Identifying and Indexing Icosahedral Quasicrystals from Powder Diffraction Patterns

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We present a scheme to identify quasicrystals based on powder diffraction data and to provide a standardized indexing. We apply our scheme to a large catalog of powder diffraction patterns, including natural minerals, to look for new quasicrystals. Based on our tests, we have found promising candidates worthy of further exploration.

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Quasicrystals are solids whose lattices exhibit a rotational symmetry, such as five-fold symmetry, that is forbidden for periodic crystals. Because the atoms are arranged quasiperiodically, the structure’s symmetry is not subject to the usual mathematical restrictions of crystallography. Quasiperiodic translational order has physical consequences. For example, since electrons and phonons in quasicrystals do not encounter a periodic potential, quasicrystals have unusual resistive and elastic properties, and these have been exploited in several applications. To date, known quasicrystals have been found by serendipity or by probing stoichiometric variations around other already-known quasicrystals. Furthermore, all known quasicrystals are synthetic; no natural quasicrystal has ever been identified. A more systematic way to search for quasicrystals, including natural quasicrystal has ever been identified. A more systematic way to search for quasicrystals, including natural quasicrystals, is desirable, and one way is to search through collections of diffraction data. Although a two-dimensional electron diffraction pattern would immediately show a quasicrystal’s salient forbidden symmetry, no large collection of such patterns exists. However, a collection of over eighty thousand powder diffraction patterns in digital form, the Powder Diffraction File (ICDD-PDF), is published by the International Center for Diffraction Data. The catalog contains synthetic inorganic and organic phases, as well as nine-thousand mineral patterns. Because the powder diffraction pattern of a material averages over all orientations, only the magnitude (and not the direction) of the scattering vector in reciprocal space is preserved, and a quasicrystal’s distinctive non-crystallographic symmetry cannot be observed directly. A priori, it is unclear if quasicrystals can be identified from their powder diffraction patterns alone.

In this paper, we present a method to identify, classify and index icosahedral quasicrystals based solely on their powder diffraction patterns. We apply the method to the ICDD-PDF and find the best-fit quasicrystal candidates. Our automated procedure picks out the known quasicrystals in the ICDD-PDF and, for the cases in which indexing has been published, produces the same indices. Although the remainder of the catalog is supposed to consist of periodic crystals, it was assembled over many years, including decades prior to the 1984 discovery of quasicrystals. Consequently, it is conceivable that the catalog includes some quasicrystals that were never identified as such. Based on our studies, we report promising materials.

The diffraction pattern of an ideal three-dimensional quasicrystal consists of Bragg peaks located on a lattice given by \( \mathbf{Q} = \sum_{i=1}^{6} n_i \mathbf{b}_i \), where the \( \mathbf{b}_i \) are basis vectors pointing to the vertices along the six five-fold symmetry axes of a regular icosahedron in three dimensions, and the \( n_i \) are integers that index each vector. The quasicrystal formula is similar to that for a crystal except that the number of basis vectors is greater than the number of dimensions (three), a consequence of the non-crystallographic symmetry. We choose the \( \mathbf{b}_i \) following the convention in [3]:

\[
\begin{align*}
\mathbf{b}_1 &= (1, \tau, 0), \\
\mathbf{b}_2 &= (\tau, 0, 1), \\
\mathbf{b}_3 &= (0, 1, \tau), \\
\mathbf{b}_4 &= (-1, \tau, 0), \\
\mathbf{b}_5 &= (\tau, 0, -1), \\
\mathbf{b}_6 &= (0, -1, \tau)
\end{align*}
\]

where \( \tau \) is the golden ratio, \((1 + \sqrt{5})/2\). An equivalent way to index the position of the three-dimensional reciprocal-space scattering vector is to use a scheme analogous to crystallographic Miller \((h\ k\ l)\) indices. Six integer indices grouped into pairs describe the distance along Cartesian basis vectors, \( \mathbf{Q} = (h + h'\tau)\hat{x} + (k + k'\tau)\hat{y} + (l + l'\tau)\hat{z} \). The \((h/h'\ k/k'\ l/l')\) indices are permutations of the \(n_i\):

\[
\begin{align*}
\ h &= n_1 - n_4, \quad h' = n_2 + n_5, \quad k = n_3 - n_6, \\
\ k' &= n_1 + n_4, \quad l = n_2 - n_5, \quad l' = n_3 + n_6
\end{align*}
\]

Because the \((h/h'\ k/k'\ l/l')\) indices express distances along Cartesian axes, the advantages of orthogonal coordinate axes are conveniently recovered. Also, associated with every \(\mathbf{Q}\) is a vector \(\mathbf{Q}_\perp\), constructed from another integer linear combination of the same basis vectors: \(\mathbf{Q}_\perp = (h' - h\tau)\hat{x} + (k' - k\tau)\hat{y} + (l' - l\tau)\hat{z} = \sum_{i=1}^{6} n_i \tilde{b}_i\), where

\[
\begin{align*}
\tilde{b}_1 &= (-\tau, 1, 0), \quad \tilde{b}_2 = (1, 0, -\tau), \quad \tilde{b}_3 = (0, -\tau, 1), \\
\tilde{b}_4 &= (\tau, 1, 0), \quad \tilde{b}_5 = (1, 0, \tau), \quad \tilde{b}_6 = (0, \tau, 1)
\end{align*}
\]
In powder diffraction patterns, the reciprocal space is collapsed to one dimension, where all vectors with the same magnitude $|\vec{Q}|$ are degenerate. The magnitude $|\vec{Q}| = Q$ is the reciprocal of the d-spacing, the quantity listed in the entries of the ICDD-PDF. $Q^2$ and $|\vec{Q}|^2 = Q^2$ can now be expressed as integer linear combinations of only two basis vectors, whose lengths are related by the golden ratio: $Q^2 \equiv N + \tau M$ and $Q^2 \perp N \tau - M$, where $N = 2 \sum_{i=1}^{6} n_i^2$ and $M = h^2 + k^2 + l^2 + 2(hh' + kk' + ll')$. Each peak in a quasicrystal powder diffraction pattern can be indexed by the two integers $N$ and $M$. The entire diffraction pattern can be scaled by a factor of $\tau^3$ along the $Q$ direction, and the support will remain the same, a consequence of the self-similarity of the pattern. That is, for each lattice vector at position $Q^2 = (N, M)$, there is another lattice vector of similar intensity at position $(N', M') = \tau^6 Q^2$. Using the relation $\tau^2 = \tau + 1$,

\begin{align*}
(N', M') &\equiv N' + M'\tau = \tau^6 (N + M \tau) = (5M + 8N) + (8M + 13N)\tau \\
(5M + 8N) &+ (8M + 13N)\tau \equiv (5M + 8N, 8M + 13N)
\end{align*}

Although three other different indexing schemes persist in the literature to describe icosahedral quasicrystal powder patterns, they are all analytically equivalent to the convention given here.

There are three distinct icosahedral reciprocal lattices: simple icosahedral (SI), face-centered icosahedral (FCI), and body-centered icosahedral (BCI). The SI, FCI and BCI reciprocal lattices correspond to real-space lattices obtained by, for example, placing identical "atoms" at each lattice point of a simple-hypercubic, face-centered hypercubic and body-centered hypercubic lattice in six dimensions, respectively, and projecting down to three dimensions. (In \([7]\), the SI, FCI and BCI lattices are referred to as $F^*$, $I^*$ and $P^*$, respectively.) For these primitive lattices, the intensity is given by:

\[ I \propto \left[ \frac{\sin(Q \perp /2)}{Q \perp /2} \right]^2 \]  

(5)

Note that $I$ increases as $Q \perp \to 0$ so that bright peaks—the ones likely to be observed experimentally—have small $Q \perp$. Eq. (3) does not account for chemical and other effects that modulate the intensities in the diffraction pattern of a real material, but it provides a guide as to which peaks should be observed when testing real patterns.

**Testing patterns.** The first step in testing a real powder pattern is to find the best possible peak-by-peak match between that pattern \{Q\}_i and the perfect quasicrystal template pattern \{q\}_i. Then, various statistical tests can be applied to compare that match to what is expected for a true quasicrystal.

If we were to match to a periodic crystal template pattern, the test would be more straightforward. For any finite interval of Q over which a pattern is measured, a real crystal has a finite number of diffraction peaks. One also has good *a priori* estimates for the nonzero minimum distance between nearest peaks, which is set by the lattice constant. These features, useful in matching the template to the real pattern, allow a unique indexing.

For the quasicrystal, the process is more complicated because the number of peaks in any finite interval of the ideal pattern is infinite (the pattern is dense) and, consequently, there is no uniquely defined lattice constant or indexing. How does one sensibly match a real pattern, with a finite number of peaks in a given interval $\Delta Q$, to a quasicrystal template pattern, with a dense set of peaks in that same interval? One must account for the intensity of the peaks, not just their $Q$. Although the quasicrystal powder pattern is dense, most of its peaks within any finite interval of $Q$ have a large $Q \perp$ and are predicted by Eq. (3) to be too dim to distinguish from the noise present in any real experiment. So, instead of finding the template $q_i$ which comes closest to the observed $Q_i$ (i.e., minimizing $|Q_i^2 - q_i^2|$ alone), we instead minimize $|Q_i^2 - q_i^2|/I_i$, which includes the intensity $I_i$ of the $i$'th template peak. This approach tends to match real $Q_i$ to the nearest *bright* peaks in the template pattern, naturally accounting for phason shifts, imperfections and experimental error that may shift $Q_i$ from its ideal value and cause an incorrect assignment to some $q_i$ with an unrealistically small intensity.

The procedure for finding the best match between the real and template patterns, then, is as follows. Choose some bright peak in the ideal pattern $(N_0, M_0)$ with a low value of $N$. An “attempted match” consists of re-scaling its magnitude to match the first real peak in the pattern $Q_1$. Identify each remaining peak $Q_{i \neq 1}$ in the real pattern with the template peak $q_i$ which minimizes $|Q_i^2 - q_i^2|/I_i$. Next, introduce a goodness-of-fit parameter $S_1$ to characterize the attempted match between the $\{Q_i\}$ and the $\{q_i\}$. Repeat the process by assigning $(N_0, M_0)$ to the second real peak $Q_2$ and compute its goodness-of-fit, $S_2$. After repeating for each real peak, use the lowest $S_j$ to decide the best overall match between the real pattern and template. Each real peak $Q_i$ is now assigned the set of indices $\{n_i\}$ or, equivalently, $\{N_i, M_i\}$ of the matching template peak.

The goodness-of-fit parameter $S_j$ depends on $\Delta = \langle |Q_i - q_i|/Q_i \rangle$ where $\langle O \rangle$ denotes an intensity-weighted average $\langle \sum_i \sqrt{O_i} \rangle/\langle \sum_i \sqrt{I_i} \rangle$. $\Delta$ measures the fractional deviation between $Q_i$ and $q_i$ and is weighted by intensity for the same reasons as above. (Results do not change significantly if $\sqrt{I_i}$ is replaced by $I_i$ or some similar function of intensity.) One challenge is that for each good fit of $Q_i$ to a template peak $q_i$ labelled by $(N, M)$, there is also an equally good fit to the peak $\tau^6(N, M)$ where $k$ is any integer, due to the self-similarity of the lattice; see Eq. (3). This leads to the practical problem of deciding which match to choose and also the annoyance that, unlike a crystal, the indexing is not unique. To produce a unique and sensibly standardized indexing, we
simultaneously minimize $\tilde{N} = \langle N_i \rangle$. The goodness-of-fit $S$ can be taken to be a linear combination of these two parameters, $S = a\Delta + \tilde{N}$. The results are relatively insensitive to the choice of $a$ (up to an order of magnitude) provided that the $\Delta$ and $\tilde{N}$ contributions to $S$ are both non-negligible for known quasicrystals; typical values are $\tilde{N} \approx 30$ and $\Delta \approx 0.3$, and we used $a = 500$ in all data runs.

If the real material is a crystal, the best attempted match to the quasicrystal template (corresponding to the lowest $S_j$) is still a poor match relative to a true quasicrystal, so we next introduce statistical tests to measure the quality of the match. These tests were found empirically by applying them first to known quasicrystals, and they involve calculating several quantities for each pattern. The first two statistical quantities, $\Delta$ and $Q_\perp$, (the intensity-weighted average of $Q_\perp$), are discussed above. Quasicrystals have low values of both, representing closer matches to brighter peaks. However, finite resolution limits the number of peaks present above the noise level; while these two parameters clearly separate out FCI quasicrystals, there are other bright peaks at $Q_\perp$. However, finite resolution limits the number of peaks present above the noise level; while these two parameters clearly separate out FCI quasicrystals, there are other bright peaks at $Q_\perp$. However, finite resolution limits the number of peaks present above the noise level; while these two parameters clearly separate out FCI quasicrystals, there are other bright peaks at $Q_\perp$. However, finite resolution limits the number of peaks present above the noise level; while these two parameters clearly separate out FCI quasicrystals, there are other bright peaks at $Q_\perp$.

Each peak in a powder pattern has a parity determined by $\eta \equiv \sum_i n_i$. Even (odd) $\eta$ corresponds to even (odd) parity. Over a finite interval, certain sequences of even and odd peaks appear. For a given bright peak at $Q_0$, there are other bright peaks at $Q = Q_0 + \Delta Q$, where $\Delta Q \equiv \Delta N + \Delta M \tau \equiv (\Delta N, \Delta M)$. All these peaks should have low values of $Q_\perp$, and will therefore be separated by small $\Delta Q_\perp^2 = \Delta N \tau - \Delta M$. $\Delta M/\Delta N$ should approximate $\tau$, the golden ratio, and as is well known, the best approximant is a ratio of subsequent Fibonacci numbers. Hence, for every peak in the powder pattern, we look for other peaks separated by “Fibonacci intervals,” $(\Delta N, \Delta M)$, where $\Delta N$ and $\Delta M$ are either successive Fibonacci integers or constant multiples of these integers. In the SI case, we search for two types of intervals: those occurring between peaks of opposite parity, which involve successive Fibonacci numbers, such as $(2, 3)$ and $(34, 55)$; and those occurring between peaks of the same parity, which involve four times successive Fibonacci numbers, such as $(8, 12)$ and $(20, 32)$. In the FCI and BCI cases, only even-parity peaks are present, and we seek only sequences with four times successive Fibonacci integers.

For each $i$th peak in the real pattern, we count the number of other real peaks that are separated from it by one of the Fibonacci intervals. If there is only one such peak, then the $i$th peak is considered part of a pair (or 2-plet); if two, part of a 3-plet; etc. We define $M_i^{(m)}$ to be 1 if the $i$th peak is part of an $m$-plet and zero otherwise. Note that $M_i^{(m)} = 1$ implies $M_i^{(m-1)} = 1$. For example, if the ninth peak in a pattern is separated from three other peaks by Fibonacci intervals, then $M_9^{(2)} = M_9^{(3)} = M_9^{(4)} = 1$ and $M_9^{(5)} = 0$. The values of $M_i^{(m)}$ for each peak are combined into intensity-weighted averages $M_i^{(m)} = \langle M_i^{(m)} \rangle$.

The three average quantities $\Delta$, $Q_\perp$, and $M^{(4)}$ are unified into a single $\chi^2$ statistic, which quantifies the degree of quasicrystallinity of a powder X-ray diffraction pattern. First, the distribution for each quantity, calculated for all sixty thousand entries in the ICDD-PDF with a dozen peaks or more, is fit to a standard Gaussian by matching percentiles. Then, $\chi^2$ is calculated from the three normalized measures. All patterns with any worse-than-average quantity are discarded and the remaining patterns with a high value of $\chi^2$ represent patterns with characteristics most like those of the known quasicrystals.

Results. The $\chi^2$ statistic has proven to be a reliable method of identifying and indexing quasicrystal diffraction patterns. For example, Fig. 1 shows a scatter plot of $\Delta$ vs. $Q_\perp$ for 60,000 patterns from the ICDD-PDF. The writer cannot be confident enough to say that the ten smallest $\chi^2$ patterns are quasicrystals; the remaining patterns are shown in grey. The clustering of the eleven quasicrystals apart from the remaining points demonstrates the success of the tests in separat-
TABLE I: Top quasicrystal candidates for SI, FCI, or BCI lattices. Type refers to whether candidates were labeled in the ICDD-PDF as quasicrystal, synthetic crystal or mineral crystal. Shown are typical quasicrystals, the top five synthetic and top mineral candidates. The best known quasicrystals have $\chi^2$ values up to 154.8 (SI) and 397.8 (FCI).

| PDF Num | Formula | Lattice | Type | $\chi^2$ |
|---------|---------|---------|------|----------|
| New Data | CdYb | SI | QC | 34.7 |
| 27-901 | SnTe$_3$O$_8$ | SI | Syn | 28.4 |
| 42-842 | InP$_3$ | SI | Syn | 27.9 |
| 44-583 | CuO$_4$ | SI | Syn | 27.4 |
| 21-117 | Cd(MnO$_2$)$_2$6H$_2$O | SI | Syn | 21.4 |
| 38-923 | K$_2$NaPdF$_6$ | SI | Syn | 19.8 |
| 25-298 | Aktashite, Cu$_4$Hg$_3$As$_5$S$_{12}$ | SI | Min | 17.9 |
| 48-1337 | A$_{608.5}$Pd$_{22.1}$Mn$_{9.4}$ | FCI | QC | 92.0 |
| 40-106 | Ba$_3$La$_{40}$V$_{12}$O$_{93}$ | FCI | Syn | 40.3 |
| 19-261 | CaYb$_2$O$_4$ | FCI | Syn | 38.9 |
| 31-1420 | Cr$_{19.9}$Ta$_{83.1}$S | FCI | Syn | 34.1 |
| 41-979 | Sr$_7$Y$_{13}$O$_2$(PO$_4$)$_3$(SiO$_4$)$_9$ | FCI | Syn | 33.7 |
| 27-863 | Tantalite, (Fe,Mn)Ta$_2$O$_6$ | FCI | Min | 25.2 |
| 22-379 | In$_3$Si$_{14}$ | BCI | Syn | 40.1 |
| 50-1335 | Co$_3$Sn$_{11}$Tb$_3$ | BCI | Syn | 36.2 |
| 42-1163 | Pb$_8$Al$_5$F$_{25}$Cl | BCI | Syn | 26.8 |
| 45-1164 | Al$_2$Mo$_{10}$S$_{66}$Th$_2$ | BCI | Syn | 25.9 |
| 36-1231 | LaNiO$_2$ | BCI | Syn | 24.9 |
| 44-1412 | Gratomite, Pb$_9$As$_4$S$_{15}$ | BCI | Min | 14.3 |

A further success is that our automated indexing of peaks for the known quasicrystals matches the available published indices. In some cases, while the published indices are aided by two-dimensional diffraction data, our automated procedure uses powder data only. Given the unique challenges in quasicrystal indexing, described earlier, the successful indexing suggests that our matching of template and real patterns automatically incorporates standards obtained by individual analysis. Hence, as more quasicrystals are discovered and added to catalogs, our procedure could provide a standardized indexing.

Future work will proceed in several directions. A number of materials merit further study, and, intriguingly, the most promising examples are in the BCI class where no quasicrystal has yet been found. Systematic studies of synthetic materials with nearby stoichiometries may also be merited. Finally, we would like to collect the powder diffraction patterns of other materials, including known quasicrystals and crystal approximant phases, to further refine our tests. We are interested in collaborating in exploring the leading candidates, only some of which have been given in Table I. Those interested are encouraged to contact PJL and PJS.

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