Indexing of icosahedral quasiperiodic crystals

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Since the definition of quasiperiodicity is intimately connected to the indexing of a Fourier transform, for the case of an icosahedral solid, the step necessary to prove, using diffraction, that an object is quasiperiodic, is described. Various coordinate systems are discussed and reasons are given for choosing one aligned with a set of three orthogonal two-fold axes. Based on this coordinate system, the main crystallographic projections are presented and several analyzed single-crystal electron diffraction patterns are demonstrated. The extinction rules for three of the five icosahedral Bravais quasilattices are compared, and some simple relationships with the six-dimensional cut and projection crystallography are derived. This analysis leads to a simple application for indexing powder diffraction patterns.

I. INTRODUCTION

The recent discovery of Shechtmanite,[1,2] a metallic phase with long-range icosahedral orientational symmetry and experimentally discrete diffraction patterns, has revealed a new class of ordered structures. The icosahedral symmetry is inconsistent with strict crystallographic periodicity, yet discrete diffraction implies quasiperiodicity. Schechtmanite is thus cited as an example of a quasiperiodic crystal or quasicrystal, for short. Since the two icosahedral groups are not part of the 32 crystallographic point groups, the possibility exists that any of the infinity of noncrystallographic point groups will be observed. Indeed, claims that specimens exhibiting two other point groups, decagonal 10/m (Ref. 3) and duodecagonal 12 (Ref. 4), have since been reported.

These quasicrystalline phases present challenging problems in crystallography. In this paper the mundane housekeeping problems of coordinate systems, indexing, and extinction rules that are the essential language of reporting experimental observations will be discussed. Indexing is not just a housekeeping procedure: it is an essential part of proving that a structure is periodic, quasiperiodic, or almost periodic. We will concentrate on the icosahedral phases and the three-dimensional aspects of descriptions that are most easily derived in higher dimensions.

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II. QUASIPERIODICITY

The Fourier transform of a periodic function is a set of delta functions that are periodically spaced and, in general, vary in magnitude. Diffraction gives information in the form of a Fourier transform of the correlations of an object. If the object is a periodic crystal, the diffraction pattern is a discrete set of spots of varying intensity that are positioned on a reciprocal lattice. Three reciprocal lattice vectors form a basis to locate any spot in a three-dimensional reciprocal space.

A mathematical function is quasiperiodic by definition if its Fourier transform is a set of delta functions that are not uniformly spaced as they would be for a periodic function, but whose spacing can be described by a finite set of lengths.[5] If an infinite number of lengths are required the function is called almost periodic. Therefore specimens that give countable diffraction spots that cannot be indexed with three reciprocal lattice vectors are quasiperiodic if they can be indexed with a finite set.

It has been shown that any D-dimensional quasiperiodic function requiring a basis of N vectors can be considered to be derived from a periodic N-dimensional function cut by a D-dimensional plane.[5] If every spot in the diffraction pattern can be indexed using a combination of N reciprocal lattice vectors, then the object that gave this diffraction pattern can be represented by a cut of a N-dimensional periodic object.

The icosahedral point group is not consistent with translational periodicity. The icosahedral diffraction pattern cannot consist of periodically spaced spots. If

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the diffraction pattern consists of discrete spots that can be indexed by a finite number of basis vectors it is quasiperiodic.

Several papers have already discussed ways of deriving quasiperiodic structures from cuts of periodic higher dimensional structures[6–10] including icosahedral structures. The converse problem of taking a particular diffraction pattern and indexing it has been attempted[11] in a way that has been criticized.[12,13] The problem centers on the fact that with a combination of incommensurate lengths any spot can be located approximately with any desired degree of accuracy. We will show that with our indexing, the observed high-intensity spots form a simple sequence in which none are missing and none left out.

III. COORDINATE SYSTEMS

Taking basis vectors along important symmetry directions simplifies the crystallographic formulation. For any group with a unique rotation axis, the z axis is taken parallel to that axis. This is the proper choice for the crystallographic groups such as hexagonal and the noncrystallographic groups such as decagonal. The icosahedral groups have 6 fivefold axes, 10 threefold axes, and 15 twofold axes. Taking one of the fivefold axes as the z axis (Fig. 1) leaves the other five in a ring 63.43° from this axis. Although these all would make acute angles with the z axis, there are obtuse angles between some of them. There is no choice of sign for the six axes that would give equal angles between all of them. A co-

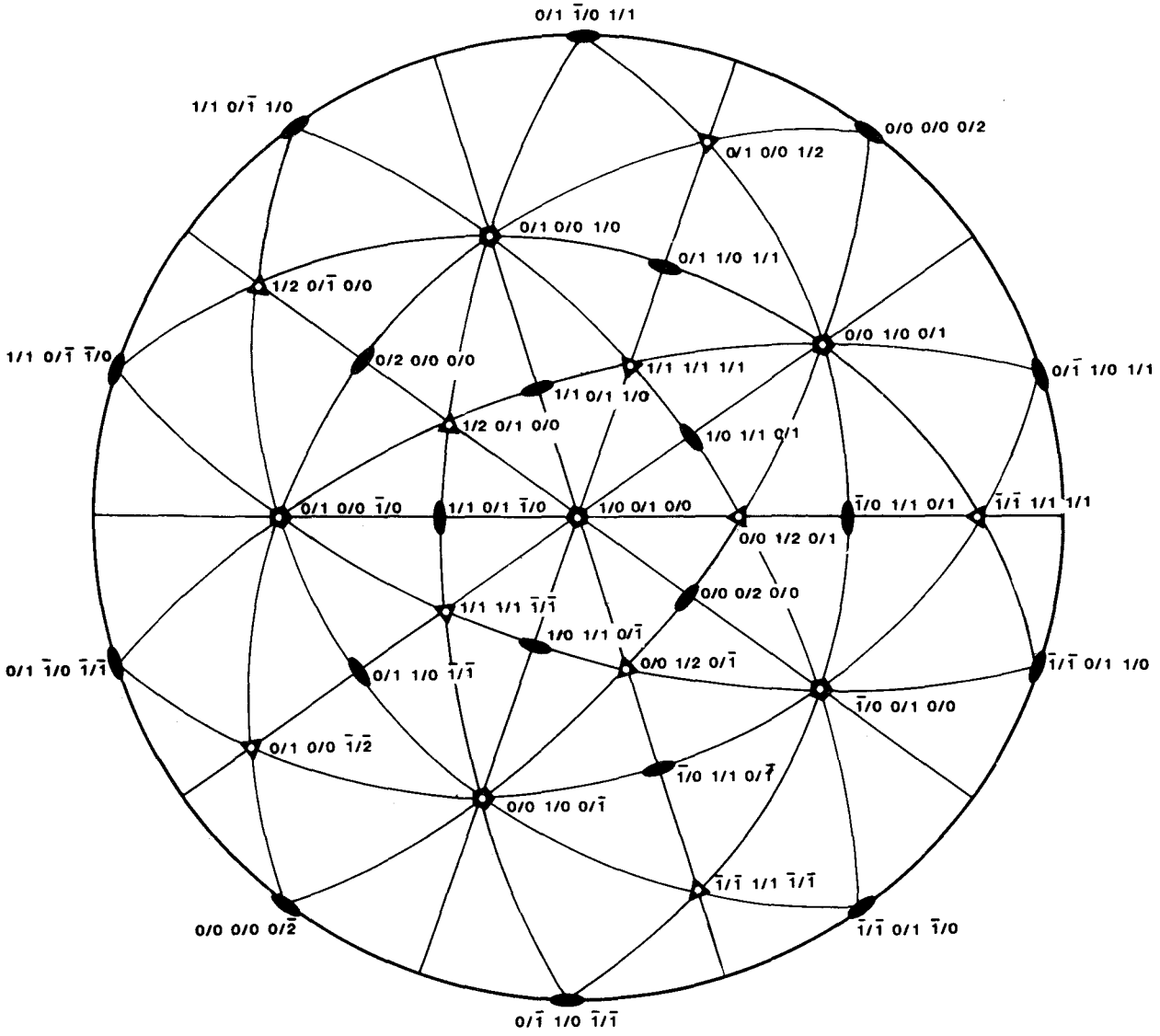

FIG. 1. The stereographic projection of the principal symmetry directions and mirror planes of the icosahedral group $m\bar{3}\bar{5}$ as seen along the fivefold direction. The number indicates the indexing system that will be described later in the text.

ordinate system based on these axes is not only skewed but encounters the difficulty of keeping track of obtuse and acute angles. There are right angles between a fivefold axis and five of the twofold axes, that could serve as a coordinate system when comparing the icosahedral phase with the decagonal phase.

If we examine the icosahedral group with a threefold axis along z (Fig. 2), we have three choices of coordinate systems that are related to familiar crystallographic ones. The 6 fivefold axes now fall into two groups, either of which could be used as a rhombohedral basis. In one set the fivefold axes make acute angles with each other. In the other set the angles are obtuse. A hexagonal coordinate system could be based on the threefold axis and the three twofold axes at right angles to it. Of special interest are the three twofold axes at 71° from z that form an orthogonal set.

The simplest system is a cubic coordinate system in which the axes of the coordinate system are aligned with a set of three orthogonal twofold axes of the icosahedral group (Fig. 3). The 15 twofold axes fall in five such sets all equivalent to each other through the operation of a fivefold axis. This is the coordinate system used in the International Tables of Crystallography, and it is the coordinate system we will use, even to describe the other coordinate systems. It has all advantages of orthogonal axes.

The three coordinate systems discussed here are all based on subgroups of the icosahedral group, as shown in Fig. 4. Using a coordinate system based on a lower symmetry than icosahedral, requires special attention for the icosahedral symmetries not used in that coordinate system: equivalent reflections will not necessarily have similar indices.

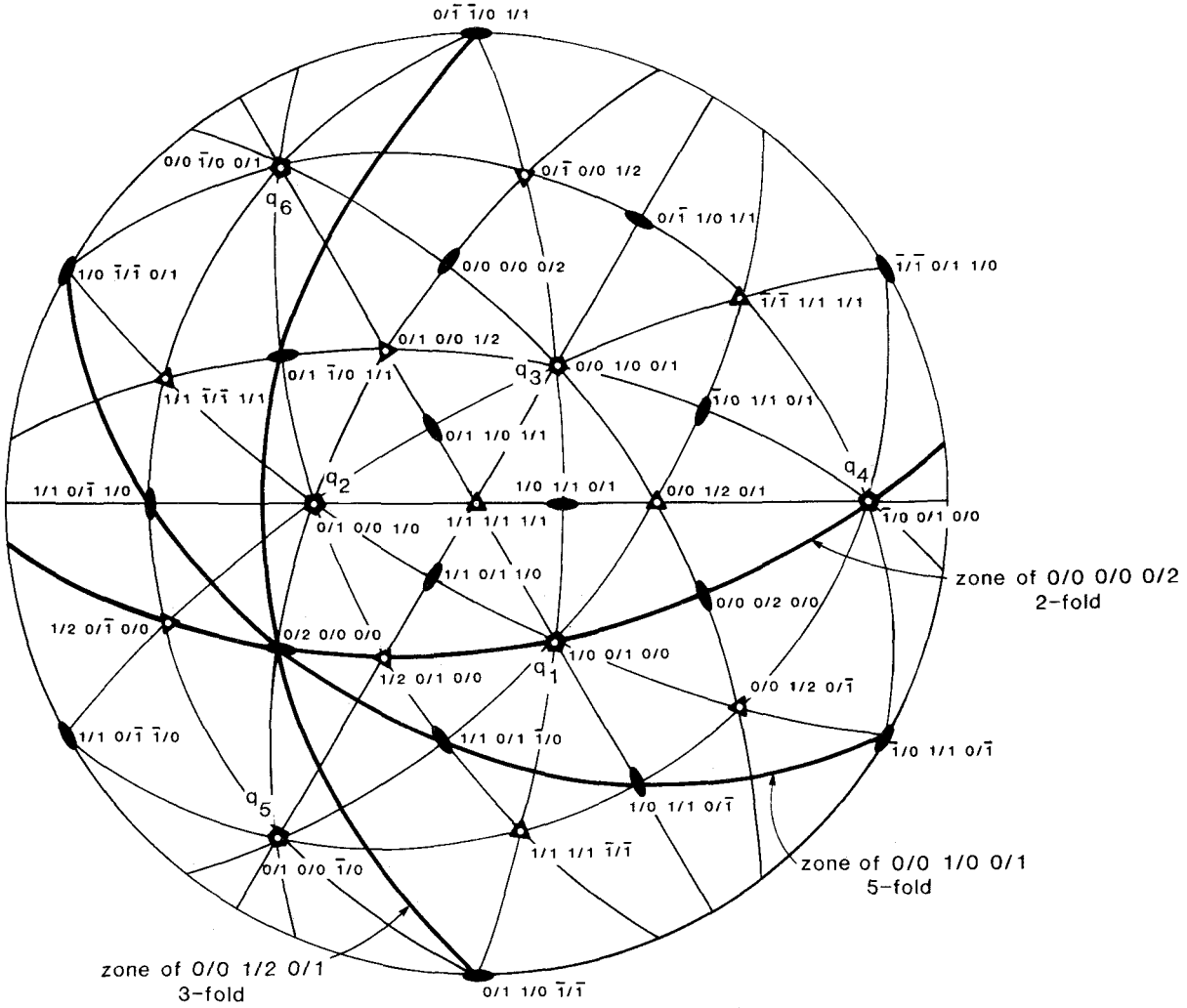

FIG. 2. The stereographic projection of the icosahedral group $m35$ as seen along a threefold direction. Note the possibility of a rhombohedral coordinate system using either set of fivefold axes, a hexagonal coordinate system using the twofold axes along the equator or the three twofold axes at 71°. The thickened great circles show the three zone axes of the diffraction pattern indexed in Figs. 5–7, namely the twofold labeled [0/0 1/0 0/1], the fivefold labeled [0/0 1/0 0/1] and the threefold axis labeled [0/0 1/2 0/1].

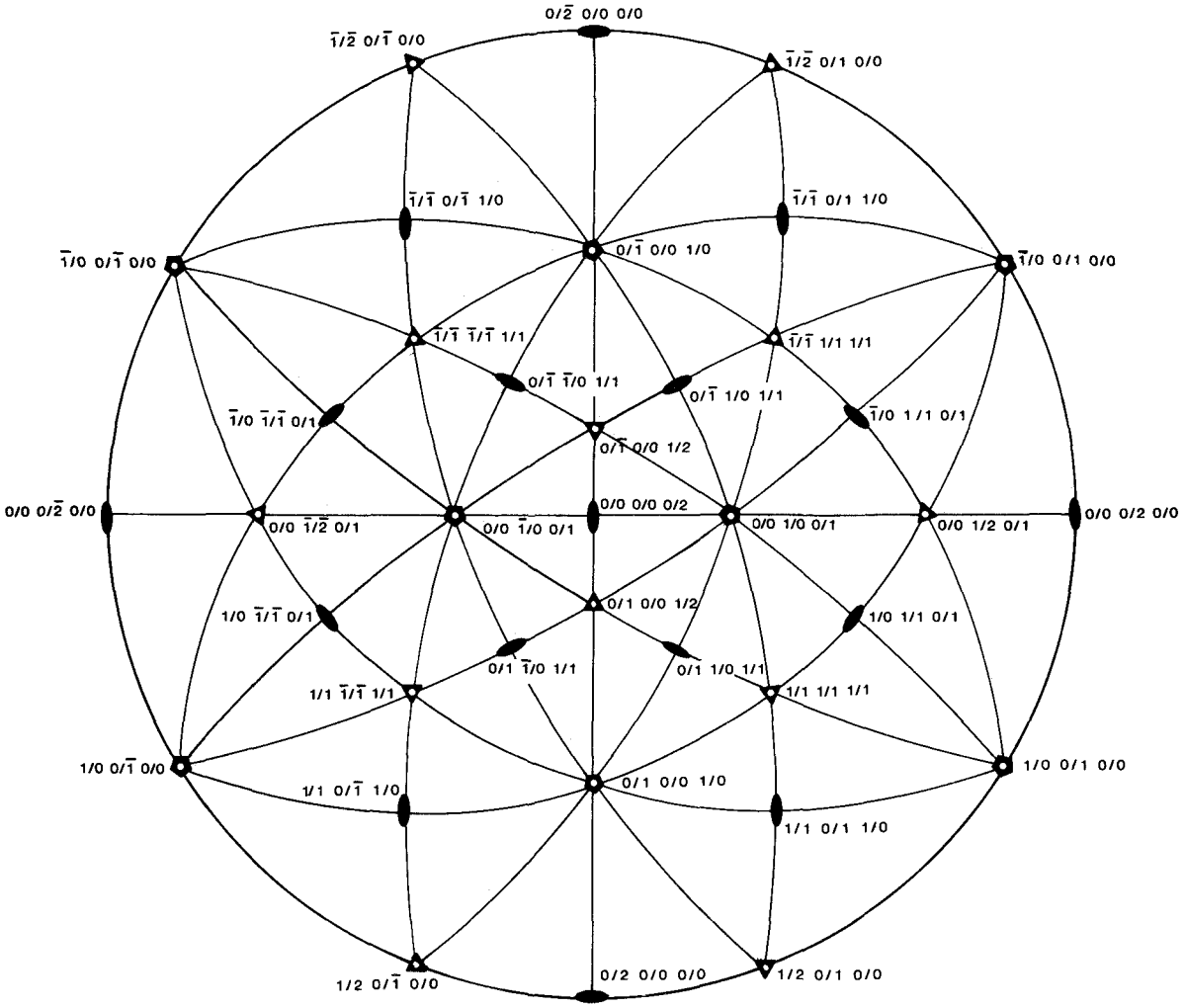

FIG. 3. The standard stereographic projection for the icosahedral group aligns the axes of an orthogonal coordinate system with one of the five sets of mutually perpendicular twofold axes. Note that four of the threefold axes are along the ⟨111⟩ directions.

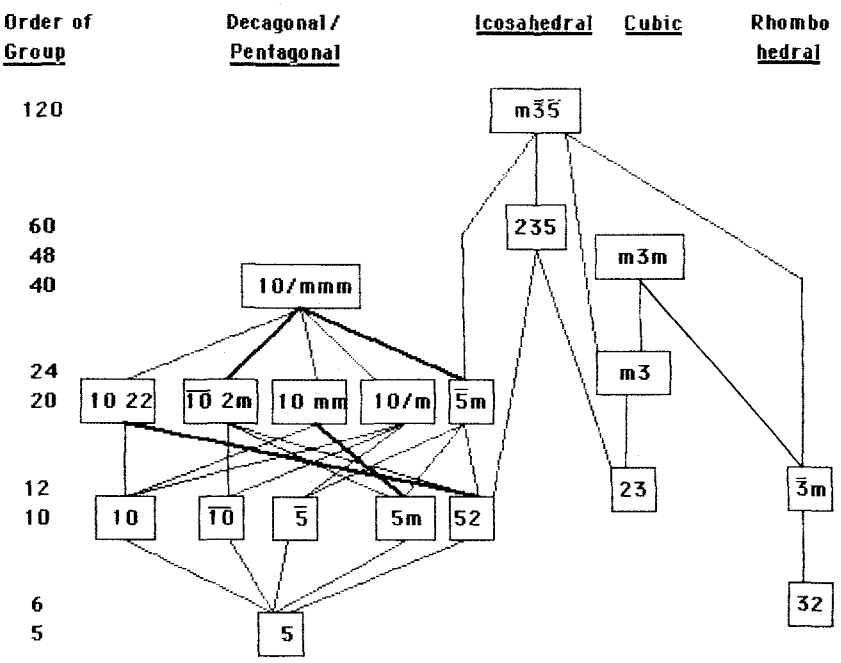

FIG. 4. The maximal subgroups of the icosahedral group $m\bar{3}\bar{5}$ and the decagonal group $10/mmm$.

IV. THE CUBIC COORDINATE SYSTEM

Having selected a coordinate system aligned along three perpendicular twofold axes, we need to describe vectors and planes in both the direct and reciprocal spaces. An immediate advantage of the choice of a cubic coordinate system is that the indices of a plane and the direction normal to it are the same. We define unit lengths a and a^* in both spaces and dimensionless lengths and position in terms of these. Consider a position (UVW) or a plane (HKL). The set of all positions or planes equivalent through the operations of the icosahedral groups (235) and $m\bar{3}\bar{5}$ is as follows:

1. The threefold axes give cyclic permutation, but note that while (UVW), (WUV), and (VWU) are equivalent, (VUW), etc., is different.

2. The twofold axes give pairs of sign changes, the mirrors give individual sign changes. Thus for 235, (UVW), $(\bar{U}\bar{V}W)$, $(U\bar{V}\bar{W})$, and $(\bar{U}V\bar{W})$ are equivalent but $(\bar{U}\bar{V}\bar{W})$, etc., is not. For $m\bar{3}\bar{5}$ all sign changes are equivalent positions.

3. The fivefold axes introduce a change of the magnitude of U, V, and W and introduce the golden section $\tau = 2\cos 36° = (1+\sqrt{5})/2 = 1.618\,034$. Because the International Tables have a misprint in the rotation matrices, we repeat them here in Table I, using their notation $G = \tau/2, g = 1/2\tau = G - 1/2$. Performing the matrix multiplication we obtain

$$\begin{aligned}(HKL)Y &= \tfrac{1}{2}[(H-K)+\tau(K-L),\\ &\quad (L-H)+\tau(H+K),\\ &\quad -(K+L)+\tau(L+H)].\end{aligned} \tag{1}$$

In this multiplication we make frequent use of the identities

$$\tau^2 = 1+\tau, \tag{2}$$

$$1/\tau = \tau - 1, \tag{3}$$

$$G^2 + g^2 + (\tfrac{1}{2})^2 = 1. \tag{4}$$

It may at first seem surprising that equivalent positions turn out to have designations with different numerical values of the components, but this is unavoidable with a Cartesian coordinate system and groups with such a high symmetry. The most symmetric crystallographic group $m\bar{3}m$ has order 48. It has 48 unit triangles. Taking all the permutations and sign changes of (UVW) generates 48 equivalent general positions, one in each unit triangle. It is impossible to generate the 60 or 120 equivalent positions needed (resp. for 235 or $m\bar{3}\bar{5}$) with just three symbols. Thus, the choice of a cubic coordinate system results in the possibility that as many as five different sets of indices may be necessary to represent equivalent positions or planes.

Now consider a plane or reciprocal space position with an index of the form

$$(h+h'\tau, k+k'\tau, l+l'\tau),$$

that is, where

$$H = h+h'\tau, \quad K = k+k'\tau, \quad L = l+l'\tau,$$

in which the h, h', k, k', l, and l' are all integers. We introduce the six-index notation $(h/h',\ k/k',\ l/l')$ or $(h/h'\ k/k'\ l/l')$ to designate such a reflection.

Operation of the fivefold rotation will change the numerical value of the six integers.

$$\begin{aligned}&(h+h'\tau, k+k'\tau, l+l'\tau)Y\\ &\quad = \tfrac{1}{2}[(h+k')-(k+l')\\ &\qquad +\tau[(-l+h')+(k-l')],\\ &\quad (-h+k')+(l+h')\\ &\qquad +\tau[(h+k')+(k+l')],\\ &\quad (-k+l')+(l+h')\\ &\qquad +\tau[(h-k')+(l+h')]].\end{aligned} \tag{5}$$

In order for this to be a close set, we impose the parity conditions that the three sums $h+k', k+l'$, and $l+h'$ are even: after fivefold rotation the six integer indices remain integers and the parity rules are conserved.

TABLE I. Matrices for fivefold rotation about $[1\ \tau\ 0]$.

$$Y = Y^{-4} = \begin{pmatrix} \frac{1}{2} & g & G \\ g & G & -\frac{1}{2} \\ G & \frac{1}{2} & g \end{pmatrix} \qquad Y^2 = Y^{-3} = \begin{pmatrix} -g & G & \frac{1}{2} \\ G & \frac{1}{2} & -g \\ -\frac{1}{2} & g & -G \end{pmatrix}$$

$$Y^3 = Y^{-2} = \begin{pmatrix} -g & G & -\frac{1}{2} \\ G & \frac{1}{2} & g \\ \frac{1}{2} & -g & -G \end{pmatrix} \qquad Y^4 = Y^{-1} = \begin{pmatrix} \frac{1}{2} & g & -G \\ g & G & \frac{1}{2} \\ G & -\frac{1}{2} & g \end{pmatrix}$$

$G = (\sqrt{5}+1)/4 = \tau/2 = \cos 36° = 0.809017$

$g = (\sqrt{5}-1)/4 = 1/2\tau = G - \frac{1}{2} = \cos 72° = 0.309017$

$Y^T = Y^{-1}$

Finding that all spots in the diffraction pattern are of this form implies quasiperiodicity.

We next turn to the indexing of the principal directions (Figs. 1–3). The six fivefold axes are all of the form $(1\tau 0)$, or in the six-index notation (1/0 0/1 0/0).

The ten threefold axes have two different designations: four are along (111) or (1/0 1/0 1/0) and six along $(\tau^2\ 1\ 0)$ or (1/1 1/0 0/0). Note that both vectors have been chosen to have a length $\sqrt{3}$.

Three of the twofold axes are along the cube axes. The remaining 12 have the form $(G, g, \frac{1}{2})$ or $(0/1\ \bar{1}/1\ 1/0)$.

V. RECIPROCAL QUASILATTICES

Consider a quasilattice in three-dimensional reciprocal space in which every spot occurs as a sum of integer multiples of a finite number (greater than three) of vectors. We will compare two lattices formed only of equivalent vectors. In particular, let us first take the six vectors along the fivefold axes,[14]

$$\mathbf{Q} = \sum_{i=1}^{6} n_i \mathbf{q}_i, \tag{6}$$

where the n_i are integers and the $\mathbf{q}_i$ are $(1\tau 0)$ which in the six-index notation is

$$\begin{aligned}
\mathbf{q}_1 &= (1/0\ 0/1\ 0/0),\\
\mathbf{q}_2 &= (0/1\ 0/0\ 1/0),\\
\mathbf{q}_3 &= (0/0\ 1/0\ 0/1),\\
\mathbf{q}_4 &= (\bar{1}/0\ 0/1\ 0/0),\\
\mathbf{q}_5 &= (0/1\ 0/0\ \bar{1}/0),\\
\mathbf{q}_6 &= (0/0\ \bar{1}/0\ 0/1).
\end{aligned} \tag{7}$$

[There are 384 ways for choosing the q_i's. All give equivalent results. The choice of the set (7) corresponds to the two rhombohedral bases: $\mathbf{q}_1$, $\mathbf{q}_2$, $\mathbf{q}_3$ define the acute rhombohedron and $\mathbf{q}_4$, $\mathbf{q}_5$, $\mathbf{q}_6$ the obtuse one (see Fig. 2).] The set of six numbers (n_i) can be considered an indexing of Q, and has been used in a number of papers. This same set can also be considered to be a six-dimensional lattice vector. To express Q in terms of the three-dimensional cubic coordinates we substitute set (7) in Eq. (6) and perform the summation,

$$\begin{aligned}
Q = [&(n_1 - n_4)/(n_2 + n_5),\ (n_3 - n_6)/(n_1 + n_4),\\
&(n_2 - n_5)/(n_3 + n_6)].
\end{aligned} \tag{8}$$

We can thus convert from the six-dimensional vector $(n_1, n_2, n_3, n_4, n_5, n_6)$ to the six-index three-dimensional vector $(h/h', k/k', l/l')$.

$$\begin{aligned}
h &= n_1 - n_4, \quad h' = n_2 + n_5,\\
k &= n_3 - n_6, \quad k' = n_1 + n_4,\\
l &= n_2 - n_5, \quad l' = n_3 + n_6,
\end{aligned} \tag{9a}$$

and vice versa

$$\begin{aligned}
2n_1 &= h + k', \quad 2n_4 = -h + k',\\
2n_2 &= l + h', \quad 2n_5 = -l + h',\\
2n_3 &= k + l', \quad 2n_6 = -k + l'.
\end{aligned} \tag{9b}$$

The form of Eq. (9b) demonstrates that Q in the six-index notation obeys the parity rules. These restrictions on the indices are extinction rules and are given in Table II under the heading of the P quasilattice (to be defined later).

These parity rules lead to four kinds of positions:

1. six even indices,
2. four even indices (odd/even, even/odd, even/even),
3. two even indices (even/odd, odd/even, odd/odd),
4. six odd indices.

If the coordinates of a spot (HKL) that is consistent with the parity rules are multiplied by τ, the results are

$$\begin{aligned}
(\tau H\ \tau K\ \tau L) = [&h'/(h + h'), k'/(k + k'),\\
&l'/(l + l')].
\end{aligned} \tag{10}$$

Only if the original $(HKL) = (h/h'\ \ k/k'\ \ l/l')$ contains two or six even indices, will $(\tau H\ \tau K\ \tau L)$ satisfy the parity rules. On the other hand, scaling by τ^3

$$\begin{aligned}
(\tau^3 H\ \tau^3 K\ \tau^3 L) = [&(h + 2h')/(2h + 3h'),\\
&(k + 2k')/(2k + 3k'),\\
&(l + 2l')/(2l + 3l')]
\end{aligned} \tag{11}$$

preserves the parity rules for all (HKL) that satisfy them. These scaling rules are tabulated for the primitive (P) reciprocal quasilattice in Table III.

In addition, the square of Q is of the form

$$Q^2 = N + M\tau, \tag{12}$$

where using Eqs. (2) and (3),

TABLE II. Extinction rules for reciprocal quasilattices.

	$P(a^*)$	$F(2a^*)$ direct lattice is $I(a)$	$I(2a^*)$ direct lattice is $F(a)$
HKL	$h + k' = 2n$ $k + l' = 2n$ $l + h' = 2n$	same as P^* plus $h + k + l = 2n$ $(h' + k' + l' = 2n)$	all even plus $h + l + h' + k' = 4n$ $h + k + l' + k' = 4n$ $(l + k + h' + l' = 4n)$
n_i	all integers	$\Sigma n_i = 2n$	all even or all odd

TABLE III. Parity and scaling properties for the P and F reciprocal quasilattices.

Parity of indexes	Scaling	P	F	$Q^2 = N + \tau M$ N	M
six even	τ	Present	Present	$4n$	$4m$
four even	τ^3	Present	Absent	$4n+2$	$4m+1$
two even	τ	Present	Present	$4n$	$4m$
six odd	τ^3	Present	Absent	$4n+2$	$4m+1$

$$N = 2\sum_{i=1}^{6} n_i^2 = h^2 + h'^2 + k^2 + k'^2 + l^2 + l'^2, \quad (13)$$

$$M = h'^2 + k'^2 + l'^2 + 2(hh' + kk' + ll'). \quad (14)$$

Equation (13) indicates that N, the integer part of Q^2, is twice the square of the length of the six-dimensional n vector and therefore must be even. Because of the parity rules, if N is divisible by 4, M also is divisible by 4, and if N is not divisible by 4, M is of the form $4m+1$. In addition, as we will show later, M conforms to the limits

$$-N/\tau < M < N\tau \quad (15)$$

and that the most intense reflections occur for the largest value of M, which we shall denote by M_0. For N divisible by 4

$$M_0 = 4\,\mathrm{L}\,(N\tau)/4\,\mathrm{J}, \quad (16)$$

where $\mathrm{L}\,x\,\mathrm{J}$ is the largest integer in x.
When N is not divisible by 4,

$$M = 4m + 1 < N\tau.$$

The largest value of the integer m is

$$m_0 = \mathrm{L}\,(N\tau - 1)/4\,\mathrm{J}$$

and

$$M_0 = 1 + 4\,\mathrm{L}\,(N\tau - 1)/4\,\mathrm{J}. \quad (17)$$

We next define a two-parameter indexing $Q(N,r)$

$$Q^2(N,r) = N + M_0\tau - 4r\tau,$$
$$r = 0,1,\ldots < \mathrm{L}\,(N/\tau + M_0)/4\,\mathrm{J}, \quad (18)$$

in which the $Q_0(N)$ will turn out to define the sequence of intense reflections.

$$Q_0^2(N) = Q^2(N,0) = N + M_0(N)\tau. \quad (19)$$

The same procedure has been used by us to find the quasilattice formed from the 15 vectors along the twofold axes. The same result is obtained in a simpler manner by putting the face-centering restrictions F on the six-dimensional lattice formed by the n_i, and then using Eq. (9a). The result for that and for the body-centered I lattice are also given in Table II.

In Table III we make a simple comparison between the P and F which share the same parity rules. It can be seen that the F lattice scales by τ, and has only $N = 4n$, the P lattice comprises, in addition, $N = 4n+2$ spots that scale by τ^3. Figure 5 is a diffraction intensity calculation using the sphere approximation in the cut and projection method.[8,9]

VI. INDEXING THE SINGLE QUASICRYSTAL PATTERNS

Figures 6–8 show the indexing of the electron diffraction patterns of Refs. 1 and 2. The stereographic projection (Fig. 2) presents the three zone axes of these diffraction patterns, namely, the [0/0 0/0 0/2] twofold, the [0/0 1/0 0/1] fivefold, and the [0/0 1/2 0/1] threefold axes. Note that all of the reflections in the fivefold and threefold zone axis conform to either the P or F reciprocal quasilattices of Sec. V. These could not be used to distinguish between the two reciprocal quasilattices.

It is easy to show that the reflections for which $h' + k' + l'$ is odd will appear in neither the five- or

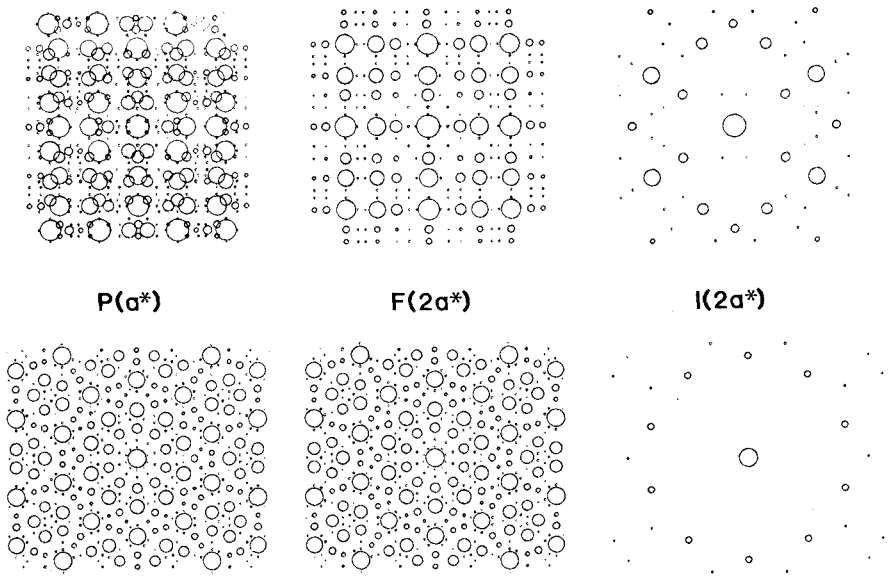

FIG. 5. Diffraction patterns calculated by the cut and projection method for all three reciprocal cubic quasilattices with the same lattice parameter a^* for the two- and fivefold zone axes.

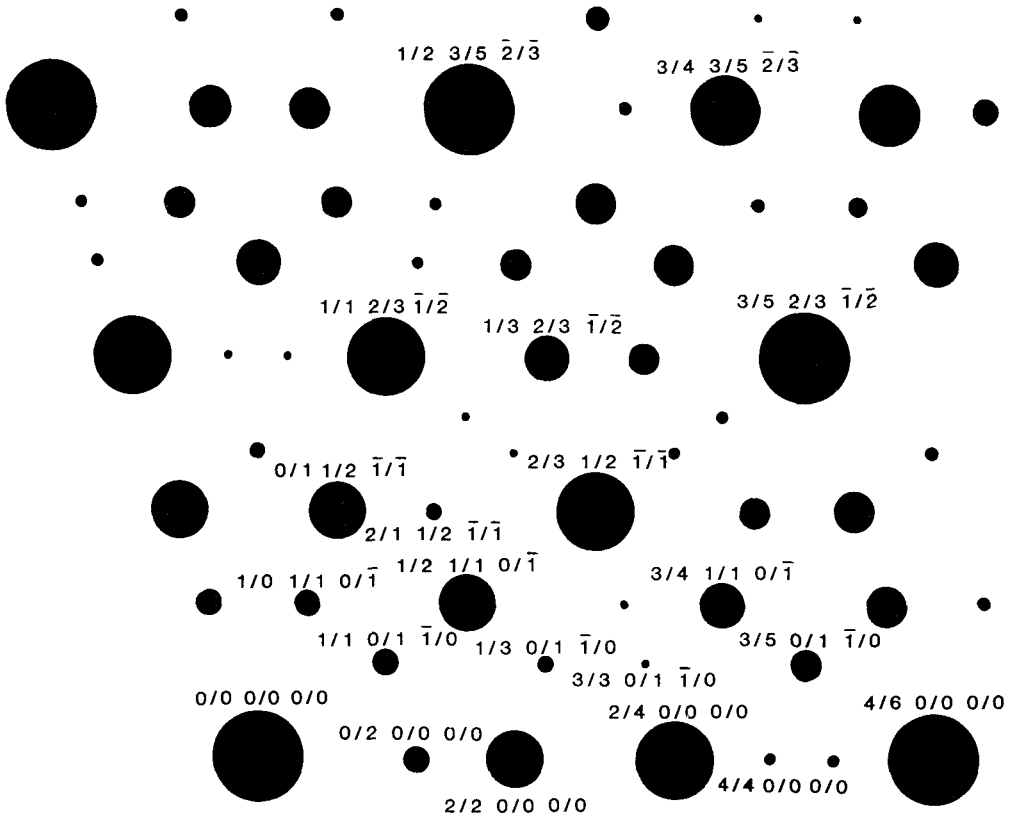

FIG. 6. Indexed diffraction pattern of a 108° sector of the [0/0 1/0 0/1] zone axis. Sizes of the circles represent calculated intensities based on the inverse of the distance of a spot in the six-dimensional primitive reciprocal lattice from the cut plane.

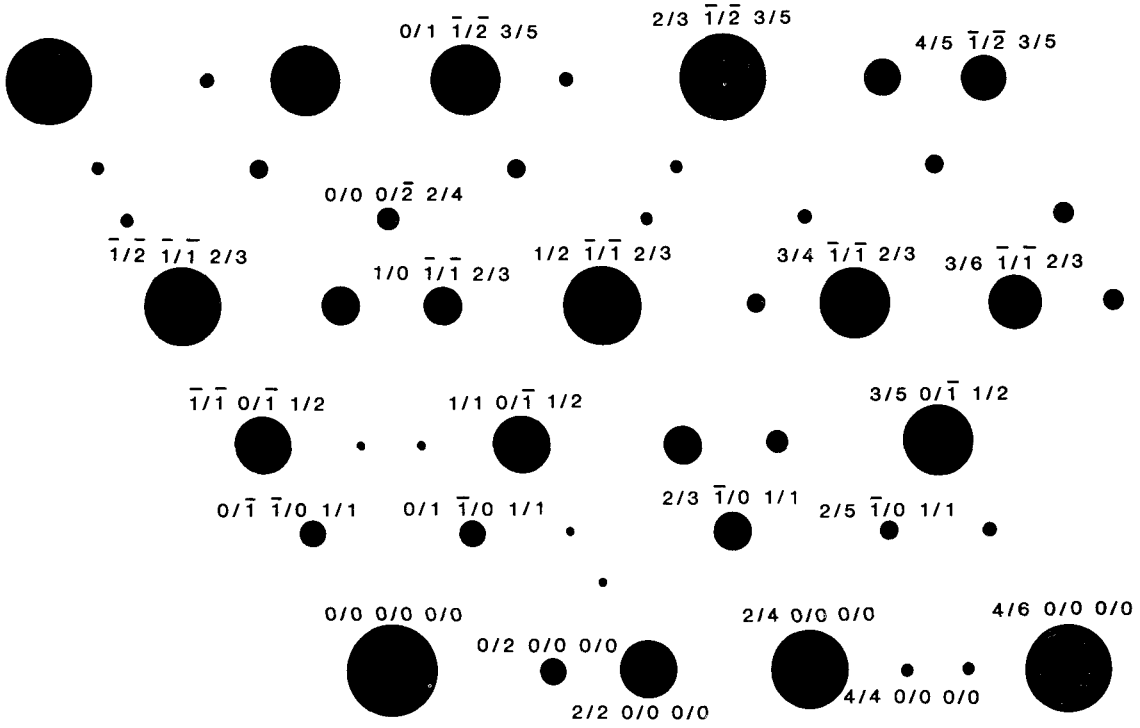

FIG. 7. Indexed diffraction pattern of a 120° sector of the [0/0 1/2 0/1] zone axis.

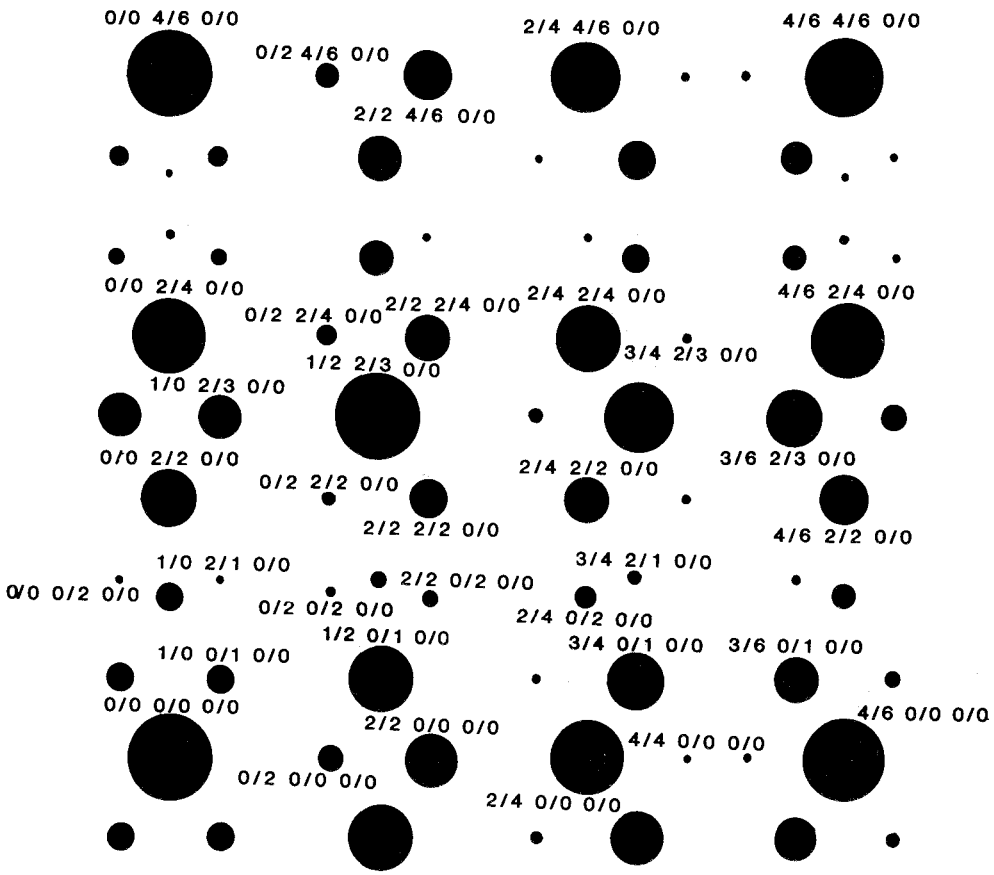

FIG. 8. Indexed diffraction pattern of the [0/0 0/0 0/2] zone axis. Note the square array made of all even and two-even spots that scale with τ. If only these spots were present, this pattern would have fourfold symmetry and scale by τ.

threefold zone axes. For example, in order for a reflection to be in the [0/0 1/0 0/1] zone axis $K + \tau L = 0$. This implies that $k + l' + \tau(k' + l + l') = 0$, which can only occur if $(k + l') = (k' + l + l') = 0$. Adding the even number $h' - l$ gives $h' + k' + l' = 2n$. The same result is obtained with the [111] zone axis. Fitting the two zone axes alone can not distinguish between P and F. Indeed the model of Levine and Steinhardt seems to fit only the three- or fivefold.[14] In the [0/0 0/0 0/2] zone axes $l = l' = 0$, but $h + k$ (and $h' + k'$) can be odd. This gives the spots with two odd indices, that can be seen in Fig. 7. Spots with six odd indices derive from these after some fivefold rotations. The twofold zone axes thus show some spots with τ^3 scaling.

The twofold zone axis for the F quasilattice show only spots with τ scaling and may show an accidental fourfold symmetry. Permutation of the x and y indices preserves the parity rules and does not change Q_c (see Sec. VII). If the intensity is only a function of Q_c the pattern will show the fourfold axis.

Observing an icosahedral diffraction pattern in which all the spots can be indexed with this six index notation proves that we have a diffraction pattern of a quasiperiodic structure. In particular the experimental pattern is not the F or I. Furthermore, because it can be indexed with six integers, the object can be represented as a slice and projection of a six-dimensional periodic structure.

Several other methods of indexing with six numbers have been successful.[11–13] They have differed from each other in ways that become significant after we examine the cut and projection method.

VII. THE CUT AND PROJECTION FROM SIX DIMENSIONS

In three dimensions the six vectors along the fivefold axes are not orthogonal. We can choose the six-dimensional cubic space in which each of these vectors is a basis vector along a hypercube axis that is perpendicular to all the others. The set of the six numbers n_i then represents a position vector in the six-dimensional cubic reciprocal lattice, and the equations (8) give the correspondence between positions in the three- and six-dimensional spaces. The cut and projection is accomplished by rotating the six-dimensional space so that what will become three axes in the three-dimensional space are in the cut plane. The six-dimensional rotation matrix corresponding to the chosen set (7) is

$$R = \frac{1}{\sqrt{2(2+\tau)}} \times \begin{bmatrix} 1 & \tau & 0 & -1 & \tau & 0 \\ \tau & 0 & 1 & \tau & 0 & -1 \\ 0 & 1 & \tau & 0 & -1 & \tau \\ -\tau & 1 & 0 & \tau & 1 & 0 \\ 1 & 0 & -\tau & 1 & 0 & \tau \\ 0 & -\tau & 1 & 0 & 1 & \tau \end{bmatrix} \quad (20)$$

The three-by-six matrix constituting the top half of the rotation matrix consists of the six fivefold directions in three dimensions as column vectors [compare with Eq. (7)], or the coordinates of the three-dimensional cube axes in the six-dimensional space as row vectors. The bottom three by six matrix consists of the complementary orthogonal space lost by the cut. It consists of projection directions from six dimensions into the real space. In the six-dimensional reciprocal space the distance of a spot from the cut plane is related to its intensity in the three-dimensional reciprocal space.

There are five Bravais lattices consistent with icosahedral symmetry in six dimensions.[10] Three of these are the P, I, F hypercubic. Consider first the primitive lattice. Its reciprocal lattice is also primitive. Because the projection of each six-dimensional lattice vector is a (1/0 0/1 0/0) vector along the fivefold axes, the reciprocal quasilattice observed experimentally to be one composed of such vectors will be denoted P. The other lattices in our example correspond to the six-dimensional face-centered F and body-centered I reciprocal lattices F corresponding resp. to I and F direct lattices.

In the P six-dimensional lattice the location of a spot in the dimensionless units that we have used in three dimensions is, using Eq. (20):

$$\mathbf{Q}_6 = \sqrt{2(1+\tau^2)}\,(n_1,n_2,n_3,n_4,n_5,n_6). \quad (21)$$

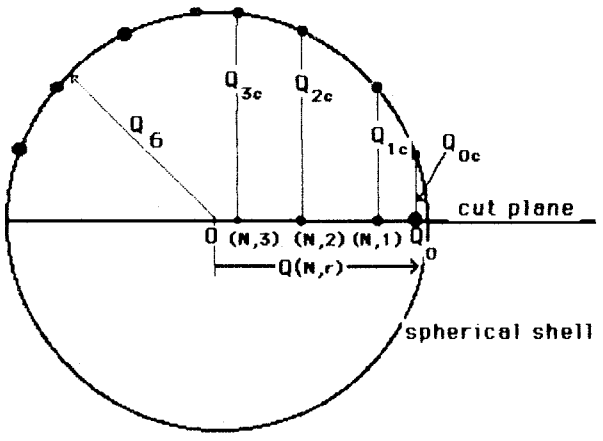

FIG. 9. Two-dimensional representation of the cut and projection procedure for the magnitude of Q and the distance from the cut plane Q_c.

As a result, using Eqs. (2) and (13),

$$Q_6^2 = 2(2+\tau)(n_1^2+n_2^2+n_3^2+n_4^2+n_5^2+n_6^2) = (2+\tau)N. \quad (22)$$

The length of Q_6 is related to the N part of the length of Q (Fig. 9). Since projection shortens Q

$$Q^2 < Q_6^2. \quad (23)$$

Using Eqs. (12) and (22)

$$N + M\tau < (2+\tau)N.$$

Therefore

$$M < [(1+\tau)/\tau]N = \tau N. \quad (24)$$

Since $Q^2 > 0$, we also have

$$-N/\tau < M \quad (25)$$

proving the inequality (15). If we define Q_c to be the distance of a spot in the six-dimensional reciprocal space from the cut plane (Fig. 8), we have

$$Q_c^2 = Q_6^2 - Q^2 = \tau(N\tau - M). \quad (26)$$

Thus the largest M for a given N will have the smallest Q_c.

Up to now we have been using a dimensionless Q. We introduce a three-dimensional quasilattice constant d_0 such that the three-dimensional diffraction vector k and the interplanar spacing are given by

$$\mathbf{k} = \mathbf{Q}/d_0, \quad (27)$$

$$d(h/h', k/k', l/l') = d_0/\sqrt{N+\tau M}. \quad (28)$$

The length of the six-dimensional reciprocal lattice constant a_6^* is related to d_0 by

$$a_6^* d_0 = \sqrt{2(2+\tau)}. \quad (29)$$

In Table IV we give the values of $Q_0(N)$ and the corresponding Q_c that according to theory should be inversely correlated with intensity. This sequence of Q's has an obvious beginning ($N=2$) and using $d_0 = 1.7466$ nm we produce for 0.155 nm radiation two further columns, the diffraction vector **k** and the diffraction angle 2θ. Comparing these with our own and published powder diffraction data[11] indicates a one-to-one correspondence with this list. The only omissions are due to overlap with fcc aluminum and low intensities in the published data.[11] The justification for our choice of d_0 is to match Table IV with experimental data. The choice of d_0 in Ref. 11 was different and this leads to complications to be discussed.

In Table V we list the $Q_0(N)$ series in three different notations each using six indices. The (n_i) and $(h/h'\,k/k'\,l/l')$ are representative of that particular $Q_0(N)$. The six-dimension (n_i) vector is that which projects into the longest possible three-dimensional vec-

TABLE IV. Scattering variables for the P lattice.

	Dimensionless			Dimensional ($d_0 = 1.74657$)	
N	M_0	Q_0^2	Q_c	$d^{-1}(\mathrm{nm}^{-1})$	2θ
2	1	3.62	1.90	1.089	9.68
4	4	10.47	2.00	1.853	16.51
6	9	20.56	1.07	2.596	23.21
8	12	27.42	1.24	2.998	26.87
10	13	31.03	2.27	3.189	28.62
12	16	37.89	2.35	3.524	31.70
14	21	47.98	1.64	3.966	35.80
16	24	54.83	1.75	4.239	38.36
18	29	64.92	0.45	4.613	41.90
20	32	71.78	0.76	4.850	44.16
22	33	75.40	2.05	4.971	45.32
24	36	82.25	2.14	5.192	47.46
26	41	92.34	1.32	5.502	50.48
28	44	99.19	1.45	5.702	52.45
30	45	102.81	2.39	5.805	53.47
32	48	109.67	2.47	5.996	55.38
34	53	119.76	1.80	6.265	58.10
36	56	126.61	1.91	6.442	59.90
38	61	136.70	0.89	6.694	62.50
40	64	143.55	1.08	6.860	64.23
42	65	147.17	2.19	6.946	65.13
44	68	154.03	2.27	7.105	66.83
46	73	164.12	1.52	7.334	69.28
48	76	170.97	1.64	7.486	70.93
50	77	174.59	2.51	7.565	71.79
52	84	187.91	0.47	7.848	74.92
54	85	191.53	1.96	7.923	75.77
56	88	198.39	2.05	8.064	77.36
58	93	208.48	1.17	8.267	79.68
60	96	215.33	1.32	8.401	81.25
62	97	218.95	2.32	8.472	82.07
64	100	225.80	2.40	8.603	83.63
66	105	235.89	1.70	8.793	85.92
68	108	242.75	1.81	8.920	87.47
70	113	252.84	0.65	9.104	89.74
72	116	259.69	0.90	9.226	91.29
74	117	263.31	2.10	9.290	92.11
76	120	270.16	2.19	9.410	93.66
78	125	280.25	1.40	9.584	95.94
80	128	287.11	1.53	9.701	97.50
82	129	290.73	2.44	9.762	98.32
84	132	297.58	2.52	9.876	99.89
86	137	307.67	1.87	10.042	102.21
88	140	314.52	1.97	10.154	103.79
90	145	324.61	1.00	10.315	106.15
92	148	331.47	1.18	10.424	107.77
94	149	335.09	2.24	10.480	108.63
96	152	341.94	2.32	10.587	110.27
98	157	352.03	1.59	10.742	112.71
100	160	358.89	1.71	10.846	114.40
102	165	368.98	0.25	10.997	116.93

TABLE V. Various indexing methods for the first 12 strong reflections.

N	M_0	(n_i)	$(h/h'\,k/k'\,l/l')$	multiplicity	Ref. 11
2	1	(100000)	(1/0 0/1 0/0)	12	$(21\bar{1}\bar{1}\bar{1}\bar{1})$
4	4	(100100)	(0/0 0/2 0/0)	30	$(2200\bar{1}1)$
6	9	(111000)	(1/1 1/1 1/1)	20	(110001)
					$(32\bar{1}\bar{1}\bar{1}2)$
8	12	$(10110\bar{1})$	(0/0 2/2 0/0)	30	$(1110\bar{1}0)$
10	13	$(11101\bar{1})$	(1/2 2/1 0/0)	60	$(2210\bar{2}0)$
12	16	(210010)	(2/2 0/2 0/0)	60	$(31\bar{1}\bar{1}\bar{1}\bar{1})$
		$(11111\bar{1})$	0/2 2/2 0/0)	12	
14	21	$(20110\bar{1})$	(1/0 2/3 0/0)	60	$(21\bar{1}001)$
					$(331\bar{0}21)$
16	24	$(21101\bar{1})$	(2/2 2/2 0/0)	60	$(21\bar{1}\bar{1}01)$
18	29	$(21111\bar{1})$	(1/2 2/3 0/0)	12	(100000)
					$[(32\bar{1}002)?]$
20	32	$(20120\bar{1})$	(0/0 2/4 0/0)	30	(110000)
22	33	$(21120\bar{1})$	(0/1 2/4 1/0)	120	
24	36	(222000)	(2/2 2/2 2/2)	20	(220002)
		$(21121\bar{1})$	(0/2 2/4 0/0)	60	$[(561\bar{0}\bar{3}3)?]$

tor, and the two are related by Eq. (9). For powder pattern intensities the multiplicity of each spot is given. The sequences of our indexing of course satisfies Eq. (13) relating N to the sum of squares of indices. As was noted earlier, the list[11] of powder diffraction angles correlates perfectly with this sequence, with only one omission in this range.

The last column gives the indexing of Ref. 11. The fundamental (100000) vector was chosen in Ref. 11 to have the length of $Q_0(18)$. As a result, all smaller reflections become higher index and the simple monotonic relation between N and Q of Eq. (13) is lost. Because of this there is no obvious start to the sequence, and it is difficult to know if any intense spots are missing. Furthermore, because of the incommensurability one can approach any angle with arbitrary precision by using high indices. The two assignments[11] labelled with question marks are probably such approximations. The question of which vector one chooses as a fundamental length in this case is uniquely resolved by the sequence of the intense reflections. Choosing a longer vector leads to the problems cited above. It will be difficult to choose a shorter vector, because intensities are likely to be very low.

We have so far concentrated on the Q_0 series. Table V lists representative spots for all the spots that occur for $N = 12$ spherical shell in six dimensions (Fig. 9). Two types of indices sum to $N = 12$. In six dimensions there are 2^6 spots of type (111111) and $2^3 6!/(2!3!)$ of type (211000). Six different lengths result from projecting in three dimensions ranging from $Q_0^2 = 37.89$ to $Q_5^2 = 5.53$. The longer Q's are from six-dimensional vectors nearly parallel to the cut plane; the shorter ones are from those nearly perpendicular. By themselves the (n_i) give no clue about projected length until the projection has been defined in Eq. (20), but in the cubic indexes the lengths obviously become shorter as the 2's shift from primed to unprimed positions and sign differences appear in the indexes.

The (111111) are high symmetry axes in six dimensions. They project into three dimensions as either three- or fivefold axes with four different lengths. The (211000) project onto mirror planes or (110) planes with six different lengths. In powders the Q_0 (12) reflection will be a superposition of 72 individual diffraction spots. These multiplicities are most readily apparent by forming ratios of the cubic indices and comparing these with the indexes of the three symmetry axes and the mirror planes.

We hope to have demonstrated that the cubic coordinate system has many advantages over either the skew coordinate system or the six-dimensional one. In addition, there is an obvious simplification when a particular lattice constant is chosen.

VIII. DISCUSSION

Several indexing methods have been introduced and need to be compared. We have introduced a method of indexing based on a three-dimensional cubic coordinate system using icosahedral symmetry. Six indexes are necessary and sufficient, indicating that the icosahedral solid is quasiperiodic and can be represented as an irrational cut of a six-dimensional periodic solid. Much of the geometry is developed without recourse to six dimensions.

The six-index notation is merely a shorthand for indexing irrational numbers of the form $h + h'\tau$. Ordinary vector addition generates the three-dimensional diffraction pattern from a single vector replicated by the

operations of the icosahedral group. There is a single basic length: the $\pi/5$ rotations introduce the algebraic number τ and, therefore, incommensurability. Unlike other incommensurate structures, in which the incommensurate ratio varies with temperature and composition, the ratio τ is part of fivefold rotation and remains the same for large changes in composition[15] and lattice parameter and a wide variety of alloy systems. The cubic coordinate system has many advantages that derive from an orthogonal coordinate system. It incorporates the cubic subgroup part of the icosahedral symmetry, but it leaves the problem of multiple notation for equivalent positions.

The multiple notation is really not a problem. We have found two convenient methods. For a particular index, multiplication by the rotation matrices quickly gives all the other notations for equivalent reflections. When dealing with a large number of indexed positions, they are quickly sorted by calculating Q^2 and sorting by N and M (or r). Just as (330) and (411) coincide in bcc powder patterns, this sorting will put nonequivalent spots in the same (N,r) box. However, since all the spots in the same (N,r) box originate from the spots in the six-dimensional reciprocal space that are the same distance from the cut plane, they are likely to have similar intensities. The other three-dimensional coordinate systems have skewed axes aligned along equivalent symmetry axes. They have all the problems of skewed axes including the problem that permutation of indices not only cause length changes but can cause the vector to rotate to a nonequivalent direction. In the cubic indexing, because the indices are primed and unprimed, cyclic permutations of (HKL) can only lead to equivalent vectors. Odd permutations do not change the length.

In six dimensions there is an orthogonal system, but the rotation matrix that defines the cut plane requires arbitrary choices of the signs of the fivefold basis vectors in three dimensions. Thus the various six-dimensional vectors of type (110000) represented two different lengths in three-dimensions differing by a factor of τ, depending on the relative orientation with respect to the cut plane, or equivalently whether the angles between the various (100000) type (010000) vectors in three dimension are acute or obtuse.

There is a geometric way of understanding the discrepancy between the various indexing methods. It might seem that any reflection along the fivefold axis could serve to define the unit length, but it must satisfy several criteria. The first is that all other spots must then be indexable with six integers that obey the parity rules. The spots that survive this criterion differ from each other in length by powers of τ^3. In six dimensions all of these vectors lie on the same $(xyyyy\bar{y})$ fivefold plane. The shortest distance in this plane is (100000) and this is the one which must be found. Only one of the fivefold reflections corresponds to this minimum distance and generates an orthogonal basis in six dimensions. The one chosen in Ref. 11 happens to be the $(21111\bar{1})$, which leads to a skewed six-dimensional basis. This destroys the hypercubic geometry that is so important to the simplicity of the indexing we have proposed. As a result the indexing fails to fit the criterion of a simple hierarchy. There are inifinitely many reflections along the fivefold axis, both longer and shorter than the one which meets this criterion. For the P quasilattice, it is the longest fivefold reflection that is shorter than any intense reflection in any direction. All shorter reflections are then projections of longer six-dimensional vectors with long Q_c and weak intensities.

These criteria not only point to a natural and unique indexing but solves the important problem of what constitutes the unit reciprocal lattice vector. Comparison of Table V indicates that while a different choice of this unit still gives a completely consistent set of indexing, there is a simplicity and completeness to the choice based on the strong reflections. The Q_0 series fits the observed intense reflections without omission and, qualitatively, is inversely correlated with Q_c, the distance from the cut plane. The next in the sequence (Table VI) $Q^2(N,1) = Q_0^2(N) - 4\tau$ all have $Q_c > 2\sqrt{\tau}$ which, of course, is longer than Q_c for any of the Q_0 spots, and are readily distinguished from the main sequence by their

TABLE VI. A complete listing of the $N = 12$ reflections.

	M	(n_i)	$h/h'\,k/k'\,l/l'$	Multiplicity
$Q_0(12)$	16	(210010)	(2/2 0/2 0/0)	60
		$(111111\bar{1})$	(0/2 2/2 0/0)	12
$Q(12,1)$	12	$(1111\bar{1}1)$	(0/2 0/2 0/2)	20
		$(20100\bar{1})$	(2/0 2/2 0/0)	60
$Q(12,2)$	8	(201001)	(2/0 0/2 0/2)	120
$Q(12,3)$	4	$(2100\bar{1}0)$	(2/0 0/2 2/0)	120
$Q(12,4)$	0	$(111\bar{1}\bar{1}\bar{1})$	(2/0 2/0 2/0)	20
		(010210)	$(\bar{2}/2\ 0/2\ 0/0)$	60
$Q(12,5)$	-4	$(\bar{1}11111)$	$(\bar{2}/2\ 2/0\ 0/0)$	12
		$(20\bar{1}001)$	$(2/0\ \bar{2}/2\ 0/0)$	60

weak intensity. Our indexing method therefore uniquely identifies the quasilattice parameter d_0 in a way that is quite equivalent to that chosen by Elser[12] based on an examination of the Fourier transform of the cut function along a systematic row. Because our method is purely geometric and does not refer to any specific cut function, it is in a sense more general.

In this paper we have taken for granted that the symmetry is truly icosahedral. The choice of the cubic axes for a coordinate system does not imply that we believe that this is a cubic crystal, as has been suggested by others.[16,17] We will address this issue in a separate paper.[18]

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