Reminiscences About a Chemistry Nobel Prize Won with Metallurgy: Comments on D. Shechtman and I. A. Blech; *Metall. Trans. A*, 1985, vol. 16A, pp. 1005–12

ILAN A. BLECH, JOHN W. CAHN, and DENIS GRATIAS

DOI: 10.1007/s11661-012-1323-1

© The Minerals, Metals & Materials Society and ASM International 2012

A paper, “The Microstructure of Rapidly Solidified Al_6Mn ,”^[1] was submitted for publication in October 1984 by D. Shechtman and I. Blech to the *Metallurgical Transactions A* (now *Metallurgical and Materials Transactions*) after having been rejected by *The Journal of Applied Physics* (JAP) in the summer of 1984. A second paper, “Metallic Phase with Long-Range Orientational Order and No Translational Symmetry,”^[2] was submitted within a week by Dan Shechtman and coworkers to the *Physical Review Letters* (PRL). Both papers announced the creation by rapid solidification, at the National Bureau of Standards (NBS)—now the National Institute of Standards and Technology (NIST)—of a sharply diffracting metallic Al-Mn solid phase that, because of its icosahedral symmetry, could not be periodic. In 2011, Dan Shechtman was awarded the Nobel Prize in Chemistry for this discovery. The Award cites him for “changing the way chemists looked at the solid state.”^[3] We, the three co-authors of these papers, are pleased to have been invited by the editor of *Metallurgical and Materials Transactions* to recount our participation in this work and to summarize its significance.

The two papers differ in several ways. The *Physical Review Letters* paper was confined to the compelling case made by the NBS experiments alone that challenged several prevailing paradigms of crystallography. The *Metallurgical Transactions A* paper had, in addition, a model created by Ilan Blech, then at the Technion, demonstrating that an icosahedral electron diffraction pattern could result from a special sort of an icosahedral glass in which the translational symmetry is broken while retaining icosahedral orientational symmetry. This model was referred to, but left out of the *Physical Review Letters*, for three main reasons: (1) The experimental case by itself was strong and sufficient to force a change in thinking, (2) the model was open to

criticism and might distract attention from the experiments, and (3) *Physical Review Letters* has a page limitation.

According to the then-prevailing crystallographic theories, crystals with icosahedral symmetry could not exist. Within a short time of publication, the existence of many others with forbidden symmetries were reported. Their undeniable existence and properties formed a classic example of the truism that experiments are unsurpassed at disproving theories. Nothing else was needed to force a change in the prevailing theories.

The discovery challenged two basic principles of crystallography. In the late 1700s, René Just Haüy^[4] postulated that all crystals were made up of clusters of atoms repeated periodically in three dimensions. The severe restrictions that periodicity places on crystals became a cornerstone of crystallography. In the 19th century, it was established that only 1-, 2-, 3-, 4-, and 6-fold rotation axes, only 14 Bravais lattices, 32 point groups, 51 crystal forms, and 230 space groups can be consistent with periodicity.^[5] Throughout the 19th century, all measured properties and external forms had been consistent with these restrictions. In 1912, the diffraction of X-rays by crystals brilliantly confirmed both that X-rays were short wavelength light and that crystals were periodic. The point group symmetries of the diffraction patterns, which are the same as those of the objects, also conformed to what was allowed by Haüy’s postulate. With no exceptions reported in almost 200 years, periodicity became the definition of a crystal and an axiom or a law of crystallography.

Diffraction from periodic objects results in sharp spots arrayed on a reciprocal lattice. The converse, that sharp diffraction spots could only come from a periodic object, was a widely accepted fallacy. By the definition of quasiperiodicity, the diffraction from quasiperiodic objects is sharp.^[6] Quasiperiodic objects have no lattice, and their diffraction spots will not form a reciprocal lattice. Because of the 5-fold axis, a frequent ratio of spacing of spots in Figures 2 and 6* is the golden mean,

ILAN A. BLECH, 25551 Burke Lane, Los Altos Hills, CA 94022. JOHN W. CAHN, Affiliate Professor, UW Physics, Senior Fellow Emeritus, is with the National Institute of Standards & Technology, Gaithersburg, MD 20899. Contact e-mail: jwcahn@gmail.com DENIS GRATIAS, Research Director, is with the Laboratoire d’Études des Microstructures CNRS ONERA, 92322 Châtillon, France.

Article published online July 31, 2012

*Figure numbers refer to figures in the *Metallurgical Transactions A* paper.

Fig. 1—(d) The Quasicrystal Team at NIST 1985: Dan Shechtman, Frank Biancaniello, Denis Gratias, John Cahn, Leo Bendersky, and Robert Schaefer.

$\tau = 2 \cos(\pi/5) = (1 + \sqrt{5})/2$. There is no reciprocal lattice in those diffraction patterns.

In 1971–1972 as a visiting professor at the Technion, John Cahn had met Shechtman, who was in his last year of graduate studies. When they met again in 1979, Cahn invited him to NBS for a 2-year sabbatical 1981–1983 to work on a large Defense Advanced Research Projects Agency-funded and National Science Foundation-funded rapid solidification project as the electron microscopist. Dan had demonstrated a skill at dealing with awkward samples. After Dan returned to the Technion, NIST hired Leo Bendersky to continue the electron microscopy work. Dan came to NIST in the summer of 1984 and continued to come to NIST every summer for more than a decade. Figure 1(d) is a photograph of the quasicrystal research group in 1985.

All of the experimental work was done at NBS/NIST. Robert J. Schaefer initiated the study of rapid solidification of dilute Al-Mn alloys because of his interest in achieving plane front solidification that would produce alloys free of microsegregation.^[7] It was Dan Shechtman's decision to explore higher manganese content. The alloys containing the quasicrystals were prepared by Schaefer and Frank Biancaniello. C.R. Hubbard did the X-ray experiments. Denis Gratias travelled to NIST from the Institute of Theoretical Physics at Santa Barbara to work with us. Special thanks are due to the NIST's internal review committee, which took unusual care to review the PRL manuscript quickly and thoroughly. The PRL paper was reviewed and in print 5 weeks after submission.

I. ACCEPTANCE

Shechtman observed the electron diffraction patterns with its icosahedral symmetry in the spring of 1982 at

NIST, but he only showed the 10-fold diffraction data to his NIST colleagues. Without seeing his dark-field images in Figure 4 (in the original *Metallurgical Transactions A* paper), the common reaction was that he was seeing multiple twinning. Most of us did not realize that twinning of periodic crystals would have resulted in overlapping reciprocal lattices and distortions; neither are found in the patterns. Quasiperiodicity was unknown to us; so was Mackay's demonstration that Penrose's aperiodic two-dimensional tiling would diffract sharply.^[7] Discussions at NIST ceased and no further work was done on quasicrystals. Before Shechtman returned to Israel in the fall of 1983, he completed another important rapid solidification work.^[8]

Although no explanation was necessary to refute both the universal periodicity of crystals and that only periodic objects can give sharp diffraction patterns, Shechtman apparently felt a need for an explanation of his finding. The observation lay dormant for 2 years. In 1984, as a result of Blech's model, Shechtman gained enough confidence to return to his findings and pursue publication.

A. The Blech Model

The second part of the *Metallurgical Transactions A* paper is devoted to the understanding of the electron diffraction pattern by considering the icosahedral phase to be a special sort of an icosahedral glass. Blech achieved this by aggregating parallel oriented icosahedra connected pairwise along common edges. The model succeeds because of two key facts:

- The icosahedra are all oriented the same way,
- Their pairwise connections form a unique set of vectors (along the 2-fold directions) that are a complete orbit of the icosahedron.

Because the actual chemical constitution of the icosahedra is not a factor, the model allows development by replacing the featureless simple icosahedra with more complicated clusters like a Bergman type cluster with 33 atoms (center + icosahedron + dodecahedron) or a Mackay type cluster with 54 atoms (two icosahedra + icosidodecahedron). The model also allows the connection vectors to be 5-fold, 3-fold, or 2-fold orbits (as in the original paper). Additional connection vectors of the icosahedral orbit are possible as long as they are equally distributed in space to satisfy an average global icosahedral symmetry. An example is shown in Figure 2(d).

By the definition of quasiperiodicity, quasiperiodic functions can always be represented by irrationally oriented cuts of higher dimensional periodic functions. In Figure 3(d), three kinds of one-dimensional cuts are sketched together with a higher (two-) dimensional periodic structure represented by the tilted lattice. Perfect quasiperiodicity is represented by the black straight line whose orientation is irrational with respect to the lattice. Large unit cell periodic structures, called approximants, can be generated by performing a high-index rational cut with respect to the lattice, as suggested by the slanted green line in Figure 3(d). Finally, the Blech model can be viewed as a wavy cut,

Fig. 2—(d) Example of parallel icosahedra built à la Blech but connected by square bridges instead of sharing common edges.

Fig. 3—(d) Quasicrystals are best described by the cut method that consists of embedding the structure in a higher dimensional space in which it is periodic and let the physical space be cut along an irrational orientation. In the figure, a one-dimensional quasicrystal is generated by a cut (the solid black line) of a periodic two-dimensional array of “atomic surfaces” (here shown as vertical line segments σ). Actual atoms would be located on the intersections of the physical space with those atomic surfaces. The black line corresponds to a perfect ideal one-dimensional quasicrystal. The green one is rationally oriented with respect to Λ generates the so-called periodic “approximants” and the blue wavy line corresponds to the Blech model, later called the “random tiling” model.

meandering about the horizontal black line, represented by the blue curve.

Icosahedral symmetry can be periodic in six dimensions, where each axis is perpendicular to the other five. Perfect icosahedral quasicrystals are given by three-dimensional straight cuts on irrational planes, oriented to retain the icosahedral symmetry and, thus, be quasiperiodic. They are the higher dimensional version of the black line in Figure 3(d). The structures in those

cuts are icosahedral in three dimensions and diffract with Bragg peaks; they are to quasicrystals what ideal crystals are for standard crystallography. Large unit cell, approximant, periodic structures, including those proposed by L. Pauling, can be generated by performing a high-index rational cut with respect to the six-dimensional lattice, as already suggested by the green line in Figure 3(d). These can only approximate icosahedral symmetry. Finally, the Blech model can be viewed as a wavy three-dimensional cut meandering about the planar cut, represented by the blue line. Icosahedral symmetry is retained as long as it fluctuates around the planar cut.

The fluctuations' contributions to background diffuse intensity were not determined in the original Blech's computations, which focused on the expected Bragg peaks. In the original *Metallurgical Transactions A* paper, the main understanding of this localized diffraction is based on the remark that the set of interplanar distances of the model form a discrete uniform ensemble of vectors. Amusingly enough, this property was shown in 2005 to be one of the main ingredients in the Strungaru theorem that states that a Delaunay distribution of atoms has a sharp diffractive component in its Fourier spectrum if the pair interatomic vectors form a uniformly discrete set.^[9] The Blech model has been the starting point of an enormous body of work on random tilings, especially in the United States, mainly by theoretical physicists.

Shechtman and Blech submitted a paper to the *Journal of Applied Physics* in the spring of 1984 reporting both Shechtman's experimental finding of the icosahedral electron diffraction pattern and Blech's computer simulation. The paper suggested the existence of a new class of solids, which they termed “multipolyhedral.” When Cahn saw the manuscript in the July of 1984, it was the first time he had seen all the data. He told Shechtman and his NIST colleagues that this work was of enormous importance, but he also told Shechtman that the paper was poorly written and that JAP was the wrong journal. In August, the paper was rejected by JAP with the suggestion that it be submitted to another journal. Shechtman told Cahn that he immediately submitted the unchanged manuscript to *Metallurgical Transactions A*, but there is no record of this. The published version was received by *Metallurgical Transactions A* early in October.

Because Cahn continued to feel that a short paper needed to be written to reach a broader audience, Shechtman invited him to write the PRL paper in August with the input from Gratias. It was finished mid-September, days before Shechtman returned to Israel.

As was his custom, Cahn sent the PRL manuscript out widely for comment. A copy of a copy reached Paul Steinhardt who, with Dov Levine, had been working on a model that was quickly submitted to PRL.^[10] They coined the name quasicrystal, and their work had enormous influence in stimulating theory.

There was immediate worldwide acceptance, excitement, and confirmation about quasicrystals. Although

the deadline for submission of abstracts for the March 1985 APS meeting was early December of 1984, 13 abstracts were received and there was an entire quasicrystal session. Lou Testardi, Division Chief of Metallurgy at NIST recommended that Shechtman be an invited speaker at that meeting. The fall 1985 meeting of the Metallurgical Society devoted a session to them. About 300 papers were submitted worldwide in 1985; by now, there are tens of thousands. Powder pattern of quasicrystals had been seen often and ignored as uninteresting intermetallic crystals with unknown symmetry and large unit cells. Stable quasicrystals, not produced by rapid solidification, were present in commercial alloys,^[11] especially in the (Al-Cu-Li) alloy where quasicrystalline intergranular grains had been observed.^[12] Quasicrystals have found all kinds of useful applications.^[13] Quasicrystals spawned a renewed interest in aperiodic tilings, higher dimensional crystallography, and mathematics.^[14]

By 1992, this realization that in a quasicrystal, the atoms are patterned in an orderly but nonperiodic manner, led the International Union of Crystallography (IUC) to alter its definition of a crystal. Previously, IUC had defined a crystal as “a substance in which the constituent atoms, molecules, or ions are packed in a regularly ordered, repeating three-dimensional pattern.” The new definition became “A material is a crystal if it has *essentially* a sharp diffraction pattern...” (emphasis added). The word *essentially* means that “most of the intensity of the diffraction is concentrated in relatively sharp *Bragg peaks*, besides the always present diffuse scattering. ...”^[15] This definition is broader and allows for possible future discoveries of other kinds of crystals.

As with any major paradigm change, there was strong opposition, most notably by Linus Pauling, who had considerable influence and access to media. By the time he began, there was much literature confirming Shechtman’s finding. Pauling initially chose to ignore electron diffraction and tried to describe the powder patterns of quasicrystals both by twinning and by very large unit cells; either would have sufficed, but his models did not fit the electron diffraction pattern from a single quasicrystal. No one ever provided experimental evidence confirming Pauling’s proposed structures, and most of the workers in quasicrystals did not take him seriously.

Within a short time Shechtman was awarded many honors, culminating thirty years later in the 2011 Nobel Prize in Chemistry.

ACKNOWLEDGMENTS

We have benefitted greatly from reminiscences and files from many involved in these events, among them, Frank Gayle, Leo Bendersky, William Boettinger, and Robert Schaefer at NIST, as well as David Brandon from the Technion. The following acknowledgement was omitted from the revised manuscript and is not in the publication. “The authors wish to thank F.S. Biancaniello for alloy preparation and R.C. Hubbard for performing (the) X-ray experiment. The work was partially supported by DARPA.” Although there is no mention of NBS at all, the original submitted manuscript contained the following affiliations: “D. Shechtman* and I. Blech, Dept. of Materials Eng., Technion, Haifa, Israel, *Center for Materials Research, The Johns Hopkins University, Baltimore, Maryland and Guest Worker at NBS, Gaithersburg, Maryland.”

REFERENCES

1. D. Shechtman and I.A. Blech: *Metall. Trans. A*, 1985, vol. 16A, pp. 1005–12.
2. D. Shechtman, I. Blech, D. Gratias, and J.W. Cahn: *Phys. Rev. Lett.*, 1984, vol. 53, pp. 1951–53.
3. D. Shechtman: Nobel Prize Lecture, http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2011/shechtman-lecture.html.
4. R.J. Haüy: *Essai d’une théorie sur la structure des cristaux*, Registres de l’Académie Royale des Sciences, Paris, 26 November 1783.
5. The International Union for Crystallography: *International Tables for Crystallography*: vol. A1, T. Hahn and D. Reidel, eds., Kluwer Academic Publishers, Boston, MA, 1983.
6. H. Bohr: *Acta Math.*, 1925, vol. 45, pp. 29–127; H. Bohr: *Almost-periodic functions*, Chelsea, reprint 1947; A.S. Besicovitch: *Almost periodic functions*, Book Cambridge University Press, New York, NY, 1932.
7. A.L. Mackay: *Physica A*, 1982, vol. 114, p. 609.
8. W.J. Boettinger, D. Shechtman, R.J. Schaefer, and F.S. Biancaniello: *Metall. Trans. A*, 1984, vol. 15A, pp. 55–66.
9. N. Strungaru: *Discret. Comp. Geom.*, 2005, vol. 33, pp. 483–505.
10. D. Levine and P. Steinhardt: *Phys. Rev. Lett.*, 1984, vol. 53, pp. 2477–80.
11. P. Sainfort, B. Dubost, and A. Dubus: *Compte Rendus A Sci.*, 1985, vol. 301, p. 10.
12. B. Dubost, J.-M. Lang, M. Tanaka, P. Sainfort, and M. Audier: *Nature*, 1986, vol. 324 (6092), p. 48.
13. J.-M. Dubois: *Useful Quasicrystals*, World Scientific, Singapore, 2005.
14. M. Senechal: *Quasicrystals and Geometry, 1995, Directions in Mathematical Quasicrystals*, Cambridge University Press, 2000, M. Baake and R.V. Moody, eds., CRM Monograph Series, vol. 13, Amer. Math. Soc., Providence, RI.
15. IUCr Commission on Aperiodic Crystals: *Acta Cryst.*, 1992, vol. A48, p. 928.

The Microstructure of Rapidly Solidified Al₆Mn

D. SHECHTMAN and I. A. BLECH

The microstructure of rapidly solidified Al-Mn alloys containing 18 to 25.3 wt pct Mn was studied by transmission electron microscopy. One of the phases found in the microstructure exhibits icosahedral symmetry manifested in electron diffraction patterns having five-fold symmetry. A new structural concept is proposed to account for the observed electron diffraction patterns. The structure is assumed to be composed of many connected polyhedra. Although not forming a regular lattice, such structures are able to produce sharp diffraction peaks. The terminal stability and transformation of the icosahedral phase was also studied and reported.

I. INTRODUCTION

THE microstructure of rapidly solidified binary aluminum-transition metal alloys was intensively investigated in the past. Most of the studies were performed on dilute solutions but some examined alloys of higher concentrations.¹⁻⁵ Rapidly solidified dilute solutions from supersaturated solid solutions and alloys of higher solute content form cellular microstructures. Beyond a certain concentration, characteristic of the alloy system, another phase forms. The phase is spherulitic in shape, and its size ranges from 0.1 μm to a few μm . Although the solidification as separate spherulites is not usual in rapid solidification, it is common in rapidly-solidified concentrated aluminum-transition metal alloys. Several examples will be given here.

Binary aluminum chromium alloys, containing up to 5 wt pct Cr are characterized^{2,3,4} by a supersaturated cell-free structure. At 5 wt pct Cr, a cellular microstructure that contains separate spherulites forms. The volume fraction of the spherulites increases with the chromium concentration of the alloy and reaches a homogeneous high density in the 15 wt pct Cr alloy.⁴ The aluminum-iron system also contains spherulites in a cellular aluminum matrix when the iron concentration exceeds 10 wt pct.⁵

The microstructure of rapidly-solidified binary aluminum-manganese alloy ribbons containing up to 15 wt pct Mn has been studied.¹ The ribbons were found to be supersaturated and cell-free up to manganese concentrations of 5 wt pct. Alloys of 9 to 15 wt pct concentration are cellular. The cell boundaries in these alloys contain fine precipitates but the cell interiors are mostly free from precipitation. In this paper we report on a spherulite phase found in rapidly solidified aluminum manganese alloys with composition exceeding 15 wt pct Mn.

II. EXPERIMENTAL

Alloy buttons with Mn concentrations of 18, 22, and 25.3 wt pct Mn were prepared by arc melting, using 99.999 pct Mn. Small pieces cut from these buttons were induction heated in zirconia-coated quartz tubes, as inputs for melt spinning. Immediately upon melting, the metal was

Table I. Heat Treatment Times and Temperatures of Rapidly Solidified Al-25.3 Wt Pct Mn

T [°C]	300	350	350	400	400
t [h]	2.5	1	6	1	6

squirted onto a copper melt-spinning wheel, 10 cm in diameter, which rotated at 6800 rpm. The process was carried out under helium at 0.9 atmospheric pressure. The material obtained had the shape of small flakes, about 40 μm thick and 3 mm in diameter. For annealing, specimens were sealed in borosilicate glass ampules with 0.5 atmosphere of helium, and heat treatments were carried out at temperatures and durations given in Table I.

Microstructural studies were performed in a 120 kV scanning transmission electron microscope. The specimens were thinned by jet electropolishing in a standard solution of 1.5 pct HNO₃ and 5 pct HClO₄ in methanol at -30 °C. X-ray diffraction patterns were taken from crushed flakes using copper radiation.

III. RESULTS

A. As-Spun Alloys

The Al-25.3 wt pct Mn alloy consists almost entirely of one phase (Figure 1).^{*} This phase will be referred to as the

^{*}The grain boundary phase was determined by electron diffraction to be aluminum.

icosahedral phase which has a composition close to Al₆Mn. The grain (Figure 2) reveals a morphology of elongated dendrites stemming from a central core. A diffraction pattern taken from one such grain is given in Figure 3. The complex pattern is unusual in that it is characterized by a five-fold symmetry. A detailed analysis of this structure will be given in the discussion portion of this article. In order to get more information on the origin of this pattern, a set of dark-field images was taken, using the diffraction spots marked in Figure 4. The whole grain was found to diffract each one of the spots and there is no indication of polycrystallinity or large scale twinning in the structure. However, the grain is heavily strained and thus requires a slight tilt to move the diffracting areas in the dark-field image across the grain. A convergent beam diffraction pattern taken from an area of about 20 nm in diameter is given in Figure 5. This diffraction pattern can be obtained from any

D. SHECHTMAN is with the Department of Materials Engineering, Technion, Haifa, Israel. I. A. BLECH is with Zoran Corporation, 710 Lakeway Drive, Sunnyvale, CA 94086.

Manuscript submitted October 2, 1984.

Fig. 1—The microstructure of rapidly solidified Al_6Mn .

Fig. 2—The spherulites in Al_6Mn are characterized by elongated branches that stem from a central core.

Fig. 3—Selected area diffraction pattern taken from a single spherulite. Note the five-fold symmetry of the pattern.

spot across the grain in this orientation. A series of tilting experiments in the microscope resulted in a set of diffraction patterns given in Figure 6. One of the results shown in this series is that the five-fold symmetry selected area diffraction (SAD) is not unique in the structure. As will be discussed later, six such patterns can be obtained from each crystal. However, since the angle between them is 63.43° , it is difficult to obtain more than two such patterns using a conventional double tilt goniometer. X-ray diffraction results are given in Table II.

The Al-18 wt pct Mn alloy consists of two phases in an aluminum matrix, one of which is a dispersion of small particles, 10 nm in diameter (Figure 7, marked A). The particles are found in regions of high volume density within the alloy and are probably a product of solid-state decomposition of a highly supersaturated solid solution. The second phase (Figure 7, marked B) is spherulitic in shape, about $0.3\ \mu\text{m}$ in diameter. Its circumference is composed of round, petal-like edges about 60 nm in diameter. The particles, identified by electron diffraction to be the icosahedral phase, are evenly distributed within the alloy, and occupy about 36 pct of the volume.

In the alloy Al-22 wt pct Mn, the icosahedral phase particles are larger and almost fill the volume. At this composition most of the particles impinge on one another upon solidification to form a grain structure similar to that found throughout the Al-25.3 wt pct Mn alloy.

B. Structural Stability

Samples of Al-25.3 wt pct Mn that were annealed for 2.5 hours at 300°C and for 1 hour at 350°C do not show any change in morphology or in crystallography. Samples that were annealed for 6 hours at 350°C are totally transformed into the stable Al_6Mn phase, as shown in Figure 8. The Al_6Mn grains obtained are about $0.2\ \mu\text{m}$ in size and contrast evidence of strain can be seen in them. Samples annealed at 400°C for 1 and 6 hours have a more relaxed grain structure, but no detectable grain growth occurred under these annealing conditions (Figure 9).

In summary, the icosahedral phase is stable at 300°C for more than 2.5 hours, at 350°C it is stable more than an hour but less than 6 hours, and at 400°C it is stable for a period of less than an hour.

IV. DISCUSSION

A. Spherulites in Rapid Solidification

The competitive solidification of spherulites in rapidly solidified Al-Mn alloys starts when the composition reaches about 18 wt pct Mn. Unlike the aluminum-iron system,⁵ these spherulites have developed an ordered structure which is found to be stable up to a temperature of 300 to 350°C . As was also found in other studies,^{5,4} the nucleation rate of the spherulitic phase becomes dominant compared to that of the Al phase, and thus upon solidification solid spherulites nucleate and grow within the liquid, depleting it from the solute before being engulfed by the solidifying aluminum front. At the composition Al_6Fe , the spherulites consume most of the liquid before nucleation of aluminum starts to form a thin layer at the grain boundaries. Spherulites that

Fig. 4—Dark-field images of a spherulite taken with four different operating reflections as marked on the diffraction pattern.

Fig. 5—Convergent beam diffraction pattern from a spherulite. Such a pattern can be obtained at any point on the spherulite with small goniometer adjustments.

Fig. 7—The microstructure of Al-18 wt pct Mn. Note small particles marked A and spherulites marked B.

Fig. 6—The sequence of selected area diffraction patterns obtained from one spherulite at various tilt angles as marked.

have the same crystallography as the Al-Mn icosahedral phase have also been observed in the Al-Fe system⁵ and in the Al-Cr system.⁶

B. The Crystallography of Rapidly Solidified Al_6Mn

The five-fold symmetry observed in the TEM diffraction patterns of Al_6Mn suggests several possible microstructures:

- (1) A series of twinned microcrystals such as previously suggested for very thin gold films.^{7,8,9}
- (2) A layered twinned structure in which the twins are layers rotated with respect to each other by 72 deg.
- (3) Five separate crystals enveloping each other (such as a helix with five branches).
- (4) A structure consisting of multiple polyhedra having limited orientations.

Table II. X-Ray Diffraction Results (Cu k Radiation)

Observed Spacing (nm)	Relative Intensity	Plane Periodicity	Calculated Spacing (nm)
0.1086	5	$r/2$	0.1084
0.11	6	$(2l + s)/3$	0.1112
0.1276	21	l	0.1274
0.1497	7	—	—
0.2056	75	—	—
0.20624	75	$l + s$	0.20624
0.21681	100	r	0.2168
0.333	2	$2l + s$	0.3337
0.383	7	—	—

Fig. 8—Following 6 h at 350 °C the icosahedral phase transforms to the stable orthorhombic Al_6Mn . Note strain contrast.

Fig. 9—The orthorhombic Al_6Mn phase following 6 h at 400 °C.

Suggestion (1) was ruled out since no twins were found in dark-field images from the main diffraction spots. Suggestions (2) and (3) were found not to be valid since a tilt of 63.43 deg out of the original plane produced another five-

fold symmetry, which was not compatible with a simple layered structure. Suggestion (4) is a new concept.

According to this suggestion, the limited ways in which certain polyhedra are connected can create a structure that is nonperiodic but can still diffract. As an example, assume a structure built from many icosahedra. Accordingly, the building block in this case can be an icosahedron shown in Figure 10. The structure consists of many icosahedra joined by their edges as seen in Figure 11. Each new icosahedron will be attached to one or more existing icosahedra, thus maintaining its orientation. The projected distances between atoms, s , repeat themselves throughout the structure

Fig. 10—A possible building block of the icosahedral structure.

Fig. 11—A view along the five-fold axis of two adjacent edge connected icosahedra.

Fig. 12—A computer modeling of the two-dimensional structure. Note s and l increments and their sequence. Some of the sites are too close (marked A in the figure).

($s = 0.3633r$, $l = 0.5878r$; s , l , and r are defined in Figure 10). Figure 12 shows a two-dimensional multiple polyhedral structure; note the periodicity in the "atomic planes." As an example, the periodicity of $2l + s$ ($= 1.539r$) is shown in the figure. The structure is assumed to form in a random fashion with new polyhedra attaching themselves to the existing ones.

Many atoms scatter in phase and therefore diffraction peaks are expected from the various "planes." There is no long-range crystalline structure, but a periodicity is still maintained by various combinations of l and s .

The three-dimensional structure can have other symmetry elements when viewed from different angles. For example, a tilt of 37.38 deg from the five-fold axis will bring in a three-fold symmetry, or a further tilt to 63.43 deg will bring in the next five-fold axis (as seen in Figure 6). The TEM diffraction pattern (Figure 13) can thus be understood by the various observed periodicities. The strongest spots appear at d spacings of 0.333 nm, 0.206 nm, and 0.128 nm corresponding to periodicities of $2l + s$, $l + s$, and l , respectively. Note that $(2l + s)/(l + s) = (l + s)/l = 1.618$ (the golden mean). Many of the other spots can be attributed to double diffraction.

The X-ray diffraction pattern (Table II) is interpreted in the following way. If the spacing of 0.206 nm is taken as $l + s$, then $r = (l + s)/0.9511 = 0.2168$ nm, and the calculated distance between the icosahedron's vertices is 0.269 nm and the vertex-center distance 0.256 nm. These distances agree quite well with the Al-Al and Al-Mn distances previously reported.¹⁰ Some of the other spacings measured by X-ray diffraction were calculated using geometrical relations. They are marked in Table II and agree quite well with the observations. The X-ray diffraction peaks at 0.2056 nm, 0.1497 nm, and 0.383 nm were not identified. These planes probably do not belong to the five-fold symmetry zone axis.

Fig. 13—Schematic partial drawing of the TEM diffraction.

Fig. 14—A stereographic projection of the main zone axes of the proposed structure. Note the agreement of model with experimental results presented in Fig. 6.

The diffracted X-ray intensity was calculated for a computer simulated random two-dimensional array containing 85 polyhedra with two additional layers totaling 255 icosahedra. The diffraction pattern showed several distinct peaks, the strongest appearing at $l + s$, r , and $(2l + s)/3$. A stereographic projection of the main zone axes of the proposed structure determined on the basis of this model is given in Figure 14. The tilting experiments presented in Figure 6 agree completely with this projection within the limit of the accuracy of the goniometer stage.

Fig. 15 — Projected lattice sites in the multiple polyhedra structure. The projection is on a plane normal to the five-fold axis. (a) Centers of the icosahedral joined by their edges. (b) All the sites of icosahedral joined by their vertices.

In summary, the multiple polyhedral structure proposed here is compatible with both the TEM and X-ray observations. The actual structure occupies space in a manner that keeps both spacing and rotation angles. Further work should be done in computer simulation of the spatial structure and its diffraction patterns.

During the reviewing procedure such simulation has been done and is added here.

A computer program was constructed to calculate the kinematical diffraction pattern from multipolyhedral structures. The diffraction from the edge connected icosahedra model was calculated and indeed, a sharp diffraction pattern was obtained having a five-fold symmetry. However, the calculated diffraction pattern fits only partially the observed one in Figure 6. Consequently, another model was tried. The model consists of parallel icosahedra joined by their vertices.

The projection of the lattice site positions on a plane normal to the five-fold axis is shown in Figure 15. Both examples of the icosahedral models are shown: Figure 15(a) represents the projection of icosahedra centers of the edge connection model, while the vertex connection model is shown in Figure 15(b). The vertex structure is different from the edge one since the lattice sites have a perfect five-fold symmetry themselves. Of course, many other models including a symmetrical edge connected are possible.

Figure 16(a) shows the calculated kinematical diffraction along the five-fold axis is obtained from a cluster of 1000 lattice points of the vertex connection model. The area of the

spots in Figure 16 is proportional to the calculated intensity. The calculated intensity has still to be multiplied by the structure factor in order to obtain the true observed intensity values. There is a great similarity between Figure 16(a) and the actual diffraction (Figure 7).

Calculated diffraction patterns were also obtained along the three-fold axis, Figure 16(b) (tilted 37.38 deg away from the five-fold axes) and the two-fold axis, Figure 16(c) (tilted 58.29 deg from the five-fold axis). Again, there is a remarkable fit between the observed and calculated patterns. All the experimentally observed diffraction spots are accounted for. Figure 16(c) offers a possibility of actually obtaining a value of r , by comparing the scale of this figure with the experimental one in Figure 6; r is calculated to be 1.732 nm.

The scattering amplitude of the strongest diffraction spots in Figure 16 is 89 pct of the maximum possible amplitude (when all atoms scatter in phase) while the background intensity is about 1 pct or less, showing that indeed sizable diffraction is possible from multipolyhedral structures.

Although the exact position of the atoms was not ascertained, we have shown here that the rapidly cooled Al-Mn alloys form a new kind of structure which is neither amorphous nor crystalline. Such a structure consists of polyhedra (one or more kinds), symmetrical or random, penetrating or tangential, connected in such a way as to preserve symmetry axes. This structure is shown here to be capable of producing sharp diffraction peaks in a similar manner to crystalline materials.

(a)

37.38°

(b)

58.29°

(c)

Fig. 16—Simulated kinematical diffraction of the a particle containing 1000 lattice sites of the vertex connection model. (a) Along the five-fold axis, (b) tilted 37.38° away from the five-fold axis, and (c) tilted 58.29° away from the five-fold axis. The areas of the circles are proportional to the calculated intensity.

REFERENCES

1. D. Shechtman, R. J. Schaefer, and F. S. Biancaniello: *Metall. Trans. A*, 1984, vol. 15A, p. 1987.
2. H. Warlimont, W. Zingg, and P. Furrer: *Mat. Sci. Eng.*, 1976, vol. 23, p. 101.
3. P. Furrer and H. Warlimont: *Mat. Sci. Eng.*, 1988, vol. 28, p. 127.
4. L. Bendersky, R. J. Schaefer, F. S. Biancaniello, and D. Shechtman: *Metall. Trans.*, in press.
5. D. Shechtman and E. Horowitz: "Metastable Phases of Rapidly Solidified Al-Rich Al-Fe Alloys", Quarterly Report DARPA order MDA 903-83-K-0400, January 1984.
6. D. Shechtman: Technion, Haifa, Israel, unpublished research, 1984.
7. C. Y. Yang: *J. Cryst. Growth*, 1989, vol. 47, p. 274.
8. C. Y. Yang, M. J. Yacaman, and K. Heinemann: *J. Cryst. Growth*, 1979, vol. 47, p. 283.
9. P. Schabes-Retchikman, A. Gomez, G. Vazques-Polo, and M. Jose-Yacaman: *J. Vac. Sci. and Technol.*, 1984, vol. A2, p. 22.
10. A. D. I. Nickol: *Acta Cryst.*, 1953, vol. 6, p. 285.