INTERPRETATION OF SO-CALLED ICOSAHEDRAL AND DECAGONAL QUASICRYSTALS OF ALLOYS SHOWING APPARENT ICOSAHEDRAL SYMMETRY ELEMENTS AS TWINS OF AN 820-ATOM CUBIC CRYSTAL

L. Pauling

Linus Pauling Institute of Science and Medicine, 440 Page Mill Road, Palo Alto, CA 94306, U.S.A.

Abstract—A summary is presented of the arguments indicating that the so-called icosahedral and decagonal quasicrystals of $MnAl_6$ and other alloys are twins of a cubic crystal with 820 atoms in the unit cube such that the complex of small individual crystallites has icosahedral or decagonal symmetry. The proposed 820-atom cubic crystal has a structure that is similar to that of other intermetallic compounds with complex structures involving clusters of metal atoms with approximate icosahedral symmetry.

In the fall of 1984 a paper was published in *Physical Review Letters* by Shechtman *et al.* in which they reported that by rapidly chilling a molten alloy with composition approx. $MnAl_6$ a solid alloy was obtained that gave electron diffraction photographs with five-, three- and two-fold axes and planes of symmetry corresponding to the holohedral icosahedral point group [1]. This report excited great interest, partially because crystallographers have believed for a long time that it is not possible for crystals to have a five-fold axis of symmetry, and partially because the alloys seemed to be of a new kind, which might well have some interesting and commercially valuable physical and electronic properties. I estimated that by the end of 1986 over 500 papers about the so-called icosahedral and decagonal quasicrystals had been published.

A number of different sets of authors had reported that they had succeeded in showing how aggregates of atoms could exist that would give diffraction patterns with sharp diffraction maxima and icosahedral or decahedral symmetry. Some of the theories involved an icosahedral unit, such as an icosahedron of 12 atoms with or without another atom in its center of a cluster with icosahedral symmetry involving a larger number of atoms, repeated in space, perhaps by sharing faces or edges or corners, in such a way that all of the clusters of atoms are in parallel orientation, but with some randomness of such a nature that the clusters are not related to one another by the three translational symmetry operations characteristic of any of the Bravais lattices. Another way of describing a possible structure involves Penrose tiling. It was knonw that a two-dimensional arrangement of points could be obtained by use of an oblate and a prolate rhomb, with equal edges. These rhombs are arranged so as to fill two-dimensional space. There are some limitations on how the rhombs are associated with one another, such that no translational operations appear, and no true five-fold axis, but only a statistical five-fold symmetry. The same kind of structure can be constructed in three-dimensional space, with use of an oblate and a prolate rhombohedron. A third way involves the consideration of possible atomic arrangement in hyper-dimensional space. Crystals with icosahedral symmetry can be constructed in four- or five- or six-dimensional space, and the authors using this treatment described a three-dimensional quasicrystal as a cross section of one of the hyper-dimensional crystals. All of these theories have in common the fact that in three-dimensional space the vectors associated with pairs of atoms constitute a finite set, with, however, the same vector not being repeated by a translational symmetry operation. These theories account in a general way for the observed electron diffraction photographs. In particular, the characteristic spacings corresponding to the diffraction maxima are often in the ratio of a power of τ, the golden mean, identified more than 2000 years ago as $(5^{1/2} + 1)/2 = 1.6180. \ldots$ It is the ratio of the diameter to the side of a regular pentagon, and appears in the dimensional relationships of the icosahedron and other polyhedra based on the icosahedron and pentagonal dodecahedron.

My own interest in the question of the nature of these quasicrystals developed rather slowly, but after some time I decided to follow up the suggestion made and rejected by the original investigators that the quasicrystals might consist of repeatedly twinned cubic crystals, twinned for example by

having an icosahedral seed that determined their relative orientation. Making use of my knowledge of values of the metallic radii and of the known tendency of intermetallic compounds involving metals with radii differing by 10 or 20%, to form icosahedral clusters, I formulated a possible structure involving about 1180 atoms in a face-centered cubic arrangement [2]. I reported that this cubic crystal, with edge 25.73 Å for $MnAl_6$, accounted reasonalbly well for the X-ray powder pattern.

It was pointed out to me by other investigators that, although the unit accounted in a moderately satisfactory way for the X-ray powder diffraction pattern, it did not seem to account for the electron diffraction patterns and the high-resolution electron micrographs. I continued to work on the problem for about a year. Finally I realized that the principal diffraction maxima on the five-fold electron diffraction pattern of $MnAl_6$ could be accounted for as orders of $h \cdot h \cdot 0$, the strongest spots being $3 \cdot 3 \cdot 0$, $5 \cdot 5 \cdot 0$, $8 \cdot 8 \cdot 0$, $13 \cdot 13 \cdot 0$, $16 \cdot 16 \cdot 0$ and $21 \cdot 21 \cdot 0$. Except for $16 \cdot 16 \cdot 0$, the values of h, 3, 5, 8, 13, 21, are Fibonacci numbers, and ratios of successive pairs are close to the golden number 1.618. . . . The value of the edge of unit cube required for this identification is 23.36 Å for $MnAl_6$. I found that all of the diffraction maxima on the electron diffraction photographs could be accounted for by a unit this size, containing 820 atoms, some of them by double diffraction. Moreover, the X-ray powder diffraction pattern was also in as good agreement with this cubic unit as with the larger one [3].

The primitive cubic unit containing 820 atoms consists of icosahedral clusters, each of 104 atoms, at the eight positions of the β–W structure. In this structure there are two kinds of clusters. Those of the first kind, at $0\,0\,0$ and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, are surrounded by 12 of the second kind, at $\frac{1}{2}\frac{1}{4}0$, $0\frac{1}{2}\frac{1}{4}$, $\frac{1}{4}0\frac{1}{2}$, $\frac{1}{2}\frac{3}{4}0$, $0\frac{1}{2}\frac{3}{4}$, $\frac{3}{4}0\frac{1}{2}$. The clusters of the second kind have ligancy 14, with two shorter interatomic distances, four (two clusters of the first kind) of intermediate length, and eight longer ones, the values being 11.68, 13.06 and 14.01 Å. The proposed structure of the 104-atom cluster is that involving 20 condensed Friauf polyhedra. The principal ligancies of the atoms are 12 and 16. This cluster is found in the 162-atom body-centered crystal $Mg_{32}(Al, Zn)_{49}$, the structure of which was discovered in 1952 [4]. All eight of the clusters in the unit have the same orientation relative to the cubic axes.

The process of twinning that has been proposed is that one of the icosahedral clusters in the microcrystal with the 820-atom structure can serve as the seed for another crystal, in which a three-fold axis of the icosahedral cluster is coincident with the three-fold axis of the new cubic crystal that rose from the seed, with each of the three-fold axes lying in the plane of symmetry. All of the clusters in the twinned crystal have the same orientation as those in the original crystal. Repeated twinning in this way can lead to a grain, containing perhaps 10^9 microcrystals, with 20 different orientations, corresponding to the icosahedral group, and with the clusters in all of the grains essentially in parallel orientation. This sort of twinning provides a mechanism for the formation of a larger structure with apparent icosahedral symmetry.

One interesting observation, made on crystallographically oriented icosahedral-phase material by implanting Mn ions directly into single crystal Al substrates by measurements of the positions of high-resolution X-ray diffraction peaks, is that the interplanar distances are not in the ratios of the Fibonacci numbers, as would be required by a perfect cubic crystal, and also are not in the ratios of the golden number, as required by icosahedral symmetry, but are in between, somewhat closer to the golden number than to the Fibonacci number ratios. Many calculations have been made of the diffraction patterns to be expected from structures involving icosahedral complexes in parallel orientations but without three-dimensional translational operations.

I have pointed out that the diffraction maxima from an array of cubic crystals of small size, perhaps 500 Å on edge, would be broad, and that the intensity distribution across the broad peak would be modulated in two ways by icosahedral interactions. First, the structure factor of the icosahedral 104-atom complex in general has its maximum values in positions different from those vectors in the cubic reciprocal lattice. Second, the diffracted beams from the different microcrystals would interact to produce maxima in positions somewhat displaced from those for the perfect cubic crystal. So far no detailed calculations have been made along these lines, but it seems to me likely that all of the diffraction observations can be explained on the basis of the twinned cubic-crystal model.

These so-called icosahedral quasicrystals are usually made by rapid quenching of the molten alloy. I think that the 104-atom complexes are already present in the molten alloy, and that if it

were to be quenched extremely rapidly a supercooled liquid (a metallic glass) would be formed. Somewhat slower quenching might lead to an alloy in which the clusters interact with one another in such a way that they are kept parallel, but that otherwise the arrangement is similar to that in the supercooled liquid. With a still smaller rate of quenching, very small microcrystals with the β–W structure could begin to form, perhaps so small as not to give well-defined X-ray powder lines. With still slower quenching the 500-Å microcrystal, with icosahedral twinning, would result. Various properties of the metallic glass, the icosahedral quasicrystals and crystalline materials with the same composition have been reported, and usually the icosahedral quasicrystals are found to be intermediate between the metallic glass and the crystalline material, as suggested by the foregoing argument.

As a crystallographer, with 65 years of experience in X-ray crystallography, I am pleased that the problem of the so-called icosahedral quasicrystals has been resolved in this way. Crystallographers have believed for many years that crystals cannot have five-fold axes of symmetry. In my model the grains with apparent icosahedral symmetry consist of cubic crystals that have a conventional structure, but that have, by repeated twinning determined by the approximate icosahedral structure of the 104-atom clusters, arranged themselves into an aggregate of microcrystals that shows icosahedral symmetry.

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