Introduction to the atomic structures of quasicrystals

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Subtiles
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Summary

- About the discovery of quasicrystals
- Quasiperiodicity and icosahedral symmetry
- Indexing schemes and experimental diffractions
- Fourier reconstructions on single grain diffractions
- Atomic clusters in F- and P- type icosahedral phases
- Conclusions and open questions
On April 8th 1982, Dan Shechtman observed at NBS the first quasicrystal in a rapidly solidified AlMn alloy:

Electron microscopy (images and diffraction) of a AlMn(Si) rapidly solidified alloy.
The first high resolution images confirmed clearly the fact that these new structures are uniformly well ordered where the pentagonal symmetry is present down to atomic scale: no traces of twinning.
The Jan. 1985 IHES meeting

Marjorie Senechal and Louis Michel

A month-long international workshop on mathematical crystallography was held at the Institut des Hautes Etudes Scientifiques (IHES), in Bures-sur-Yvette, France, in January 1985. Organized by Professor Louis Michel, a physicist and permanent member of the Institute, the purpose of the workshop was to bring together mathematicians, physicists, and crystallographers to discuss some of the fundamental problems in the field. The speakers, who came from seven countries, stayed at the Institute for varying lengths of time, from five days to the entire month; the other participants in the workshop — which was open to everyone — were faculty members of nearby universities and institutes. There were two or three lectures on one day each week (January 4, 10, 17, 24, 31); during the rest of the time the participants discussed problems, did their own research, and visited nearby Paris. The atmosphere was informal and the discussions very stimulating; it was a workshop that really was one.

The first lectures, on January 4, were introductory: Marjorie Senechal (USA) opened the workshop with an historical-expository talk, Introduction to Mathematical Crystallography; she was followed by Louis Michel, who spoke on Crystallography in n Dimensions. Geoffrey Shephard (UK) was the first speaker on January 10, with a lecture on The Classification of Patterns with Respect to Symmetry. The next speaker was Hans Raszillier (FRG), who spoke on Crystallography in Quantum Mechanical Spectral Problems. The third lecture was also by Shephard: The Aperiodic Tilings of Penrose and Amman. The three lectures on January 17 were Laminated Lattices by John H. Conway (UK), Modulated Crystals by Aloysio Janner (Netherlands) and Conjugation Classes of Crystallographic
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Groups by Jan Mozrzymas (Poland). Conway also gave an unscheduled lecture the next day on aperiodic tilings. On January 24, Peter Engel (Switzerland) spoke twice, first On the Uniqueness of Crystal Structure Analysis and later on Geometrical Crystallography. In between these talks, Denis Gratias (France) talked about the Discovery of Quasi-Crystals with Icosahedral Symmetry. (Two of the three co-discoverers, Daniel Schectman (Israel) and J.W. Cahn (USA) were also present.) The final session of the workshop, January 31, included a lecture by André Katz (France) on his work with Michel Duneau, Étude et généralisation des pavages de Penrose, a lecture on Bravais Lattices of Coxeter Groups by Pierre Cartier (France) and a discussion of the lectures of the month and open problems, led by Louis Michel.

Despite the variety of titles, the lectures can be grouped together around a few basic themes. Thus Michel’s lecture, and Shephard’s first lecture were concerned with aspects of the problem of unifying and clarifying the foundations of mathematical crystallography; Raszillier spoke on an unusual application of the crystallographic groups; and Conway’s first lecture and the talks by Mozrzymas and Cartier dealt with some theoretical aspects of n-dimensional crystallographic groups. Engel’s first lecture concerned the interpretation of x-ray diffraction patterns, while in the second he summarized his computer computations of the Dirichlet regions of the four-dimensional lattices and recent work on the local (near neighbor) conditions that ensure the isohedrality of tilings in n-dimensional space. In retrospect one could say that these eight lectures provided a prerequisite context for the rest of the talks, which were concerned with what may be called generalized crystallography.
The basic questions

- How are the atoms arranged in these structures?
- what physical properties are special to those solids with long range order but no periodicity?
- what kinds of order are necessary and sufficient for a pattern of points to exhibit a diffraction with well defined bright spots?

(from Marjorie Senechal and Jean E. Taylor, Quasicrystals : the view from Stockholm, to appear 2013)

The first theoretical model by D. Levine and P. Steinhardt has been published three weeks after Shechtman’s announcement independently of the experimental discovery. Levine and Steinhardt designated these new solids as quasicrystals (for quasiperiodic crystals).
Indexing the electron diffractions: a 3-D $\mathbb{Z}$-module of rank 6
The diffractions peaks $\mathbf{\tilde{Q}}$ can all be indexed with 6 arithmetically independent vectors $\mathbf{\tilde{e}}_i$ oriented along the 5-fold direction of the regular icosahedron with integer coefficients

$$\mathbf{\tilde{Q}} = \sum_{i=1}^{n} n_i \mathbf{\tilde{e}}_i, \quad n_i \in \mathbb{Z}$$

*Shechtman’s alloy can be viewed as a 3-D cut of a periodic object in a 6-D space: it is a quasiperiodic crystal.*
The cut method

Cut method: (black) perfect quasicrystal*, (green) periodic approximant, (blue) random tiling

*defined by Levine and Steinhardt; Katz and Duneau; Kalugin, Kitayev and Levitov; Elser
Understanding the cut method

Using $\mu_k = 1_k \otimes \delta_{k\perp}$ we obtain:

$$\varrho_{||} = (((\Lambda \ast \eta) \cdot \mu_c) \ast \mu_{\perp}) \cdot \mu_{||}, \quad \hat{\varrho}_{||} = (((\Lambda^* \ast \hat{\eta}) \ast \hat{\mu}_c) \cdot \hat{\mu}_{\perp}) \ast \hat{\mu}_{||}$$

The argument of the form factor is $q_{\sigma}$; the location of the diffraction peak is $q_{||}$, projection of $Q$ on $E_{||}$ along $E_{c\perp}$. 

Examples

![Diagram of quasicrystal structures](image)

- **Quasicrystal discovery**
- **Quasiperiodicity**
- **Understanding the first experimental data**
  - Powder diffraction data
  - Single grain diffraction data
- **Structural models**
  - Atomic surfaces
  - Cell (Klötzé) decomposition
- **Conclusion**
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Where are the atoms? Quasicrystallography

A quasicrystalline structure is defined by:

- the dimension of the high dim space $n$ de $E^n$ and the kind of lattice $\Lambda$ in $E^n$;
- the orthogonal projectors $\widehat{\pi}_\parallel$ and $\widehat{\pi}_\perp$ in $E_\parallel$ and $E_\perp$:
  $$\forall V \in E^n \quad \widehat{\pi}_\parallel V \in E_\parallel, \quad \widehat{\pi}_\perp V \in E_\perp$$
- the (super) space group $G$ is the set of the symmetry group $\mathcal{N}$ of the N-dim object that keep $E_\parallel$ et $E_\perp$ parallel to themselves:
  $$G = \{ g \in \mathcal{N} \text{ tels que } [g, \widehat{\pi}_\parallel] = 0 \quad ([g, \widehat{\pi}_\perp] = 0) \}$$
- the list of the atomic surfaces: shapes in $E_\perp$ and locations on $\Lambda$ (in $E^n$)
Application to the icosahedral phases

Group $m35$ (or 235), diffraction spectrum indexing on a $\mathbb{Z}$-module of rank 6.
Projectors

Let \( \{ |i\rangle \} \) a vector of the orthonormal canonical basis of \( \mathbf{E}^6 \); let \( \{ |\alpha\rangle \} \) and \( \{ |\bar{\alpha}\rangle \} \) the internal orthonormal bases of respectively \( \mathbf{E}_\parallel \) and \( \mathbf{E}_\perp \). The operator

\[
\hat{M} = \sum_i \left( \sum_{\alpha \in \mathbf{E}_\parallel} |\alpha\rangle \langle \alpha| i \rangle \langle i | + \sum_{\bar{\alpha} \in \mathbf{E}_\perp} |\bar{\alpha}\rangle \langle \bar{\alpha}| i \rangle \langle i | \right)
\]

relates the coordinates in \( \mathbf{E}^6 \) of a vector \( X \) with its internal coordinates in \( \mathbf{E}_\parallel \) and \( \mathbf{E}_\perp \). For icosahedral quasicrystals, the 6 unit vectors \( |i\rangle \) project in \( \mathbf{E}_\parallel \) along the 6 5-fold directions of the icosahedron:

\[
\hat{M} = \frac{1}{\sqrt{2(2 + \tau)}} \begin{pmatrix}
1 & \tau & 0 & -1 & \tau & 0 \\
\tau & 0 & 1 & \tau & 0 & -1 \\
0 & 1 & \tau & 0 & -1 & \tau \\
-\tau & 1 & 0 & \tau & 1 & 0 \\
1 & 0 & -\tau & 1 & 0 & \tau \\
0 & -\tau & 1 & 0 & \tau & 1 \\
\end{pmatrix}
\]

Up to the scaling factor \( 1/\sqrt{2(2 + \tau)} \), a vector \( X = (x_1, x_2, x_3, x_4, x_5, x_6) \) in \( \mathbf{E}^6 \) projects according to:

\[
X_\parallel \begin{cases}
X_x = u + u' \tau \\
X_y = v + v' \tau \\
X_z = w + w' \tau
\end{cases} \quad X_\perp \begin{cases}
X'_x = u' - u \tau \\
X'_y = v' - v \tau \\
X'_z = w' - w \tau
\end{cases}
\]

with \( u = x_1 - x_4 \), \( u' = x_2 + x_5 \), \( v = x_3 - x_6 \), \( v' = x_1 + x_4 \), \( w = x_2 - x_5 \), \( w' = x_3 + x_6 \).
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Neutrons (X-ray) powder diffraction spectra
Interpretation

Using

\[
\begin{align*}
N & = h^2 + k^2 + \ell^2 + h'^2 + k'^2 + \ell'^2 = 2 \sum_i n_i^2 \\
M & = h'^2 + k'^2 + \ell'^2 + 2(hh' + kk' + \ell\ell')
\end{align*}
\]

one finds \( q^2_{\parallel} \propto (N + M\tau) \) and \( q^2_{\perp} \propto \tau(N\tau - M) \); the most intense peaks are those defined by \( M = \lfloor N\tau \rfloor \):

\[
q_{\parallel} \propto \sqrt{N + \lfloor N\tau \rfloor \tau} \quad q_{\perp} \propto \sqrt{\tau(N\tau - \lfloor N\tau \rfloor)}.
\]

This was the first remarkable result in studying the powder spectra.
1985 The first stable quasicrystals

- Stable quasicrystals are found in ternary metallic systems obtained through strongly non congruent peritectic transformations.

Most of the stable quasicrystals have been discovered by A. P. Tsai and his group in Japan.
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Single (quasi) crystal Diffraction

Neutrons (left) and X-rays (right) of $i$-AlCuFe: the intensities plotted versus $|Q^2|$ distribute on four branches depending on the parities of $N$ and $M$. 
Phase changes at special points

Phases changes at special points \([m35]\) in \(F(2)\) lattice

- \(R = (0, 0, 0, 0, 0, 0), \ Y(Q) = 1\)
- \(R = (1, 0, 0, 0, 0, 0), \ Y(Q) = (-1)^N, \ (P(1) \rightarrow F(2))\)
- \(R = (\bar{1}, 1, 1, 1, 1, \bar{1})/2, \ Y(Q) = (-1)^M, \ (D(1) \rightarrow F(2))\)
- \(R = (1, 1, 1, 1, 1, \bar{1})/2, \ Y(Q) = (-1)^{N+M}, \ (D'(1) \rightarrow F(2))\)

The experimental results are consistent with ASs located at the special points of the \(Fm35\) group.
The atomic surfaces appear as segments along 2D (rational) planes in $E_\perp$. They are located on special positions (strata of dimension 0) of $Fm\bar{3}5$ on the 6-D lattice $\Lambda$. Indeed...
Atomic surfaces (AS)

The simplest AS are high symmetry polyhedra aligned along $\mathbf{E}_\perp$. They give an acceptable density and lead to a relatively small number of different local configuration.
Parametrisation for possible ASs

We require ASs to follow a few simple criteria:

- be such that they do not generate atoms at too short distance from each others whatever cut is chosen;
- being connected at short distances to insure easy phasons jumps during a translation of the cut along $E_\perp$.
- being bounded by borders with planes of low indices to insure the possible existence of matching rules at short distances in physical space.
Cell decomposition

The local atomic configurations are listed by examining in $E_\perp$ the cell (klötze) decomposition. It is a hierarchical analysis that becomes finer and finer when the exploration radius increases.
Atomic models of F-type structures (\(i\)-AlCuFe and \(i\)-AlPdMn)

The atomic structure is reasonably well described using 3 ASs localized at the special points \(n = (0, 0, 0, 0, 0, 0)\), \(n' = (1, 0, 0, 0, 0, 0)\) and \(bc = 1/2(1, 1, 1, 1, 1, 1)\) of a 6D F-type Lattice \(F(2A)\).
Example of a typical atomic cluster: the M-cluster
The idea consists in attributing the same chemical species to the same local environments. Here is a simple chemical decoration that describes both \textit{i-}AlPdMn and \textit{i-}AlCuFe using the same cells.
Atomic structure in physical space
Example of possible Atomic clusters for P-type icosahedral phases

Because AS’s are located at special points of \( Pm35 \), the atomic structure will be of high symmetry (icosahedral) atomic shells.

<table>
<thead>
<tr>
<th>Translation</th>
<th>( R^2 )</th>
<th>type</th>
<th>location</th>
<th>AS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (1, 0, 0, 0, 0, 0)/2 )</td>
<td>( (2 + \tau)/4 )</td>
<td>icosahedron</td>
<td>edge</td>
<td>( e_1 )</td>
</tr>
<tr>
<td>( (1, -1, 1, 1, 1, 1)/2 )</td>
<td>3</td>
<td>dodecahedron</td>
<td>bc</td>
<td>( b_1 )</td>
</tr>
<tr>
<td>( (1, 0, 0, 0, 0, 0) )</td>
<td>( 2 + \tau )</td>
<td>icosahedron</td>
<td>node</td>
<td>( n_1 )</td>
</tr>
<tr>
<td>( 1/2(1, 2, 0, 0, 0, 0)/2 )</td>
<td>( (10 + 9\tau)/4 )</td>
<td>pentakisdodecahedron</td>
<td>edge</td>
<td>( e_2 )</td>
</tr>
<tr>
<td>( 1/2(1, 1, 1, 1, 1)/2 )</td>
<td>3 + 3( \tau )</td>
<td>dodecahedron*</td>
<td>bc</td>
<td>( b_2 )</td>
</tr>
<tr>
<td>( (1, 1, 0, 0, 0, 0) )</td>
<td>3 + 4( \tau )</td>
<td>icosahedron*</td>
<td>bc</td>
<td>( b_3 )</td>
</tr>
<tr>
<td>( 0, 1, 1, 1, 0, 0 )</td>
<td>4 + 4( \tau )</td>
<td>icosidodecahedron</td>
<td>node</td>
<td>( n_2 )</td>
</tr>
<tr>
<td>( 1/2(1, 1, 1, 1, -1)/2 )</td>
<td>6 + 5( \tau )</td>
<td>pentakisdodecahedron</td>
<td>node</td>
<td>( n_3 )</td>
</tr>
<tr>
<td>( (2, 0, 2, 1, 0, 0)/2 )</td>
<td>( (18 + 25\tau)/4 )</td>
<td>trisicosahedron</td>
<td>edge</td>
<td>( me )</td>
</tr>
<tr>
<td>( (2, 1, 1, 1, 1, -1)/2 )</td>
<td>( (18 + 29\tau)/4 )</td>
<td>icosahedron</td>
<td>mid-edge</td>
<td>( \ldots )</td>
</tr>
<tr>
<td>( (2, 2, 0, 1, 2, 0)/2 )</td>
<td>( (26 + 33\tau)/4 )</td>
<td>pentakisdodecahedron</td>
<td>edge</td>
<td>( \ldots )</td>
</tr>
</tbody>
</table>
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Typical AS for Primitive phases
At node $(0, 0, 0, 0, 0, 0)$:

At $bc (1, 1, 1, 1, 1, -1)/2$:

At mid-edge $(1, 0, 0, 0, 0, 0)/2$ and $(0, 1, 1, 1, 1, -1)/2$: 
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Typical Cluster
Conclusions

- (Stable) Quasicrystals are well described by the cut method: they are quasiperiodic objects.
- All actually known quasicrystals have ASs located on special points of the 6D periodic object.
- They can be viewed as assemblages of large highly symmetric atomic clusters (interpenetrating) located on the nodes of a tiling: the tiles form the *skeleton* of the structure (like the lattice in the ordinary crystals) and the atomic clusters are the *muscle* (as the motif in ordinary crystals). . .
Open Questions

- how quasiperiodic order propagates during the growth of quasicrystals (matching rules are not growth rules)?

- what kind of (long range) order gives pure point diffraction with peaks of intensity larger that a finite threshold distributing on a discrete set

- what kind of analytical tool can be (experimentally) used to decipher the long range order in solids beyond diffraction?

How to improve the new (1991) IUCr definition of crystals

*In the following, by "crystal" is meant any solid having an essentially discrete diffraction diagram, and by "aperiodic crystal" is meant any crystal in which three dimensional lattice periodicity can be considered to be absent. As an extension, the latter term will also include those crystals in which three dimensional periodicity is too weak to describe significant correlations in the atomic configuration, but which can be properly described by crystallographic methods developed for actual aperiodic crystals.*
A few basic papers on quasicrystals...

- Y. Meyer, "Algebraic numbers and harmonic analysis" (North Holland) (1972)
- M. Duneau M et A. Katz A; PRL (1985) 2688