

QUASICRYSTALS: NOVEL FORMS OF SOLID MATTER

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An ordered state of solid matter called quasicrystalline, discovered in the early 1980's, possesses symmetries forbidden in crystals. The growing number of quasicrystalline compounds and the variety of methods used to synthesize them in the laboratory suggest that quasicrystals may be an as yet undiscovered facet of the mineral kingdom.

INTRODUCTION

Since the time of René Just Haüy (1743–1822) it has been generally recognized that the wonderful polyhedral shapes of crystals and their naturally occurring planar faces are a manifestation of their internal atomic order. On the other hand, amorphous solids (glasses) such as obsidian have a very disordered internal structure, and do not naturally occur in the polyhedral shapes we so readily identify with crystals. Until the recent discovery of "quasicrystals," solids have been identified as being either crystalline or amorphous. Quasicrystals, however, are less ordered than crystals but are more ordered than glasses. Perhaps their most striking feature is their appearance as certain polyhedral shapes that are *not* allowed in crystals. For examples, the shape of the Al-Li-Cu quasicrystals in Figure 1 is called a triacontahedron,

possessing 30 equivalent faces and six axes of 5-fold rotational symmetry (Fig. 2), a symmetry forbidden in crystals.

BACKGROUND

In his works, Haüy championed the theory that for a given mineral, any of its varied crystal shapes could be constructed by the appropriate stacking of many identical building blocks or integrant molecules (*molécules intégrantes*) of the same orientation (Fig. 3). Based on such constructions, Haüy proved that the regular icosahedron and dodecahedron (Platonic solids which possess 5-fold symmetry) violated his law of rational intercepts, and thus are impossible shapes

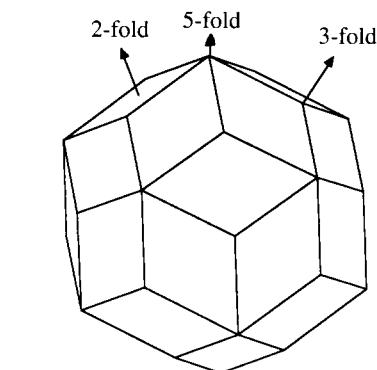
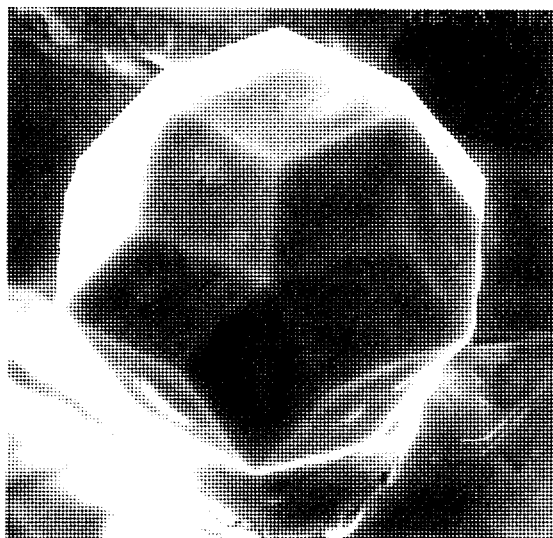


Figure 2. An idealized triacontahedron with one of its six 5-fold axes indicated.

Figure 1. SEM photo of an isolated, triacontahedral quasicrystal of $Al_{5.1}Li_3Cu$ made at AT&T Bell Laboratories. The grain is 0.1 mm across. SEM photo courtesy of A. R. Kortan, AT&T Bell Laboratories.

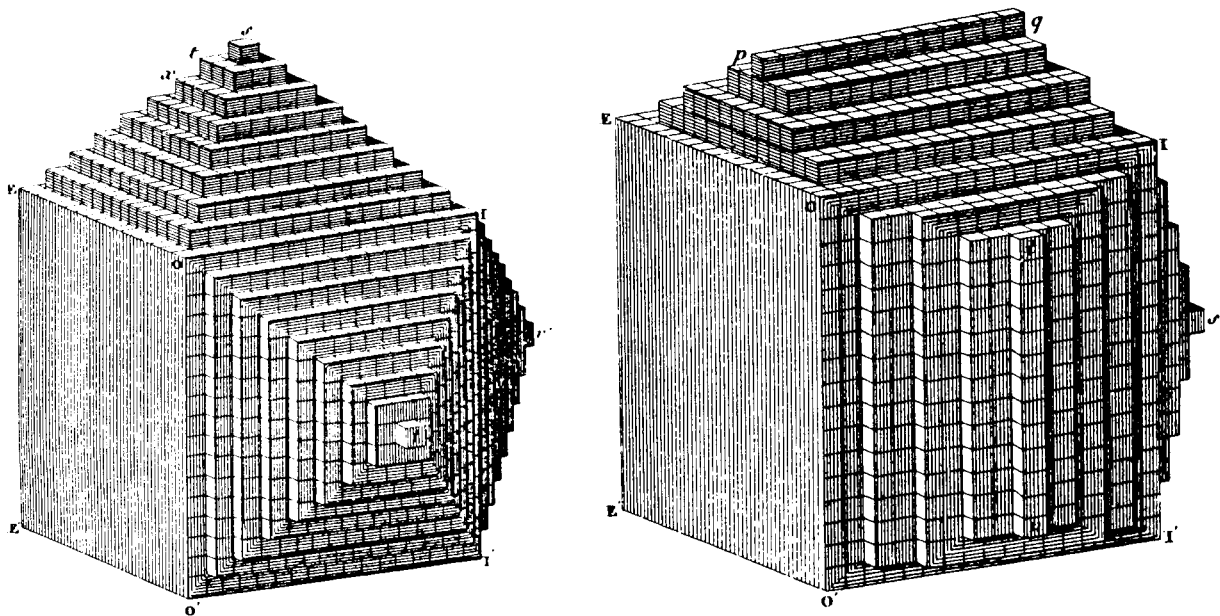


Figure 3. An illustration of Haüy showing how stacking integrant molecules can account for the habit of crystals (Haüy, 1801).

for crystals (Haüy, 1801).¹ Subsequently, the existence of flat faces on crystals has become intimately associated with their being composed of a regular stacking of a single type of building block for a given crystal. Haüy's concept of an integrant molecule has since developed into what is known today as the unit cell—a hypothetical volume decorated with atoms, which when many are stacked together in the same orientation, make up the entire crystal structure. In an infinite crystal, each unit cell has the same surroundings as every other unit cell. One can then imagine a point (say at the center of each cell) as representing the position of each unit cell. This set of regularly spaced points is known as a lattice. If one imagines moving from one lattice point to another by going a certain distance in a certain direction, one will always come to another lattice point by again going the same distance in the same direction but starting from any other lattice point—a property called *periodic translational symmetry*. Using the fact that each point in a lattice has the same surroundings as every other point, Auguste Bravais (1811–1863) showed that there are only fourteen different lattices in three-dimensional space.² In two-dimensional space there are only five different lattices (Fig. 4).

Throughout the early development of the science of crystallography the classification of crystals based on their external form has played an important role. Christian Samuel Weiss (1780–1856) and Frederick Mohs (1773–1839) set up classifications based on the concept of external symmetry, and laid the foundation for the mathematical treatments of the 19th century. The external symmetry of crystals³ can be

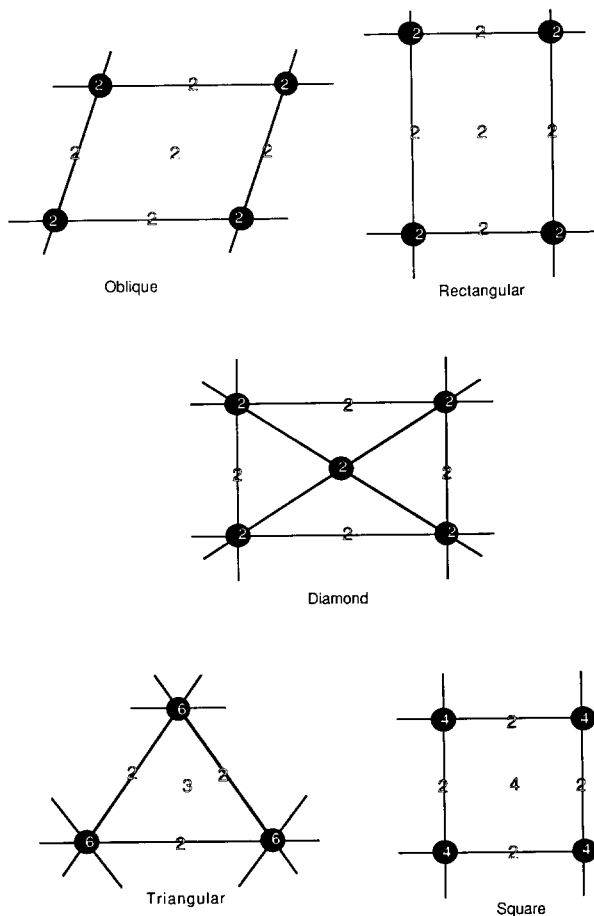


Figure 4. The five two-dimensional lattices: square, triangular, rectangular, centered and oblique. The numbers correspond to the type and position of rotational symmetry axes of the lattice.

¹For a detailed history of the science of crystals, Burke (1966) and Schneer (1977) are highly recommended.

²Illustrations of the fourteen Bravais lattices can be found in most introductory mineralogy texts.

³Since the conditions in which crystals grow, such as close proximity to other crystals or a varying chemical composition or temperature, can distort their shapes compared to what their shapes would be given enough room in a uniform environment, the following discussion refers to ideal crystals—those whose internal structures are without defects or flaws, and that grew in such a way that their external form is consistent with their internal symmetry.

understood in terms of two basic symmetry operations: rotation and reflection. A crystal has rotational symmetry about an axis (an imaginary line through the center of the crystal) if it repeats itself in appearance⁴ one or more times as it is rotated one complete revolution about that axis. Axes of rotational symmetry are classified according to the number of times a crystal repeats itself in appearance during such a rotation about the axis. For example, a crystal with 3-fold symmetry will repeat itself in appearance three times when rotated by 360 degrees about a 3-fold axis. A crystal has reflection (or mirror) symmetry if a plane can be found which divides the crystal into two halves which are mirror images of each other. The cube, for example, has six mirror planes perpendicular to its six 2-fold axes, and three mirror planes perpendicular to its three 4-fold axes. Other symmetry operations can be derived by combining rotations and reflections into a single operation, e.g., inversion symmetry can be thought of as a 2-fold (180 degree) rotation followed by a reflection through a plane perpendicular to the rotation axis.⁵ Various minerals possess different groupings of the symmetry operations, and it is these groupings which determine a crystal's allowed forms, such as cube, tetrahedron, pinacoid, etc. Johann F. C. Hessel in 1830, and Bravais independently in 1848, mathematically proved that there were *only* 32 possible different groupings of the symmetry operations in crystals. These different groupings are known as the 32 crystal classes (Buerger, 1956; Boisen and Gibbs, 1985).

There are two main reasons why the number of crystal classes is limited to only 32. First, the set of symmetry operations in a class must not generate an infinite number of equivalent crystal faces. This would occur, for example, if one combined a 4-fold axis perpendicular to a 6-fold axis. The second reason is more basic to the very nature of crystals. Since by definition crystals are composed of a stacking of identical unit cells on a lattice, only 1-fold, 2-fold, 3-fold, 4-fold and 6-fold symmetry axes are allowed. These are precisely the rotational symmetries of the fourteen Bravais lattices. To illustrate why the concept of a lattice limits the rotational symmetries, consider the two-dimensional lattices in Fig. 4. All of the allowed rotational symmetries are represented. Notice that each unit cell (lattice point) has identical surroundings as every other unit cell (lattice point), as is required. Figure 5, on the other hand, illustrates what happens when a unit cell with 5-fold symmetry is used to try to form a lattice. Here, the pentagonal "tiles" neither fit together to fill the plane, nor do all the pentagonal tiles have the same surroundings as every other tile. While some tiles have five tiles bordering them, others have as few as two. Furthermore, some pentagons actually overlap each other. Similar problems occur when one tries to form a lattice out of unit cells with 7-fold or higher symmetry. Thus, 5-fold, 7-fold, and higher rotational symmetries are not allowed in crystals.

One might wonder why the concept of the lattice has been kept since it is so restrictive. After all, is nature *constrained* to grow ordered solids based on lattices or a single unit cell? In 1912 Max von Laue predicted that the orderly arrangement of atoms on a lattice should diffract a beam of X-rays in a mathematically predictable pattern of spots that could be verified by exposing a photographic plate to the diffracted X-rays (Arem, 1971). Within the year von Laue, Walter Friedrich and Paul Knipping confirmed the hypothesis experimentally and set the concept of the lattice on firm ground (Ewald, 1962). In addition, the symmetries of the crystal are clearly evident in the symmetry of the diffraction patterns. Since amorphous materials dif-

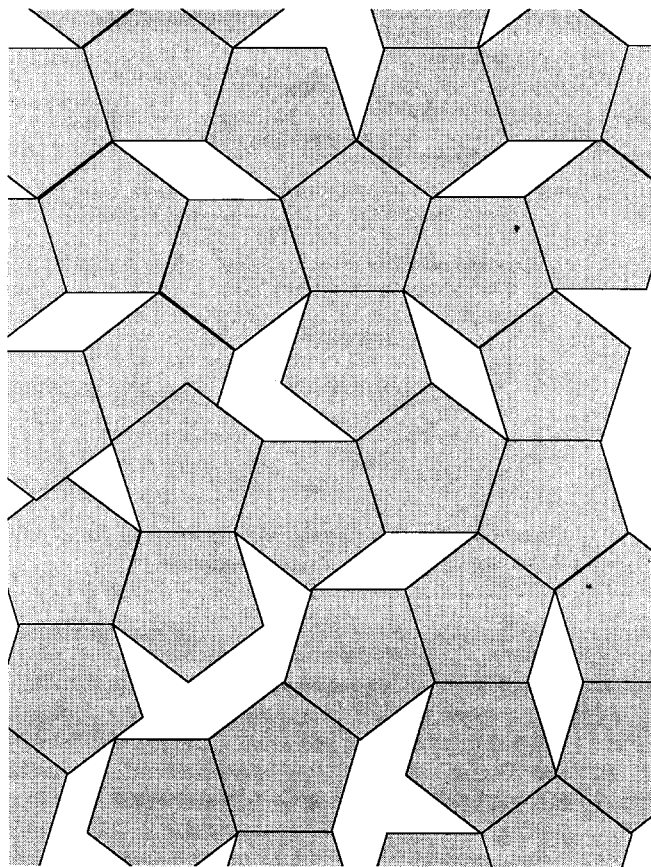


Figure 5. A two-dimensional pattern formed by trying to "tile the plane" with cells that have 5-fold symmetry.

fract X-rays in only diffuse rings, it became commonly believed that only structures that were based on a lattice could produce a diffraction pattern of spots. In the following years, X-ray analysis proved to be immensely successful in determining the crystal structure of hundreds of thousands of compounds. Thus, in a system where crystals are defined as being structures based on a lattice, the empirical *observation* that 5-fold symmetry did not seem to occur in solids became a law that ordered solids *could not* have 5-fold symmetry.

A NEW ORDERED STATE OF SOLID MATTER

Given the mathematical foundation and the phenomenal experimental successes of crystallography, it is no wonder that the world of crystallography was taken by surprise in November, 1984 when D. Shechtman, I. Blech, D. Gratias and J. W. Cahn at the U.S. National Bureau of Standards (now the National Institute of Standards and Technology) announced that they had observed 5-fold symmetry in rapidly cooled alloys of aluminum with 10 to 14 atomic percent manganese, iron or chromium (Shechtman *et al.*, 1984). Using electron diffraction (which is similar to X-ray diffraction) these alloys were shown to have the symmetry of the icosahedron. The icosahedron is a Platonic solid with six 5-fold axes through the vertices, ten 3-fold axes through the centers of its triangular faces, and fifteen 2-fold axes through the edges (Fig. 6). A sample diffraction pattern is shown in Fig. 7. Because the quasicrystals also possess inversion symmetry, the diffraction pattern along a 5-fold axis appears to have 10-fold symmetry.⁶ A diffraction technique called "convergent beam" electron

⁴More precisely, the rotated crystal *structure* must appear to be in the same orientation as the unrotated structure in order to truly possess the symmetry. For example, even though pyrite forms cubes, its structure does *not* possess 4-fold symmetry. This fact is revealed, for example, when pyrite cubes are striated, or by the pyritohedron itself. ⁵See Arem (1971) pp. 63, 192 for illustrations.

⁶It is interesting to note that, in 1956, X-ray photographs of a disordered crystal of bushy stunt virus showed a symmetrical pattern of 10 spots among diffuse rings (Caspar, 1956). D. Shechtman first observed the 10-fold diffraction pattern of his Al-Mn alloy on April 8, 1982 (La Brecque, 1987/8).

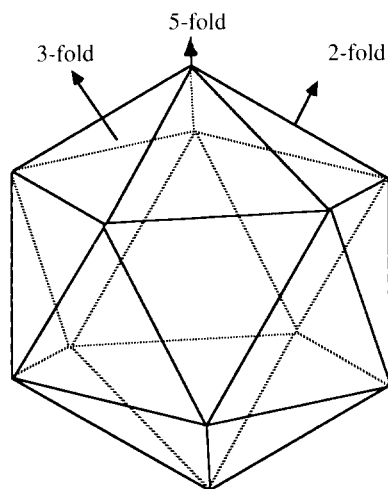


Figure 6. The icosahedron showing one of its 5-fold axes, 3-fold axes and 2-fold axes.

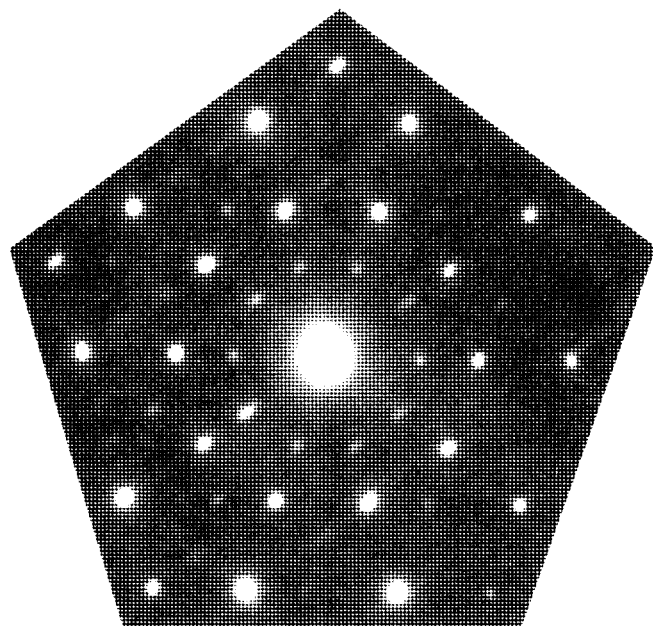


Figure 7. Electron diffraction pattern of $\text{Al}_6\text{Li}_3\text{Cu}$ along a 5-fold axis. Courtesy of Frank W. Gayle, Reynolds Metals Co.

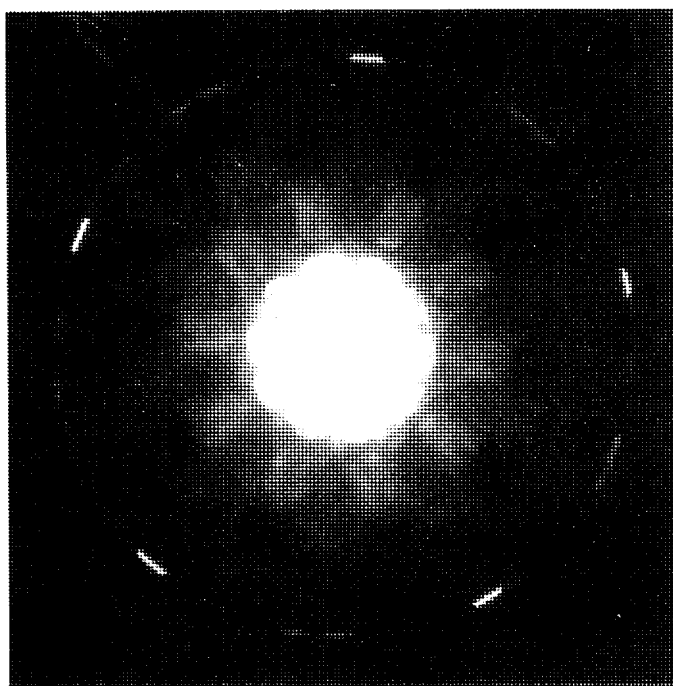


Figure 8. Convergent beam electron diffraction pattern of $\text{Al}_6\text{Li}_3\text{Cu}$ along a 5-fold axis. Note the clear 5-fold symmetry in the outer diffraction ring. Courtesy of Frank W. Gayle, Reynolds Metals Co.

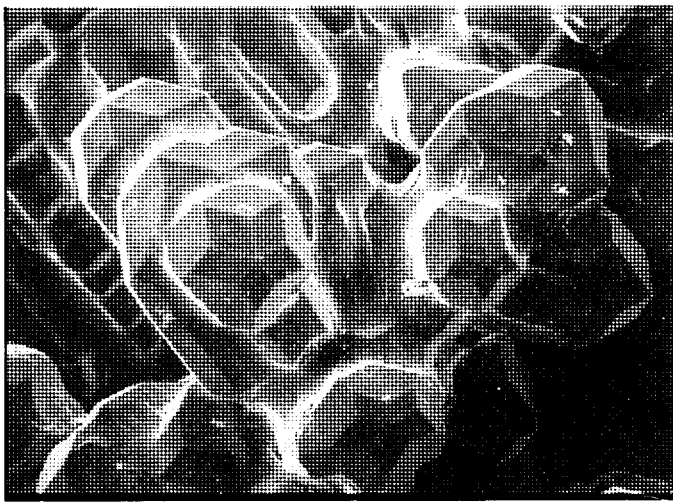
diffraction can distinguish the difference between 5-fold and 10-fold and clearly shows the 5-fold symmetry in Fig. 8 for the Al-Li-Cu alloy.

Since 1984, immense interest has been generated among crystallographers, chemists, physicists, mathematicians, metallurgists, and materials scientists in this new class of compounds that exhibits symmetries forbidden in crystals. Through all the effort, dozens of alloys have been synthesized which possess 5-fold (icosahedral), 8-fold (octagonal) (Wang *et al.*, 1987), 10-fold (decagonal) (Bendersky, 1985; Chattopadhyay *et al.*, 1985; Schaefer and Bendersky, 1986; Kortan *et al.*, 1989b), and 12-fold (dodecagonal) (Ishimasa *et al.*, 1985; Chen *et al.*, 1988) symmetries. Among the icosahedral alloys, which comprise the largest group, are compositions Al-M (where M = Cr, Mn, or Fe), Al-Cu-Li, Al-Cu-Fe, Al-Cu-Ru, Ga-Mg-Zn, Al-Pd-Mn, Ni-Ti-V, Pd-U-Si and others. Octagonal quasicrystals have been formed

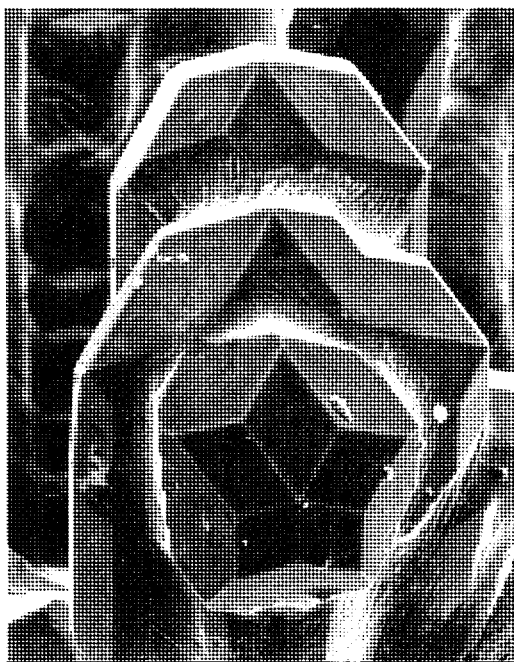
with alloys of V-Ni-Si and Cr-Ni-Si, whereas decagonal quasicrystals are alloys of Al-Mn, and Al-Cu-M, where M = Mn, Fe, Co, or Ni. Doceagonal alloys have been made using V-Ni-Si, V-Ni, and Ni-Cr. While the compounds with these symmetries can not be crystals—based on the well established framework of crystallography, their diffraction patterns of rather sharp spots (Fig. 7) reveal an ordered atomic structure. Thus, the term “quasicrystal” has generally been applied to these compounds. Nature does not, in fact, appear to be constrained to grow ordered solids based only on lattices and single unit cells. As will be discussed below, crystallographic concepts can be generalized to allow for the new structures, by allowing, for example, two or more unit cells to form the entire structure. In fact, the crystallographic concepts of space groups have recently been generalized to include the new symmetries (Mermin, 1992).

In addition to the kinds of quasicrystals produced, the methods of producing quasicrystalline alloys have also steadily increased over the years. The first quasicrystals were made by rapid solidification methods, such as spin quenching, whereby the molten alloys are sprayed onto a rapidly spinning chilled copper wheel producing metallic ribbons. Other methods have been developed which include ion-beam mixing, laser quenching, sputtering, ion implantation, solid-state reaction, and casting.

Of great current interest are the icosahedral alloys, Al-Li-Cu (Dubost *et al.*, 1986; Gayle, 1987), Al-Cu-Fe (Tsai *et al.*, 1987; Ebalard and Spaepen, 1989), Ga-Mg-Zn (Ohashi and Spaepen, 1987), Al-Cu-Ru (Guryan *et al.*, 1989), Al-Pd-Mn and Al-Pd-Re (Tsai, *et al.*, 1989) which appear to be thermodynamically stable—a property often thought to be reserved for crystals. Also of great interest is the recently discovered stable decagonal alloy Al-Cu-Co (Kortan *et al.*, 1989b). In contrast to the very rapid cooling spin quenching techniques which produce most of the other quasicrystalline alloys as metastable phases (Chen *et al.*, 1985; Knapp and Follstaedt, 1987), the stable alloys are synthesized by a rather slow-cooling casting technique—one which is conducive to the formation of faces in both crystals and quasicrystals. By this method, quasicrystals form wonderfully faceted shapes (shapes with flat faces) that are reminiscent of crystals (despite their lack of a structure based on a lattice), and which reveal their surprising 5-fold (or 10-fold) symmetry.



a.



b.

Figure 9. (a) SEM photo of triacontahedral quasicrystal dendrites of $\text{Al}_6\text{Li}_3\text{Cu}$ made at Reynolds Metals Co. by Frank W. Gayle (Gayle, 1987), showing 2-fold faces. The grains are 0.1 mm across. (b) Same as (a) at higher magnification.



a.

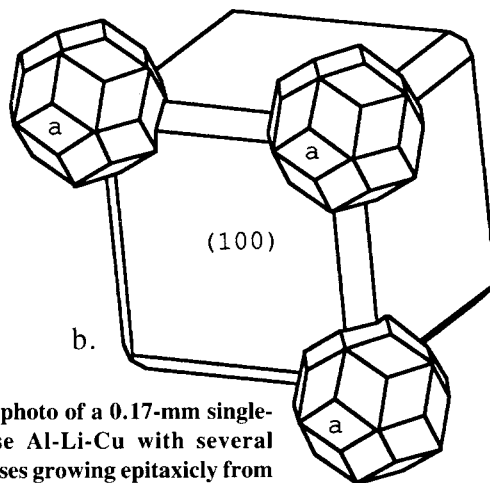


Figure 10. (a) SEM photo of a 0.17-mm single-crystal cubic phase Al-Li-Cu with several quasicrystalline phases growing epitaxially from the corners. Courtesy of A. R. Kortan, AT&T Bell Laboratories. (b) Idealized SHAPE drawing of the epitaxial relationships in (a).

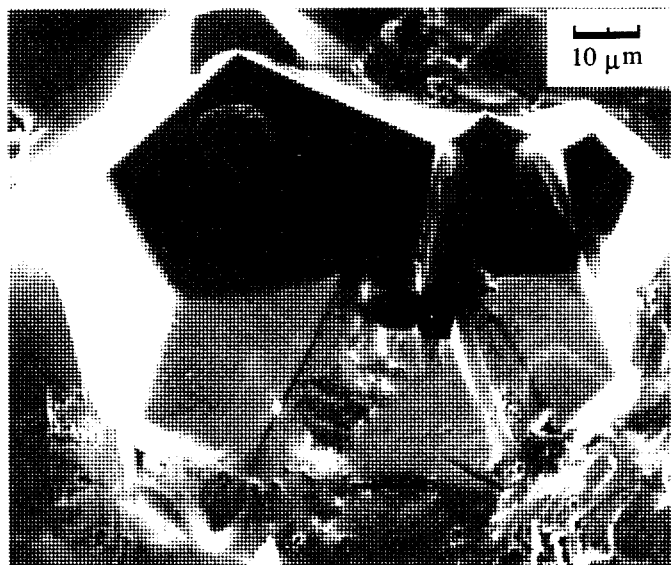


Figure 11. SEM photo of pentagonal dodecahedral $\text{Ga}_{1.0}\text{Mg}_{2.1}\text{Zn}_{3.0}$ quasicrystal, 0.1 mm across (Ohashi and Spaepen, 1987). Courtesy of Frans Spaepen, Harvard University.

Most of the early experiments synthesized, quasicrystals with interesting but highly dendritic morphologies. In 1986, however, crude pentagonal dodecahedra up to 0.01 mm on an edge were observed in Al-Mn-Si quasicrystal alloys (Ishimasa and Nissen, 1986; Robertson *et al.*, 1986). More recent papers report faceted dendrites that resemble stellated dodecahedra (Nishitani *et al.*, 1986; Nissen *et al.*, 1988). The most beautiful morphologies, however, have been observed in the stable phases mentioned above. The Al-Li-Cu quasicrystal has only been observed showing one form—the rhombic triacontahedron (Fig. 1). This 30-faced polyhedron has the symmetry of the icosahedron, as can be seen by replacing the edges of the icosahedron with diamond-shaped (2-fold) faces. The triacontahedra are typically 0.1 mm across, and usually compose coarse dendrites in shrinkage cracks of the cast alloy (Fig. 9).

A cubic crystalline phase of similar composition to the Al-Li-Cu quasicrystal is known to be composed of icosahedral clusters of atoms



Figure 12. SEM photo of pentagonal dodecahedral Al-Cu-Fe quasicrystal, 0.1 mm across, made at Reynolds Metals Co. by Frank W. Gayle. Note the small pentagon, rotated by 180°, on one of the pentagonal faces.

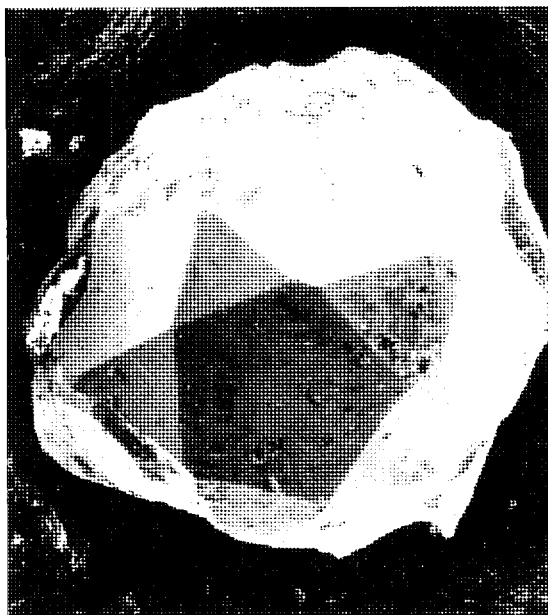


Figure 14. SEM photo of a quasicrystal grain 0.4 mm wide of $Al_{65}Cu_{23}Fe_{12}$ showing 5-fold and 3-fold faces after annealing for 10 days at 830C. Courtesy of Peter Bancel, IBM.

stacked in a body-centered-cubic lattice (Audier *et al.*, 1986). What is most interesting is that the cubic and the quasicrystalline phases have been found to coexist, and in fact, can grow together in an oriented fashion. Figure 10 shows a single cubic Al-Li-Cu crystal with at least three triacontahedral quasicrystal grains growing epitaxially on the crystal corners (Kortan *et al.*, 1989a), and is yet another demonstration that the quasicrystals have ordered internal structures.

In contrast to the Al-Li-Cu alloys, Ga-Mg-Zn (Fig. 11), and Al-Cu-Fe (Fig. 12) quasicrystals form regular pentagonal dodecahedra, with faces in the orientation of the icosahedral vertices (i.e., normal to the 5-fold symmetry axes). Recently, the Al-Cu-Fe quasicrystal has been observed to possess faces related by 2-fold axes and faces related by 5-fold axes on a single grain (Fig. 13). In another grain, faces related by 5-fold axes occur with the first observed icosahedral faces related by 3-fold axes (Fig. 14). Very recently, grains to 0.3 mm of icosahedral Al-Pd-Mn alloys have shown either faces related

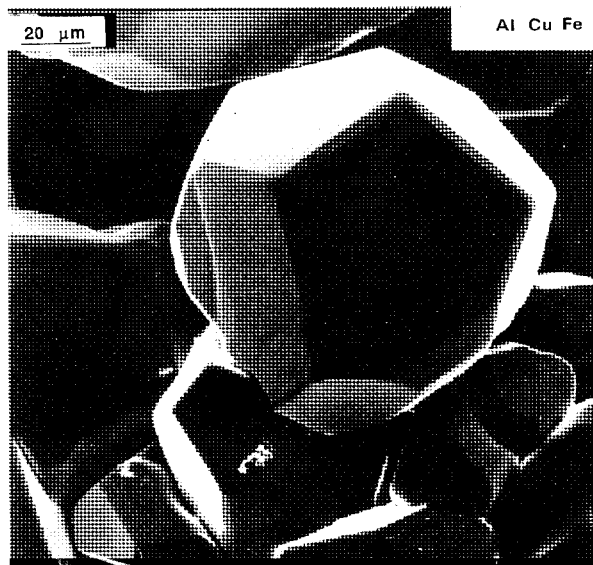


Figure 13. SEM photo of quasicrystal grains of $Al_{63}Cu_{25}Fe_{12}$ showing 5-fold and small 2-fold faces after annealing for 15 hours at 870C. Courtesy of Annick Quivy, Centre d'études de Chimie Métallurgique, C.N.R.S., France. The size of the largest face is 0.07 mm.

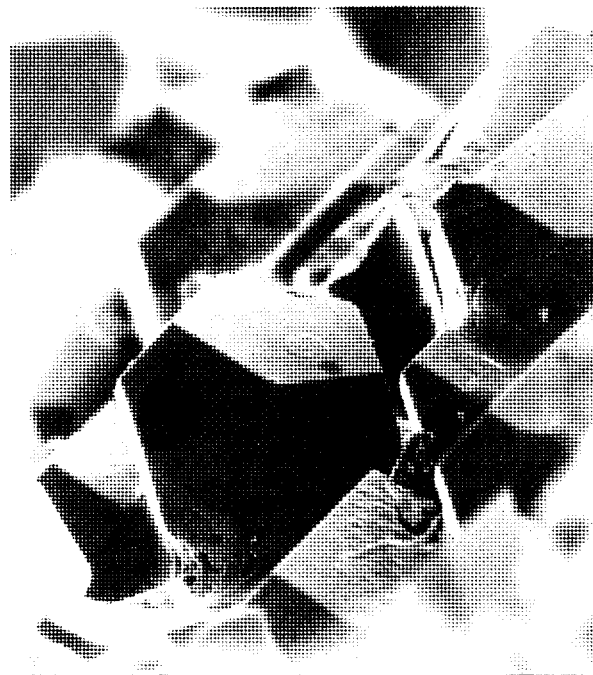
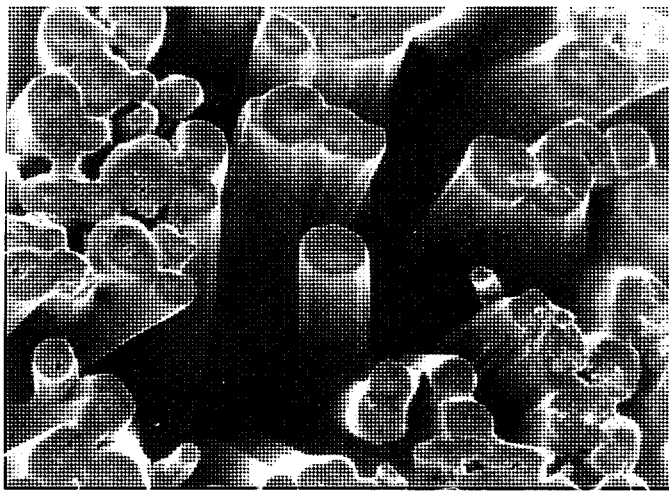


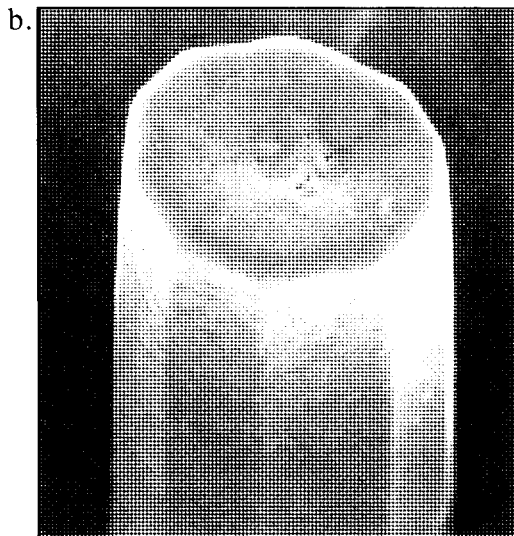
Figure 15. SEM photo of quasicrystal grains of $Al_{75}Pd_{15}Mn_{10}$ up to 0.08 mm showing 5-fold faces. Courtesy of A. P. Tsai, Tohoku University.

by 5-fold axes, or a combination of faces related by 3- and 5-fold axes, depending on the composition and cooling rate (Fig. 15).

The recently discovered decagonal alloy of Al-Cu-Co, shown in Fig. 16, exhibits elongate 10-fold prisms that are terminated by dimpled pinacoids. The 10-fold faces are often striated and show growth steps. These decagonal quasicrystals are some of the largest yet grown, reaching up to 4 mm in diameter (Kortan *et al.*, 1989b). These remarkable alloys are interesting because their structures are periodic in the direction parallel to the 10-fold axis, but are quasiperiodic in the planes perpendicular to that axis.



a.



b.

Figure 16. (a) SEM photo of decagonal grains of Al-Cu-Co which are approximately 0.07 mm across. (b) Enlargement of the decagonal grain in the center of (a). Courtesy of A. R. Kortan, AT&T Bell Laboratories.

MODELS

Inspired by the *local* icosahedral order in dense liquids (Steinhardt *et al.*, 1981), Dov Levine and Paul J. Steinhardt, independently and simultaneously to the experimental discovery of quasicrystals, found that the ordered yet *aperiodic* Penrose tiling (Fig. 17) and its three dimensional generalizations would yield crystal-like diffraction patterns despite their lack of periodic translational symmetry (Levine and Steinhardt, 1984, 1986). Also independently, Alan MacKay had pondered about the physical realizations of a Penrose tiling as early as 1982 (MacKay, 1982), and Peter Kramer and R. Neri considered three-dimensional generalizations of the Penrose tiling well before the discovery of Schectman *et al.* (Kramer and Neri, 1984).

Penrose tilings, named after their inventor, Oxford University mathematical physicist Roger Penrose, are marvelously beautiful patterns that are constructed out of *two* types of "unit cells" (referred to as tiles) that completely tile the plane in an *aperiodic fashion*.⁷ Many of their wonderful mathematical properties have been discussed by Gardner (1977). In these tilings, any particular pattern of any given size

⁷A pentagonal aperiodic tiling, related to the Penrose tiling, covers the Blue Tomb at Maragha, Iran, built 1196–1197 A.D. (Makovicky, 1990).

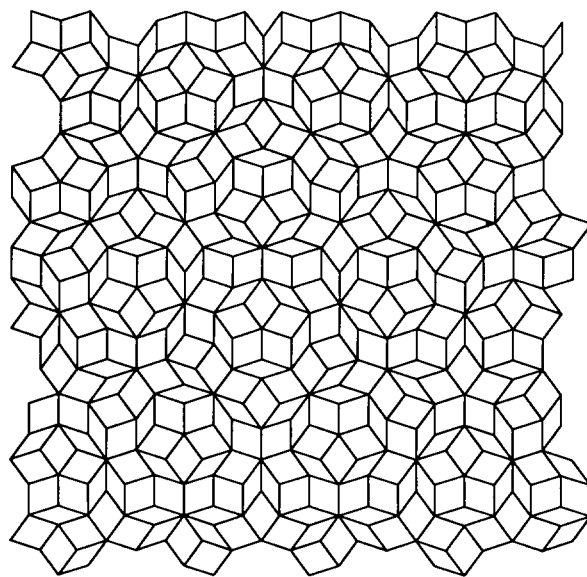


Figure 17. A portion of the Penrose tiling, made up of only two types of tiles—fat and thin rhombi.

always repeats itself again elsewhere in the tiling. Though not periodic, this is a kind of long-range translational order. Another important property is that all of the tile edges are oriented in one of ten directions everywhere in the tiling—a property called *long-range orientational order*, which is 10-fold in the Penrose tiling. Crystals also have long-range orientational order, but as a consequence of their periodic translational symmetry. Ho *et al.* (1987) have shown that the long-range orientational order, and not necessarily periodic translational order (i.e. a lattice), is sufficient for solids to exhibit faces. One can see a special order in the Penrose tiling, and even how faces might be able to exist in structures based on them, by noting the layer-like structure which is manifest when one shades all tiles with edges parallel to a given direction (Fig. 18). It is particularly interesting to note that some shaded layers touch adjacent layers, while others do not. The

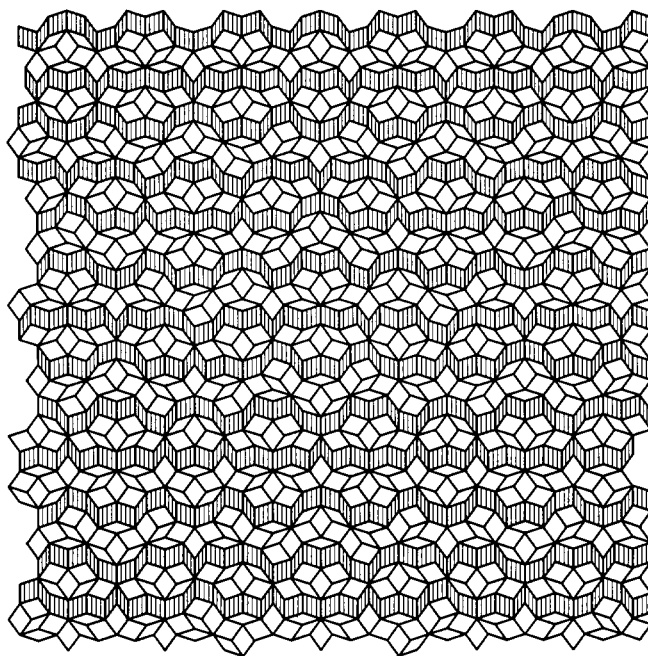


Figure 18. A Penrose tiling showing a layer-like structure when all tiles with edges parallel to one direction are shaded.

order in which adjacent layers touch or not is not random, but can be described mathematically by the so-called Fibonacci sequence, named after the thirteenth century mathematician who first studied the sequence (Steinhardt, 1986). Since this order is neither random nor periodic, the Penrose structures are known as quasiperiodic. There are strict matching rules which govern how to assemble the tiles to make a Penrose tiling, and controversy exists over how real quasicrystals can grow while maintaining these complex matching rules (Onoda, *et al.*, 1988, 1989; Jarić and Ronchetti, 1989).

Other models for quasicrystal structure are based on more random systems, or glasses, analogous to the one illustrated in Fig. 5. Glass models constructed by randomly packing icosahedra in the same orientation have been shown to generate fairly sharp diffraction patterns in computer calculations (Shechtman and Blech, 1985; Stephens and Goldman, 1986). These glasses also possess long-range orientational order, and might be expected to form faces as well. However, the glass models appear to have too great a degree of disorder to adequately explain Al-Cu-Fe and Al-Cu-Ru quasicrystals. By flipping groups of tiles in a Penrose tiling (thus breaking the matching rules), a complete spectrum of possible structures can be shown to exist between the ordered Penrose tiling models and the more disordered glass models. These "random tiling models," which fill space in contrast to the glass models, but do not satisfy the strict order of the Penrose tiling, are currently popular because it is suggested that they may be stabilized by entropy (Strandburg *et al.*, 1989).

The atomic structure has not yet been conclusively solved for any of the quasicrystalline alloys, despite extensive studies using X-ray, electron and neutron diffraction, high resolution electron microscopy, and field-ion microscopy. The task is clearly more complicated than for simple crystals since the latter can be described by the periodic repetition of a single unit cell. Quasicrystals do not have a single unit cell, and local structures are not periodically repeated throughout the quasicrystal. The situation is further complicated by the fact that the different quasicrystalline materials may belong to rather different structural classes. It is generally believed, with the exception of supporters of the multiple-twin model (Pauling, 1987), that the icosahedral quasicrystals are some kind of *aperiodic* packing of icosahedral clusters of atoms. A great deal has been learned about the local atomic structures of icosahedral quasicrystals by means of comparison with the known structures of similar crystalline materials which have very large unit cells containing icosahedral clusters of atoms. In particular, the complicated structures of *crystalline* Al-Mn-Si and Al-Zn-Mg compounds, solved some time ago, are body-centered-cubic packings of clusters of atoms. These clusters are composed of two shells of atoms, have icosahedral symmetry about their centers, and are all connected along their 3-fold and 2-fold axes in the crystalline phases. An overall icosahedral order is achieved when crystallinity conditions are relaxed, and the clusters pack more randomly. The close relationship between the crystalline and quasicrystalline phases of Al-Li-Cu alloys (similar to the Al-Zn-Mg alloys) is demonstrated by the epitaxial growth in Fig. 10.

SUMMARY

A new ordered state of solid matter been discovered, which is neither crystalline nor amorphous, and has generally been called quasicrystalline. A wide variety of quasicrystalline compounds, manifesting several new rotational symmetries, have been produced by a number of different techniques. Several stable quasicrystalline materials have been synthesized using conventional slow-cooling methods, and show beautifully faceted surfaces that are reminiscent of crystals. The stability of quasicrystalline materials, their ease of manufacture and their variety of compositions suggest that quasicrystals may be an as yet undiscovered component of the mineral kingdom awaiting the careful inspection of a diligent mineral collector who does not disregard 5-fold symmetry *a priori*.

ACKNOWLEDGMENTS

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ADDITIONAL READING

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