not only represent a new phase of matter, but it might also serve as a more natural template.[7]

Motivated by this possibility, we began a long, systematic investigation of the properties of the Penrose lattice to see if other such lattices might exist in 2D and 3D. We find that the Penrose lattice is just one of an infinite set of 2D and 3D lattices that exhibit the BOO and self-similarity properties of a crystal, but have quasiperiodic (QP), rather than periodic, translational order. We term such lattices "quasicrystals." We find that the simple quasicrystals can be classified according to their bond orientational symmetry and the minimum number of incommensurate length scales that characterize their QP translational order. [By simple quasicrystals or crystals we shall mean lattices with BOO with the rotational symmetry of a regular polygon or polyhedron; the further extension to irregular polyhedra (the analog of monoclinic, triclinic, etc.) and decorated lattices (fcc as opposed to simple cubic) should be straightforward.] This new classification scheme is the natural extension of the classification of simple crystals in 2D and 3D. We find that for every allowed crystal BOO symmetry there are an infinite number of quasicrystal lattices. We further find that there is an infinite list of disallowed crystal BOO symmetries that are allowed quasicrystal symmetries.

Perhaps the most physically relevant example is the 3D icosahedral quasicrystal. We have found two polyhedra that can be packed to fill space in only nonperiodic arrays such that the vertices form a 3D icosahedral quasicrystal.[8] We further find that the diffraction pattern of the infinite, ideal simple quasicrystal can be computed analytically. The pattern is characterized by a *self-similar arrangement of Bragg peaks (true δ functions) which densely fill reciprocal space*—very different from what one would expect from a glass with long-range BOO.

We have used conjugate gradient static relaxation techniques to show that a 2D state with long-range decagonal BOO is (at least) locally stable for special binary and ternary mixtures of Lennard-Jones atoms or for a colloidal suspension of two types of oppositely charged polystyrene (or latex) spheres whose atomic radii and densities are in special ratios. Steric hindrance to the formation of similar structures in 3D is expected to be less. The electronic wave functions appear to obey a modified Bloch theorem.[9] We have also studied the electronic density of states and the phonon spectrum of the quasicrystal, both of which appear to exhibit a self-similar sequence of gaps. These results will be presented in separate publications.[7]

By comparison of our computed diffraction pattern of the icosahedral quasicrystal with the electron diffraction pattern found by Shechtman *et al.*,[10] for a rapidly spin-cooled alloy of 86% Al and 14% Mn, it is apparent that the atomic arrangements in the alloy must be closely related to the arrangement of lattice points in the quasicrystal. The position of each electron diffraction peak matches with the position of a peak in the calculated quasicrystal pattern, and a hierarchy of intensities characteristic of quasiperiodicity is observed to several orders. It is intriguing to note that Shechtman *et al.* claim that the phase transition to the peculiar alloy state is first order, as would be predicted by Steinhardt *et al.*[1] Whether the QP translational order is long range, as in a 2D hexagonal crystal, or is short range, as in a 2D hexatic phase, will be determined by high-resolution x-ray diffraction, although relating the width of powder averaged x-ray diffraction peaks to the QP translational correlation length is not straightforward.[7] In either case, the symmetries of the icosahedral quasicrystal will play a crucial role in determining the structural and electronic properties of the alloy.

The defining properties of a simple quasicrystal lattice are as follows: (i) The distance between any two lattice points is greater than some $r > 0$. Every lattice point lies within some distance $R > 0$ of another lattice point. (ii) The lattice is self-similar in the sense that one can eliminate a subset of the lattice points and obtain another quasicrystal lattice with nearest-neighbor distances increased by a constant factor. (iii) The lattice has perfect long-range BOO. (iv) The lattice has QP translational order with k linearly independent (incommensurate) lattice spacings along each lattice vector direction. (A simple crystal can be thought of as the degenerate case of a $k=1$ quasicrystal, in which case, "quasiperiodicity" reduces to periodicity.)

The lattice positions of a 2D (3D) simple k quasicrystal are given by a set of vectors, $\vec{x}$, such that

$$\vec{x}\cdot\vec{e}_i = x_{in}, \quad \vec{x}\cdot\vec{e}_j = \bar{x}_{jn'} \quad (\vec{x}\cdot\vec{e}_k = x_{kn''}), \qquad (1)$$

where n, n' (and n'') run over all the integers; $\vec{e}_i$ are unit vectors along the axes of a regular polygon (polyhedron); $i > j$ ($> k$) and i runs from 1 to N, where N is the number of axes of the polygon (polyhedron). In this paper, we shall define the BOO of a quasicrystal according to the polygon (polyhedron) determined by the $\vec{e}_i$, even though two different polygons (polyhedra) may ultimately correspond to the same BOO rotational symmetry group (as is the case, say for pentagonal and decagonal quasicrystals).

The x_{in} for each i are given by the lattice positions of a discrete, one-dimensional (1D) k-component QP lattice, i.e., a 1D k quasicrystal. The lattice points can be defined in terms of the sequence of k incommensurate intervals, r_i (where i runs from 1 to k), that separate neighboring points. The sequence of intervals is characterized by a substitution law, $r_i = M_{ij} r_j$, where M is a $k \times k$ nonsingular matrix with nonnegative integer matrix elements where the characteristic polynomial cannot be factored into polynomials with rational coefficients. If each interval, r_i, in a finite or infinite QP sequence is replaced by a string of intervals, $M_{ij} r_j$, one gets another QP sequence. The most famous example of a 1D QP sequence is for $k=2$, $M_{12} = M_{21} = M_{11} = 1$, $M_{22} = 0$, which is the sequence studied by Fibonacci and is the basis of the Penrose tiling.[11] In this case, the ratio of intervals r_1/r_2 is equal to τ. Beginning with a QP string of intervals (e.g., the one-element string, r_1) and iteratively substituting $r_1 r_2$ for each r_1 and r_1 for each r_2 in the string, one can generate another QP string (e.g., $r_1 r_2 r_1 r_1 r_2 \ldots$). The set of all 1D quasicrystals that can be generated for fixed k and M have the following properties: (1) Both the number of intervals of any pair of incommensurate lengths and the lengths of any two incommensurate intervals must be in ratios that are algebraic numbers of degree k; that is, they satisfy a polynomial equation with integer coefficients of degree k, but no lower. For $k>1$ this is necessarily irrational, and so clearly the quasicrystal cannot be periodic. (2) There are no uncountable number of distinct k quasicrystals, only a finite number of which have a distinct "center." Any finite sequence of intervals in one k quasicrystal appears an infinite number of times in every other. (3) If one builds a QP lattice out to a distance L, the sequence of intervals that may be added to extend the lattice is "rather restricted" out to arbitrarily large distances beyond the edge of the original lattice.[5,7,12]

All of these properties carry over to the 2D and 3D quasicrystals. The last would undoubtedly play an important role in the nucleation and growth of an atomic quasicrystal.[7]

For a quasicrystal in greater than 1D there are the additional restrictions required to have BOO and yet maintain quasiperiodicity and self-similarity. We have determined a set of conditions that is necessary to satisfy all restrictions, but we have not yet rigorously proven that the conditions are sufficient. However, all known 2D and 3D quasicrystals satisfy these conditions. We have shown that the conditions are satisfied for all k for 2D and 3D quasicrystals with a BOO that corresponds to an *allowed* simple crystal rotational symmetry. For all disallowed crystalline symmetries in 2D constructed from some regular polygon with E edges, a quasicrystal is possible for $E=8$, p, or $2p$, where p is a prime number greater than 3; then $k=[E/2]$ for E odd and $[E/4]$ for E even, where $[n]$ is the greatest integer less than n. A similar argument can be used for 3D to show that icosahedral, tetrahedral, and octahedral quasicrystals are possible with $k=2$.

Because of their possible relation to metallic glasses,[1,7] we have studied the 3D icosahedral quasicrystal in some detail. The quasicrystal is generated by the same 1D QP sequence as the Penrose tiling. We have generated a pair of polyhedra which are the analog of the Penrose tiles; our polyhedra or "bricks" can form space-filling volumes of infinite extent, but only ones which are nonperiodic. The resulting structure can be decomposed into overlapping clusters of rhombic triacontahedra (RT).[7] It is our conjecture that for each k quasicrystal lattice there is a set of k polygons (polyhedra) that can fill the plane (space) only nonperiodically.

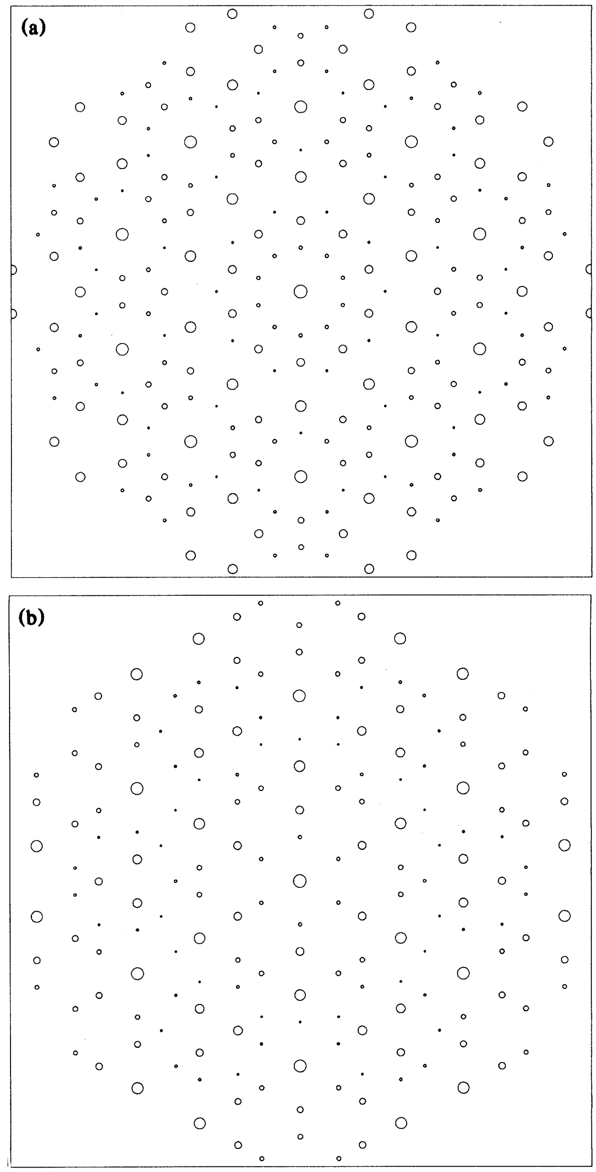

FIG. 1. Computed diffraction pattern for an ideal icosahedral quasicrystal (displaying only peaks above some given intensity). The circles are centered at the location of Bragg peaks and have a radius proportional to their intensity: (a) in a plane normal to a fivefold axis (a characteristic feature is that the peaks lie along quasiperiodically spaced lines oriented parallel to the faces of a pentagon); (b) in a plane normal to a threefold axis. From Eq. (2) it can be shown that the bright peaks of equal intensity lie at the centers of the faces of a RT.

The diffraction pattern of a quasicrystal lattice is given by the Fourier transform, $F(\vec{k})$, of $\sum_{\vec{x}'}\delta(\vec{x}-\vec{x}')$, where $\vec{x}'$ are given by Eq. (1). For 3D,

$$F(\vec{k})=\sum_{\vec{i}>\vec{j}>\vec{k}} F_1(\vec{k}\cdot\vec{u}_{ijk})F_1(\vec{k}\cdot\vec{u}_{jki})F_1(\vec{k}\cdot\vec{u}_{kij}) \quad , \tag{2}$$

where $\vec{u}_{ijk}=\vec{e}_j\times\vec{e}_k/[\vec{e}_i\cdot(\vec{e}_j\times\vec{e}_k)]$. The transform is simply related to the Fourier transform of a 1D quasicrystal, $F_1(k)$. We have proven that $F_1(k)$ is given by a countably infinite number of δ functions with positions in reciprocal space that densely fill the real line. The peaks obey a scaling relation so that their positions, heights, and phases are analytically calculable. For the Fibonacci sequence, for example, we find that the δ-function peaks lie at $k=2\pi(m+m'\tau)/\sqrt{5}$, where $\tau=(1+\sqrt{5})/2$ is the "golden mean" and m and m' are integers.

Substituting $F_1(k)$ into Eq. (2), we can compute the 3D diffraction pattern (see Fig. 1).[13] The pattern is composed of Bragg peaks which densely fill reciprocal space in a self-similar pattern. The positions of the diffraction peaks of the Al-Mn alloy observed by Shechtman *et al.*[10] correspond exactly with Fig. 1, up to experimental resolution. This very strongly suggests that the alloy not only has icosahedral BOO, but is in a quasicrystal phase. From our study of the icosahedral quasicrystal bricks, we conjecture that an atomic arrangement with quasicrystal symmetries should be less dense than a dense-random-packed solid, with confined vacant volumes distributed quasiperiodically throughout the structure.[7]

If real quasicrystalline materials exist (with short- or long-range QP order), as suggested by Shechtman *et al.,* they are sure to possess a wealth of remarkable new structural and electronic properties.[7]

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[13]Note the similarity of Fig. 1(a) to the optical transform of a Penrose tiling found by A. L. Mackay, Physica (Utrecht) **114A**, 609 (1982).