
THE SO-CALLED ICOSAHEDRAL QUASICRYSTALS OF MANGANESE-ALUMINUM AND OTHER ALLOYS

Linus Pauling

Linus Pauling Institute of Science and Medicine
440 Page Mill Road, Palo Alto, California 94306

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I am glad to participate in the celebration for Dr. Ricardo Ferreira. I remember with much pleasure my first contact with him some thirty years ago, and the interesting conversations that we had about structural chemistry and other matters. I extend congratulations to him on his successful career.

Because of our common interest in the structure of molecules and crystals and the explanation of the properties of substances in terms of structure, I have decided to write an account of recent work on the so-called icosahedral quasicrystals. This paper is dedicated to Ricardo Ferreira.

In 1984 it was reported by Shechtman, Blech, Gratias, and Cahn¹ that when a molten alloy of manganese and aluminum is very rapidly cooled, by being squirted onto the surface of a rotating copper cylinder, the solidified alloy, with composition $MnAl_6$, gives electron-diffraction photographs showing fivefold, threefold, and twofold axes of symmetry, at angles corresponding to the icosahedral point group. The investigators suggested that this alloy represented a new kind of crystal, later named a quasicrystal, inasmuch as crystallographers for over 150 years had claimed that crystals cannot have fivefold axes of symmetry. Because of the possibility that these quasicrystals (which have been found to be formed by rapidly quenching many different alloys) might have quite unusual electronic and other physical properties, the discovery led to a tremendous amount of activity, with hundreds of solid-state physicists, mathematicians, and metallurgists in many countries carrying out theoretical and experimental studies in this field. I estimated that by the end of 1986 there had been more than 500 papers on these quasicrystals published.

Many attempts to develop a theory of icosahedral quasicrystals have been published. Some of them involve Penrose tiling, the construction of a structure without icosahedral symmetry by piling together, to some extent in random positions but with definite orientations, two rhombohedral units, a prolate one and an oblate one. Other investigators have assigned structures, which do not have the three-dimensional translation operations characteristic of ordinary crystals, by formulating a structure in four, five, or six dimensions, and then taking three-dimensional cross sections of the structure. Another attack has been to take an icosahedron, of 12 atoms or perhaps 13, including one at the center, and to stack these icosahedra, all with the same orientation, by sharing edges or faces in a somewhat random manner. It is found that, so long as

the icosahedra are all in parallel orientation with some cluster-cluster vectors repeating, the structure gives rise to a predicted pattern of electron or x-ray diffraction maxima resembling the observed patterns.

I did not find any of these proposals to be satisfactory, in that we know from the many crystal structure determinations that have been made of intermetallic compounds that in these compounds the atoms of the various elements arrange themselves in quite definite ways, as determined by their metallic radii, and none of the proposed structures seemed to satisfy the expectations about the detailed atomic arrangement. An alternative explanation, discussed to some extent by several investigators, is that the so-called icosahedral quasicrystals are really cubic or rhombohedral crystals of the ordinary sort, which, however, undergo repeated twinning about an icosahedral seed, to give an aggregate that has icosahedral symmetry. During the last two years I have gathered much evidence supporting the idea, and it seems likely that before long a definite decision can be made between the twinning theory and the other theories.

In my first attempt to solve this problem I pointed out that the x-ray powder diffraction could be accounted for by a face-centered cubic unit of structure 25.73 \AA on edge, containing about 1180 atoms. The suggested structure was similar to the known structure of NaCd_2 . I published an account of this work in *Nature* in 1985². It soon was evident, however, that this structure did not account satisfactorily for the electron diffraction photographs. After many months of work on the problem, I found that the electron diffraction data and the x-ray powder pattern could all be accounted for by a cubic unit with edge 23.36 \AA ³.

The reason that the x-ray powder data could be accounted for by the 25.73 \AA unit as well as by the 26.36 \AA unit is that these two values for the edge of the unit cell, when squared, give the ratio 4/3. Since the interplanar distances are inversely proportional to the sum of the squares of the indices of a plane, $h^2 + k^2 + l^2$, for a cubic crystal, many of the powder lines can be explained by either unit. For example, the plane 200, with $h^2 + k^2 + l^2 = 4$, corresponds to 111, with $h^2 + k^2 + l^2 = 3$. For some powder lines, however, the primitive cubic unit with edge 23.36 \AA provided a better explanation of the observed spacing the large unit did.

Consideration of atomic volumes showed that the unit with 23.36 \AA contains about 820 atoms. No intermetallic compounds had been previously reported to have a

primitive cubic unit containing this number of atoms, but it was possible to make a suggestion about these structures from a consideration of how atoms tend to pack together.

The most compact way or packing together rigid spheres of the same size is cubic or hexagonal close packing, in which each sphere has 12 neighbors at the corners of a cubo-octahedron. (for cubic closest packing) or a closely similar polyhedron. The interstices in this structure are tetrahedra, formed by four atoms, or octahedra, formed by six atoms. If it were possible to fill space with regular tetrahedra, so that the interstices were all tetrahedral, the packing would be closer than close packing, but it has been found that such an arrangement is not possible for rigid spheres of the same size. With spheres of somewhat different sizes, however, this sort of tetrahedrally packed structure becomes possible.

The simplest example of tetrahedral packing is achieved by arranging 12 atoms around a central atom which is ten percent smaller. Tetrahedral packing can also be achieved with larger coordination numbers, especially 14, 15, or 16. Many intermetallic compounds with structures involving only tetrahedral packing are known. In general they involve a decrease in the average atomic volume, compared with the constituent metals in their close-packed structures.

A good example of a tetrahedrally-packed intermetallic compound is $Mg_{32}(Al,Zn)_{49}$, the structure of which was determined by two of my students and me and reported in 1952.⁴ This structure is shown in Figure 1. It involves clusters of 105 atoms, a central atom with an icosahedral shell of 12, then an outer shell of 32, and an outermost shell of 60 atoms. Twenty of the atoms have liganacy 16. The 105-atom atom cluster is shown in Figure 2. In the 162-atom crystal these clusters are at the corners of the unit cube and the center, and some of the atoms in the outer shell are shared by the cluster with neighboring clusters, to reduce the number of atoms in the unit to 162.

We may consider a molten alloy of manganese and aluminum, in which there is a tendency for the smaller manganese atoms to surround themselves by 12 atoms at the corners of the icosahedron and for larger atoms to have larger coordination numbers, permitting tetrahedral packing to occur, and perhaps giving rise to clusters of 105 atoms, or possibly 104, if the position at the center is not occupied. In the melt we may consider these 104-atom clusters to be rolling around over one another, losing and picking up atoms occasionally in the way characteristic of liquids. If the liquid alloy is very rapidly quenched, one might obtain a supercooled liquid, with the clusters of metal atoms having various orientations and somewhat different compositions. For a somewhat less rapid quenching, however, the clusters might settle into some crystalline arrangement, in which they have parallel orientation and are at definite distances from one another.

A cubic crystal with 820 atoms would contain eight of these clusters. There is only one arrangement that is compatible with the x-ray powder pattern. It is the β -W arrangement, shown in Figure 3. I decided accordingly that the so-called icosahedral quasicrystal of $MnAl_6$ really consists of icosahedrally-twinned cubic crystals with a structure in which the 104-atom complexes are located in the β -W position.

A characteristic of the electron diffraction photographs taken with the electron beam along various axes is the occurrence of a radial sequence of spots, intensity weak, medium, strong, medium, at the radial distances approximately 3, 5, 8, 13. The ratios of successive distances approximate 1.618, which is the golden mean $(5^{1/2} + 1)/2$. Calculations show that the structure factor for a cluster of atoms with icosahedral symmetry tend to have maxima in these positions. The numbers 3, 5, 8, 13, 21 are successive terms in the Fibonacci series, in which each term is the sum of the two preceding ones (the series starts with 1, 2). With the lattice constant 23.36 Å for $MnAl_6$, the measured positions of these spots on the electron diffraction photographs correspond to the planes 3 3 0, 5 5 0, 8 8 0, and 13 13 0. Other spots corresponding to h h 0 also appear, as weaker diffraction maxima.

An important step forward was made when it was discovered that the stable form of Li_3CuAl_6 gives electron diffraction patterns corresponding to icosahedral symmetry.⁵ It is possible to grow grains of this alloy as much as a millimeter in diameter, and to make single-grain precession x-ray diffraction photographs with them. I found that all of the spots on these precession photographs could be accounted for by a twinned-cubic unit 23.81 Å on edge. The value 23.81 Å is obtained independently in two ways. One way is to index the x-ray powder photograph of the icosahedral preparation. The second way, which gives complete agreement, is to translate the cube edge of the unstable 162-atom form of the same substance by multiplying its cube edge by $(820/162)^{1/3}$.

Several other kinds of evidence have been found to support the postulate that the so-called icosahedral quasicrystals are twins of an 820-atom cubic crystal.

Another form of icosahedral quasicrystal has also been discovered. A rapidly chilled specimen of $Ni(Ti,V)_2$ gives electron diffraction photographs showing icosahedral symmetry. The pattern is similar to that of $MnAl_6$, but with a quite different scale, corresponding to cube edge 14.93 Å. This unit cube contains only 224 atoms, rather than 820. The structure that I assigned to it is similar to that of the 820-atom crystal, except that the clusters at the points of the β -W arrangement are 45-atom icosahedral clusters, with successive shells 1, 13, and 32, rather than 104-atom clusters.

During the 20th century, after the discovery of the electron and of atomic nuclei, the field of structural chemistry has developed rapidly. We now have an excellent theoretical understanding of the nature of organic compounds and of many inorganic compounds. There is, however, one field that is not well understood. This is the field of metallurgy, the study of metals and intermetallic compounds.

Sixty-five years ago I heated some mercury, dissolved some potassium in it, and then let it cool slowly, to allow the compound of potassium and mercury to crystallize. From the crystallizing dish I removed beautiful crystals, cubes with the corners truncated by octahedral faces. The composition of this intermetallic compound is KHg_{11} . For decades I have thought about the question as to why the compound has this formula, and why potassium and mercury also form the compounds KHg_8 , KHg_3 , K_5Hg_7 , KHg_2 , and KHg . and also why, copper and tin form the compounds

$\text{Cu}_{41}\text{Sn}_{11}$, $\text{Cu}_{10}\text{Sn}_3$, $\text{Cu}_{17}\text{Sn}_3$, as well as several others. I have seen some regularities, with limited application, but for the most part we must admit that even such a simple property as the chemical composition of intermetallic compounds is not well understood. Through application of the technique of x-ray diffraction for determining the structure of crystals, there is now a great body of empirical information. In Pearson's Handbook of Crystallographic Data for Intermetallic Phases by P. Villars and L. D. Calvert,

three volumes, over 4,000 pages, one finds crystallographic data for over 24,000 intermetallic compounds. Although I have studied the chemical bond for 70 years, I have to admit that my understanding of the nature of the chemical bond in metals and intermetallic compounds is still far from complete. Metals and alloys play a very important role in modern life. I hope that the chemists of the future will have a far better understanding of them than I now have.

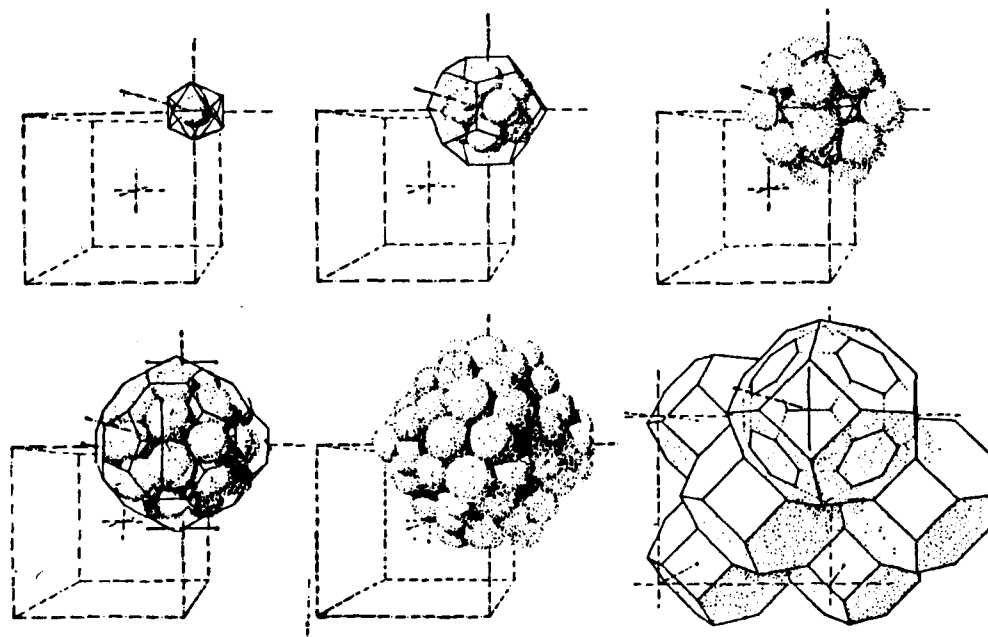


Fig. 1 – The atomic arrangement in the cubic crystal $\text{Mg}_{32}(\text{Zn}, \text{Al})_{49}$. The six drawings, from left to right in the top row and then left to right in the bottom row, have the following significance: A central atom surrounded by 12 atoms at the points of a nearly regular icosahedron; the icosahedral group of 13 atoms surrounded by 20 atoms at the points of a pentagonal dodecahedron; the outermost shell of 60 atoms at the corners of a truncated icosahedron, plus 12 atoms out from the centers of 12 of the hexagons of this polyhedron; packing drawing showing the outer shell of 72 atoms surrounding the central complex of 45 atoms; the structure of the crystal, in which these complexes located about the points of a body-centered cubic lattice share all of the 72 atoms of the outer most shell with neighboring complexes.

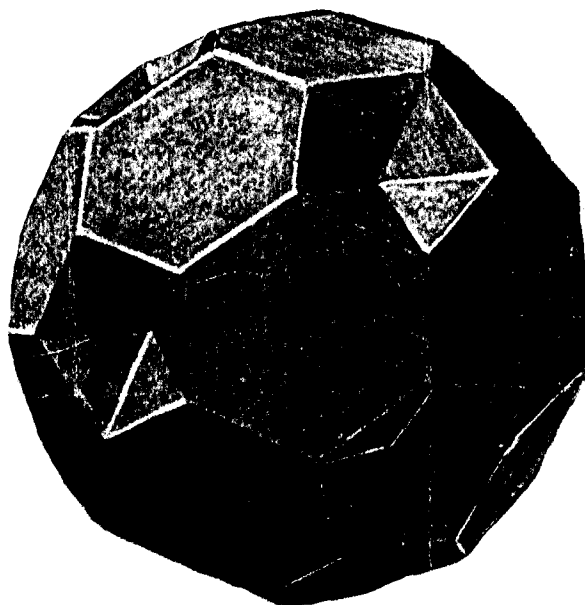


Fig. 2 – The 105-atom complex formed by condensation of 20 Friauf polyhedra. The complex has icosahedral symmetry. It was first found in the compound $\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$.

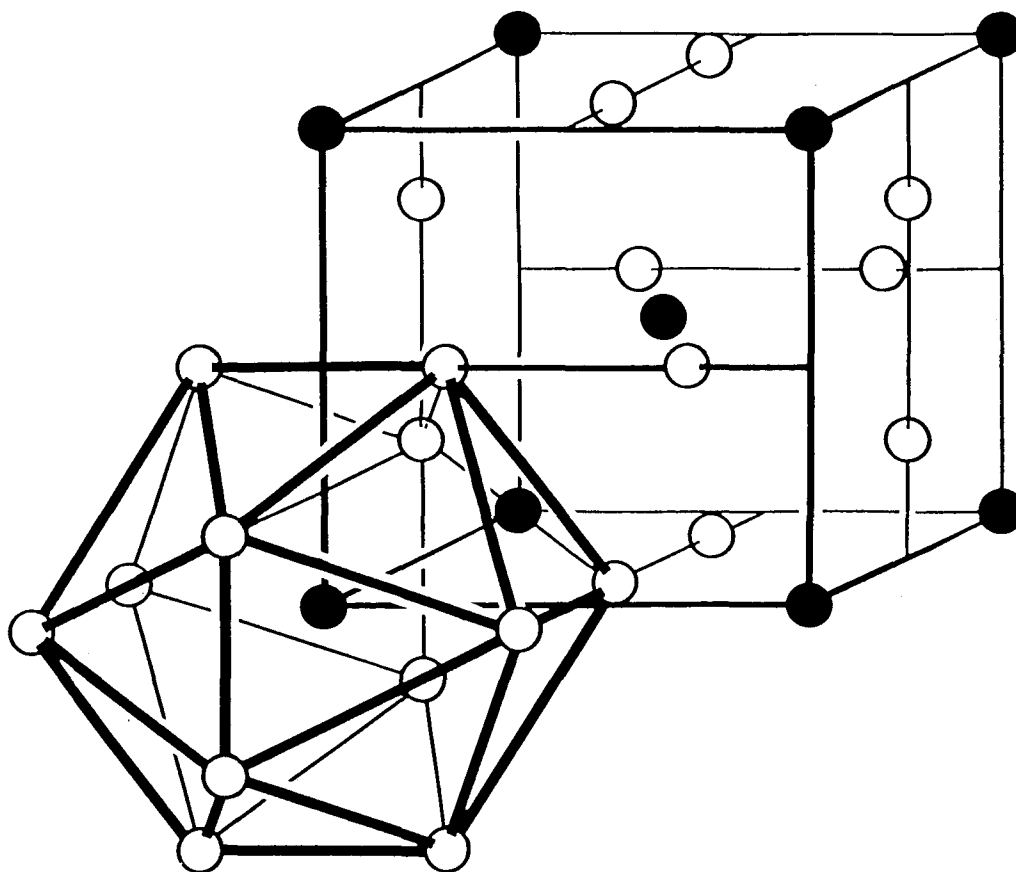


Fig. 3 – The arrangement of atoms in the β -tungsten structure. There are 8 atoms in the primitive cube. An atom at 000 or $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ is surrounded by 12 atoms at the corners of a slightly distorted icosahedron. In CuLi_3Al_6 , MnAl_6 , and other icosatwins and decautwins there are complexes of 104 atoms centered at each of the 8 atomic positions of the β -W structure.

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