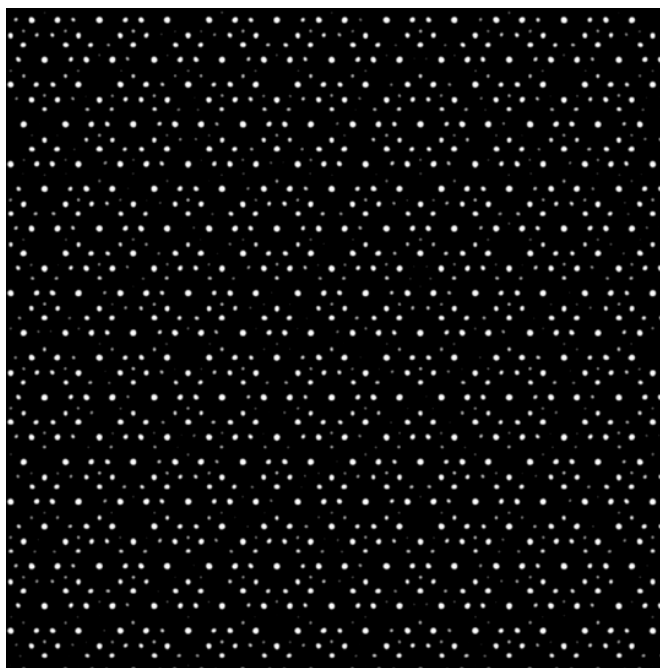


MATH 300-902

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# QUASICRYSTALS – A CAPTIVATING EXCEPTION

*TOPIC 18: CRYSTAL STRUCTURES AND SYMMETRY*



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## TABLE OF CONTENTS:

Abstract .....	1
1. Introduction .....	1
2. Some Crystallographic Concepts.....	2
3. Crystallographic Restriction Theorem.....	3
4. Quasicrystals – An Astonishing Discovery.....	7
5. Tiling and Quasicrystals.....	9
6. Fibonacci Sequence in Quasicrystals.....	12
7. Applications of Quasicrystals.....	13
8. Conclusion.....	13
References.....	15

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*Abstract:* The majesty of crystal structures is a great obsession in science due to their periodic and highly ordered pattern. In order to distinguish crystals from other materials, scientists had been using the arrangement and symmetry rules of atoms, which is called the crystallographic restriction. However, Shetchman's discovery of an unprecedented material – quasicrystal – unveiled a new type of matter which extends the paradigm of crystallography due to their aperiodicity and 5-fold rotational symmetry. This new type of matter gives rise to a variety of exciting applications in mathematics, chemistry, crystallography, and material science.

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## 1. INTRODUCTION

From the ancient Greeks, Egyptians, and Chinese to the Renaissance and today's world, crystals have attracted people by their aesthetic perfection and value<sup>[12,20]</sup>. However, it took centuries for scientists to effectively systematically distinguish crystals from other solids. In the 18<sup>th</sup> century, the first observations of symmetry in rocks and minerals had been made by Abbe Hauy when he noticed the repetition in calcite fragments<sup>[19]</sup>. The idea of symmetry in crystallography was further developed by Johann Hessel – a German mineralogist – in 1830 with the use of group theory, by which, the *crystallographic restriction theorem* was established and used to determine crystals. However, people at that time only knew the superficial structure of matters in micro scales by using microscopes. The study of symmetry in crystallography was only at its zenith for the first time, when the technique of X-ray diffraction (XRD) elucidated the atomic structure (Angstrong scale) of table salt and diamond in 1914 by Max Theodor Felix von Laue<sup>[12,19]</sup>. This technique gives a real two-dimensional pattern of the molecule's structure (Laue pattern), from which the three-dimensional structure can be calculated and pictured.

With the power of the XRD technique, scientists were able to resolve thousands of crystal structures and picture them on papers and computers. But also by XRD, a violating yet captivating and substantial phenomenon of quasicrystals was revealed. In 1982, Dan Shechtman et al., while analyzing the structure of aluminum-manganese alloys with XRD, asserted the existence of a 3-D icosahedral symmetry with 5-fold rotational symmetry<sup>[23]</sup>. This discovery raised a contentiousness in the crystallographic society because the 5-fold rotational symmetry breaks the crystallographic restriction theorem. In other words, quasicrystals have a structure with symmetry that does not obey the fundamental law of crystallography. However, the experimental results of Shechtman showed the crystalline properties of the quasicrystal materials<sup>[23]</sup>.

In this paper, basic characteristics of quasicrystals and their differences from real crystals will be discussed. Moreover, the fascination of quasicrystals is also expanded to the mathematical and material science. The connections of quasicrystals with Penrose tiling and the golden ratio are great interests for mathematicians of recent decades. The outstanding electrical properties of quasicrystals have also been researched and shown promising results. Since quasicrystals study can be considered as a young field in science, more intriguing features of this novel type of material are expected to be seen more often in this century.

## 2. SOME CRYSTALLOGRAPHIC CONCEPTS

In order to understand quasicrystals, one must be introduced to crystals and related concepts. A matter is considered as a crystal if its atomic structure is arranged in a three-dimensional periodically repeating pattern. Such a highly arranged and periodic network is called a *lattice* of the crystal. In mathematics, there are more than one definition for lattices and one is shown here:

DEFINITION 1: For  $n$  linearly independent vectors  $a_1, a_2, \dots, a_n \in \mathbb{R}^m$ , the lattice ( $\mathcal{L}$ ) is determined as

$$\mathcal{L}(a_1, a_2, \dots, a_n) = \{ \sum x_i a_i \mid x_i \in \mathbb{Z} \}$$

The lattice can be divided into many smallest identical units which are called unit cells. In other words, a space or an area can be completely filled by a number of identical 3-D shaped or 2-D shaped unit cells respectively. In XRD technique, it is sufficient to evaluate the whole crystal by just analyzing one unit cell because the unit cell has all the characteristic of the crystal<sup>[6]</sup>.

An important property of crystals is that every crystal has symmetry and this symmetry can be operated on. Symmetry operation is a movement of a symmetric body such that after the movement, the body looks exactly the same as before the movement. For instance, if a 90° rotation operation around the center axis is carried out on a cube, the cube will look exactly the same as before the operation. Symmetry operations include rotation ( $C_n$ ), improper rotation ( $S_n$ ), inversion operation ( $i$ ), and mirror plane ( $\sigma$ ). A crystal must have translational symmetry and rotational symmetry meaning that if a unit cell is shifted or rotated by a certain degree, the unit cell will match one of the other unit cells in the lattice. These two properties are important because they guarantee the periodicity of the crystal structure and the identity of the unit cells.

For the rotation operation, the angle of the rotation has to be  $\theta = \frac{2\pi}{n}$  for some  $n \in \mathbb{N}$ , where  $n$  is also called the order of rotation. A lattice is said to have a  $n$ -fold rotational symmetry if all points in the lattice coincide with themselves after a rotation about one point by an angle of  $\theta = \frac{2\pi}{n}$ . For example, an equilateral triangle has a 3-fold rotational symmetry because after a 120° rotation about its centroid, all of its points coincide.

By symmetry operations, possible types of crystals (or lattices) were identified by Auguste Bravais. Although there is an infinite number of crystals their lattice can only be one of the 14 Bravais lattices (figure 1)<sup>[18]</sup>. These lattices have been extensively used in crystallography, chemistry, physics, and materials science to classify crystals and their properties.

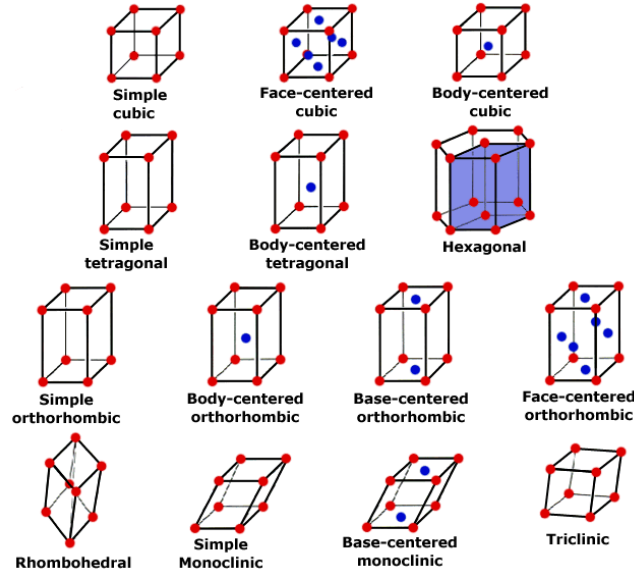


Figure 1. 14 Bravais Lattices<sup>[18]</sup>

### 3. CRYSTALLOGRAPHIC RESTRICTION THEOREM

Regardless of their difference in their lattice, crystals have to follow a symmetry rule which is called the crystallographic restriction theorem. There are several approaches to prove this theorem including lattice proof, trigonometry proof, matrix proof, etc. Here, a trigonometry proof is given for a 2D lattice.

**THEOREM 1. (The crystallographic Restriction):** For all lattices in  $\mathbb{R}^2$ , only 2-, 3-, 4-, and 6-fold rotational symmetry exist.

Proof:

By contradiction, assume that for all lattices in  $\mathbb{R}^2$ , 5-fold and n-fold ( $n > 6$ ) do exist.

Let A and B be two closest points of a 2D lattice and let r be the distance between A and B.

Since A and B are in the same lattice, they have the same n order of rotational symmetry.

Hence, there is a point  $A'$  resulting from a  $\frac{2\pi}{n}$  rotation of  $A$  about  $B$  and there is a point  $B'$  resulting from a  $\frac{2\pi}{n}$  rotation of  $B$  about  $A'$  such that  $AB=A'B=A'B'=r$ . Consider the following cases:

Case 1:  $n = 5$ . Hence,  $\frac{2\pi}{n} = 72^\circ$  and  $ABA'B'$  is a trapezoid.

Therefore,  $AB' = A'B(1 - 2\cos\frac{2\pi}{5}) < r$  (a contradiction because  $r$  is the smallest distance in the lattice)

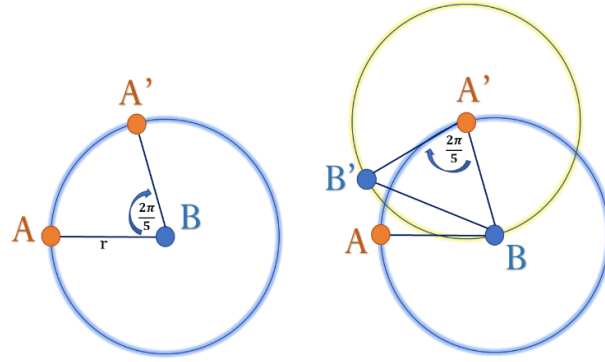


Figure 2.  $\frac{2\pi}{5}$  rotational operation of two lattice points  $A$  and  $B$ .

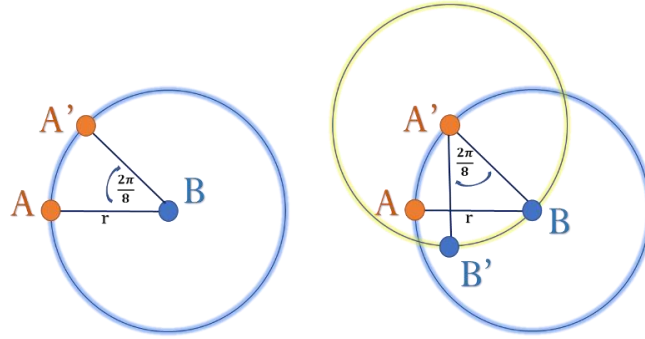


Figure 3.  $2\pi/8$  rotational operation of two lattice points  $A$  and  $B$ .

Case 2:  $n > 6$ . Consider the isosceles triangle  $ABA'$ :

Because  $AA' = \sqrt{2r^2(1 - \cos\frac{2\pi}{n})}$  and  $r = \sqrt{2r^2(1 - \cos\frac{2\pi}{6})}$ ,  $AA' < r$  (a contradiction because  $r$  is the smallest distance in the lattice). ■

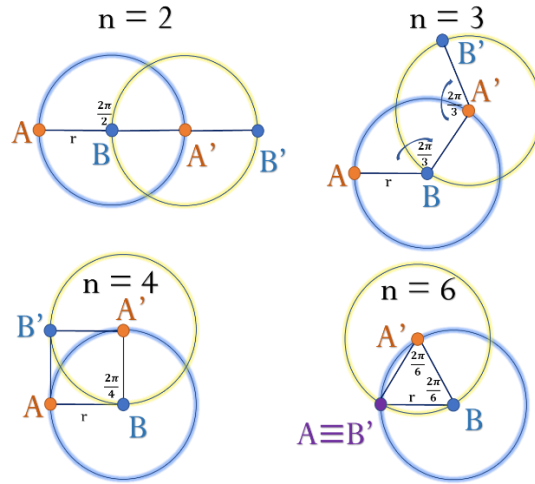


Figure 4. Four possible rotational symmetries of two points  $A$  and  $B$  in 2D lattices

In fact, all crystals structures of regular materials and minerals obey the crystallographic restriction theorem. In their 2D Laue patterns (figure 2)<sup>[1,18]</sup>, only the allowed rotational symmetries can be seen. For example, NaCl (a) shows 4-fold rotational symmetry; and sapphire (d) exhibits 3-fold rotational symmetry.

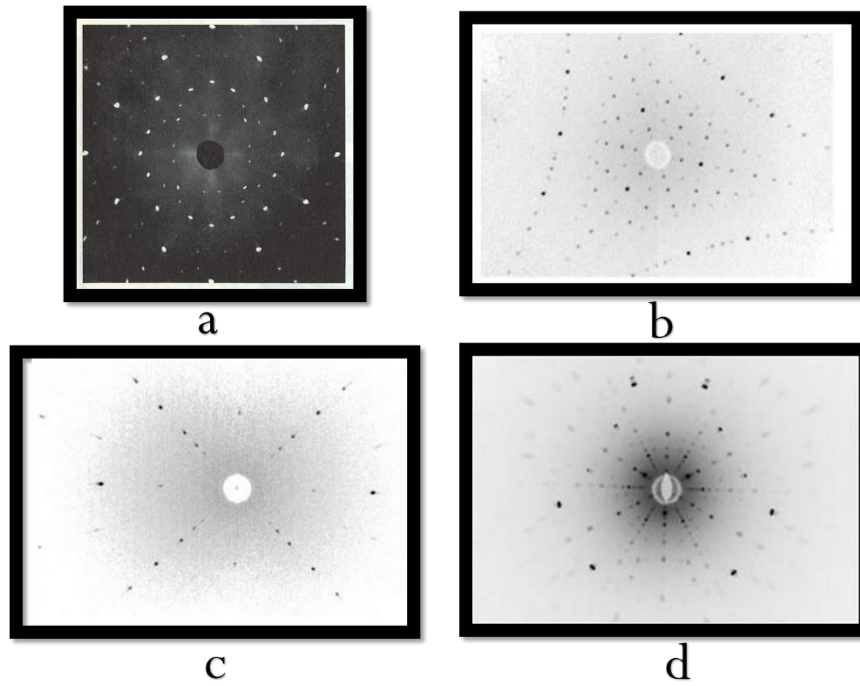


Figure 5. Laue pattern (electron diffraction) of a) NaCl<sup>[1]</sup>, b) Tungsten<sup>[18]</sup>, c) Diamond<sup>[18]</sup>, and d) sapphire<sup>[18]</sup>.

#### 4. QUASICRYSTALS – AN ASTONISHING DISCOVERY

The story of quasicrystals embarked in 1984 with the groundbreaking paper titled “*Metallic Phase with Long-Range Orientational Order and No Translational Symmetry*” by Dan Shetchman and coworkers<sup>[23]</sup>. In the paper, the authors demonstrate a highly ordered structure of alloys of Al with 10 – 14% Mn, Fe, or Cr. The structure displays a forbidden 5-fold rotational symmetry<sup>[7,23]</sup> of atoms built from pentagons. This means if the molecule is rotated by  $72^\circ$  about its central axis, the resulting position of the molecule will be exactly the same as before the rotation<sup>[23]</sup>. In addition, quasicrystals, unlike real crystals, do not have a periodic pattern. Put differently, while having rotational symmetry, quasicrystals do not have translational symmetry meaning that if the pattern is shifted, it will not match the original pattern. Hence, this type of crystals shatters the crystallographic restriction theorem not by falsifying the logic of the theorem, but by indicating that periodicity does not guarantee the long-range order of matters<sup>[7,20]</sup>.

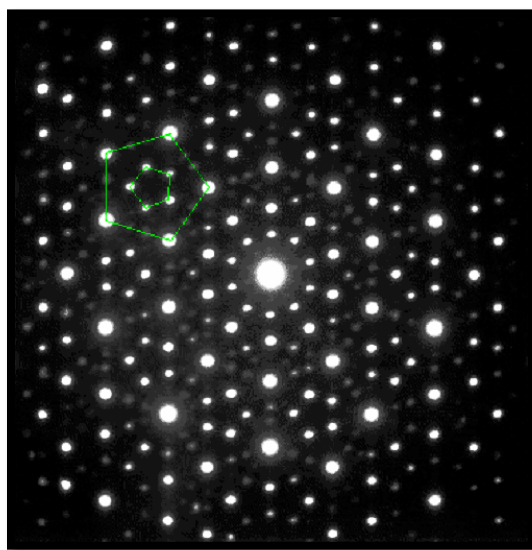
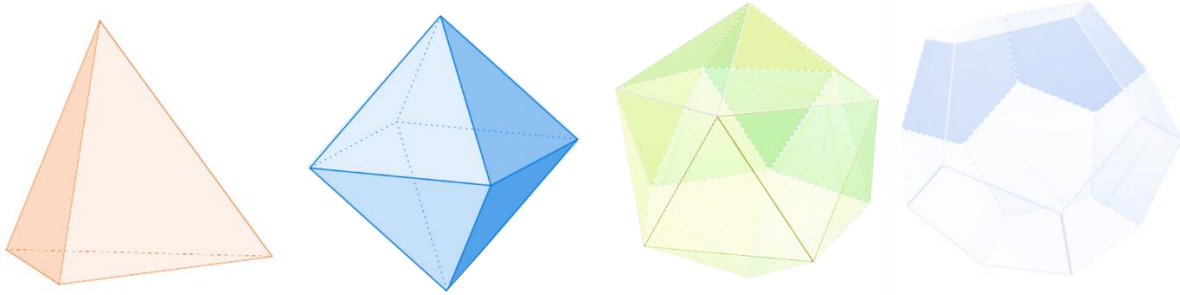


Figure 6. Electron diffraction of the first quasicrystal<sup>[20]</sup>

Another peculiar feature of quasicrystals is that they show the icosahedral symmetry in high dimension<sup>[16,20,23]</sup>. Among high symmetry polyhedra, while tetrahedron and octahedron are ubiquitously seen in crystal structures, icosahedron is not considered as a point group symmetry for crystals<sup>[2,6,16,23]</sup> simply because an attempt to completely fill a space with icosahedra would not be succeeded. However, quasicrystals show that it is possible to have atoms arranged in an icosahedral way<sup>[7,20,23]</sup>. This mystery can be explained by the quasi-periodicity of the arrangement. Captivatingly, the quasi-periodicity closely relates to geometry progression with irrational common ratio<sup>[10,20]</sup>. Therefore, by understand this geometry sequence, the whole structure of quasicrystals can be resolved albeit the lack of unique unit cells.



*Figure 7. From left to right: tetrahedron, octahedron, icosahedron, dodecahedron.*

Since the first quasicrystal was made, thousands of other quasicrystals have been published<sup>[26]</sup> along with their varied properties. It has been shown that quasicrystals can even exhibit 8-, 9-, 10-, 11-, and 12-fold rotational symmetry in 2D image<sup>[8,24,25]</sup>. Accordingly, octagonal, decagonal, and dodecahedral quasicrystals were also discovered. Different compositions of the quasicrystals have also been identified but limited to just alloys<sup>[20,24]</sup>, which are mixtures of metals. Some of such quasi-crystalline alloys are Al-Pd-Mn,  $\text{Cr}_5\text{-Ni}_3\text{-Si}_2$ , Sc-Zn-Mg, Al-Cu-Fe, and Ag-In-Yb<sup>[8,10,23,24,25]</sup>. This variety in structure and composition give rise to creativity in designing and modifying quasicrystals for desired properties and perhaps just for curiosity.

## 5. TILING AND QUASICRYSTALS

Instead of filling a 3D space by blocks, the periodicity of crystals is commonly simplified as 2D tiling because by knowing the other and examining one tile, the whole floor can be speculated. Tiling or tessellation is to cover a plane with polygons so that they do not overlap each other and there is no gap left on the plane. It is apparent that a floor can be tile with equilateral triangles, squares, and hexagons but not pentagons or octagons. These tiling ways were first recognized by Archimedes and was later fulfilled by Johannes Kepler in 1619<sup>[15,20]</sup>. In his famous book “*Harmonices Mundi*”, Kepler discovered the full list of 11 Archimedean tilings of plane (plane tilings by convex alike or non-alike polygons with identical arrangement at each vertex, figure 9)<sup>[15,20,21]</sup>.

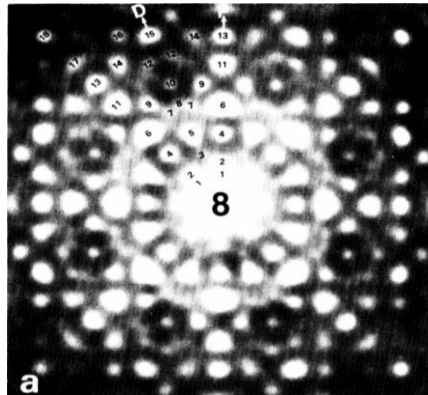


Figure 8. Electron diffraction of Cr-Ni-Si showing 8-fold rotational symmetry<sup>[23]</sup>

Also from Archimedean tilings, it had been noticed and believed for a long time that it is only possible to tile a floor in a periodic way. For example, in figure 10, an Archimedean tiling is divided into identical parallelograms; every parallelogram can be shifted and still looks the same. This means Archimedean tilings have both translational symmetry in addition to rotational symmetry. Therefore, filling a plane by this way is just the task of placing copies of the parallelogram next to each other.

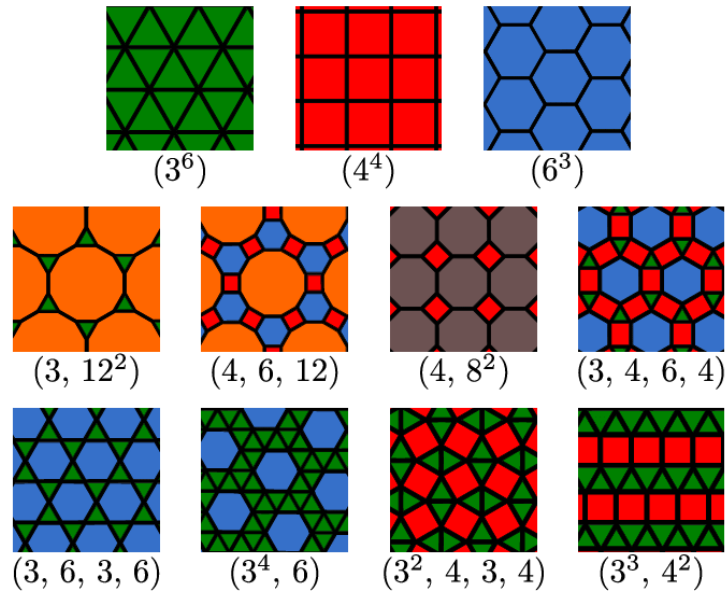


Figure 9. 11 Archimedean tilings<sup>[15]</sup>

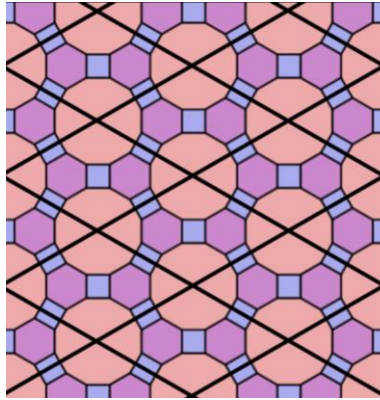


Figure 10. Dividing an Archimedean tiling into parallelograms

However, in the 1970s, Sir Roger Penrose found different systematic methods to fill a floor in a non-periodic way (Figure 11)<sup>[4,5,21]</sup>. Penrose only needs a small number of types of identical polygons to cover the entire plane which Kepler failed to achieve. Figure 11 (left) shows a Penrose tiling with two types of rhombs and figure 11 (right) indicates five types of polygons. Penrose tiles have special shapes that closely relate to pentagons. For the Penrose tiling with 2 rhombs (Figure 11 left), the angles of one rhomb are  $2\theta$  and  $3\theta$ ; and

the other rhomb has angles of  $\theta$  and  $4\theta$  where  $\theta = \frac{\pi}{5}$ . Consequently, the length of one of the diagonals of the two rhombs is  $(1+\sqrt{5})/2$  and  $\frac{1}{(1+\sqrt{5})/2}$  respectively, where  $(1 + \sqrt{5})/2$  is  $\varphi$ , the golden ratio.

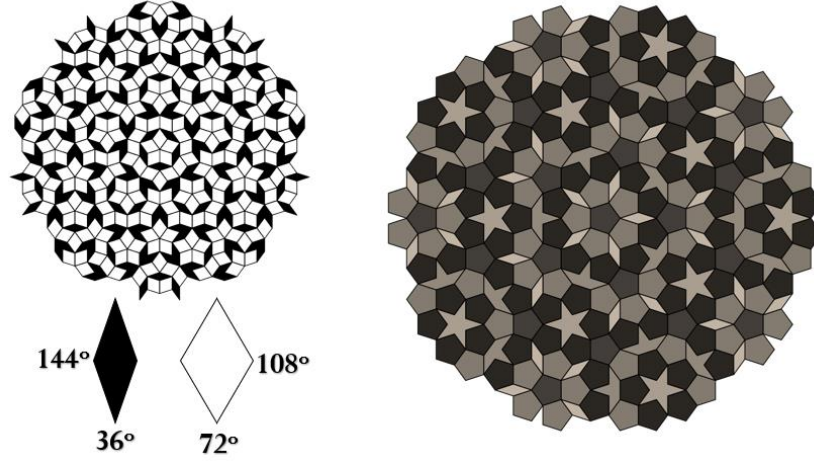


Figure 11. Two Penrose tilings

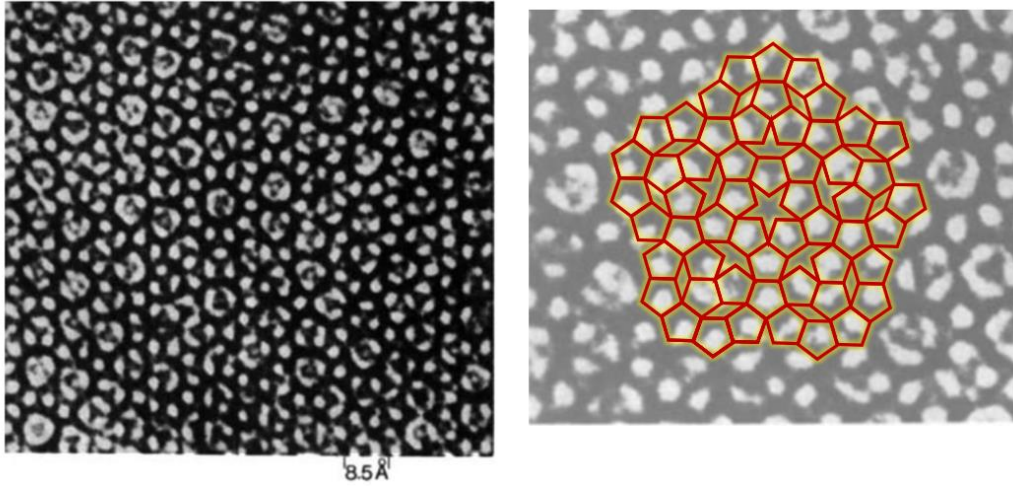


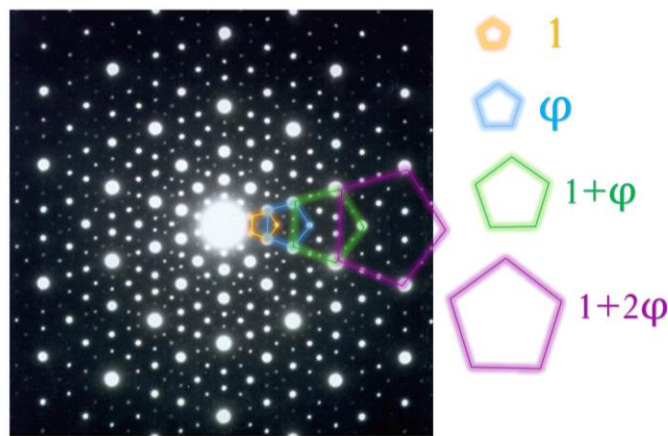
Figure 12. Electron diffraction pattern of an Al-Mg alloy<sup>[5]</sup>.

It is noticeable that Penrose tiling includes 5-fold rotational symmetry and lacks translational symmetry. This property is similar to the behavior of quasicrystals in three-dimensional. As expected, quasicrystals can be projected as a two-dimensional Penrose tiling<sup>[5,21]</sup>. By the technique of electron microscope which is

conceptually similar to XRD, a two-dimensional electron diffraction of Al-Mg alloy is pictured, and it is consistent with a Penrose tiling (figure 12). Conversely, there has been an intriguing topic in the mathematical society that construct the theoretical quasicrystals by representing Penrose tiling in higher dimensions<sup>[3,14]</sup>.

## 6. FIBONACCI SEQUENCE IN QUASICRYSTALS

As mentioned, the quasi-periodic arrangement in quasicrystals displays a geometric progression and the Penrose tiling is closely related with the golden ratio. Therefore, it suggests that quasicrystal also show the golden ratio characteristic; and this is true. Taking the electron diffraction picture of the first quasicrystal – Al-Mg alloy as an example, the golden ratio feature can be seen. If the vertexes of a pentagon are placed on 5 points closest to the core and the next pentagons are placed on 5 points such that 2 points of the bigger pentagon coincide with 2 points of the smaller pentagon, then the lengths of the side of each pentagon from smaller to greater will be the Fibonacci sequence or a geometric progression in which  $\varphi$  is the common ratio (Figure 13)<sup>[9,20]</sup>. Since the Fibonacci sequence is commonly observed in nature, a question is raised: can quasicrystals be obtained in biological systems?



*Figure 13. Fibonacci sequence found in quasicrystals*

## 7. APPLICATIONS OF QUASICRYSTALS

Not only showing their enchantment, but quasicrystals also propose various practical applications in material and nanotechnical science. The very first product made from quasicrystals was nonstick cookware where quasi-crystalline materials are used instead of Teflon<sup>[13]</sup>. They are superior than Teflon because Teflon layers are not healthy and easily scratched out of the coating, while quasi-crystalline layers are hard almost impossible to be damaged by knives. Moreover, brittle quasicrystals have been studied and show extraordinary ductility over 50% strain with a strength of 4.5GPa<sup>[26]</sup>. This suggest that quasi-crystalline materials can be used as plastics.

Another prospective application of quasicrystals is their ability to store hydrogen gas for advancement in stationary power, portable power, and transportation involving hydrogen fuels. Because the icosahedral quasi-periodicity in quasicrystalline materials have a larger free volume than periodic crystalline materials, hydrogen gas can access to the porous structure much more easily<sup>[17]</sup>. Also, because quasicrystals are usually alloys, the efficiency of hydrogen absorption can be enhanced by using two elements that have high affinities for hydrogen such as Ti and Zr<sup>[22]</sup>. Although it is not easy and may be impossible to industrialize quasicrystals-based products, other applicable properties of quasicrystals such as adherence, heat insulation, friction, corrosion, etc. have also been studied in order to bring this novel kind of material to daily life<sup>[11]</sup>.

## 8. CONCLUSION

Quasi-crystalline structure is a fascinating discovery to science, especially among mathematical, crystallographic, and physical communities. The 5-fold rotational symmetry in quasicrystals is attractive not only because it does not obey the crystallographic restriction theorem, but also because its relations to Penrose tiling and the Fibonacci sequence. Studies in quasi-crystalline structures are open fields which are only in their infancy and will potentially bring significant applications. Despite to the sterility of large-scale

applications, quasicrystals are certainly important because they further explain the atomic order of matters in a crystallographic, chemical, and mathematical way.

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