

So-called Icosahedral and Decagonal Quasicrystals Are Twins of an 820-Atom Cubic Crystal

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It is proposed that a molten alloy may contain a 104-atom cluster with icosahedral symmetry and largely icosahedral packing. The cluster may be described as involving twenty interpenetrating Friauf polyhedra. On rapid freezing these clusters form cubic crystals related to the β -W structure. The structure is compatible with x-ray and neutron powder diffraction patterns, the single-crystal precession x-ray patterns of CuLi_3Al_6 , the electron diffraction photographs, and the high-resolution electron micrographs.

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The discovery by Shechtman *et al.*¹ that a rapidly cooled alloy with composition MnAl_6 and some other alloys seem to have icosahedral symmetry has aroused great interest, with about 500 papers having been written on this subject during the last two years, many of them dealing with Penrose tiling, six-dimensional space, and other efforts to explain the observations. Decagonal quasicrystals have also been reported.^{2,3} The few efforts to discuss the phenomena in terms of twinning⁴⁻⁶ have been largely ignored.

I suggested last year⁶ that an icosahedral or decagonal seed orders twenty or ten cubic crystals into orientations such as to give the twinned clusters icosahedral or decagonal point-group symmetry. The structure that I proposed, on the basis of arguments about icosahedral packing of larger atoms (Al) about smaller ones (Mn), was the 1168-atom face-centered-cubic NaCd_2 structure⁷⁻¹⁰ with cube edge 26.73 Å. This structure accounted reasonably well for the x-ray powder pattern, but it was pointed out^{11,12} that other large units might also account for this pattern and that I had not provided a satisfactory discussion of the electron-diffraction (ED) patterns and the high-resolution electron micrographs (HREM's).

During the past year I made considerable progress with the 26.73-Å unit, but kept having difficulties. One problem was that a sequence of ED diffraction maxima on essentially all the ED photographs had surely, on the twinning hypothesis, to be $hh0$ rather than $h00$, because the cubic crystals are oriented with their body diagonals and symmetry planes coincident with the threefold axes and symmetry planes of the icosahedral seed, and $hh0$ of the 26.73-Å cube could not give the correct ED spacings if the scale published by Shechtman and Blech¹³ were correct. I suggested to these authors and also to Bendersky² that there was an error by the factor $3^{1/2}/2$ in their scales. They kindly sent me calibrating ED's proving that my suggestion was wrong. The alternative was that the error lay in my value of the cube edge, and I soon found that a primitive unit cube with edge length 23.36 Å and containing about 820 atoms is in complete agreement with the high-resolution x-ray

powder diffraction pattern reported by Bancel *et al.*¹⁴ The longest interplanar distances, 3.850, 3.349, and 2.856 Å correspond, respectively, to the indices 610, 632, and 733; the other values also agree with this unit. The unit also accounts for the neutron diffraction patterns,^{15,16} including one strong line (2.622 Å, 840) that does not appear on the x-ray pattern.

The single-crystal x-ray photographs of the CuLi_3Al_6 decagonal quasicrystals sent to me before publication by Bartges *et al.*¹⁷ were of great help to me in substantiating the 820-atom cubic structure. Diffractions 550, 880, 13130, and 16160 are seen as the principal features on the fivefold axis, threefold axis, and twofold axis precession x-ray photographs.

It is of interest that this is the most complicated structure to have been reported for an intermetallic compound. It has 820 atoms in the Bravais unit, nearly three times as many as the NaCd_2 structure.

Representative ED photographs with the beam along a fivefold axis (kindly given to me by Dr. K. K. Fung³) are shown in Fig. 1. Analysis of the spots on the meridional (P - P) plane of symmetry is given in Table I. All of the spots are orders of $hh0$, with the stronger ones representing the first six terms of the Fibonacci series, as is expected from the icosahedral packing of the atoms in the assigned structure (described below).

There are only three equatorial spots. Each of the three can be accounted for by double diffraction (of 330, 550, and 880, with the factor for R of $1.9021 = 2\sin 72^\circ$). By vector addition it is seen that the other spots can be accounted for by multiple diffraction of $hh0$.

Whereas only $hh0$ can diffract with the beam along a fivefold axis of the icosatwin because of the tilt of the cubic crystals, any plane in the zone $1\bar{1}0$ of the decatwin can diffract because the seed orients the cubic crystals with this zone axis parallel to the fivefold axis of the twin. It is seen from Fig. 1(b) that the meridional spots of decagonal FeAl_6 are the same as for icosahedral MnAl_6 , representing orders of $hh0$, but that there are many more equatorial spots, eleven instead of three. Indices are assigned in Table II; some spots involve double

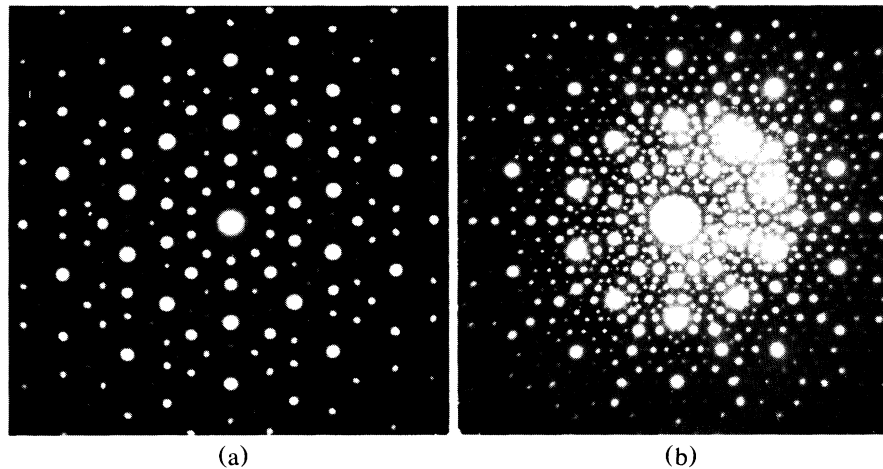


FIG. 1. Fivefold ED photographs of icosahedral MnAl₆ (left) and decagonal FeAl₆ (right) (Ref. 3).

diffraction. Inspection of Fig. 1 (vector addition) shows that all of the spots between the symmetry planes can be accounted for by multiple diffraction or primary diffraction (the two strongest, spacings 2.565 and 1.835 Å, have indices 119 and 3312).

I have analyzed many other ED photographs, with similar success in accounting for the observed patterns with the 23.36-Å unit.

Recognition that the crystals have a cubic unit with edge 23.36 Å required that I reconsider the nature of their structure. The relative sizes of Mn and Al indicate icosahedral packing. This packing was first reported by Friauf¹⁸ for the copper atoms in the 24-atom face-centered compound MgCu² and then by other investigators for some of the atoms in α -Mn, β -Mn, and β -W. In 1950, I recognized that the 39-atom cubic structures of Mg₃Cu₆Al₅ and Mg₂Zn₁₁ (Samson^{19,20}) could be obtained from a centered icosahedron surrounded by a shared shell of 32 atoms, and I used this idea to predict the structure of Mg₃₂(Al,Zn)₄₉. This structure was refined by Bergman, Waugh, and Pauling^{21,22} who pointed

out that the central position may not be occupied. Samson²³ has emphasized that the structure may be described as involving a complex of twenty interpenetrating Friauf polyhedra (Fig. 2).

This complex is especially appealing as a unit in a very rapidly quenched alloy. The Mg₃₂(Al,Zn)₄₉ structure, with its outer 72-atom shell shared, would be slow to form, but a packing of the 104-atom complexes of Fig. 2 into a crystal without sharing atoms could form rapidly. The cube edge 23.36 Å corresponds to eight of these complexes in the unit. One simple way of arranging them is the NaCl structure, with two orientations alternating; it is ruled out because it is face centered. The other way, the β -W structure (two atoms at 000, $\frac{1}{2} \frac{1}{2} \frac{1}{2}$, 6 at $\frac{1}{2} \pm \frac{1}{4} 0, \curvearrowright$), is not ruled out. With this structure each complex C_1 at 000 or $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ is surrounded icosahedrally by twelve complexes C_2 of the second sort at 13.06 Å, and each C_2 has four C_1 at this distance, two C_2 at 11.68 Å, and twelve C_2 at 14.31 Å, its coordination polyhedron being a hexagonal antiprism with two polar caps. The three distances 11.68, 13.06, and 14.31

TABLE I. The meridional (P - P) diffraction maxima of the MnAl₆ icosatwin fivefold-axis ED photograph (Ref. 3). Values of intensity, I ; radius, R ; observed and calculated interplanar distances, d_{obs} and d_{calc} ; and indices. Scale $Rd = 75.6 \text{ mm } \text{Å}$, $a_0 = 23.36 \text{ Å}$.

	I	R (mm)	d_{obs} (Å)	d_{calc} (Å)	hkl
1	vvvw	9.1	8.3	8.26	220
2	w	14.0	5.40	5.51	330
3	s	22.8	3.32	3.304	550
4	vs	36.6	2.066	2.065	880
5	vvw	45.5	1.662	1.652	10100
6	vvvw	50.5	1.497	1.502	11110
7	s	59.2	1.277	1.271	13130
8	w	73.2	1.033	1.032	16160
9	vvw	81.8	0.924	0.918	18180
10	w	95.6	0.791	0.787	21210

TABLE II. The equatorial (D - D) diffraction maxima of the FeAl_6 deca twin fivefold-axis ED photograph (Ref. 3). Values of intensity, I ; radius, R ; observed and calculated interplanar distances, d_{obs} and d_{calc} ; and interpretation. Scale $Rd = 72.6 \text{ mm } \text{\AA}$, $a_0 = 23.36 \text{ \AA}$.^a

	I	R (mm)	d_{obs} (\AA)	d_{calc} (\AA)	Interpretation ^b
1	m	7.0	10.3	10.14	$d(006)$, $d(550)$, 18°
2	m	11.5	6.29	6.300	$d(006)$, $d(006)$, 36°
3	s	18.5	3.91	3.893	$d(006)$
4	m	22.9	3.157	3.150	$d(0012)$, $d(0012)$, 36°
5	m	25.6	2.824	2.833	$d(550)$, $d(550)$, 72°
6	ms	30.3	2.386	2.384	$d(448)$ ^c
7	m	37.1	1.949	1.947	$d(0012)$
8	s	41.7	1.734	1.737	$d(550)$, $d(550)$, 144°
9	s	49.6	1.458	1.460	$d(0016)$
10	s	60.6	1.193	1.192	$d(8816)$ ^c
11	s	68.0	1.063	1.062	$d(0022)$

^aThe value of a_0 is uncertain. If Rd were the same as for Fig. 1(a), a_0 would be 24.4 \AA .

^bThe factor for double diffraction by equivalent planes at 36° is τ , the golden number, with retention of orientation (D - D stays D - D). At 72° the factor is 1.756 and at 144° it is 1.9021, with rotation P - P to D - D or the reverse.

^cCrystals rotated by $\pm 36^\circ$ diffract $h h 2h$ at $\pm 0.7^\circ$ from the D - D plane.

\AA correspond, respectively, to about six, seven, and eight effective shell thicknesses. The distance along the cube edges, 11.68 \AA , involves the sharing of pairs of atoms between C_2 and C_2 , the distance 13.06 \AA involves the juxtaposition of two five-rings rotated by 36° relative to one another, and the distance 14.01 \AA involves the juxtaposition of pairs of hexagons to form a dicapped hexagonal prism, as found by Samson²⁴ in the 184-atom face-

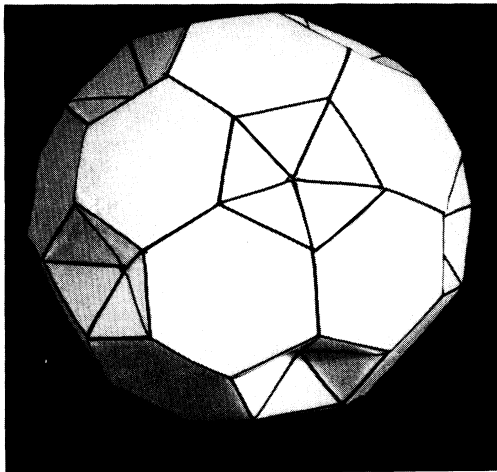


FIG. 2. A complex of twenty Friauf polyhedra, with icosahedral symmetry (Samson, Ref. 23). This complex contains 104 atoms, if the central icosahedral position is not occupied. Most of the atoms show approximate icosahedral ligan- cy; twenty atoms, at the centers of the Friauf polyhedra, have ligan- cy 15 or 16. The complex was first identified in $\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$. In the cubic crystals that form the icosatwins and deca twins these complexes are packed in such a way as to approximate an icosahedral arrangement of twelve complexes about a central one, the structure being similar to that of β -W.

centered-cubic crystal $\text{Mg}_3\text{Cr}_2\text{Al}_{18}$ (cube edge 14.53 \AA). The eight 104-atom complexes lose twelve atoms by the sharing of pairs between C_2 and C_2 , giving 820 in the unit cube. This number leads to atomic volume 15.5 \AA^3 and to density 3.31 g ml^{-1} for MnAl_6 , in agreement with the observed values^{25,26} 3.287 ± 0.038 and $3.26 \pm 0.06 \text{ g ml}^{-1}$. If the intercluster icosahedra and hexagonal prisms were centered, the calculated density would be 6% larger and unacceptable; it is accordingly to be concluded that these polyhedra remain empty, perhaps because of such low activity of single atoms as to decrease their availability during the process of very rapid freezing of the melt.

This structure, based on the space group $O_h^3 Pm 3n$, involves about fifty atomic positional parameters, for which approximate values can be estimated from the $\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$ parameters. Refinement of the structure would be laborious.

The structure factor for the 104-atom complex with almost perfect icosahedral symmetry determines the intensities of the diffraction maxima, in correspondence with the inverse relationship between intensity in reciprocal space and the atom-pair vectors in real space that was discovered fifty years ago by Patterson.²⁷ The icosahedral nature of the clusters in the cubic crystal explains the appearance of the Fibonacci numbers and the golden ratio.

I conclude that the evidence in support of the proposal that the so-called icosahedral and decahedral quasicrystals are icosatwins and deca twins of cubic crystals is now convincingly strong. I point out that there is no reason to expect these alloys to have unusual physical properties.

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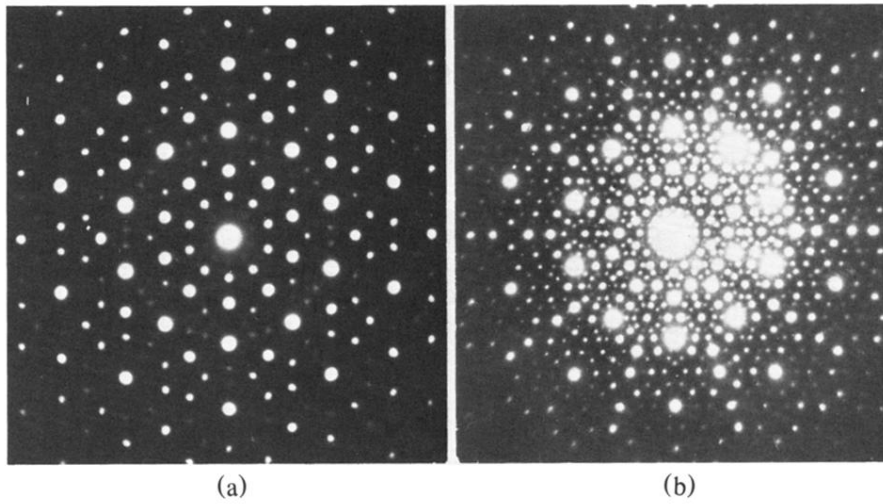


FIG. 1. Fivefold ED photographs of icosahedral MnAl_6 (left) and decagonal FeAl_6 (right) (Ref. 3).

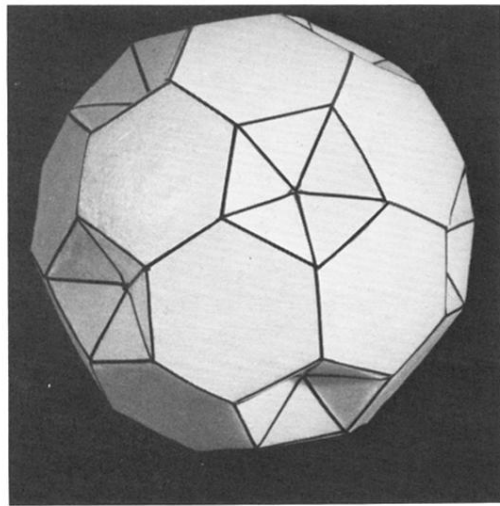


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