

Review Article

An Overview of Quasicrystals, Their Types, Preparation Methods, Properties

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Abstract

Quasicrystals, unlike crystals that contain regular and repetitive patterns, are composed of regular patterns that are not repetitive. Moreover, the symmetry of quasicrystals in crystals is impossible. For example, ordinary crystals can have triple symmetries from the repetition of a triangle or quadruple symmetries from the repetition of a cube. Quasicrystals are a special type of real crystals that are artificially formed only in laboratories, under certain conditions and temperatures, and it is not possible to form them like the earth. Evidence suggests that quasicrystals can form naturally under conditions contrary to astrophysical laws and remain stable for long periods. Quasicrystals are a group of new materials with unique mechanical, physical, and chemical properties. Among the known properties of these materials are low adhesion and friction, high resistance to corrosion, very high hardness, electrical insulation at low temperatures, and light absorption. Quasicrystals are used in non-stick coatings, nanoparticles, hydrogen storage, reinforcing phases in composites, catalysts, thermal insulation, infrared light absorption, and corrosion protection. In this article, we refer to some of the main topics related to quasi-crystal.

Keywords: Quasicrystal, Structure, Mechanical and Chemical Properties.

1. Introduction

In traditional segmentation in a Crystalline structure, a cell repeats itself to form a very large order (long order). While the amorphous structure lacks such an order. Daniel Shechtman first discovered a regular structure in an alloy in 1984, in which space was filled with rotational symmetry and 10 axes of symmetry. His discovery led to a change of heart in chemistry and he was awarded the Nobel Prize in 2011. These new materials were called quasicrystals. Quasicrystals can have five, ten, or even twelve symmetries that form strange shapes that are impossible to create in crystalline materials. Shaktman and colleagues first discovered the quasicrystal structure in the Mn-Al alloy by a rapid freezing process from the molten state. These structures are mostly discovered in Al, Ti, Mg, Zn, Zr based alloys [1-4]. Quasicrystal structures existed in ancient Iranian architecture in mosques and buildings before being discovered in materials. Lu and Steinhardt [5] examined thousands of photos taken from mosques of different countries including Pakistan, Uzbekistan, Turkey, Iran, and Iraq where girih tiles were used for decoration. They showed that the decagonal girih pattern is the most popular since 1200 and almost all the patterns were periodic. However, they found agirih pattern which was used to decorate the Darbi-i Imam shrine, in Isfahan, Iran,

builtin 1453, which shows quasicrystalline symmetry. A photograph of the half spandrel, which exhibits decagonal motifs with two different length scale, is shown in Fig. 1.

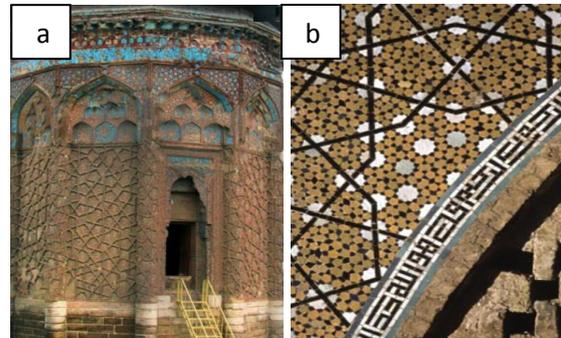


Fig. 1. a: Photograph of the tomb in Maragha in Iran, built-in 1197, b: Photograph of half of the spandrel of Darbi-i Imam shrine, in Isfahan, Iran 1453. [5].

This is a telltale of a quasicrystalline pattern [5]. After examination of the photo, Lu found that the girih pattern can be mapped onto the Penrose tiling including a few defects which could be made by workers during construction or repair. Lu suggested that the architects had understood quasicrystals since the 15th century [6]. The properties of alloys with this unique atomic structure distinguish them from previously known solids. These properties include hardness, electrical resistance, heat resistance, high wear and corrosion resistance, low

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By arranging these components with one of the shapes of triangle, square, rectangle, parallelogram, and hexagon, no space is created [10].

2.2. Quasicrystal

Structures with rotational symmetry of fifty or greater than six are prohibited in periodic spaces (the existence of symmetries other than 1, 2, 3, 4, and 6 for atomic arrangement in materials is prohibited). For a pentagon, the vertex angle is 108 degrees. If we place three pentagonal structures around a point to form a network, the pentagonal units do not stick to each other and a triangular slit is obtained which has an angle of 36 degrees (Fig. 5.) [9].

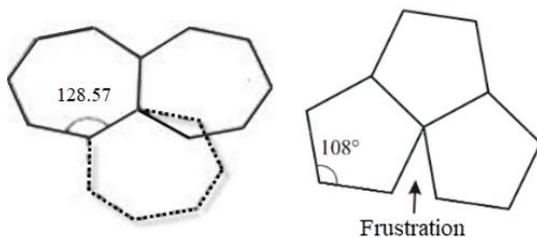


Fig. 5. Unauthorized shapes in two-dimensional space [9].

Also, hexagonal structures are not acceptable in periodic spaces. The angles of the vertex of a hexagon are equal to 120, which if two hexagons are placed next to each other, an angle of 120 is left empty. If we want to discuss in general, they are n-sided structures whose vertex angle is equal to $(\pi(n-2)/n)$ [9].

The existence of such an arrangement for atoms is a structure that has a long-range and is not repeated periodically, has forbidden symmetries of 5, 7, 8, 10, 12, 14, 30, 36, and is called a quasicrystal [9,10]. Table. 1. given the general differences between the three structures of crystal, quasicrystal, and amorphous.

Table. 1. General differences of three crystal structures, quasicrystal and amorphous [10].

Structure	Regular	Periodic	Rotational symmetry
Crystal	✓	✓	2, 3, 4, 6
Quasicrystal	✓	❖	5, 8, 10, 12
Amorphous	❖	❖	❖

3. Types of Quasicrystals

A quasicrystal is distinguished by two basic features in their structure: quasi-periodic transition order and forbidden rotational symmetries [11,12]. Putting a quasicrystalline pattern together can not fill the page putting two separate patterns together can fill the page. The Penrose model expresses this. Fig. 6.

shows several models of Penrose drawn with the help of two or more fat and thin rhombuses

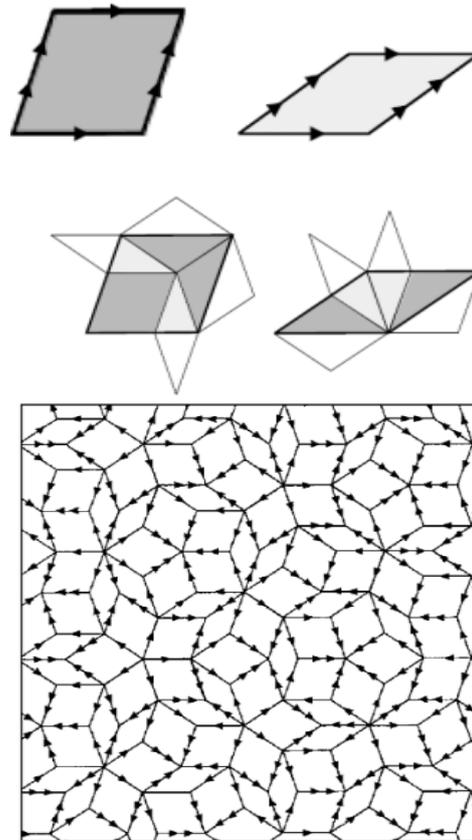


Fig. 6. Penrose Model [11].

Experimental quasi-alternating crystals with cubic symmetry such as tetrahedral, tetragonal as well as structures with hexagonal symmetry have been observed that are quasicrystal [12].

There are two types of quasicrystal: The first type is along the alternating path, which is called dehydral (polyhedral) quasicrystal. Dehydral quasicrystal can be called octagonal, decagonal, and dodecagonal crystals, which have axes of symmetry, 8, 10, and 12, respectively. While the second type of quasicrystal is not alternating along their path and is called an icosahedral (twenty-faceted) quasicrystal. Polyhedral quasicrystals have six-fold axes, ten triple axes, and fifteen binary axes that form a polyhedral structure [13].

Icosahedral consists of 20 quadrilaterals that are partially distorted from their natural shape and are arranged around a common axis. This structure, as a dense, stable, and configurable body, explains the possibility of local symmetry in many phases between complex crystals, often occurring in glass and rapidly cooled liquids [14]. Fig. 7. shows the diffraction pattern of a quasicrystal specimen as well as a three-dimensional view of the icosahedral structure of the first and most common type of quasicrystal known in nature and its symmetries.

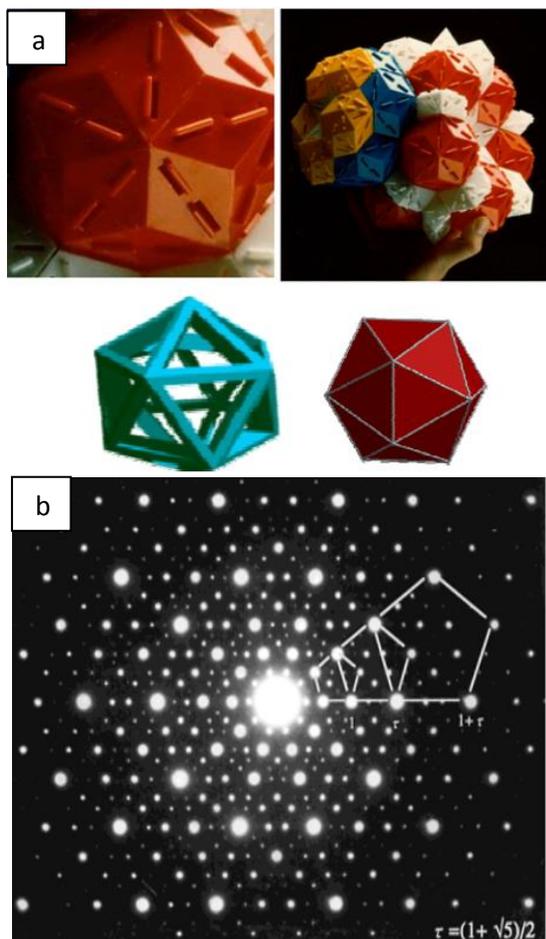


Fig. 7. a: Three-dimensional view of icosahedral structure ,b: Electron diffraction pattern along a quasicrystal pentagon [14].

Transitional symmetry determines the amount of displacement between individual atoms in one direction. While crystals have atomic plates that form periodically, quasicrystals have plates that are non-periodically aligned. Despite the non-periodicity of the pages, they have a long amplitude order and their position can be predicted with a special odd number τ , $1.617034 = \tau = (1 + \sqrt{5})/2 = 2 \cos \pi/5$ (Fig. 7-b).

The most common example of quasiperiodic is the Fibonacci series (... 8, 5, 3, 2, 1, 1, 0) where each component of the series element is the sum of the previous two elements. The correlation of the atomic arrangement distance in quasicrystals with the Fibonacci sequence is presented in the form of a special sequence of long (L) and short (S) parts (... SLSLSLSL...), while the ratio of the number of parts L to S is τ [15,16].

4. Types of Quasicrystal Alloys

Quasicrystal can be divided into stable and quasi-stable categories, many of which are in the quasi-stable phase. The first known Al-Mn alloy crystal is a quasi-stable phase.

The first known quasicrystal in the stable phase is a ternary alloy called Al-Cu-Li, which has icosahedral symmetry.

The most important stable quasicrystal alloys are Al-Cu-Fe, Al-Pd-Mn with icosahedral order.

Quasicrystal structures are mostly discovered in Al, Ti, Mg, Zn, Zr based alloys [17-20]. Table. 2. given the different types of alloys with a quasi-crystal structure.

Table. 2. Types of alloys with quasicrystal structure [21].

Type of Structure	Chemical Formula
Octagonal	Mn-Si
	Mn-Si-Al
	Mn-Fe-Si
Decagonal	Al-Tm (TM=Ir, Pd, Pt, Os, Ru, Rh, Mn, Fe, Co, Ni, Cr)
	Al-Ni-Co
	Al-Cu-Mn
	Al-Cu-Fe
	Al-Cu-Ni
	Al-Cu-Co
	Al-Cu-Co-Si
	Al-Mn-Pd
Dodecagonal	Cr-Ni
	V-Ni
	V-Ni-Si
Icosahedral	Al-Mn
	Al-Mn-Si
	Al-Li-Cu
	Al-Pd-Mn
	Al-Cu-Fe
	Al-Mg-Zn
	Zn-Mg-RE (RE=La, Ce, Nd, Sm, Gd, Dy, Ho,Y)
	Ti-TM (TM=Fe, Mn, Co, Ni)
	Pd-U-Si

5. Properties of Quasicrystal Alloys

5.1. Resistance to Oxidation

The study of the oxidation of quasicrystals by exposing them to oxygen shows that the layer of aluminum oxide formed on their surface prevents further oxidation.

As soon as it is exposed to water, whether in the form of vapor or liquid, the thickness of the oxidized layer increases relative to when it is exposed to oxygen. Moskalewicz et al. In creating AlCuFe, AlCuFeCr, and AlCoFeCr multicomponent coatings on titanium alloy by magnetron sputtering showed that the oxidation resistance of the alloy at high temperature (750 ° C) was significantly improved by deposition of coatings.

The improvement in oxidation resistance by the deposited coatings in the present work has been mainly due to the occurrence of α -Al₂O₃ protection

[22]. Also, Riabsio et al. investigated the effect of adding Al-Cu-Fe coating on materials and showed that this film reduced the susceptibility to corrosion in saline solutions. The corrosion tests of the model for 1, 2, 3, 4, 8 days with a 5% NaCl solution showed that all the examined films remained practically intact against corrosion. At the surface affected by the saline solution, no signs of normal radiation were observed for Al-Cu-Fe alloys [23].

5.2. Friction Coefficient

Numerous comparisons have shown that quasicrystals have a lower coefficient of friction than other metals. Careful studies of friction between quasi-crystalline pairs in a vacuum show that the friction between clean surfaces from the surface exposed to air and a thin layer of oxide that reduces friction is very noticeable [22, 23]. For example, Kang et al. studied several aspects of three thermal-spray quasicrystal coatings.

During single-pass diamond indenter tests, friction coefficients of 0.08 were reported for AlCuFe quasicrystal coatings [8]. Multiple pass $\delta n > 400\text{P}$ indenter tests performed by Brunet et al. reported friction coefficients of 0.2 versus a WC-Co indenter [24].

5.3. Level

One of the special properties of quasicrystals is their smooth surface, which despite the irregular atomic structure, the surface of quasicrystals can be smooth and flat. The surface of the quasicrystals also has an abnormal chemical reactivity and is used as a model for molecular surface adsorption [22].

5.4. Application of Anisotropy

The anisotropy phenomenon causes the emergence of properties in crystals that have various and important applications in the industry. For example, if we pull or press crystals such as quartz or tourmaline on both sides in a direction perpendicular to the pressure or tension, they will have opposite electric charges. If we change the direction of this pressure or tension, the type of electric charge changes, this phenomenon is called piezoelectric.

Heat generates electricity in some crystals, causing a positive charge on one side and a negative charge on the other, resulting in a difference in electrical potential between the two. Also, if we connect an alternating current to this crystal, the crystals expand and contract alternately, and sound is produced by vibration.

This property is used to produce sound, ultrasonic, electrical oscillations, crystal microphones, and phonograph needles [23].

5.5. Semiconductor Properties

Some crystals, such as germanium, silicon, and carbon, have semiconductor properties and conduct electrical currents to some extent. If semiconductor crystals are heated or placed in the path of light radiation, their electrical resistance is reduced and they conduct electricity better. Semiconductors are used in the electronics and telecommunications industries in the form of diodes, transistors, and electronic components. A diode or rectifier is made of two pieces of semiconductor crystal and is used to rectify alternating currents. A transistor consists of three semiconductor crystal pieces and is used to amplify weak currents and rectify alternating current [23].

5.6. The Phenomenon of Double Failure

Some crystals split light into two beams, causing double refraction in transparent minerals, such as calcium carbonate. If we put an inscription under calcium carbonate, it will be seen as two inscriptions.

Some crystals have selective absorption properties, such as the tourmaline crystal, which splits light rays into two groups. It absorbs one batch and passes through the other. This property is used to make films and polarizing lenses and to reduce the light intensity of car headlights [24].

5.7. Hardness

Some properties of crystals depend on the type and position of the bond between their molecules. For example, the stronger the bond between the components of a crystal, the higher its melting point, and the higher its hardness and strength, such as diamond and graphite crystals, which are chemically identical [23]. Carbon is formed, but due to the difference in chemical bonding between their atoms, the hardness and strength of graphite are low, but the hardness and strength of the diamond are very high. Some crystals break easily in certain lengths, due to the shape of internal bonds, such as NaCl crystals, and some easily break down into laminates, such as mica crystals [24].

The hardness and strength of the crystals are used in the manufacture of various papers and abrasive blades, as well as in watchmaking [24, 25]. In a study of the Al-Cu-Fe alloy produced by the arc melting method, Lee et al. observed that the alloy consists of three structures: λ -Al₁₃Fe₄, icosahedral phase, and τ -AlCu. They showed that the hardness of 334 HR15T alloy due to these structures is 3.65 times higher than bearing steel (88.8 HR15T) and 12.3 times higher than comparable aluminum alloy (Al 6061, 0.6 GPa). [25].

5.8. Low Thermal Conductivity

Quasicrystals are also used as thermal insulators. For example, the thermal conductivity of AlCuFe and AlPdMn pseudocrystals is much lower than that of aluminum, steel, and zircon (recently recognized as one of the best thermal insulators) [25]. Much attention was devoted to physical property investigations of these alloys [23].

It was found that Al–Cu–Fe quasicrystals showed peculiar physical properties such as high electrical resistivity, diamagnetism, and a pseudogap at the Fermi level [24]. Moreover, the magnetoresistance of quasicrystals is anomalously large at low temperatures. The study of Al₆₅Cu₂₀Fe₁₅ quasicrystalline ribbons exhibited paramagnetic spectra in the temperature range from 4 to 300 K [25]. The behavior of the icosahedral Al–Cu–Fe quasicrystal phase determined by some important magnetic factors is crucial in some industrial sectors [26].

5.9. Color of Crystals

When most of the light passes through the crystal and only a small amount of it is absorbed, the crystal is seen as transparent, and if the amount of light absorbed and the light passing through the crystal is approximately equal, the crystal appears semi-transparent if all the incoming light is absorbed. A dark crystal is seen. When the light absorption is different for different wavelengths, the crystal appears colored [25].

In addition to the properties mentioned in the above sections, we can mention other properties such as high thermal resistance, high Young modulus (100–200 GPa), good abrasion resistance, and high strength along with suitable softness for quasicrystals [2].

6. Application of Quasicrystal Alloys

Due to the properties mentioned above, alloys with this structure can be suitable for the following applications:

Anti-wear coatings, non-viscous coatings, thermal insulation coatings, corrosion-resistant coatings (medical industry), reinforcements for polymer-based composites, and adsorbents in solar cells hydrogen storage [23].

An Al–Cu–Fe quasicrystal is widely used in industry due to its advantages such as non-toxicity, availability of constituent elements, and their cheapness. Low thermal conductivity and coefficient of thermal expansion close to steels [3,5] make this alloy suitable for TBC applications.

Thermal stress due to mismatch between the substrate and the coating material is the most important cause of failure of traditional ceramic

thermal coatings such as zirconium, which is partially stabilized [18].

Many attempts have been made to use quasicrystalline phases in soft metals to improve their strength and hardness. The best method is to use aluminum powder and quasi-crystalline phase after homogenizing them in a low energy mill and using hot press or casting to produce composite [25, 26].

A significant increase in the mechanical properties of these composites has been observed so that the hardness of these materials has reached 1200 MPa, which is twice as much as the basic aluminum composites reinforced with SiC with the same volume percentage [25].

Low thermal conductivity as well as good corrosion resistance at high temperatures, in addition to the superplastic behavior of quasi-crystalline coatings at high temperatures, make the use of these coatings more valuable and have replaced one of the best insulators today, including zircon [26].

Today, these coatings are used in rocket engines and aircraft turbines [26]. The quasi-crystalline phase of Ti–Zr–Hf is more capable of storing hydrogen than the crystalline phases in this system. Recent advances show that hydrogen storage devices using Ti_{41.5}Zr_{41.5}Ni₁₇ quasicrystals can withstand high pressures (100–200 psi) and absorb three hydrogen atoms per metal atom [27,28].

Quasicrystal buds precipitate and grow during the tempering of stainless steels, and it has been observed that under ideal annealing conditions, the quasi-crystalline phase remains unchanged [27]. The hardness of these steels reaches 700 Vickers and their tensile strength reaches 3000 MPa. The surface of some quasi-crystalline phases has a high reactivity that can be used as a catalyst. These quasicrystals include Al–Pd alloy which can replace Pd particles [28].

One of the most important disadvantages of quasicrystals is that at temperatures below 80–70% of the melting point, these alloys are very brittle and have limited their range of application. For example, the i-Al–Pd–Mn quasi-crystalline hardness at room temperature does not exceed that of steel, but it has much lower hammering. One solution to overcome this limitation is to coat them as coatings on stronger substrates [29].

7. Types of Processes of Forming Quasicrystal Structures

Quasicrystals are produced in different ways. One of these methods is rapid cooling from molten to solid. In this method, the cooling rate is about 10⁵ to 10⁶ K/s, which is very important. The lower the value, the more likely it is that crystalline phases will form next to the quasicrystals [24].

Another method of producing these materials is the use of induction melting furnaces, which are based on a variable magnetic field, Metals are placed

inside this magnetic field, the induced current created in them causes the metals to heat up and eventually melt [25].

The use of electric arc furnaces is another method for producing quasi-crystals. In this method, two or three electrodes are used, which are created after the electric current of the electric arc is established, and the resulting heat melts the metals. Mechanical alloying is another method of creating a quasi-crystal and produces a compound with a very fine and uniform structure [26].

The basis of this method is the use of high energy mills based on the failure, deformation, cold welding, and penetration at short distances between layers of powder. Its kinetics depend on the energy transferred from the pellets to the powder during milling. The production of nanostructures is also possible with this method [24-29].

Other reported processes for forming a quasi-crystalline structure are rapid solidification (melt spinning and gas atomization), gentle cooling of the melt, physical vapor deposition, electron-beam superficial fusion, low-temperature annealing of amorphous phases, electrodeposition [29].

The most common method used in the preparation of stable quasicrystals in the laboratory is the melting of pure components and casting and melting in the form of ingots or tubes.

For most alloys and their components, the quasi-crystalline phases are due to the peritectic solidification reaction of the high-temperature crystalline phases with the residual liquid phase [14, 30].

8. Conclusion

Quasicrystals are new materials that can be used in many fields of advanced technology. Quasicrystals are essentially solids with ordered structures that are quite strange along with one or more crystallographic directions and often show five to ten times symmetries. They are usually binary and triple metal alloys, which often contain 60% -70% aluminum.

This unusual atomic structure results in a combination of special mechanical and physical properties that provide a wide range of applications. quasicrystals are a group of intermetallic tributaries that have high hardness and strength.

Studies have shown that quasi-crystals have a low coefficient of friction, corrosion resistance, and high abrasion resistance.

These materials are commonly found in the base alloys of aluminum, magnesium, zirconium, titanium, zinc, and copper.

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