

# *The Discovery of Quasi-Periodic Materials*

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and  
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**Surprising Discoveries  
on the Structure of  
matter and its  
properties in the  
Mid-1980s**

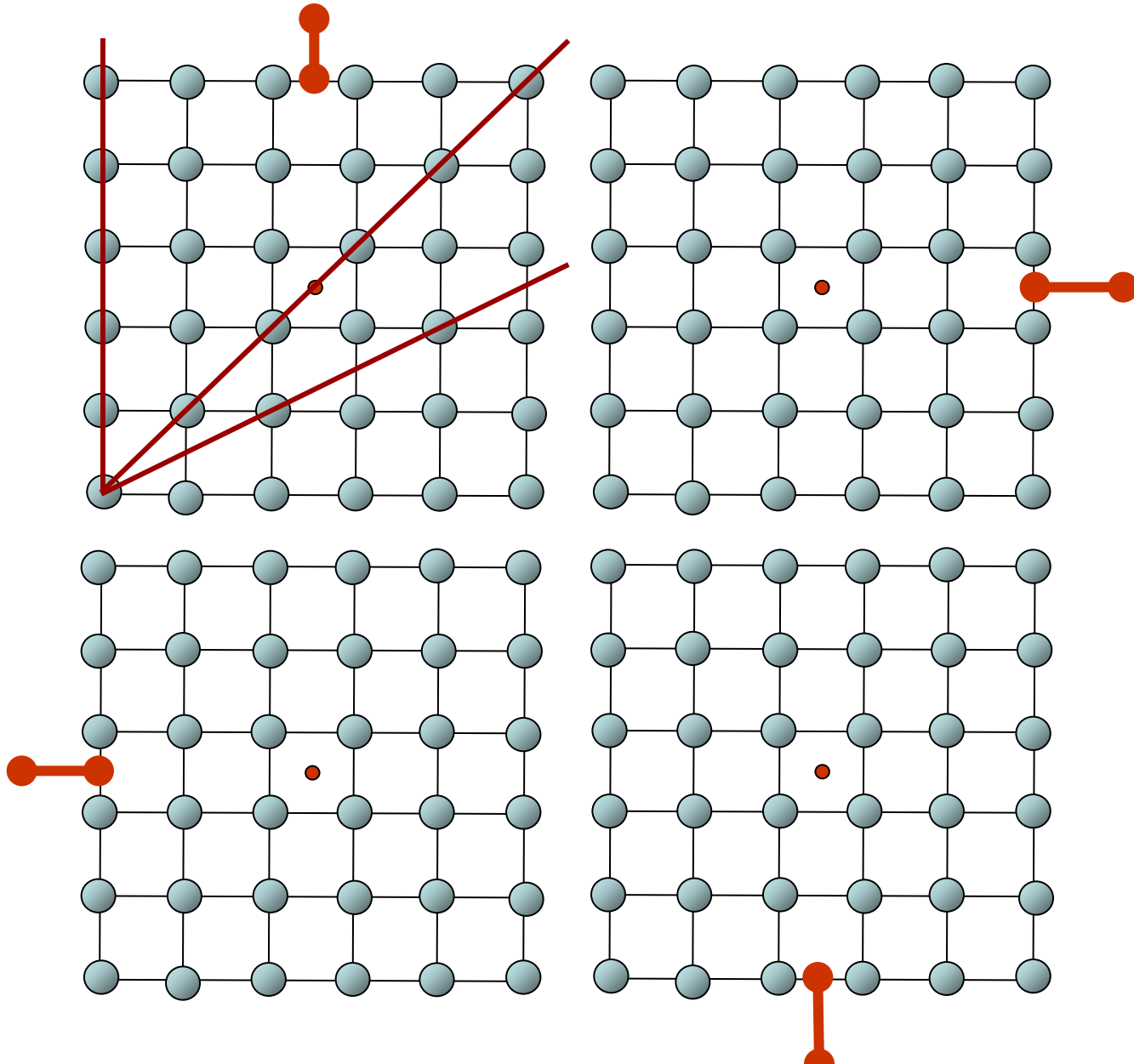
Quasi-Periodic Crystals  
(1984)  
Dan Shechtman  
Ilan Blech,  
Denis Gratias and  
John Cahn

Fullerens  
(1985)  
Herold Kroto, JR Heath,  
SC Obrian, Robert Curl  
And Richard Smalley

High Temperature  
Superconductivity  
(1986)  
Georg Bednorz  
And Alex Muller

# Order, periodicity and rotational symmetry

Four-fold rotational symmetry



# Rotational Symmetry

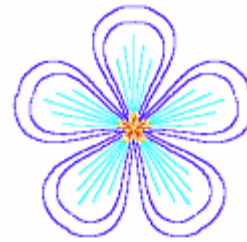
An image has **Rotational Symmetry** if there is a center point around which the object is turned a certain number of degrees and the object still looks the same, ie it matches itself a number of times while it is being rotated.



Two-fold



Three-fold



Five-fold



Six-fold

# Crystallography

Modern crystallography started in 1912 with the seminal work of von Laue who performed the first x-ray diffraction experiment.

The crystals von Laue studied were ordered and periodic, and all the hundreds of thousands crystals studied during the 70 years from 1912 till 1982 were found to be ordered and periodic.

Based on these observation, a paradigm was created that all crystals are periodic and the following definitions of "crystal" was accepted by the community of crystallographers and by the scientific community in general.

## Crystal definition till 1991

A crystal may be defined as:

A solid composed of atoms arranged in a pattern periodic in three dimensions

*"X-ray Diffraction", Cullity 1959*

Atoms in a crystal are arranged in a pattern that repeats itself in three dimensions throughout the interior of the crystal

*"Structure of Metals"*  
*Barrett and Massalski, 1966*

# Crystallography in 1982

CHARLES KITTEL

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*Introduction  
to  
Solid State  
Physics*

THIRD EDITION

John Wiley & Sons, Inc., New York, London, Sydney

## FUNDAMENTAL TYPES OF LATTICES<sup>10</sup>

Crystal lattices can be carried into themselves not only by the lattice translations  $T$  of Eq. (2), but also by various other symmetry operations. A typical symmetry operation is that of rotation about an axis which passes through a lattice point. Lattices can be found such that one-, two-, three-, four-, and six-fold rotation axes are permissible, corresponding to rotations by  $2\pi$ ,  $2\pi/2$ ,  $2\pi/3$ ,  $2\pi/4$ , and  $2\pi/6$  radians and by integral multiples of these rotations. The rotation axes are denoted by the symbols 1, 2, 3, 4, and 6.

We cannot find a lattice that goes into itself under other rotations, such as by  $2\pi/7$  radians or  $2\pi/5$  radians. A single molecule can have any degree of rotational symmetry, but an infinite periodic lattice cannot. We can make a crystal from molecules which individually have a five-fold rotation axis, but we should not expect the lattice to have a five-fold rotation axis. In Fig. 9a we show what happens if we try to construct a periodic lattice having five-fold symmetry: the pentagons do not fit together neatly. We see that we cannot combine five-fold symmetry with translational symmetry. The argument against seven-fold symmetry is given in Fig. 9b. The lines of an algebraic argument are indicated in Fig. 10.

A lattice point group is defined as the collection of the symmetry operations which, when applied *about a lattice point*, leave the lattice invariant. The possible rotations have been given earlier. We can also have mirror reflections  $m$  about a plane through a lattice point. The inversion operation is made up of a rotation of  $\pi$  followed by reflection in a plane normal to the rotation axis; the total effect is to replace  $r$  by  $-r$ .

<sup>10</sup>The original 1848 study by A. Bravais is reprinted in his *Etudes cristallographiques*, Gautier-Villars, Paris, 1866; a German translation appears in Ostwald's *Klassiker der exakten Wissenschaften* 90, (1897). For a full discussion of crystal symmetry, see F. Seitz, *Z. Krist.* 88, 433 (1934); 90, 289 (1935); 91, 336 (1935); 94, 100 (1936); and Vol. 1 of *International tables for x-ray crystallography*, Kynoch Press, Birmingham, 1952. A particularly readable discussion of space groups is given by F. C. Phillips, *An introduction to crystallography*, Wiley, 1963, 3rd ed.

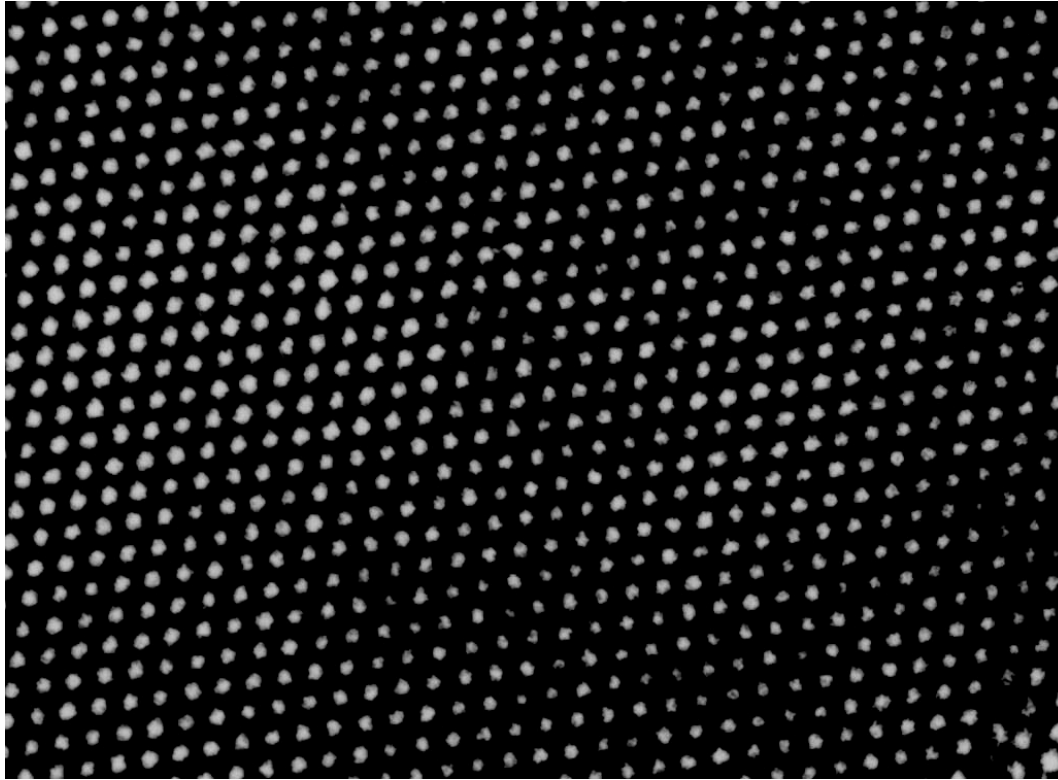
# Crystallography in 1982

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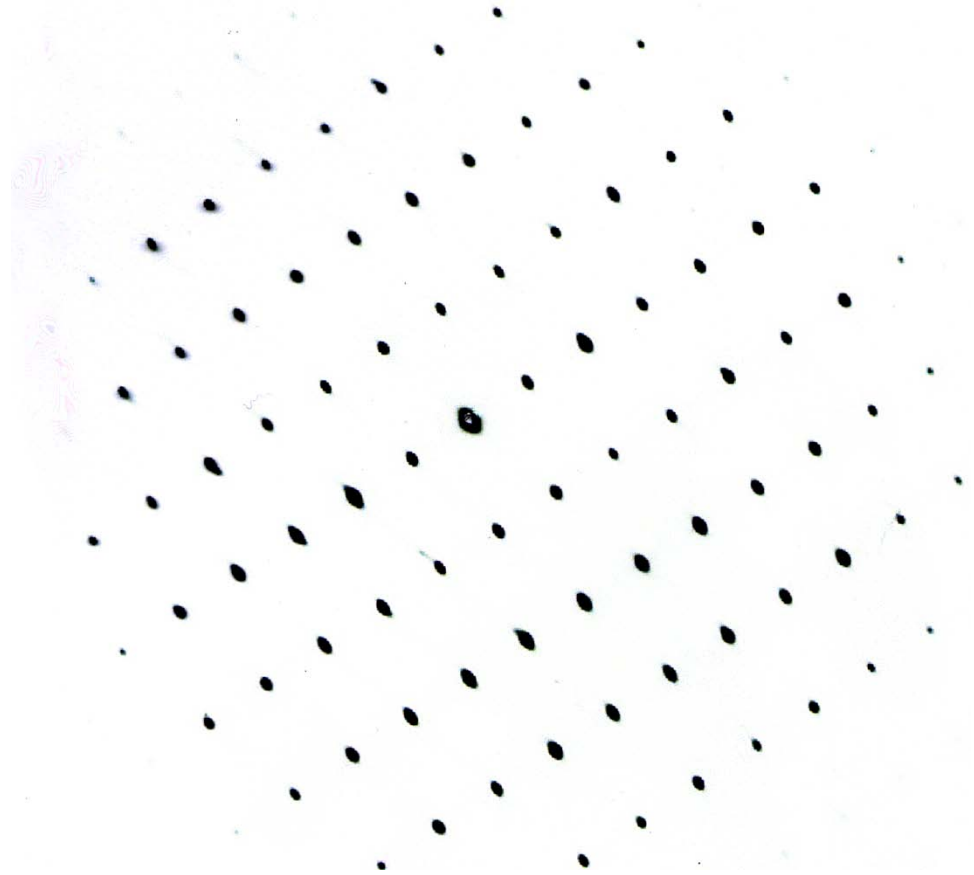
# Atoms in diamond – periodic order



The order of carbon atoms in diamond is periodic. The allowed rotational symmetries are 1, 2, 3, 4, and 6. 5-fold rotational symmetry as well as any other symmetry beyond 6 is forbidden in periodic structures.

# A diffraction pattern from a periodic crystal is characterized by:

- ♣ Periodicity of diffraction peaks in the reciprocal Space
- ♣ Rotational symmetries: 1,2,3,4 and 6-fold
- ♣ No 5-fold rotational symmetry and nothing beyond 6-fold



# A new definition for Crystal

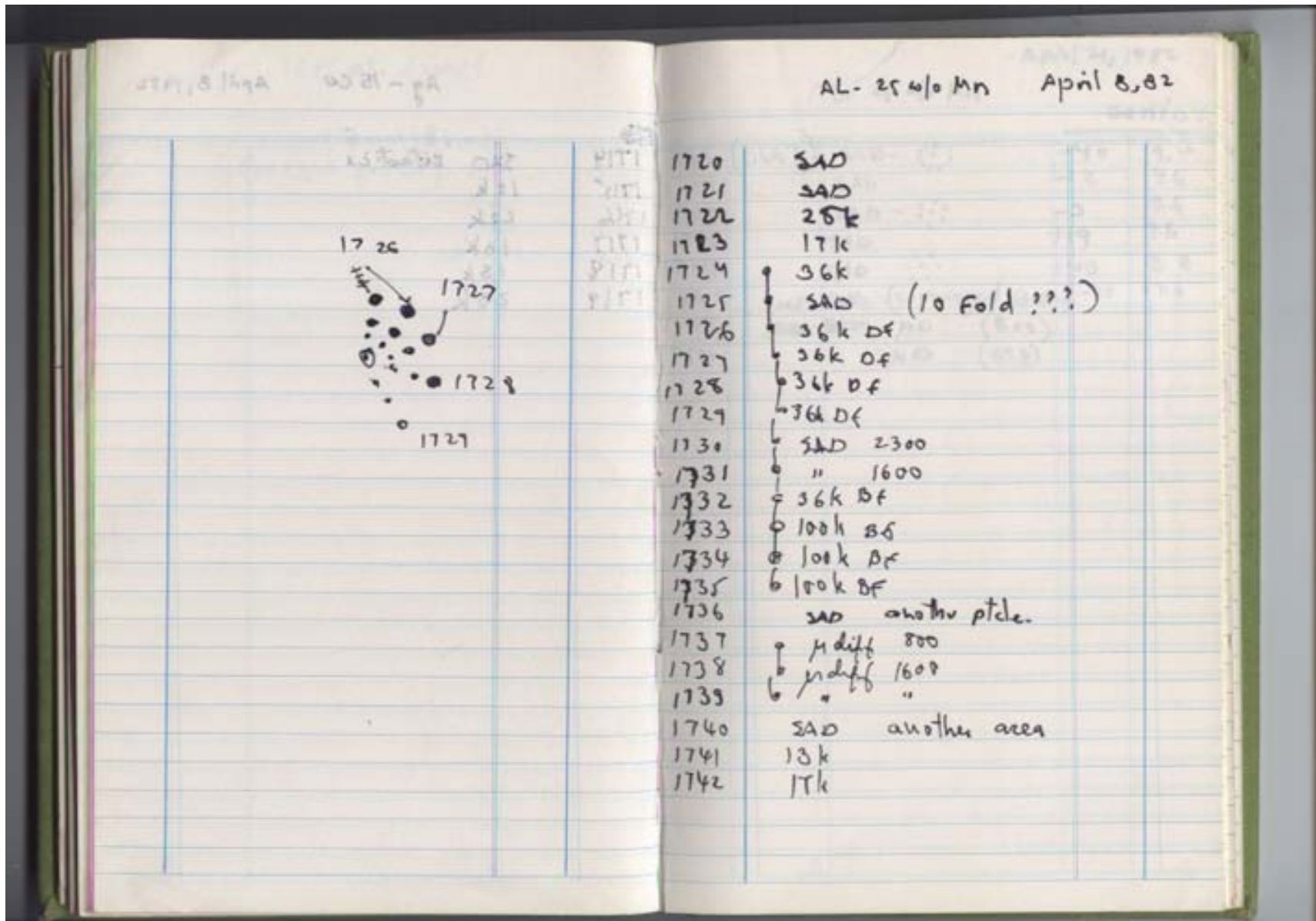
“..... By crystal we mean any solid having an essentially discrete diffraction diagram, and by aperiodic crystal we mean any crystal in which three dimensional lattice periodicity can be considered to be absent.”

*Reference: International Union of Crystallography,  
"Report of the executive Committee for 1991",  
Acta Cryst. A48 (1992) 922-946*

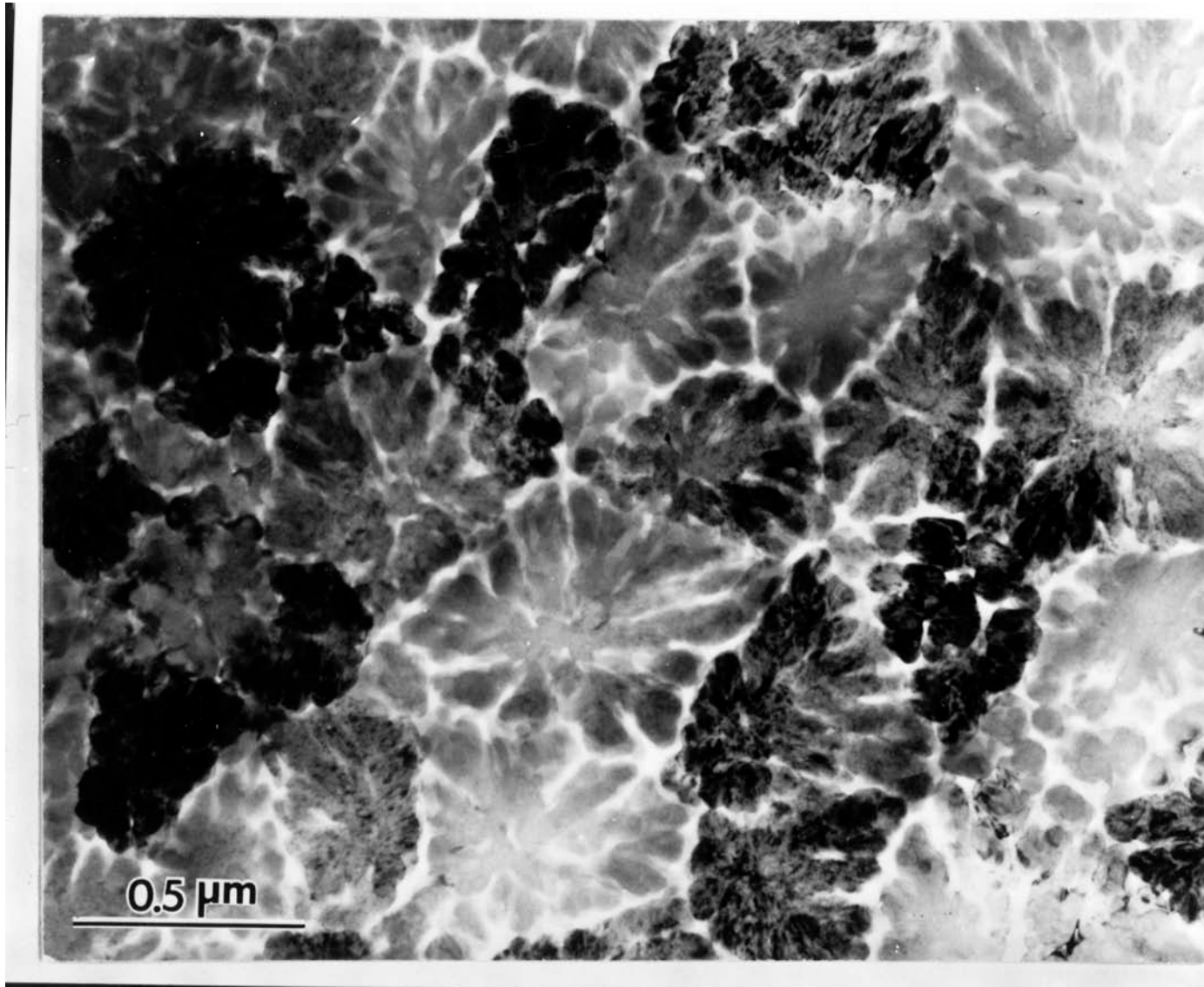
1982 – the 70th birthday of crystallography

The year Quasi-periodic Crystals were discovered

# Shechtman's NBS TEM logbook records of the first observation of 10 (5)-fold symmetry



# The first view of the Icosahedral Phase

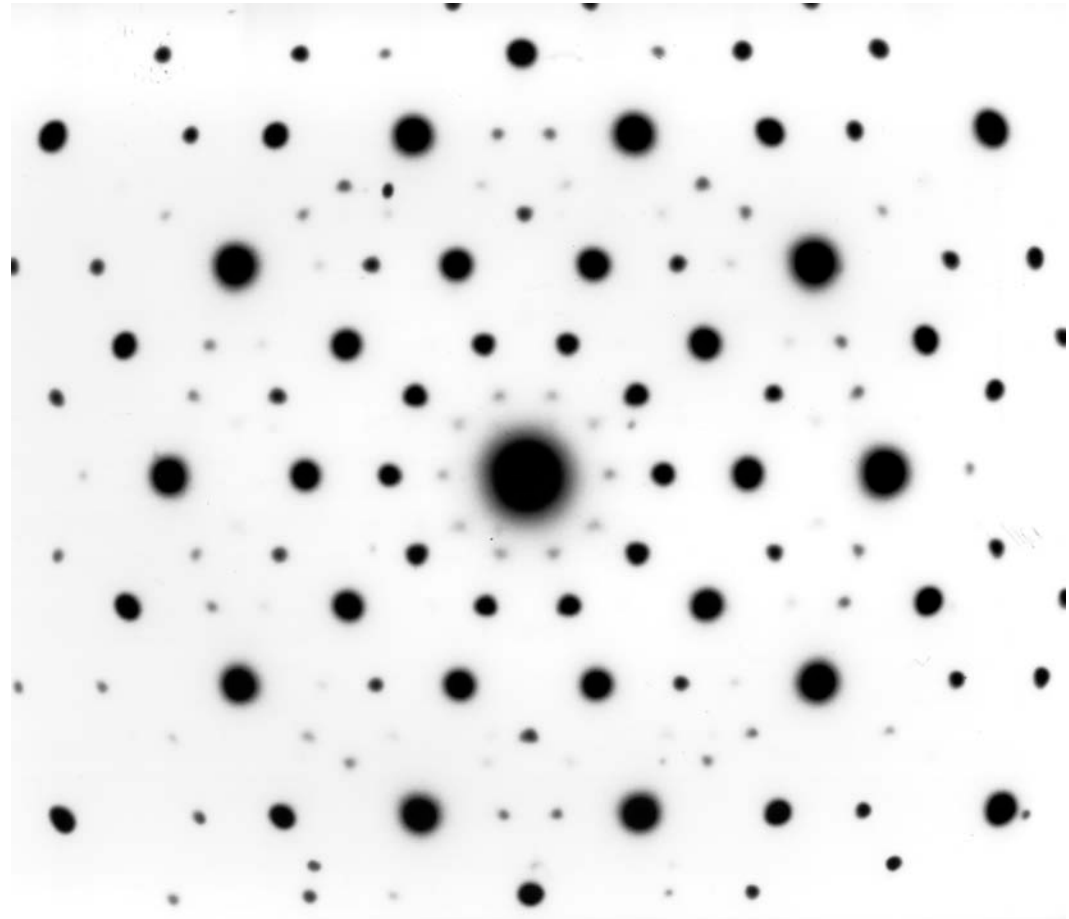


# 10-fold electron diffraction pattern

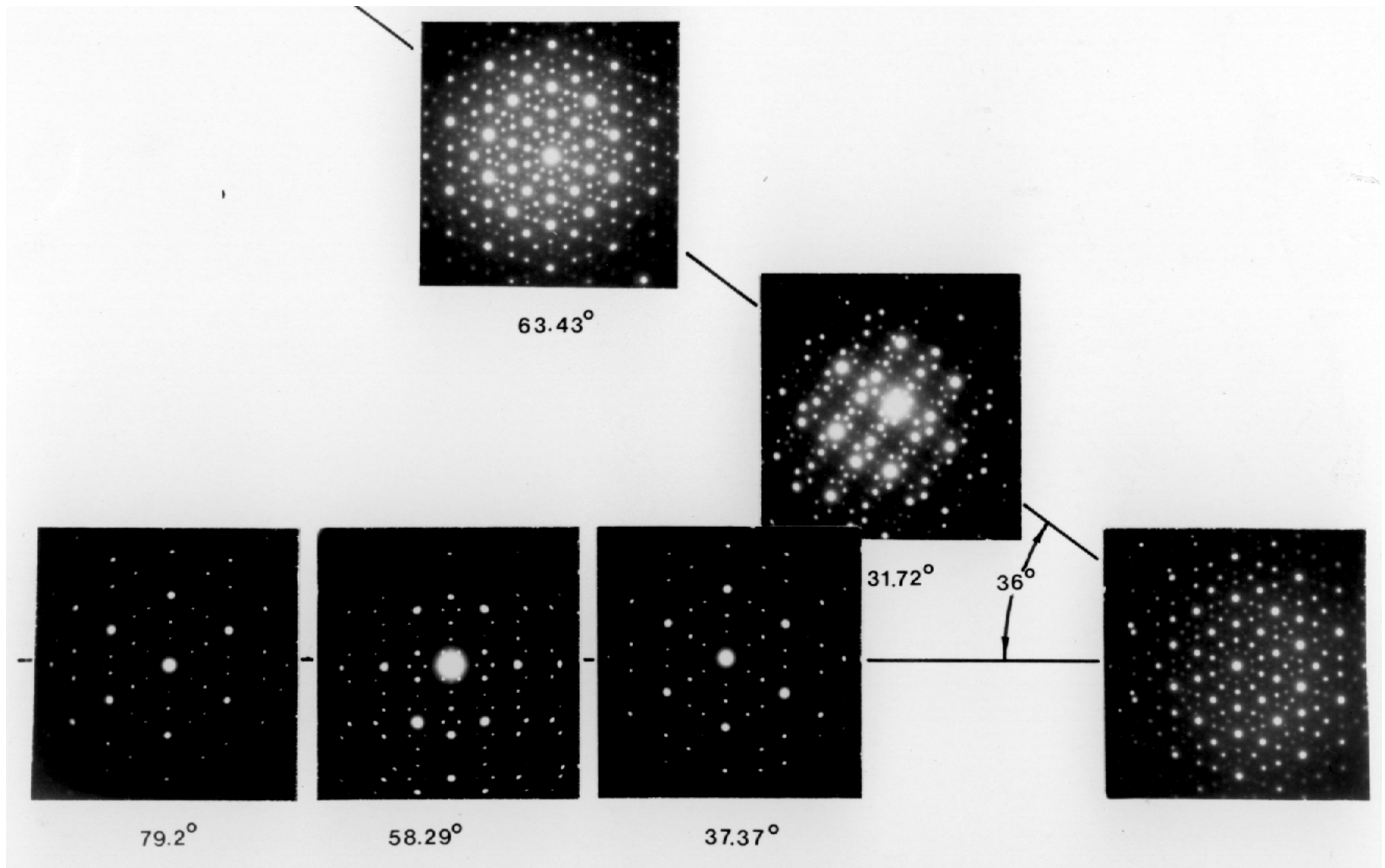
Electron diffraction from the Icosahedral Phase has five-fold rotational axes and it is not periodic.

The ratio of distances between the central spot and other spots is the Fibonacci Number  $\tau$  or  $\varphi$  known also as the "Golden Mean".

$$\tau = \frac{1 + \sqrt{5}}{2} \approx 1.618\dots$$

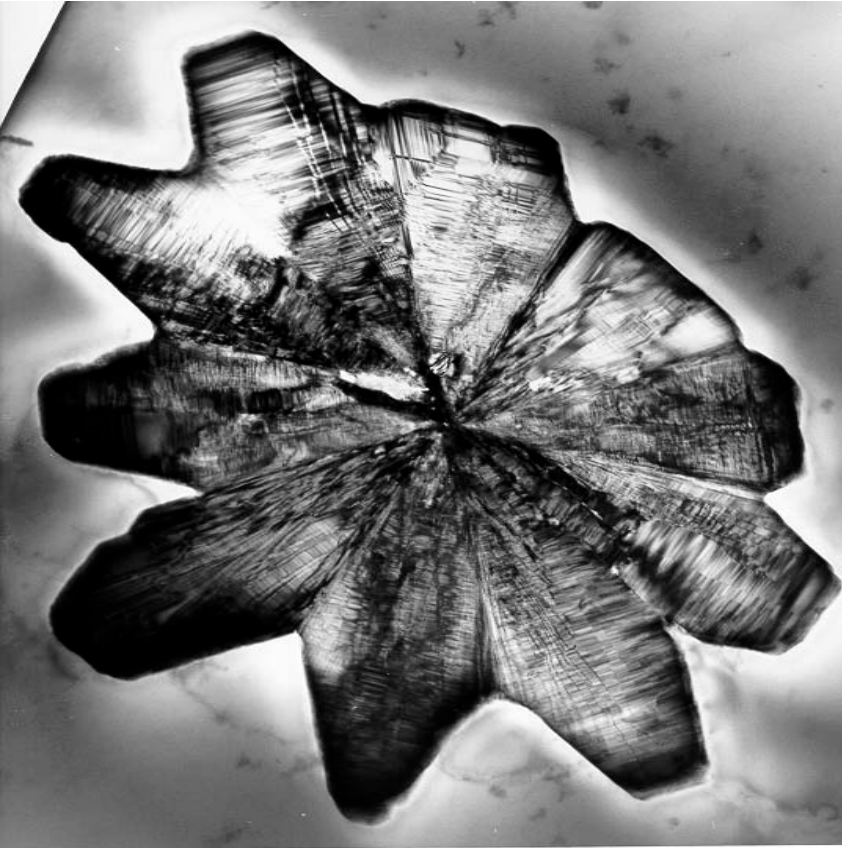


# TEM diffraction from the Icosahedral phase

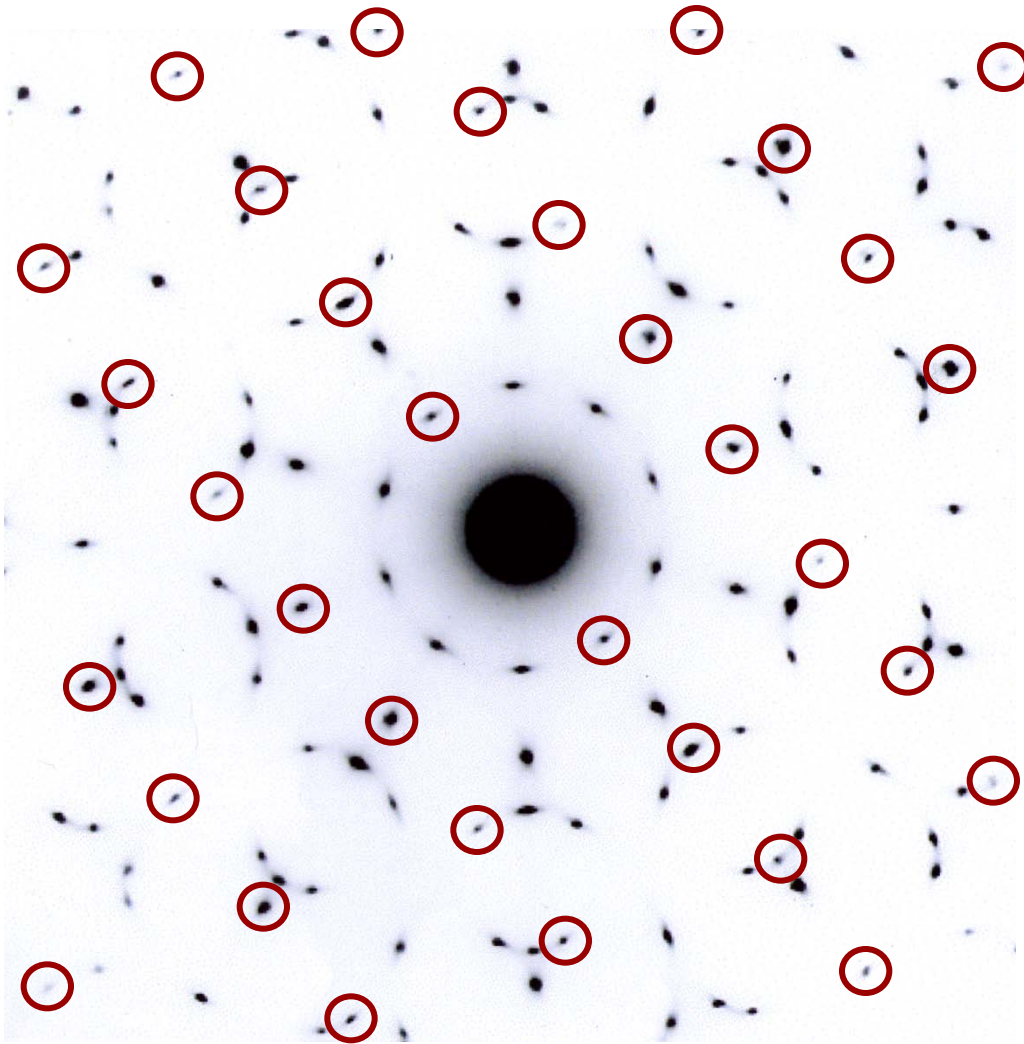




## Pseudo five-fold symmetry



Ten twins in an Fe-Al intermetallic compound. Each twin diffracts like a single crystal, but superposition of all ten patterns results in a pseudo five fold rotational symmetry.



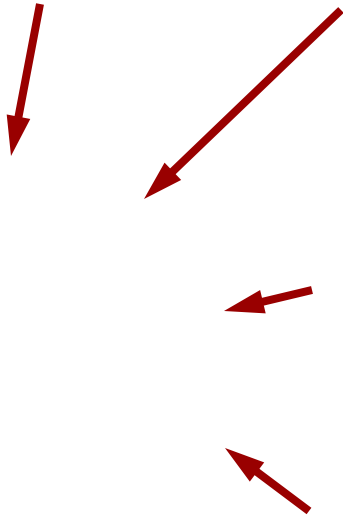
Pseudo five-fold rotational symmetry in an electron diffraction pattern taken from a twinned Al-Fe periodic crystal.

The pattern is similar to a combination of patterns taken from 10 twinned single crystals

The identical patterns are rotated 72 degrees to one another.

# Dark field experiments

A set of four dark field images shows that the same region is illuminated in all four.



No twins or other types type boundaries can be seen at the resolution of the images.

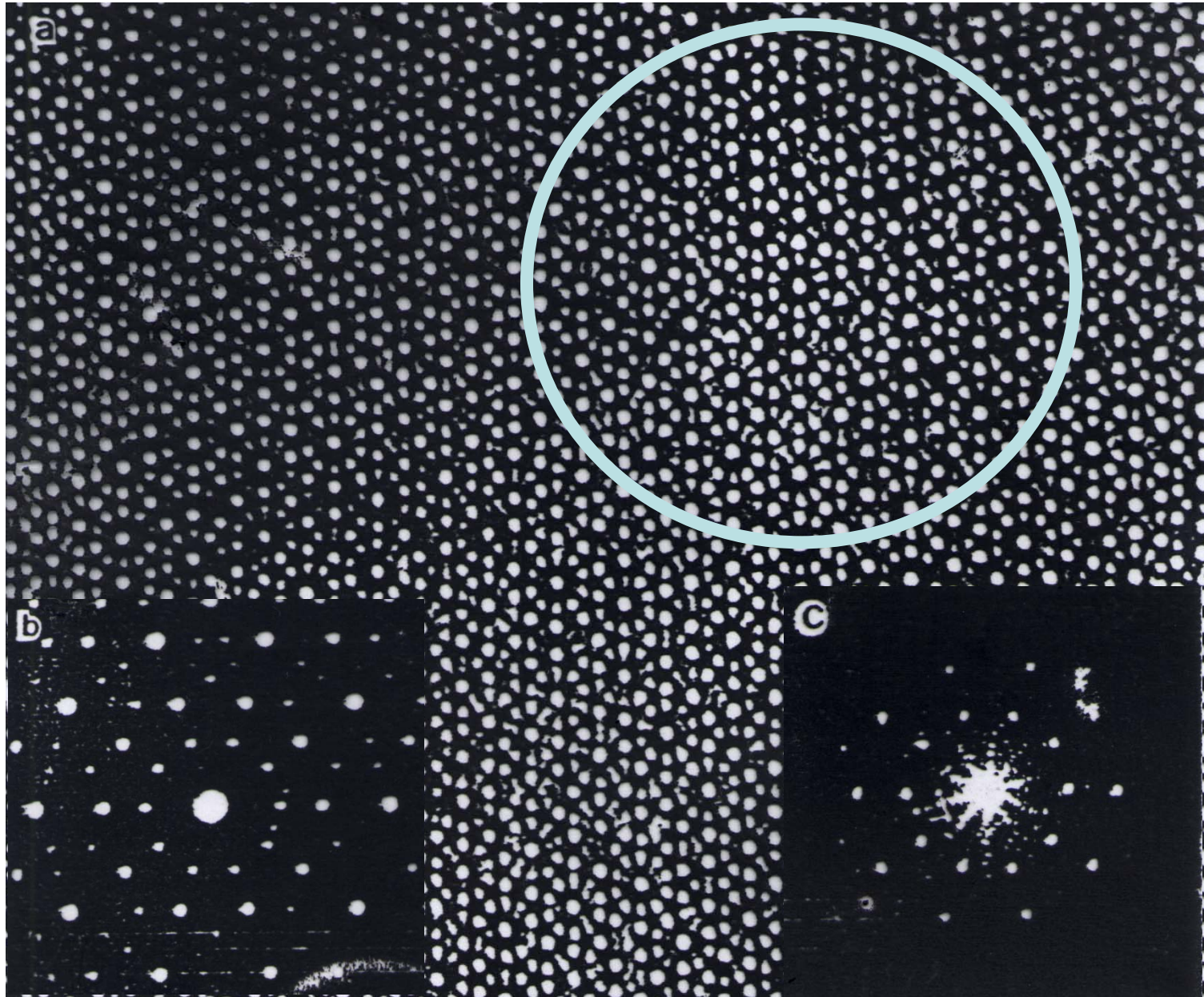
# Micro-diffraction experiment



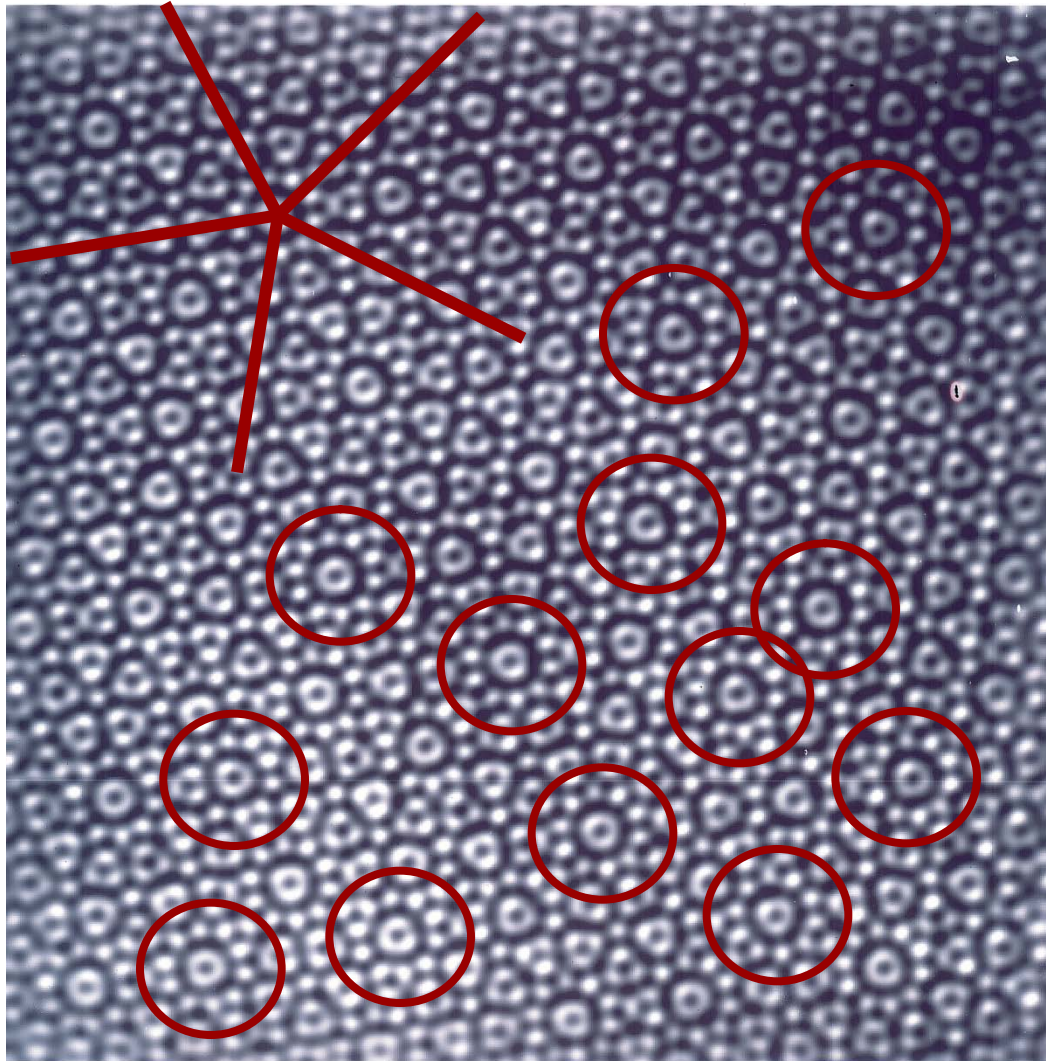
A micro-diffraction pattern taken from a single QC grain. The size of the convergent beam spot on the specimen was about 40 nm.

If there are twins or particles in this grain, They must be smaller than the size of the beam.

# Atomic arrangement in the Icosahedral Phase



# Atomic resolution TEM image of Icosahedral quasi-periodic crystal



The Shechtman-Blech article was rejected by JAP in September 1984.

I then submitted it to Met. Trans. on October 2, 1984. The article was accepted and published in June, 1985

The article includes the crystallographic information of the Icosahedral phase, and a model that explains the structure, including simulations of the reciprocal space of the model and comparison of the simulations with the observed diffraction patterns obtained from the Icosahedral phase.

## The Microstructure of Rapidly Solidified Al<sub>6</sub>Mn

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.<sup>1-5</sup> 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  $\mu\text{m}$  to a few  $\mu\text{m}$ . 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<sup>2,3,4</sup> 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.<sup>4</sup> The aluminum-iron system also contains spherulites in a cellular aluminum matrix when the iron concentration exceeds 10 wt pct.<sup>5</sup>

The microstructure of rapidly-solidified binary aluminum-manganese alloy ribbons containing up to 15 wt pct Mn has been studied.<sup>1</sup> 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

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Manuscript submitted October 2, 1984.

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  $\mu\text{m}$  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 HNO<sub>3</sub> and 5 pct HClO<sub>4</sub> 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 Al<sub>6</sub>Mn. 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

In September 1984 I gave the Shechtman-Blech article to John Cahn who was on his way to Santa Barbara. Upon John's return we had a conversation about the article and John suggested to bring Denis Gratias to NBS for discussion. Denis came to NBS for several days and the three of us composed a focused article based on the 1982 TEM observations and analysis.

A week or so later we sent the article to Phys. Rev. Lett. The article was received on October 9 and published a month later, on November 12, 1984

### Metallic Phase with Long-Range Orientational Order and No Translational Symmetry

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(Received 9 October 1984)

We have observed a metallic solid (Al-14-at.%-Mn) with long-range orientational order, but with icosahedral point group symmetry, which is inconsistent with lattice translations. Its diffraction spots are as sharp as those of crystals but cannot be indexed to any Bravais lattice. The solid is metastable and forms from the melt by a first-order transition.

PACS numbers: 61.50.Em, 61.55.Hg, 64.70.Ew

We report herein the existence of a metallic solid which diffracts electrons like a single crystal but has point group symmetry  $m\bar{3}5$  (icosahedral) which is inconsistent with lattice translations. If the specimen is rotated through the angles of this point group (Fig. 1), selected-area electron diffraction patterns clearly display the six fivefold, ten threefold, and fifteen twofold axes characteristic<sup>1</sup> of icosahedral symmetry (Fig. 2). Grains up to  $2\ \mu\text{m}$  in size with this structure form in rapidly cooled alloys of Al with 10–14 at.% Mn, Fe, or Cr. We will refer to the phase as the icosahedral phase. Microdiffraction from many different volume elements of a grain and dark-field imaging from various diffraction spots confirm that entire grains have long-range orientational order. If the orientational order decays with distance, its correlation length is far greater than the grain size. We have thus a solid metallic phase with no translational order and with long-range orientational order.

The remarkable sharpness of the diffraction spots (Fig. 2) indicates a high coherency in the spatial interference, comparable to the one usually encountered in crystals. The diffraction data are qualitatively well fitted by a model consisting of a random packing of nonoverlapping parallel icosahedra attached by edges.<sup>2</sup> The invariance of the local orientational symmetry from site to site and the finite number of possible translations between two adjacent icosahedra seem to be sufficient for insuring highly coherent interferences. Icosahedra are a common packing unit in intermetallic crystals with the smaller transition element at the center sur-

rounded by twelve larger atoms arranged like the corners of an icosahedron.<sup>3</sup> The symmetries of the crystals dictate that the several icosahedra in a unit cell have different orientations and allow them to be distorted, leaving the overall crystal consistent with the well-known crystallographic point and space groups. Even though icosahedral symmetry is of great importance as an approximate site symmetry in crystals, it cannot survive the imposition of lattice translations: Crystals cannot and do not exhibit the icosahedral point group symmetry.

Elementary crystallography indicates that fivefold

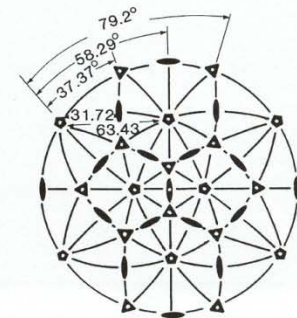


FIG. 1. Stereographic projection of the symmetry elements of the icosahedral group  $m\bar{3}5$ .

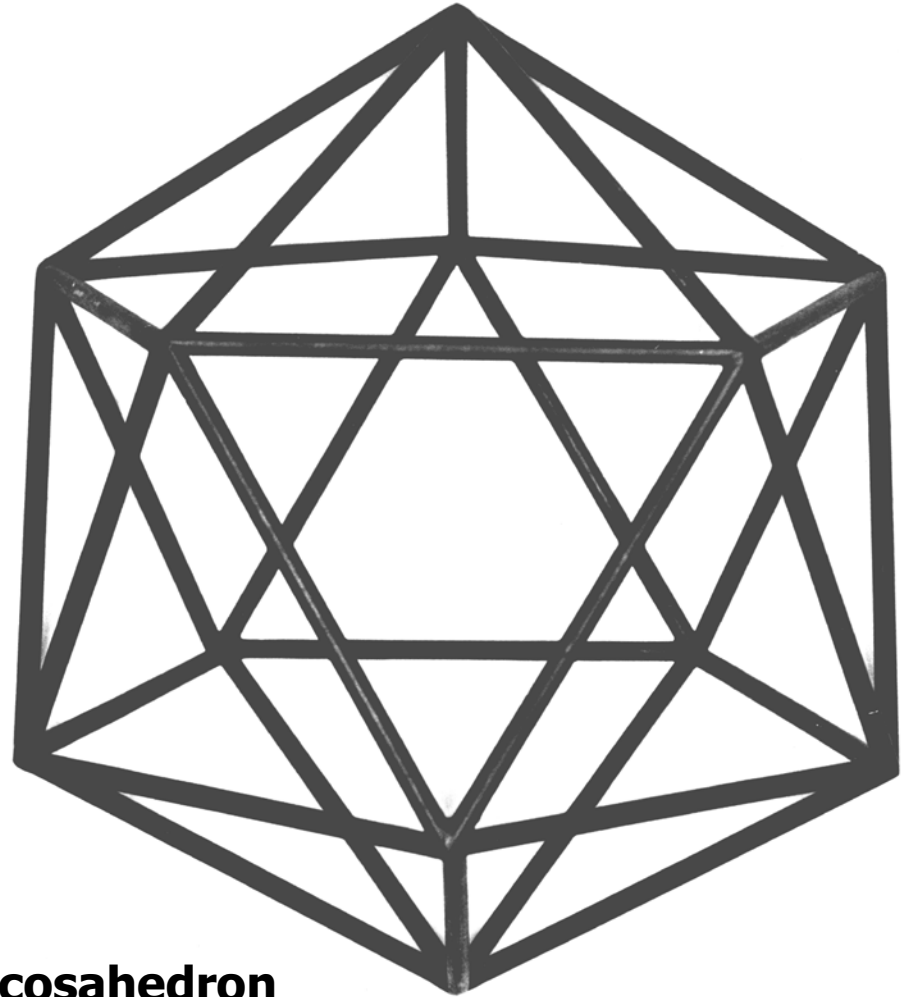


# Icosahedral symmetry

Many of the  
quasi-periodic crystals  
have Icosahedral  
symmetry

With:

6 five-fold axes  
10 three-fold axes  
and  
15 two-fold axes



**The Icosahedron**

The main rotational symmetries of the Icosahedron



1982 – 1987 Years of rejection



גם כִּי-אַלֶּךָ בְּגֵיאַ צְלֻמוֹת לֹא-אִירָא רַע תְּהִלִּים כ"ג

"Yea, though I walk through the valley of the shadow of death, I will fear no evil" Psalm 23

# Professor Linus Pauling

The main objection to the quasiperiodic nature of QCs came from Professor Linus Pauling

Linus Carl Pauling (February 28, 1901-August 19, 1994), was a distinguished American chemist, two time Nobel Laureate.

During the last decade of his life he tried to prove that QCs are really just twinned periodic crystals. He did that by proposing larger and larger periodic unit cells. All his models were proven wrong.

At the end of his life he remained the only prominent opponent to quasiperiodicity in crystals.

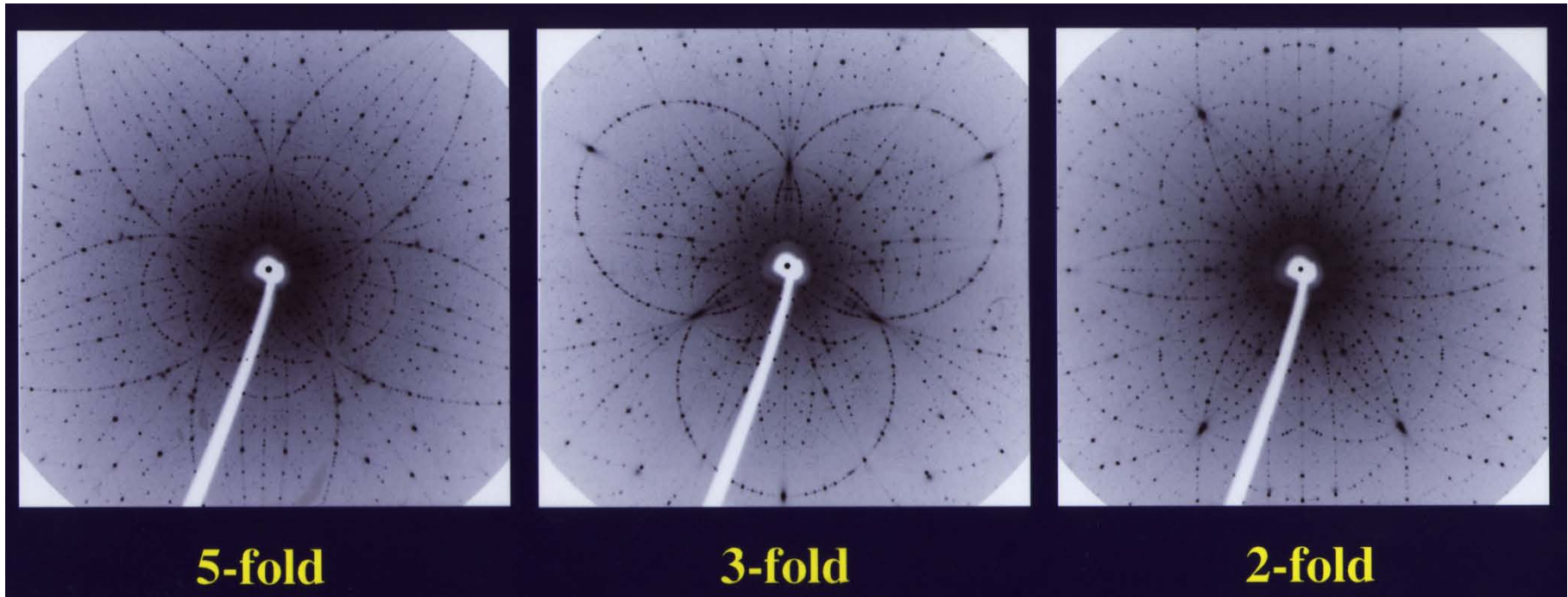


As large single QCs became available, so did x-ray diffraction patterns.

## X-ray transmission Loue photograph of i-ZnMgHo QC

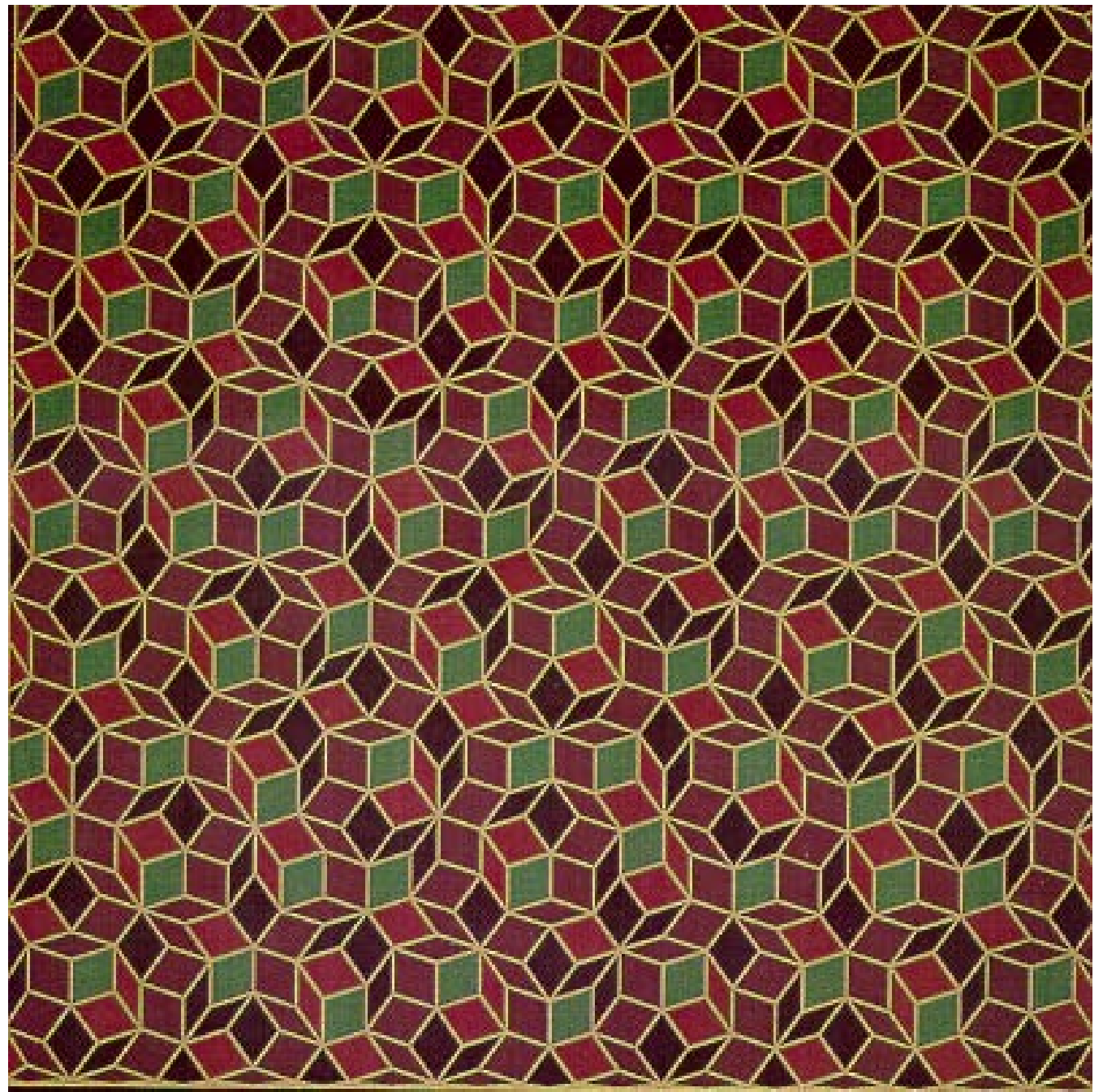
Curtsey: An-Pang Tsai

Mo radiation 40kV-50mA

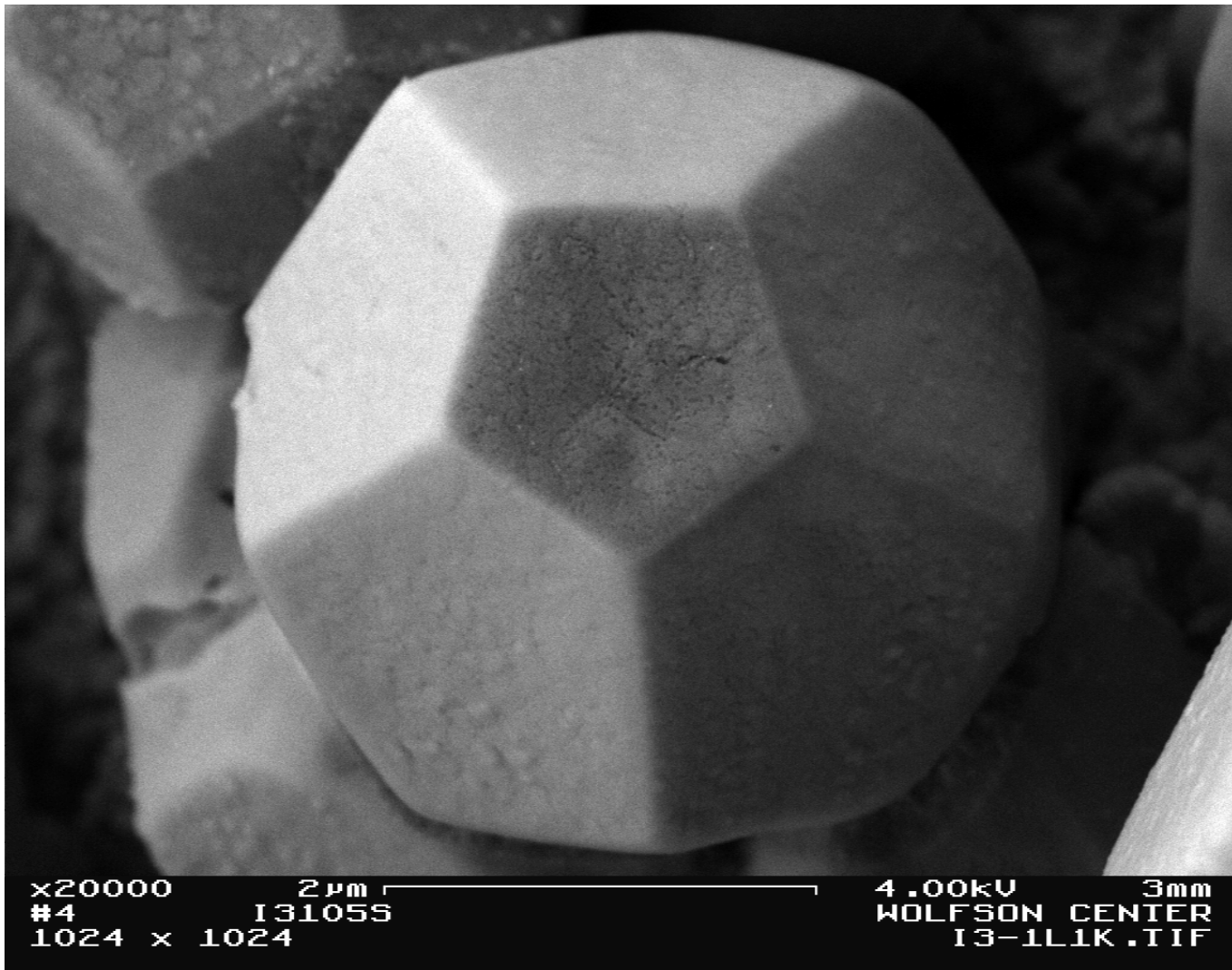


It is this x-ray diffraction pattern that convinced the community of crystallographers that 5-fold symmetry can exist in crystals. This became available only in 1987. Only electron diffraction patterns were taken before that time.

# Penrose tiles

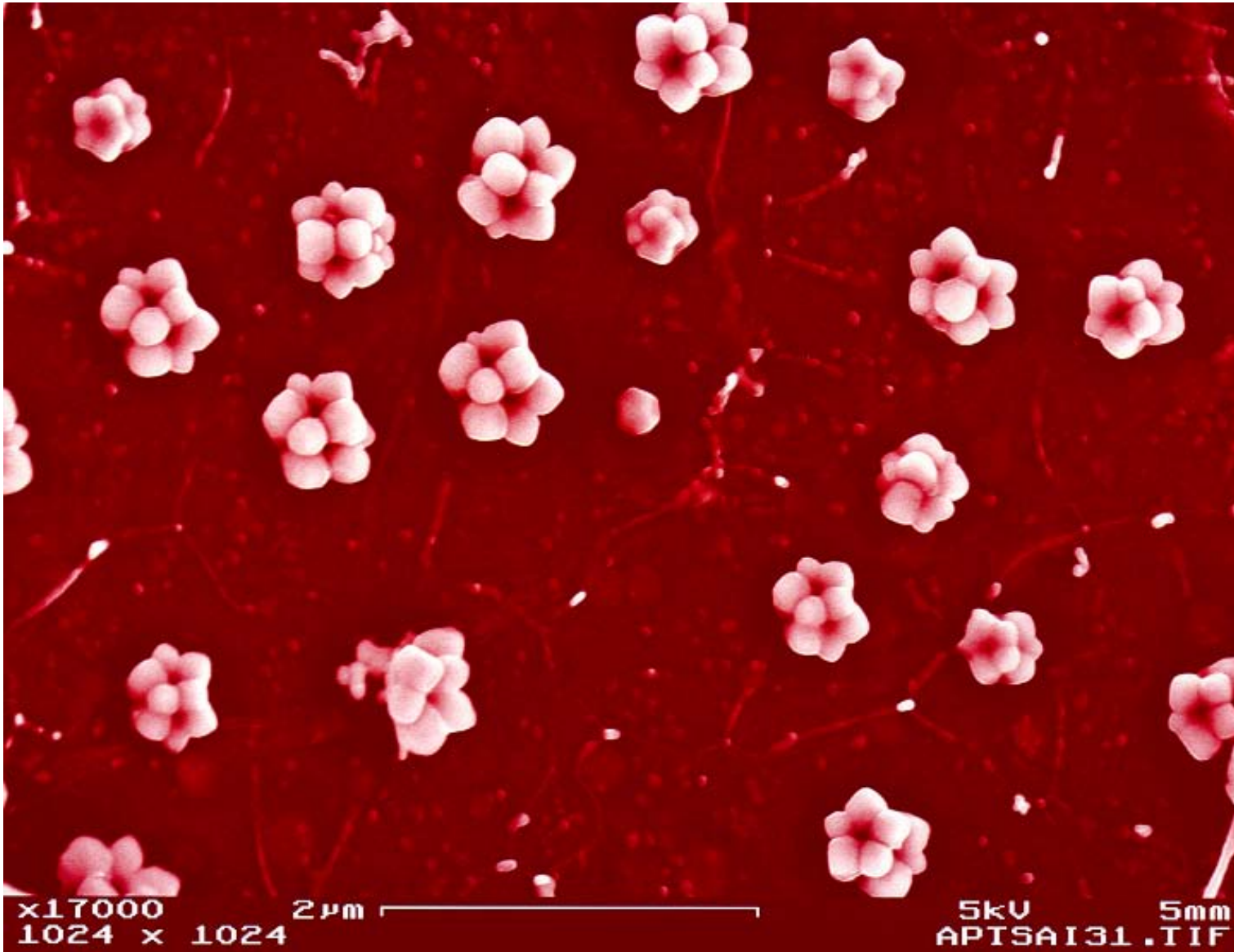


# A quasi-periodic crystal of the system Mg-Zn-Ce





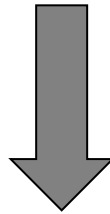
# Icosahedral QCs in an Al-Mn alloy



SEM image by  
An-Pang Tsai

Order

Periodicity



Order

Periodicity and Quasi-periodicity

# Why QCs were never discovered before 1982?

♣ **Are they very rare?**

♣ **Are they not stable?**

♣ **Are they difficult to make?**

# Are QCs rare?

QCs are not rare there are hundreds of them.

## ALLOY COMPOSITIONS KNOWN TO FORM THE ICOSAHEDRAL PHASE

<b>Al</b>	Al-Co				
	Al-Cr	Al-Cr-Ge	Al-Cr-Si	Al-Cr-Mn-Si	Al-Cr-Zr-Mn
	Al-Fe	Al-Fe-Mn	Al-Fe-Si	Al-Fe-Mn-Si	
	Al-Mn	Al-B-Mn	Al-Ge-Mn	Al-Ni-Mn	Al-Ru-Mn
	Al-Ni				
	Al-Pt				
	Al-Ti				
	Al-V				
	Al-Cu	Al-Cu-Li Al-Cu-Fe	Al-Cu-Mn	Al-Cu-Mn-Zn	Al-Cu-V
		Al-Ag-Mg Ga-Mg-Zn	Al-Au-Li	Al-Zn-Li	Al-Mg-Zn

## Are QCs not stable?

Many are, and transform to periodic structures at high temperatures, but QCs can be thermodynamically stable. Examples are -

Most of these stable QCs were discovered by An Pang Tsai and his coworkers at Tohoku University, Sendai, Japan

Al-Li-Cu

Mg-Zn-Ga

Mg-Pd-Al

Al-Cu-(Fe, Ru, Os)

Al-Pd-(Mg, Re)

Zn-Mg-RE

Cd-(Ca, Yb)

# Are QCs difficult to make?

Not at all, QCs are easy to make

QCs can be made by many manufacturing technologies

- ♣ Casting
- ♣ Rapid solidification
- ♣ Single crystal growth
- ♣ Electrodeposition
- ♣ CVD
- ♣ PVD

So, why QCs were never discovered before 1982?

1. TEM

2. Professionalism

3. Tenacity

4. Believing in yourself

5. Courage



Thank you