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An introductory note on Quasicrystals

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Abstract

This paper presents a brief introduction of the research on a new class of materials called quasicrystals. Starting from history of its development, paper discusses about its growth mechanism and its applications. Contents of the paper are based on various sources available and no originality of the article is claimed by the author.

Keywords: Quasicrystals

INTRODUCTION

Quasicrystals are materials with an ordered but nonperiodic structure. These are a unique class of ordered solids that display long-range aperiodicity, which distinguishes them from ordinary crystals. The term quasicrystalline is applied to a pattern with unusual symmetry. An ordering is said to be non-periodic if it lacks translational symmetry, which means that a translated copy will never match exactly with its original. A quasicrystalline pattern can continuously fill all available space, but it lacks translational symmetry. If a plane surface is to be filled by tiles of different shapes, only tiles of certain shapes fit together snugly without creating unsightly holes. These tiles can be rectangles or triangles or squares or hexagons, any other simple shape won't work, because it will leave a gap. However, in a quasicrystal, pentagonal and other symmetries, which are not possible in crystals, are found. The tiling displayed in a quasicrystal may have translational symmetry in some dimensions but may lack periodicity in other dimensions [1, 2]. Quasicrystals are found most commonly in aluminium alloys (Al-Li-Cu, Al-Mn-Si, Al-Ni-Co, Al-Pd-Mn, Al-Cu-Fe, Al-Cu-V, etc.), but many other compositions are also known (Cd-Yb, Ti-Zr-Ni, Zn-Mg-Ho, Zn-Mg-Sc, In-Ag-Yb, Pd-U-Si, etc.)[3].

The History of Quasicrystal Research

The possibility of Quasicrystal structure had been investigated and observed earlier [3] but, until the 1980s, they were disregarded in favor of the prevailing views about the crystal structure of solids. Crystallographic restriction theory states that crystals can only have symmetry's of the order of 2, 3, 4 and 6. Quasicrystals were found to have an order of symmetry of 5, 8, 10 and 20, with ordered but aperiodic structure.

Aperiodic structures were discovered by mathematicians in the early 1960s, and, some twenty years later, they were found to apply to the study of quasicrystals[4]. In 1961, Hao Wang's conjecture [5] initiated a debate on whether determining a set of tiles that admits a tiling of the plane is algorithmically a solvable problem. Two years later Robert Berger [6] constructed a set of some 20,000 square tiles which are called Wang tiles. This pattern can tile the plane in an ordered but in a nonperiodic fashion. As the number of known aperiodic sets of tiles grow, each set seems to contain even fewer tiles than the previous one. In 1976, Roger Penrose[7] proposed a set of just two tiles known as Penrose tiles that produces only ordered non-periodic tilings of the plane. These tilings displayed instances of fivefold symmetry. In 1972, de Wolf and van Aalst[8] reported that the diffraction pattern produced by a crystal of sodium carbonate cannot be labeled with three indices but needed one more, which implied that the underlying structure had four dimensions in reciprocal space. Some other puzzling cases [9] were also reported, but until the concept of quasicrystal came to be established, they were either ignored or denied [10]. In 1977 Alan L. Mackay [11] showed experimentally that the diffraction pattern from the Penrose tiling had a two-dimensional Fourier transform consisting of sharp delta peaks arranged in a fivefold symmetric pattern. During the same time, Robert Ammann [12] created a set of aperiodic tiles with eightfold symmetry.

Mathematically, quasicrystals have been shown to be derivable as projections of a higher-dimensional lattice where various (aperiodic or periodic) arrangements in two and three dimensions can be obtained from postulated hyperlattices with four or more dimensions. Icosahedral quasicrystals in three dimensions were projected from a six-dimensional hypercubic lattice by Peter Kramer and Roberto Neri in 1984[13]. The tiling is formed by two tiles with rhombohedral shape.

On the experimental side the first quasicrystalline materials were found to be thermodynamically unstable. When heated, they formed regular crystals. The first stable quasicrystals was discovered in 1987 However, by 1987, many stable quasicrystals have been discovered making it possible to produce large samples and opening the door to potential applications in diverse branches of technology. In 2009 scientists reported the first natural quasicrystal, a mineral found in in Russia[14]. The natural quasicrystal phase, with a composition of $Al_{63}Cu_{24}Fe_{13}$, was named icosahedrite. Quasicrystals are most commonly found in aluminium alloys (AlLiCu, AlMnSi, AlNiCo, AlPdMn, AlCuFe, AlCuV, etc.), but many other compositions also may exhibit quasicrystal structure (CdYb, TiZrNi, ZnMgHo, ZnMgSc, InAgYb, PdUSi, etc.).

The discovery of quasicrystals gradually opened up a whole new avenue of understanding of crystallography. Quasicrystals are now used almost everywhere ranging from fry pans to diesel engines and so on. By the end of the eighties, the idea became acceptable, and in 1992 the International Union of Crystallography altered its definition of a crystal, broadening it as a result of Shechtman's findings, reducing it to the ability to produce a clear-cut diffraction pattern and acknowledging the possibility of the ordering to be either periodic or aperiodic. The term "quasicrystal" was first used in print by Steinhardt and Levine[15] after Shechtman's paper [16] was published. Shechtman was awarded the Nobel Prize in Chemistry in 2011 for his work on quasicrystals.

Growth mechanism

Quasicrystals are formed via nucleation and growth process. A microscopic nucleus of the solid phase spontaneously arises in the supercooled liquid and spreads outward, converting the system from liquid to solid [17, 18]. One of the fundamental problems in quasicrystal physics is to reconcile the typical picture of nucleation and growth with the formation of an aperiodic solid. Quasicrystals cannot grow like crystals, where the nucleus surface acts as a template for copying a unit cell via local interactions. Rather, quasicrystals, require specialized growth rules that describe their formation [19].

Quasicrystal growth models fall into two categories: energy-driven quasiperiodic tiling models[15,20] and entropy-driven random tiling models[21,22]. The energy- driven models are based on matching rules to describe how atomic clusters or tiles attach to the nucleus whereas entropic models allow tiles to attach randomly to the nucleus with some probability. Although these models provide important insight into the mechanism that systems must follow to grow quasicrystals, they do not provide a detailed physical grounds to justify why such mechanisms exist. The physical driving force underlying quasicrystal growth, and whether it is based on local interactions or long-range correlations, is still not well understood.

Types of Quasi Crystals

Quasicrystals can be classified into two types [23]. The first type, polygonal (dihedral) quasicrystals, have an axis of eight, ten, or 12-fold local symmetry. They are periodic along this axis and quasiperiodic in planes normal to it. The examples are:

Octagonal symmetry : Mn_4Si, $Cr_5Ni_3Si_2$ etc.
Decagonal symmetry : Al-Co-Ni, Al_5Ir) etc. and
Dodecagonal symmetry : V_3Ni_2, $Cr_{70}Ni_{29}$) etc.

The second type is called the icosahedral quasicrystals having 5- fold symmetry. These structures are aperiodic in all directions. Examples of such type of quasicrystals are: Al-Pd-Mn, Al-Cu-Fe, Ag-In-Yb etc.

Depending on thermal stability the quasicrystals are classified as Stable quasicrystals, which are grown by slow cooling or casting with subsequent annealing and Metastable quasicrystals, which are prepared by melt spinning, or by the crystallization of the amorphous phase[24].

Structure of Quasicrystals

The structures of crystals are determined using electron microscopes or X-ray diffraction. By measuring how the X-rays or electrons are diffracted, the patterns can be determined in which atoms are arranged inside the crystals. Most crystals are composed of a three-dimensional arrangement of atoms that repeat in an orderly pattern. Depending on their chemical composition, they have different symmetries. Contrary to the crystallographic restriction theory, quasicrystals behave differently than other crystals. They have an orderly pattern that includes pentagonal, octagonal, decagonal, or dodecagonal or icosahedral structures but unlike other crystals, the pattern never repeats itself exactly.

Shechtman observed the tenfold electron diffraction patterns in 1982. These results were not published until two years later when Ilan Blech, using computer simulation, suggested that the diffraction patterns obtained by Shechtman resulted from an aperiodic structure. Blech simulations as well as the diffraction patterns were published in 1984 in a joint paper with Shechtman[25]. Later on another paper was submitted for publication demonstrating a clear diffraction pattern with a fivefold symmetry [16]. In 1985, Ishimasa [26] reported twelvefold symmetry in Ni-Cr particles. Soon, eightfold diffraction patterns were recorded in V-Ni-Si and Cr-Ni-Si alloys [27]. Over the years, hundreds of quasicrystals with various compositions and different symmetries have been discovered.

Potential Applications

Many properties of quasicrystals combine effectively to give technologically interesting applications. The combination of nonsticking, hardness, corrosion resistance, and low thermal conductivity gives almost ideal material for coating frying pans or other cookware. Quasicrystalline coatings, usually 10μm to 1mm in thickness, are made by plasma spraying powders produced by gas atomization of a melt. Cost largely depends on the alloy composition. Quasicrystalline powders are presently manufactured under the trade-name CRISTOME for coating cooking utensils. Similarly combining the low friction coefficient and the high hardness and corrosion resistance is obviously very efficient in reducing both surface damage and energy dissipation in the moving contact between two solids. Quasicrystalline cylinder liners and piston coatings in motor-car engines would result in reduced air pollution and increased engine lifetimes. The same set of associated properties combined with biocompatibility is very promising for introducing quasicrystals in surgical applications as a coating on metallic parts used for bone repair and prostheses. Low thermal conductivity and corrosion resistance of quasicrystals become useful at high temperatures when quasicrystalline coatings are superplastic. They constitute thermal screens that can easily accommodate thermal constraints and the thermal expansion of the protected bulk material. Rocket motors and aero-engine turbine would benefit from this technology. Hydrogen storage is a key issue preventing the development of hydrogen powered automobiles. TiZrHf-based quasicrystals have been demonstrated to efficiently absorb hydrogen atoms into either interstitial sites or on their surfaces. This property gives these novel materials potential technological importance in hydrogen fuel technology. Their optoelectronic properties are used in manufacturing high efficiency light emitting diodes.

CONCLUSION

Over the last three decades, hundreds of quasicrystals have been synthesized in laboratories. Now the quasicrystals exist universally in many metallic alloys and some polymers. The discovery of quasicrystals has shown to be much more than just academic and conceptual. Quasicrystals have been used in surgical instruments, LED lights. Quasicrystals have non-stick surfaces which makes them suitable for surface coating of non stick frying pans. Quasicrystals are very hard and are also bad conductors of heat and electricity, making them useful as so-called thermoelectric materials. Potential uses also include components for energy-saving light-emitting diodes (LED) and heat insulation in engines. Properties of quasicrystals vary depending on their direction. In one direction might conduct electricity easily and in another direction it might not conduct electricity at all. By now quasi crystals have shown high potential for various application in diverse fields of technology. Of course, there are still many problems in this field. Producing industrial quantities of good quality quasicrystals is not that simple. Material cost is another challenge. Moreover their low tolerance has also limited their practical applications. However the present status is promising the real implications of the discovery may still lie in the future.

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