Periodic Quasicrystal

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It is shown that the icosahedral quasicrystal and the recently observed T phase are closely related to each other. The latter is a periodic stacking of two-dimensional quasilattices with mirror symmetry. Their diffraction patterns, though appearing very different, can be indexed by a set of primary vectors that are only small deformations of each other. However, because of the mirror symmetry, their quasilattices are not related by small deformations. A calculation based on the model free energy of Kalugin *et al.* shows that this periodic quasicrystal is very competitive with (and in fact energetically more favorable than) the icosahedral quasicrystal.

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The recent discovery[1] of Al-Mn alloys with diffraction patterns containing sharp Bragg peaks with icosahedral symmetry has found an explanation in the suggestion that although they are positionally ordered, that ordering cannot be periodic in any direction. Such structures have been called quasicrystals. Real-space structures for such quasicrystalline lattices have recently been proposed by a number of people.[2–5] A particularly powerful and suggestive approach has been the "projection method,"[3–5] which constructs lattices by projecting higher-dimensional periodic structures into suitably chosen three-dimensional subspaces.

More recently it has been discovered that there is also a phase of these alloys (referred to as the "T phase"[6] or "decagonal phase"[7]) that has a diffraction pattern characteristic of a periodic stacking of two-dimensional quasicrystalline structures. I shall refer to such atomic arrangements as "periodic quasicrystals," in contrast to the "icosahedral quasicrystals" which lack periodicity in any direction. In addition to the periodicity, the diffraction pattern of the decagonal phase also has a plane of mirror symmetry. The decagonal phase is *a periodic quasicrystal with mirror symmetry.*

In the first part of this paper I show that there is a periodic quasicrystalline structure, referred to as the pentagonal-bipyramid (PB) structure, that (1) has all the observed symmetries of the decagonal phase, (2) has a k-space structure generated by a set of "primary" vectors (defined below) that is only a small deformation of the corresponding icosahedral set, and (3) is, at least within the simple Landau theory of Kalugin, Kitaev, and Levitov,[3] energetically more favorable than the icosahedral structure.

In the second part of the paper, I show that although the primary vectors of the PB quasicrystals and the icosahedral ones are related by small deformations, their real-space lattices are not—as a result of the mirror symmetry of the PB structure. A nontrivial extension of the projection method is developed to construct and to reveal some rather subtle properties of the real-space lattice.

The diffraction patterns of icosahedral quasicrystals can be indexed by a set of six "primary" vectors $\{\mathbf{k}_n\}$. The densities of these structures are of the form

$$\rho(\mathbf{r}) = \sum\nolimits_\lambda \psi_\lambda e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} + \text{c.c.}, \quad \mathbf{k}_\lambda = \sum_{n=0}^{5} \lambda_n \mathbf{k}_n, \tag{1}$$

where $\lambda \equiv [\lambda_0, \lambda_1, \ldots, \lambda_5]$, and λ_n are integers. The set $\{\mathbf{k}_n \equiv k\hat{\mathbf{a}}_n^0\}$ and its negative are the vertex vectors of a regular icosahedron,

$$\hat{\mathbf{a}}_0^0 = \hat{\mathbf{z}}, \quad \hat{\mathbf{a}}_n^0 = \cos\theta\,\hat{\mathbf{z}} + \sin\theta\,R^n\hat{\mathbf{x}}, \quad n = 1 \text{ to } 5, \tag{2}$$

where R is a rotation about the $\hat{\mathbf{z}}$ axis by $2\pi/5$, and $\cos\theta = 1/\sqrt{5}$.

The periodic quasicrystals considered here are specified by the following ["pentagonal-bipyramid" (PB)] set of primary vectors $\{\mathbf{k}_n = k\mathbf{a}_n\}$:

$$\mathbf{a}_0 = 2\cos\alpha\,\hat{\mathbf{z}}, \quad \mathbf{a}_n = \cos\alpha\,\hat{\mathbf{z}} + \sin\alpha\,R^n\hat{\mathbf{x}}, \quad n = 1 \text{ to } 5. \tag{3}$$

The vectors $\{\mathbf{a}_n\}$ and $\{\mathbf{a}_0 - \mathbf{a}_n\}$ are lower and upper edges of a pentagonal bipyramid. Densities (1) generated by the PB set are clearly periodic along z with a period $\Gamma = 2\pi/(k\cos\alpha)$. Since $2\cos\theta = 2/\sqrt{5} \sim 0.9$, there is a range of angles α in the neighborhood of $\alpha = \theta$ for which the PB set (3) is very close to the icosahedral set (2).

From the icosahedral set (1), one can generate a diffraction pattern with icosahedral symmetry by making wave vectors of the same length to have the same amplitude, (i.e., $|\psi_\lambda| = |\psi_{\lambda'}|$ if $|k_\lambda| = |k_{\lambda'}|$). Under this construction, the PB set will generate a structure, referred to as the pentagonal-bipyramid (PB) structure, whose diffraction pattern has the same symmetries as the one observed in the decagonal phase: a tenfold axis z, and two sets of ten twofold axes $\{\pm R^n x\}$ and $\{\pm R^n y\}$ for $n = 1$ to 5. The xy plane is a plane of mirror symmetry.

To demonstrate the plausibility of this periodic quasicrystal, I have used the model of Kalugin, Kitaev, and Levitov[3] to study the energy barrier between the isotropic phase and the PB structure and compared it with the icosahedral case. In this model, the free energy [to the third order in density $\rho(\mathbf{x})$] can be written as

$$F=\int d^3r\{\rho^2-\rho^3\}+y\sum_{\mathbf{k}}(k/q_0-1)^2|\rho_{\mathbf{k}}|^2, \quad y>0, \tag{4}$$

where $\rho(\mathbf{r})=\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}\rho_{\mathbf{k}}$. For very large y, the last term tends to lock the wave vectors at q_0. Even when y is large, however, the free energy can favor the appearance of many wave vectors all *close* to q_0 that form many triangles, if the gain in bulk energy through the ρ^3 term can compensate for the extra "elastic" energy y.

Several authors[8] pointed out some years ago that for infinite locking $(y=\infty)$, the structure with smallest energy barrier against the isotropic phase (and hence most likely to appear from the melt) is a bcc structure. Recently, Kalugin, Kitaev, and Levitov,[3] by taking the edge and vertex vectors of the icosahedron as the only k vectors in (1), showed that this icosahedral structure has an energy barrier lower than that of this bcc structure for $y<69$. (I obtain 69.52.) In this case, the icosahedral vertex and edge vectors together can form triangles that would be absent if only one type of vector were considered. Because their lengths only differ by 5%, the cost in elastic energy is moderate even for large values of y $(y\leqslant 69)$.

Since the PB set (3) can be viewed as a slightly distorted icosahedral set for a range of angle α, one might think that the PB structure in k space is simply a distorted (edge and vertex) icosahedral structure and therefore has the same bulk free energies and similar elastic energies. This is not true. The mirror symmetry of the PB structure demands an additional set of vectors, which can form many more triangles while costing only a small increase in elastic energy. In fact, there is a PB structure that is favored over the (edge and vertex) icosahedral structure for all values of y where the icosahedral structure is favored over the bcc.

To understand the relations and difference in energy between the icosahedral and PB structure, it is useful to group the vertex and edge vectors of an icosahedron in the following five sets, with the numbers of vectors in each set denoted as $2n_i$, $i=1$ to 5 (see Fig. 1): (S1), the upper and lower "umbrella" vertex vectors, $\pm\mathbf{a}_n^0$, $n=1$ to 5, $n_1=5$; (S2), the "backbone" vertex vectors, $\pm\mathbf{a}_0^0$, $n_2=1$; (S3), the upper and lower "cap" edges, $\pm(\mathbf{a}_0^0-\mathbf{a}_n^0)$, $n=1$ to 5, $n_3=5$; (S4), the upper and lower horizontal "ring" edges, $\pm(\mathbf{a}_n^0-\mathbf{a}_{\langle n+1\rangle}^0)$, $n=1$ to 5, $n_4=5$; (S5), the "waist" edges, $\pm[\mathbf{a}_n^0-(-\mathbf{a}_{\langle n+3\rangle}^0)]$, $n=1$ to 5, $n_4=5$. There are altogether 42 vectors (thirty edges and twelve vertex vectors).

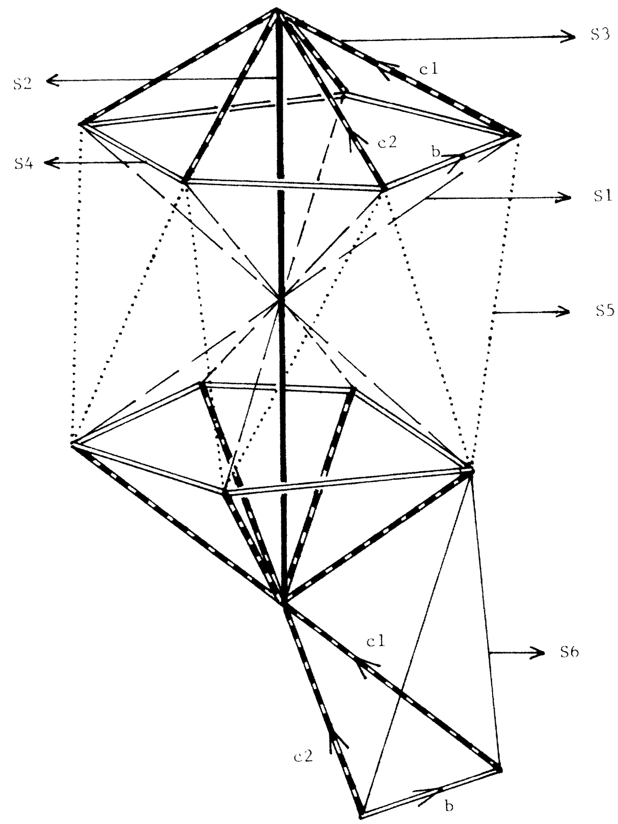

FIG. 1. The vertex and edge vectors of an icosahedron are separated into five sets S1 to S5, represented by five different kinds of straight lines. S6 is the mirror image of S5. (Not all S6 vectors are shown). The cap vectors c1 and c2 in S3 and the ring vector b in S4 are repeated at the bottrom of the figure to show the additional triangles formed by the S6 waist vectors.

With these two sets of vectors, icosahedral symmetry implies two amplitudes, one for the vertex set $\{S1+S2\}$, and another for the edge set $\{S3+S4+S5\}$.

One can form a PB analog of the above set of vectors by replacing the $\mathbf{a}_n^0$'s by the $\mathbf{a}_n$'s. Immediately, one notices that the sets of umbrella vectors S1 and cap vectors S3 are mirror images of each other about the xy plane, while the sets of backbone vectors S1 and ring vectors S4 are mirror images of themselves. The waist vectors S5, however, are without a mirror image. In order to restore the mirror symmetry, one must include the image of S5, denoted as S6, which can be expressed as the differences between the upper and lower cap vectors. There are ten vectors in S6, $2n_6=10$. The total number of vectors is now increased from 42 to 52, as compared with the icosahedral structure. This set S6, when included, can generate additional triangles through the combinations of two S6 waist vectors and one S4 ring vector, as well as one S6 vector and two S3 cap vectors (see Fig. 1).

These six sets of vectors demand four different amplitudes ζ_i ($i=1$ to 4), one for each of the following sets: $Y1 \equiv \{S1+S3\}$, $Y2=\{S2\}$, $Y3\equiv\{S4\}$, and $Y4 \equiv \{S5+S6\}$. Taking the "trial" density to be $\rho(\mathbf{r}) = \sum_j \sum_{v_j} \zeta_j e^{ik\mathbf{v}_j\cdot\mathbf{r}}$, $j=1$ to 4, with $\mathbf{v}_j$ in Y_j, and k the length scale of the wave vectors, I have found that the energy barrier of the PB structure is lower than that of the bcc for $y<74.48$ with optimum values $\cos\alpha = 0.4981$ and $k/q_0=0.9948$. Moreover, the PB barrier is lower than the icosahedral one[3] for all values of y where the icosahedral barrier is lower than that of the bcc.

That the crossover value of y of the PB structure (to bcc) is greater than that of the icosahedral structure may well be due to the truncation in the density waves in (1), or it may be a peculiar property of the model of Kalugin, Kitaev, and Levitov.[3] However, the present results certainly suggest that the two structures will be competitive with each other, so that more sophisticated energy calculations ought to take the PB structure into consideration to be complete.

Next, I consider the quasilattice of the PB quasicrystals. In this case, a generalization of the projection method is necessary to incorporate the mirror symmetry of the PB structure. An application of the method below shows that all points of the PB lattice lie on a set of equally spaced lattice planes with a spacing equal to one half of the period. This periodic stacking of alternating layers also implies an alternating layer structure in the diffraction pattern, which is observed in experiments.[7]

Scheme of projection.—Given any primary set $\{\mathbf{k}_n, n=0 \text{ to } 5\}$ that spans the 3D physical k space, one can find a set of 3D vectors $\{\mathbf{q}_n, n=0 \text{ to } 5\}$ in an orthogonal k space, so that the direct sums $\mathbf{k}_n \oplus \mathbf{q}_n$ form a basis in a 6D k space. This 6D basis also determines a basis $\{\mathbf{A}_n \oplus \mathbf{B}_n\}$ in a 6D real space (which is a direct sum of the 3D real space and a 3D orthogonal space) through the completeness relation

$$\sum_{n=0}^{5} (\mathbf{A}_n \oplus \mathbf{B}_n)^{\mu} (\mathbf{k}_n \oplus \mathbf{q}_n)^{\nu} = 2\pi\delta^{\mu\nu}, \tag{5}$$

where μ and ν denote the six directions in the 6D real space. In terms of the 3×3 block components, this matrix equation becomes

$$\sum_{n=0}^{5} (A_n)^i (k_n)^j = \sum_{n=0}^{5} (B_n)^i (q_n)^j = 2\pi\delta^{ij}, \tag{6}$$

$$\sum_{n=0}^{5} (A_n)^i (q_n)^j = \sum_{n=0}^{5} (B_n)^i (k_n)^j = 0, \tag{7}$$

where i,j denote the x, y, and z directions. The lattice vectors of this 6D real-space lattice are $A_\tau \oplus B_\tau$, where $\mathbf{A}_\tau = \sum_{n=0}^{5} \tau_n \mathbf{A}_n$, $\mathbf{B}_\tau = \sum_{n=0}^{5} \tau_n \mathbf{B}_n$, $\tau \equiv [\tau_0, \tau_1, \ldots, \tau_5]$, τ_n integers.

A quasilattice is defined as the projection onto the 3D real space of those 6D lattice points which lie inside a specified region in the orthogonal space,

$$\rho_{\rm ql}(\mathbf{r}) = \sum\nolimits_\tau \delta(\mathbf{r}-\mathbf{A}_\tau) f(\mathbf{B}_\tau), \tag{8}$$

where f, referred to as the "acceptance" function, is 1 or 0 depending on whether $\mathbf{B}_\tau$ lies inside or outside the specified region in the orthogonal space. Equation (8) can be rewritten as

$$\rho_{\rm ql}(\mathbf{r}) = \sum\nolimits_\lambda \int d^3r' f(\mathbf{r}') \exp(i\mathbf{k}_\lambda\cdot\mathbf{r} + i\mathbf{q}_\lambda\cdot\mathbf{r}'), \tag{9}$$

which is of the form (1) with the identification

$$\psi_\lambda = \int d^3r\, f(\mathbf{r}) \exp(i\mathbf{q}_\lambda\cdot\mathbf{r}) \equiv \tilde{f}(\mathbf{q}_\lambda). \tag{10}$$

As we shall see below, the translational and mirror symmetry of the PB structure imposes stingy constraints on its acceptance function.

Choosing the real-space vectors $\{A_n\}$ for the PB structure.—As seen from the preceding Section, the choice of $\{\mathbf{q}_n\}$ is not unique. For the icosahedral quasicrystal, $\mathbf{k}_n^0 = k\mathbf{a}_n^0$, it has been shown[4] that the 6D vectors $\mathbf{k}_n^0 \oplus \mathbf{q}_n^0$ will be proportional to an orthonormal set if $\{\mathbf{q}_n^0\}$ are chosen to be $\mathbf{q}_0^0 = -\mathbf{k}_0^0$, $\mathbf{q}_n^0 = \mathbf{k}_{\langle 2n\rangle}^0$, where $\langle\ \rangle$ means modulo 5. Equation (8) then implies $\mathbf{A}_n^0 = (2\pi/k)(\mathbf{a}_n^0/2)$, and $\mathbf{B}_0^0 = -\mathbf{A}_0^0$, $\mathbf{B}_n^0 = \mathbf{A}_{\langle 2n\rangle}^0$.

For the PB set, (3), the choice of $\{q_n\}$ is again not unique. As a natural generalization of the icosahedral case, I choose

$$\mathbf{q}_0 = -\mathbf{k}_0, \quad \mathbf{q}_n = \mathbf{k}_{\langle 2n\rangle}, \quad n=1 \text{ to } 5. \tag{11}$$

Equation (8) then implies

$$\mathbf{A}_0 = (2\pi/4k\cos\alpha)\hat{\mathbf{z}} = (\Gamma/4)\hat{\mathbf{z}}, \tag{12}$$

$$\mathbf{A}_n = \tfrac{2}{5}(\Gamma/4)(\hat{\mathbf{z}} + 4\cot\alpha R^n\hat{\mathbf{x}}), \quad n=1 \text{ to } 5, \tag{13}$$

and $\mathbf{B}_0 = -\mathbf{A}_0$, $\mathbf{B}_n = \mathbf{A}_{\langle 2n\rangle}$.

Symmetry constraints on f.—As seen from Eq. (8), to generate a quasilattice, one needs both the 6D lattice $\mathbf{A}_\tau \oplus \mathbf{B}_\tau$ and the function f. Since the magnitudes $|\psi_\lambda|$ must be the same for all $\mathbf{k}_\lambda$'s that are related by symmetry operations, f in (10) must have a functional form to preserve this symmetry. In the icosahedral case, this symmetry is guaranteed by choosing f to have icosahedral symmetry. In Ref. 4, f is taken as a triacontahedron $\sum_{n=0}^{5} x_n \mathbf{B}_n^0$, $0<x_n<1$, with a diameter $\hat{\mathbf{z}}\cdot(-\mathbf{B}_0^0 + \sum_{n=1}^{5}\mathbf{B}_n^0)$.

From the icosahedral quasilattice, one can generate a periodic quasilattice by replacing all the icosahedral lattice vectors $\sum_{n=0}^{5}\lambda_n\mathbf{A}_n^0$ by their PB analog $\sum_{n=0}^{5}\lambda_n\mathbf{A}_n$ [with $\mathbf{A}_n$ given by (12) and (13)]. This amounts to projecting the 6D oblique lattice $\mathbf{A}_\tau \oplus \mathbf{B}_\tau$ with an acceptance function f which is a distorted triacontahedron, i.e., one that is generated by $\{\mathbf{B}_n\}$ instead of $\{\mathbf{B}_n^0\}$. In fact, f has a simpler form. Since $\hat{\mathbf{z}}\cdot\mathbf{B}_\tau$ is an integer multiple of $\Gamma/20$ [as seen from $\hat{\mathbf{z}}\cdot\mathbf{B}_\tau = (-\tau_0 + \frac{2}{5}\sum_n \tau_n)\mathbf{A}_0$ and $A_0 = \Gamma/4$], the orthogonal vectors $\mathbf{B}_\tau$ all lie on a set of disks which are the intersections between the distorted triacontahedron and a set of equally spaced planes perpendicular to the z axis and with a spacing $\Gamma/20$. Since $\hat{\mathbf{z}}$ is a fivefold axis, all disks have pentagonal symmetry. Moreover, the diameter of the distorted triacontahedron is $\hat{\mathbf{z}}\cdot(-\mathbf{B}_0+\sum_{n=1}^5\mathbf{B}_n)=3A_0=3\Gamma/4$, and there are fifteen such disks. The function f is therefore of the form

$$f(\mathbf{r})=\sum\nolimits_m \delta(z-\Gamma m/20)f_m(x,y), \tag{14}$$

where m is an integer labeling the disks. The amplitude ψ_λ is, by (10),

$$\psi_\lambda=\sum\nolimits_m \exp(iq_\lambda^z\Gamma m/20)\tilde{f}_m(q_\lambda^\perp), \tag{15}$$

where $\tilde{f}_m$ is the Fourier transform of f_m.

This is probably the simplest way to generate a periodic quasilattice from the icosahedral one. However, the diffraction pattern of this periodic quasilattice *does not have* a plane of mirror symmetry and is therefore *not* appropriate for the decagonal phase. To see this, and to understand the proper way to restore the mirror symmetry, we note that if $\mathbf{k}_\lambda$ and $\mathbf{k}_{\lambda'}$ as generated by (3) are mirror images, the corresponding $\mathbf{q}_\lambda$ and $\mathbf{q}_{\lambda'}$ need not be; though it is always true that $\mathbf{q}_\lambda-\mathbf{q}_{\lambda'}$ is an integer multiple of $\mathbf{k}_0$. [For example, while the vectors $\mathbf{k}_1$ and $-\mathbf{k}_0+\mathbf{k}_1$ are mirror images, the vectors $\mathbf{q}_1(=\mathbf{k}_2)$ and $-\mathbf{q}_0+\mathbf{q}_1(=\mathbf{k}_0+\mathbf{k}_2)$ are not.] The amplitude ψ_λ is therefore (15) with an additional phase factor $\exp(isk_0\Gamma m/20)=\exp(i4\pi sm/20)$ in the sum, where s is an integer depending on the λ's. In order to satisfy the symmetry constraint $|\psi_\lambda|=|\psi_{\lambda'}|$, we must have $m=10p$, p integer, and

$$f(\mathbf{r})=\sum\nolimits_p \delta(z-\Gamma p/2)f_p(x,y). \tag{16}$$

Thus, the mirror symmetry eliminates many of the acceptance disks. (Only two disks in the distorted triacontahedron are kept.) The resulting PB quasilattice cannot be obtainable from the icosahedral one by small distortions.

The layer structure of the lattice and the diffraction.— By (8) and (16), a lattice vector $\mathbf{A}_\tau$ must have an orthogonal partner $\mathbf{B}_\tau$ satisfying $(\Gamma/2)p=\hat{\mathbf{z}}\cdot\mathbf{B}_\tau=(-\tau_0+\frac{2}{5}\sum_{n=1}\tau_n)A_0$. Since $A_0=\Gamma/4$, we have $2\sum_{n=1}^5\tau_n=5(\tau_0+2p)$, which can only be satisfied for $\tau_0=2\mu$, $\sum_{n=1}^5\tau_n=5(\mu+p)$, μ integer. We then have

$$\hat{\mathbf{z}}\cdot\mathbf{A}_\tau=A_0(\tau_0+\tfrac{2}{5}\sum\nolimits_{n=1}\tau_n)=\tfrac{1}{4}\Gamma(2\tau_0+2p)=\Gamma(\mu+\tfrac{1}{2}p).$$

The lattice points are therefore confined to a set of planes perpendicular to the z axis separated by half the period.

The diffraction pattern can be obtained from (10) and (16), which implies

$$\psi_\lambda=\sum\nolimits_{p(\mathrm{even})}\tilde{f}_p(k_\lambda^\perp)+\exp(i2\pi k_\lambda^z/k_0)\sum\nolimits_{p(\mathrm{odd})}\tilde{f}_p(k_\lambda^\perp), \tag{17}$$

where the relations $q_\lambda^\perp=k_\lambda^\perp$ and $\exp(i2\pi k_\lambda^z/k_0)=\exp(i\pi\sum_{n=1}^5\lambda_n)$ have been used. Since $\hat{\mathbf{z}}\cdot\mathbf{k}_\lambda$ is an integer multiple of $k_0/2$, ψ_λ alternates between two different values. The diffraction pattern along an axis in the xy plane will therefore have an alternative layer structure. In the decagonal phase, there is in fact a prominent alternating layer structure in the diffraction pattern along one of its two sets of twofold axes.[6,7]

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