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## Discovery of quasicrystals: The early days

*Découverte des quasicristaux : les premiers pas*

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## ABSTRACT

This paper is a survey of the initial developments of the research on quasicrystals starting from their discovery by Daniel Shechtman (Nobel Prize in Chemistry in 2011) in 1982 at the National Bureau of Standards (now National Institute for Standard and Technology) in Gaithersburg (Maryland, USA) up to the beginning of the early 1990s, a time when the crystallographic methods were well developed and mastered enough to decipher the ultimate atomic structures of quasicrystals. These early works have enlarged our understanding of spatial order in solids through a strong multidisciplinary effort between mathematicians, physicists, chemists and material scientists.

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## R É S U M É

Cet article relate le développement initial des recherches sur les quasicristaux depuis leur découverte par Daniel Shechtman (prix Nobel de chimie en 2011) en 1982 au National Bureau of Standards (aujourd'hui National Institute for Standards and Technology) à Gaithersburg (Maryland, États-Unis) jusqu'au début des années 1990, période durant laquelle se sont développées les méthodes cristallographiques adaptées à l'analyse de ces structures atomiques quasicristallines. Ces premiers travaux ont permis d'élargir notre compréhension de l'ordre dans les solides grâce à une forte pluridisciplinarité alliant mathématiciens, physiciens et spécialistes de la science des matériaux.

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## 1. Introduction

## 1.1. A short chronology of Shechtman's discovery

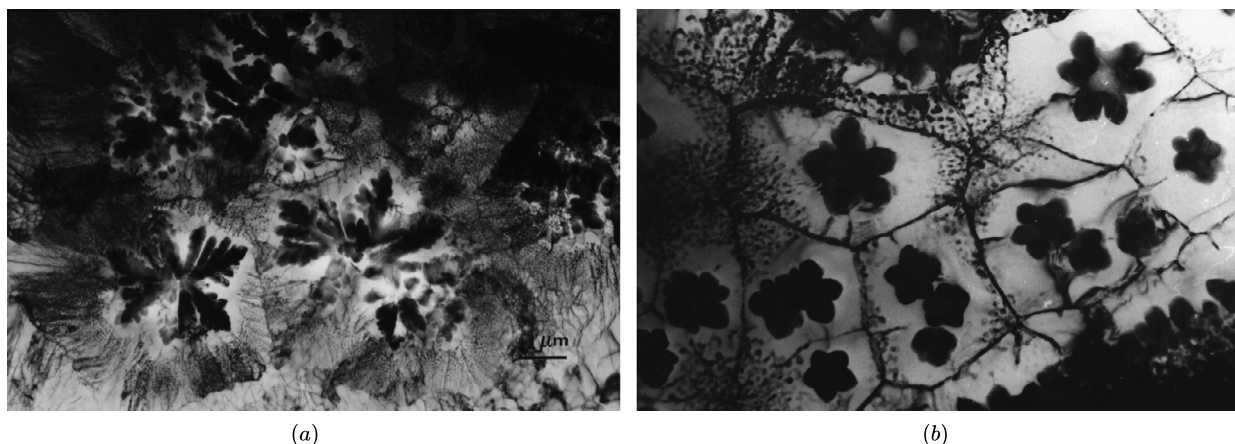
The first observation of quasicrystals by electron microscopy was made by Daniel Shechtman in early April 1982 during his study of the structural morphology of a rapidly solidified (Al, Mn) alloy at the Metallurgy Institute of the National Bureau

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**Fig. 1.** Typical dendritic morphologies of precipitates of the icosahedral phase in (Al, Mn) along various crystallographic orientations (a) and (b) of the aluminum matrix.

of Standards, now National Institute of Standards and Technology (NIST, Gaithersburg-Maryland, USA). This work was part of a two-year sabbatical 1981–3 DARPA–NSF<sup>1</sup> project on rapid solidification, where Shechtman was hired as an electron microscopist.<sup>2</sup>

This group on rapid solidification of binary alloys was created by Robert J. Schaefer, who was interested in partitionless solidification and precipitation, and all of the experimental work of the DARPA–NSF project was done at the Metallurgy Institute at NIST. The project included several Aluminum based alloys (Al, X) with X = Cr, Mn, Fe, Co, and Ni for low compositions in X roughly up to 10 at. %. The fruitful decision of extending the composition range up to Al<sub>6</sub>X and beyond was made by Shechtman himself.

On 8 April 1982, looking at a new set of rapidly solidified Al<sub>6</sub>Mn samples prepared by Robert Schaefer and Frank Biancanello, Shechtman discovered a new precipitation in the aluminum matrix grains with the typical dendritic morphology shown in Fig. 1. As a highly experienced microscopist, he noticed an unusually strong contrast variation in standard bright field imaging mode according to the precipitate orientation with respect to the incident electron beam. After a careful examination of the sample under various orientations, he eventually obtained a set of diffraction patterns exhibiting an astonishing 3D icosahedral symmetry, inconsistent with 3D periodicity, but with still a remarkable sharpness of the diffraction spots comparable to the one observed in the best-quality crystals.

This paradoxical discovery has been made possible because electron microscopy allowed him to observe 3D diffractions of single grained precipitates as shown in Fig. 1 where he could recognize at once the long range order of these precipitates together with their overall non-crystallographic icosahedral symmetry as revealed by the diffraction patterns as the one of Fig. 2. Transmission Electron Microscopy (TEM) has indeed been here the key tool necessary to allow for the discovery of quasicrystals.

The TEM diffraction pattern perpendicular to a 5-fold rotation axis shown in Fig. 2, very emblematic of quasicrystals, deserves particular attention:

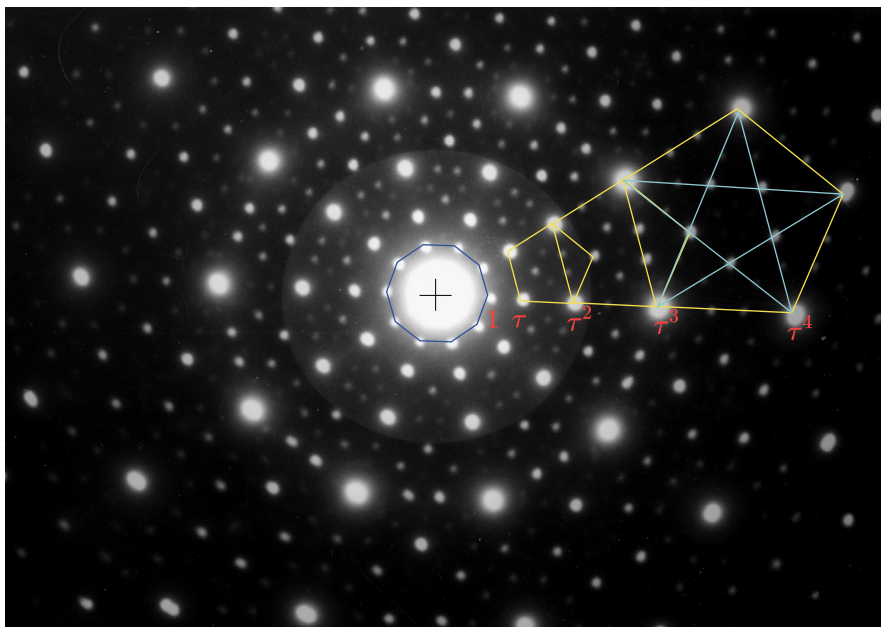
- the 5-fold symmetry (icosahedral symmetry in 3D) is inconsistent with periodicity;
- the sharpness of the diffraction spots are comparable to those obtained from best crystalline silicon standards;
- the locations of the diffraction spots can be obtained by a simple geometric construction using simple homothetic inflation by the golden mean  $\tau = (1 + \sqrt{5})/2$  of elementary regular pentagons;
- whatever the direction, there are no single rows of periodically spaced spots in the pattern: this rules out the possible hypothesis of the structure resulting from possible multiple twins of usual crystals.<sup>3</sup>

Hence, this new structure appeared as a paradoxical object: on the one hand, it exhibited a long-range order like in crystals because of the sharpness of the diffraction spots; on the other hand, it could not be crystalline because of its overall pentagonal symmetry.

<sup>1</sup> Joined program between the Defense Advanced Research Projects Agency and the National Science Foundation.

<sup>2</sup> As a visiting professor at the Technion, Cahn had met Shechtman in 1971 when he was in his last year of graduate studies. When they met again in 1979, Cahn invited him to NIST to participate in the DARPA project on rapid solidification. After 1984, NIST hired Leo Bendersky at a permanent position to continue the electron microscopy work of the group.

<sup>3</sup> Although this point was obvious from the very beginning, the idea of the 5-fold symmetry resulting from possible microtwinning of crystalline material kept being regularly opposed to Shechtman and his colleagues during a very long time after the first high-resolution image published in the *Comptes rendus de l'Académie des sciences* in 1985 by Shechtman et al. [1].



**Fig. 2.** The famous electron diffraction pattern observed by Dan Shechtman of the icosahedral phase in  $\text{Al}_6\text{Mn}$  is characterized by sharp diffraction spots, comparable to those in high-quality crystals, but distributed according to an overall pentagonal symmetry that forbids this material from being a periodic distribution of atoms.

At that time, Shechtman felt a need for an explanation of his unbelievable finding before thinking in publishing these results. As he said, “*there is no such animal*”; the notion of quasiperiodicity and Mackay’s experimental demonstration that Penrose’s quasiperiodic two-dimensional tiling would diffract sharply, were unknown to the initial metallurgy group, so that the discussions at NIST ceased and no further work was done on quasicrystals. Moreover, all tentative explanations that Shechtman received from knowledgeable scientists in the field of crystallography and metallurgy were simply that quinary structures cannot appear in crystals – that he knew perfectly well – so that his observations should most probably be artefacts due to a multiple twinning of standard crystals. But because this twinning was impossible to be experimentally revealed in electron microscopy, Shechtman completed other work before returning to Israel in the fall<sup>4</sup> of 1983.

This extraordinary observation lay relatively dormant for two years, although it was still very present in Shechtman’s mind. In spring 1984, he met Ilan Blech – one of his former professors at the Technion (Haifa, Israel) – at a congress in San Diego (California, USA). Blech was very impressed by Shechtman’s 5-fold diffraction patterns and he devised a very clever and simple model of random stacking of *parallel regular icosahedra connected by their edges*, sort of an *icosahedric glass* similar to the drawings shown in Fig. 3. This model – although leading to a much too low density for being realistic – gave remarkably good results for the numerically calculated diffraction patterns with well-localized strong peaks at the wavevector positions<sup>5</sup> observed by Shechtman. The main understanding of this localized diffraction was there based on the remark that the set of interplanar distances of the model form a discrete uniform ensemble of vectors.<sup>6</sup> Blech’s model has been the starting point of an enormous body of work on random tilings, especially in the USA, mainly by theoretical physicists.

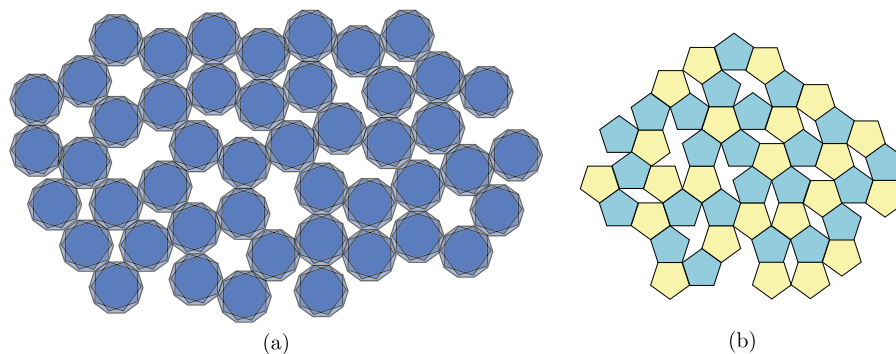
This gave Shechtman enough confidence to return to his findings and write a first publication [4] together with Blech, entitled “The Microstructure of Rapidly Solidified  $\text{Al}_6\text{Mn}$ ” and submitted to the *Journal of Applied Physics* (JAP). Incredibly enough, the paper was rejected by the referee on the basis that the subject was too narrow to be of possible interest to the usual reader of JAP...

The authors then submitted in summer a revised version of the paper to *Metallurgical Transactions A* (now *Metallurgical and Materials Transactions*), and Shechtman presented a copy to John-Werner Cahn, a very famous senior scientist at the NIST Metallurgy Institute worldwide known for his works in thermodynamics of solids (in particular the so-called spinodal decomposition with the famous Cahn–Hilliard equations). John-Werner Cahn read the paper in his way to Santa Barbara where he was implied in a long-term seminar, “Theoretical physics and materials sciences”, at the Institute of Theoretical Physics (UCSB California). Although he was already aware of Shechtman’s work, it was there that he had seen all the data at

<sup>4</sup> After his return to NIST in the summer of 1984, Shechtman continued to come to NIST every summer for more than a decade.

<sup>5</sup> The fluctuation to background diffuse intensity was not discussed in these original computations by Blech, focused only on the locations of the expected Bragg peaks.

<sup>6</sup> Interesting enough, this property was shown in 2005 to be one of the main ingredients in the Strungaru theorem [2] 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.



**Fig. 3.** (a) The initial atomic model of  $\text{Al}_6\text{Mn}$  proposed by I. Blech was a so-called icosahedral glass or *icosahedric phase*, made of a set of randomly distributed *parallel regular icosahedra attached by edges*. (b) Blech's model (a) is one of the many examples of random tilings of non-crystallographic polygons as those regular pentagons connected by edges and first imagined by A. Dürer [3].

once for the first time and realized that this work was of real importance. He thought that the way the paper was written did not give enough emphasis to this icosahedral phase and that neither JAP nor Met. Trans. were the right journals for publishing this finding.

The day after his arrival in Santa Barbara in mid-August 1984, Cahn presented Shechtman's experimental results at a blackboard lunch to the seminar group. Denis Gratias was a member of this group invited by Cahn as a crystallographer specialized in group theory and incommensurate structures in metallurgy (the so-called long-period alloys). He was immediately fascinated by these diffraction patterns and convinced by the veracity of the icosahedral symmetry compared to twinning. After a short discussion where Gratias explained why these patterns could not be the results of twins (see previous paragraphs), Cahn convinced Gratias to join the metallurgy group at NIST<sup>7</sup> – soon called the *quasicrystal group* (see Fig. 4) – as a crystallographer. Thus, Shechtman, Cahn and Gratias started working together at NIST at the end of August 1984. Shechtman proposed to Cahn to write a short manuscript specifically on the icosahedral phase to be submitted to *Physical Review Letters* (PRL) with the input from Gratias on incommensurate phases. There, the main idea was that sharp diffraction like Bragg diffraction could occur outside periodicity.<sup>8</sup> This paper [7], entitled “Metallic Phase with Long-Range Orientational Order and No Translational Symmetry”, was finished in mid-September, a few days before Shechtman returned to Israel.

Although both papers [4,7] announced the creation by rapid solidification of a sharply diffracting aperiodic metallic Al–Mn solid phase, they differed in several ways. The first paper [4] was more explicitly focused on the metallurgical aspects of the experiment, whereas the PRL paper [7] was confined to the compelling case made by the experiments alone at NIST that challenged several prevailing paradigms of fundamental crystallography. Whatever model could be proposed that might distract attention from the experiments, the experimental result by itself was strong and sufficient to force a change in thinking of the possibility of ordered solids to exhibit Bragg diffraction outside periodicity. In that sense, the PRL paper posed the very basic question of a new possible long-range atomic ordering in solids that would go beyond periodicity. It was sent to PRL on 7 October and disseminated out for comments.

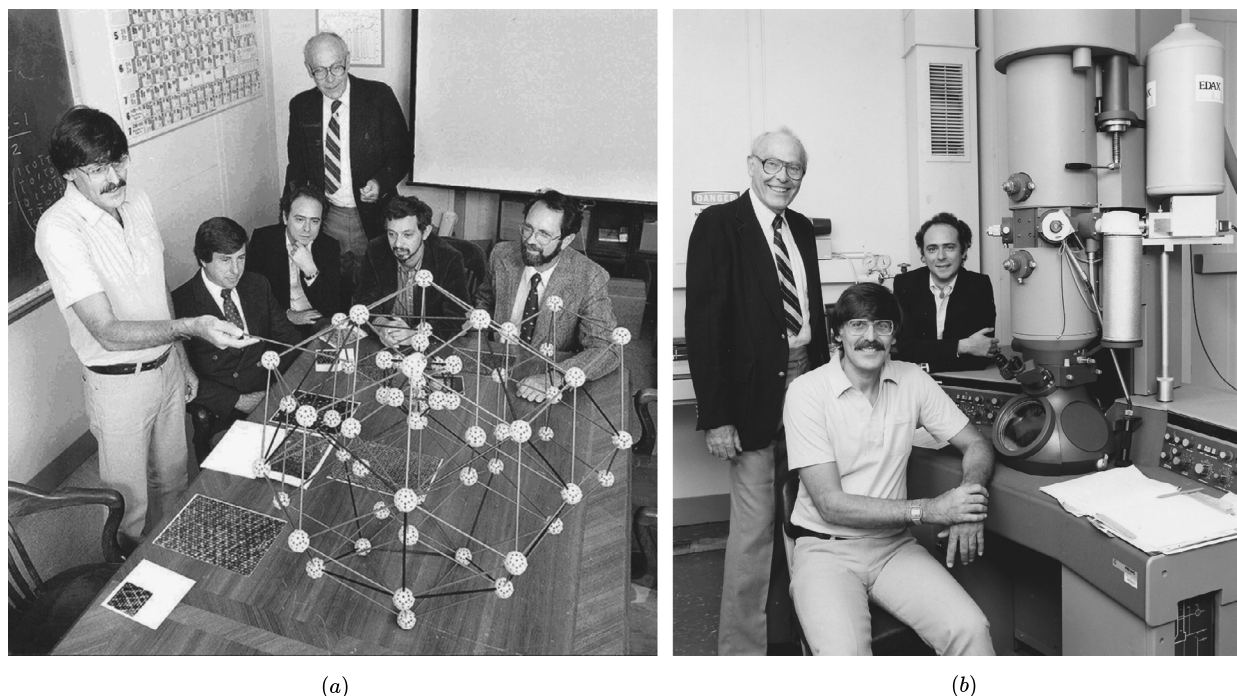
One of those copies reached Paul Steinhardt and Dov Levine, who were working on a theoretical model of a hypothetical icosahedric phase, the calculated diffraction patterns of which were identical along the 5-fold and 3-fold directions to the experimental patterns<sup>9</sup> obtained by Shechtman. They submitted their model [8] to PRL a couple of weeks after Shechtman et al. and coined the name *quasicrystal* as an abbreviation for *quasiperiodic crystal*. Their work had enormous influence in stimulating theory: quasiperiodicity entered for the first time in the field of solid-state physics and crystallography. The two publications of Shechtman [7] and Levine [8] in PRL appeared in November 1984; they received an immediate worldwide acceptance and excitement, and confirmation about the name *quasicrystals* for this new kind of ordering in metallic alloys.

In the meantime, the NIST experiments of metallurgical elaboration, TEM, and X-rays characterizations were successfully reproduced and confirmed in France at the “Centre d'étude de chimie métallurgique” (CECM, Vitry, France). The first TEM high-resolution images obtained in France in early January 1985 by Shechtman et al. [1] and Portier et al. [9], were theoretically calculated in dynamical electron diffraction a couple of months later by Marianne Cornier (Quiquandon) et al. [10]. They definitely ruled out the multiple twinning explanation. In view of these results, the famous French scientists Louis

<sup>7</sup> Cahn was unsuccessful in requesting additional funds from DARPA, but received funding from the NIST internal management to begin a major effort on the subject.

<sup>8</sup> Gratias was aware of the works of H. Bohr [5] and A. Besicovic [6] on almost-periodicity, thus confirming on mathematical bases the possible existence of Bragg diffraction beyond periodic objects.

<sup>9</sup> The 2-fold patterns were slightly different, Levine and Steinhardt's model showing more spots than observed; in fact, as it has been understood later, this model was built on a F-type 6D lattice, whereas the real structure, at that time, had a P-type 6D lattice; F-type 6D lattices were indeed discovered a couple of years later.



**Fig. 4.** (a) The research group on quasicrystals in early 1985 at NIST (from left to right, Dan Shechtman, Frank Biancianiello, Denis Gratias, John Cahn, Leonid Bendersky, and Robert Schaefer); a set of high-resolution TEM micrographs is to be seen on the table that had been taken by R. Portier in January 1985 at CECM, Vitry; they were the first HREM observations along the 2-fold orientation of  $Al_6Mn$  quasicrystals. (b) The electron microscope of the Metallurgy Institute at NIST where Dan Shechtman (sitting in front) discovered quasicrystals (on the back, John Cahn and Denis Gratias).

Michel, André Guinier, and Jacques Friedel, among others, gave their full support to engage new research efforts in France on the subject.

Michel Fayard, head of the Chemistry department of the CNRS, created in early January 1985 a “Programme international de collaboration scientifique” (PICS) between the Institute of Metallurgy at NIST (Gaithersburg, USA), the CECM/CNRS (Vitry, France) and the department of Materials Sciences at Technion (Haifa, Israel). This gave the opportunity to Shechtman, Cahn, and Gratias to meet in January 1985 at the CECM, Vitry, France, where a new research team had formed around Yvonne Calvayrac and Jean Bigot to elaborate and study these new aluminum-based alloys, research that lasted many years.

It turns out that, at the same time, an international seminar of mathematical crystallography was organized at IHES by Louis Michel and Marjorie Sénéchal [11]. Both knew about the quasicrystal discovery through Gratias, who learned group action theory a couple of years earlier at IHES under the supervision of Louis Michel. The three authors were thus invited to give a presentation of their experimental results. Gratias insisted in his talk on almost-periodicity as the plausible concept for understanding the apparent paradox of Bragg diffraction of solids exhibiting pentagonal symmetry. Michel Duneau, André Katz, and Aloysio Janner were in the audience and immediately after Gratias’ talk, André Katz [12] explained on the blackboard the technique of the cut-and-project method<sup>10</sup> he had derived with Michel Duneau (see Fig. 5), whereas Aloysio Janner (see [15]) made the connection with the superspace description. It was during this extraordinary session – where most of the interventions were improvised and spontaneous – that many of the basic concepts of quasicrystallography were enounced for the first time. This started a renewal of interest in higher-dimensional crystallography and aperiodic tilings in mathematics (see, for instance, [16]).

In the USA, the APS meeting of March 1985 at Baltimore opened the first quasicrystal session with already 13 abstracts received in December 1984. Shechtman was invited as a key-note speaker and Gratias gave a lecture explaining the cut-and-project method. About 300 papers were submitted worldwide in 1985 followed by tens of thousands several years later. A new quasicrystalline decagonal phase was discovered in 1985 by Leonid Bendersky [17]. Stable quasicrystals<sup>11</sup> phases were found in commercial alloys (Al–Cu–Li) by Dubost et al. [18] at CEGEDUR–Péchiney, where large quasicrystalline single grains were obtained for the first time. Numerous new stable icosahedral quasicrystals were then found in many aluminum-based ternary alloys, in particular the (Al, Cu, Fe) system by An-Pang Tsai and his group [19].

<sup>10</sup> This method has been independently proposed by the Russian group of Pavel Kalugin, Alexei Kitayev, and Leonid Levitov [13], and by the American Veit Elser [14].

<sup>11</sup> They are now hundreds of stable icosahedral and decagonal phases in binary and ternary metallic systems. They are obtained by the standard metallurgical technics used to grow large single crystals. They are stable in the sense that they are part of the equilibrium phase diagrams like any other metallurgical crystalline phase.

It is only in 1992 that the International Union of Crystallography (IUCr) eventually altered its definition of crystals (see [20]). Previously IUCr 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...” The word essentially is to be understood here as “most of the intensity of the diffraction is concentrated in relatively sharp Bragg peaks, besides the always present diffuse scattering...” Although quite unsatisfactory, this broader definition allows for possible future discoveries of other kinds of crystals.

Although no scientific revolution has ever been easier in Europe than quasicrystals, this ten-year delay for changing the definition of crystal came mostly from an opposition in the USA against this major paradigm change. In fact, in a letter [21] to *Nature* dated October 1985, the famous double Nobel Prize chemist and crystallographer Linus Pauling rebelled strongly against these quasicrystals that he considered as simple multi-twinned ordinary crystals: “*crystallographers can now cease to worry that the validity of one of the accepted bases of their science has been questioned*” and “*There are no such things as quasicrystals, there are only quasicientists.*” Strong refutations have immediately been published [22] in the issue of *Nature* dated January 1986, with the letter “Pauling’s model not universally accepted”, signed by several groups, but most of the US crystallographers stayed outside the field during years.

This has been the opportunity for European and Asiatic scientists to take some advance in sample preparation techniques and crystallography, whereas the US physicists developed mostly the entropy aspects of the random tiling models that are an important part of the stability of quasicrystals. No one ever provided experimental evidence confirming the structures proposed by Pauling for quasicrystals<sup>12</sup> and there was so much literature confirming Shechtman’s finding that Linus Pauling’s opposition eventually failed.

Quasicrystals received an unanimous enthusiastic interest from the mathematics and solid-state physics communities. The research developed very quickly in Europe: in France, with a joined research program (PICS) with the NIST, the first International Workshop on Aperiodic Crystals in Les Houches (March 1986), the creation of the “Groupe de recherche CNRS quasicristaux”, which lasted until the 1990s, and then, starting 1997, in Germany with the DFG “Schwerpunkt Quasikristalle”. Together, more than a hundred European laboratories have been involved in those programs with quite comfortable financial support. In the 2000s, an European Network of Excellence on Complex Metallic Alloys (CMA) gathered 21 European countries. Nowadays, the most active research on the subject has moved to Asia, in particular in Japan, with the group of Tsai (see, for instance, [23]).

## 1.2. Prolegomena of quasicrystals (see J. Friedel in [24])

As very often in science, the concepts that were at the basis of quasicrystals were already known for quite a long time.

In 1972, Yves Meyer [25] had published a book entitled *Harmonic Analysis and Number Theory*, in which he invented non-periodic sets of points that diffract on dense enumerable sets of Bragg peaks with hierarchical intensities. These ensembles are now clearly recognized as the first quasicrystalline frameworks now called *Meyer sets*. In 1977, Peter Martin de Wolff [26], followed by Aloysio Janner and Ted Janssen [15], invented the superspace description for describing incommensurate phases. A few years before, in 1974, R. Penrose [27] built a non-periodic tiling made of two kinds of tiles with an overall 5-fold symmetry. In 1981, Alan Lindsay Mackay chose the Penrose tiling as a prototype of possible atomic distributions with 5-fold symmetries in a magnificent pioneer paper [28], “De Nive Quiquangula: on the pentagonal snowflake”, where he concluded: “*it gives an example of a pattern of the type which might well be encountered but which might go unrecognized if unexpected*”. The link between the Penrose tiling and the superspace description started with the 1981 paper “Algebraic theory of Penrose’s non-periodic tilings of the plane” by Nicolaas Govert de Bruijn [29], who discovered the hidden properties of this tiling in considering internal variables that would later be recognized as the basis of the cut method. Soon after, in 1984, Peter Kramer and Roberto Neri [30] found new periodic and non-periodic space fillings by projection from higher dimension spaces. Finally, as previously discussed, a few weeks after Shechtman’s publication, Dov Levine and Paul Steinhardt [8] proposed the first explicit ideal structural model that they designated as *quasicrystals*, an abbreviation for *quasiperiodic crystals*.

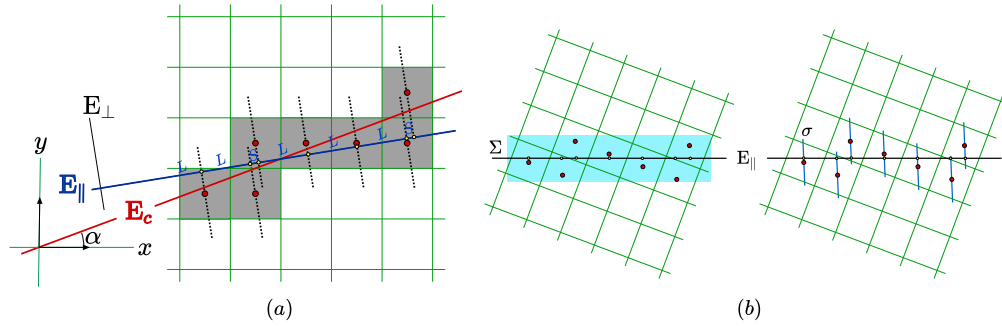
## 2. The $N$ -dimensional crystallography

Shechtman’s discovery challenged two principles of crystallography.

First, in 1784, René-Just Haüy postulated that all crystals were made up of clusters of atoms repeated periodically in three dimensions [31]. This periodicity implies 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 are possible to describe crystals anywhere in the universe. During 200 years, all measured crystals entered that scheme, periodicity becoming the definition of a crystal and an axiom of crystallography.

Secondly, it is well known since the beginning of the 20th century that diffraction from periodic objects results in sharp spots arrayed on the nodes of a reciprocal lattice. But the converse, that sharp diffraction spots could only come from a

<sup>12</sup> Although regular periodic phases have been found with atomic clusters similar to those observed in quasicrystals called *approximant phases*, those are easily distinguished from quasicrystals by their diffraction patterns.



**Fig. 5.** (a) The simplest geometric construction of a quasiperiodic sequence of points consists in collecting all the centers of the unit squares of the graph paper that are intersected by a straight line  $E_c$  of irrational slope designated as the cut (red line), and project them perpendicularly to another line  $E_{\parallel}$  in blue designated by the physical space. The sequence of points in yellow along  $E_{\parallel}$  is a quasiperiodic distribution of short and long segments. (b) Choosing  $E_c$  parallel to  $E_{\parallel}$  for simplicity, we observe that collecting the centers of the unit squares hit by the line  $E_{\parallel}$  is equivalent for selecting the centers that are located inside a strip extending along  $E_{\parallel}$  with thickness  $\Sigma$  being the convex envelope of the projection of the unit square along the line  $E_{\perp}$  perpendicular to  $E_{\parallel}$ . This, in turn, is equivalent in attaching a segment  $\sigma$  to each center – called an atomic surface – and collecting their intersections with  $E_{\parallel}$ .

periodic object, was a *widely accepted fallacy*, which is the main and unique responsible cause of the apparent paradox of Shechtman’s results: the concept of almost-periodicity under its simplest form, called quasiperiodicity after the works of Ernest Esclançon [32], Harald Bohr [5], and Abram Besicovitch [6] on almost-periodic continuous functions, was enough to pretend solving this apparent paradox.

Indeed, a function (of  $d$  real variables) on an affine ( $d$ -dimensional) space  $E_{\parallel}$  is said to be *quasiperiodic* if it is the restriction to  $E_c$  (embedded as an affine subspace) of a periodic function of  $n$  real variables defined in a higher-dimensional space  $\mathbb{R}^n$  where the direction of the cut is irrational (i.e. if the vector subspace parallel to the cut contains no point of the lattice besides the origin). For example, the function  $f$  of two real variables  $x$  and  $y$  defined by:  $f(x, y) = \cos x + \cos \sqrt{2}y$  is *periodic* in the  $(x, y)$ -plane. But, if we take the diagonal restriction of this function along the line  $y = x$ , i.e. the function  $\phi$  of one variable  $\phi(x) = \cos x + \cos \sqrt{2}x$  is not periodic because of the incommensurability between the two arguments in the cosine functions;  $\phi(x)$  is a *quasiperiodic* function.

### 2.1. The cut method

The simplest extension for generating quasiperiodic sets of points was explained by Katz in an improvised talk at IHES in the afternoon of 21 January 1985 using the following scheme.

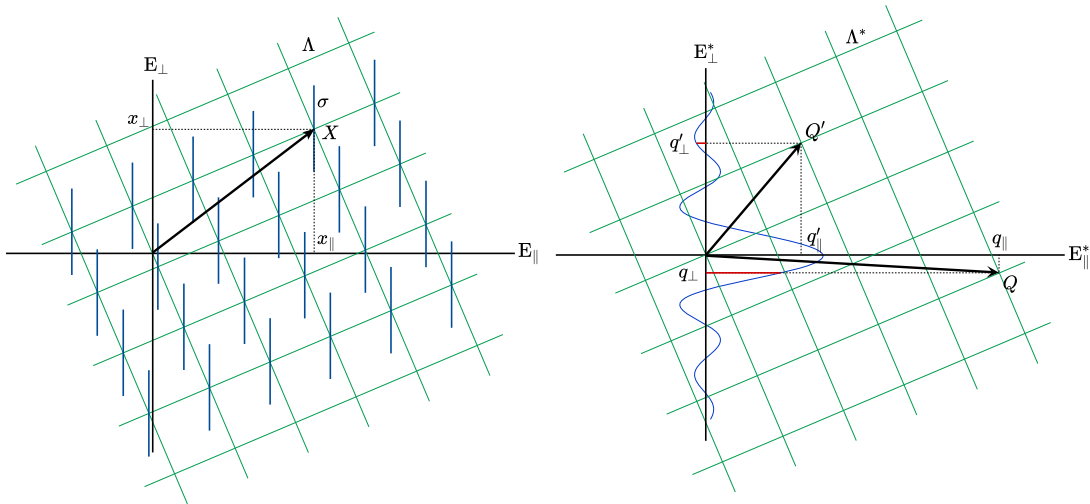
Take a graph paper made of square units, designate by  $x$  and  $y$ , respectively, the horizontal and vertical directions; draw a generic straight line  $E_c$  of angle  $\alpha$  with the  $x$  direction and collect all the unit squares that are hit by the line as shown in Fig. 5(a); choose whatever distinguished points in those squares, for example their centers, and project them on another line say  $E_{\parallel}$ . One obtains a sequence of points separated by long and short segments that do not repeat periodically if  $\tan \alpha$  is an irrational number: the sequence is quasiperiodic.

This simple scheme is highly instructive. Quasiperiodicity is induced uniquely by the *irrationality of the slope*  $\tan \alpha$  of the cut  $E_c$  and not by its localization in the plane nor by the orientation of the projection of the distinguished points onto the line  $E_{\parallel}$ . Indeed, the way the projection on  $E_{\parallel}$  is achieved has no influence on the quasiperiodicity of the sequence: if the projection direction has a rational slope, the relative lengths of the long and short segments are in a rational ratio: this is a *quasiperiodic* sequence built out of a *periodic* set of points. Also, moving the cut  $E_c$  line results in exchanging here and there some  $L$  and  $S$  segments, this generates infinitely many different sequences that are all equivalent.

This simple technique succeeds in generating a discrete set of points because the intersection of the line with the graph paper generates a set of connected unit squares that cover a non-zero surface: in fact, generic irrational cuts of lattices are empty or contain at most one point. To collect an infinite discrete set of lattice points like the red ones in Fig. 5, it is necessary either to consider a cut by a slice with finite thickness transverse to the cut, or to attribute a non-zero but finite extension to the lattice nodes transverse to  $E_{\parallel}$  as shown in Fig. 5(b) where, for simplicity,  $E_{\parallel}$  and  $E_c$  are a same line. In the first case, we collect the lattice points that are inside a strip of thickness  $\Sigma$ ; in the second case, we attach to each lattice node a segment of length  $\sigma$ , called an *atomic surface*, and collect the intersections of these atomic surfaces with the cut. These two constructions are made equivalent in choosing  $\Sigma = \sigma$ . Crystallographers prefer the second one, using atomic surfaces, for two reasons:

- it is very convenient for defining the distribution of several different atomic species by a collection of different atomic surfaces located at different sites with different shapes;
- this scheme enters the technique of  $N$ -dimensional crystallography invented by de Wolf [26] and set up in a general framework by Janner and Janssen [15] for the incommensurate phases.

All quasiperiodic structures generated by the previous technique share the following properties [33].



**Fig. 6.** The spectrum of the Fourier transform of a quasiperiodic chain of scatterers of equal weight generated by the cut method on the left, is located on the dense set of all projected nodes of the reciprocal lattice  $\Lambda^*$  where each projected node located at  $q_{\parallel}$  is weighted by  $\sin(\sigma q_{\perp})/q_{\perp}$  as drawn in blue on the right.

- The *repetitivity property* states that any finite packing of atoms that appears in a given quasiperiodic structure appears infinitely many times in the same tiling uniformly with a well-defined frequency. For any given finite radius  $r$ , there exists only a *finite* number of different atomic configurations called the  $r$ -atlas within any ball of radius  $r$ . This number grows with  $r$ , whereas it remains bounded for a periodic crystal.
- The *local isomorphism property* asserts that, if the projection of  $\Lambda$  is everywhere dense in  $\mathbf{E}_{\perp}$ , any finite packing of atoms that appears in a given quasiperiodic structure in  $\mathbf{E}_{\parallel}$  also appears in any other structure defined by a cut parallel to  $\mathbf{E}_{\perp}$ .

These two properties are often stated together as the *local isomorphism* property. They are however quite different by essence. The first one describes the repetitivity of finite-size patterns in one given tiling and may be considered as the quasiperiodic version of the standard repetitivity property (or homogeneity) in ordinary crystals. The second one has no simple counterpart in standard crystallography; it relates two *different* tilings; the closest relation that can be found with standard crystallography is the so-called *homometric* property of certain degenerate structures that have same self-correlation functions.

## 2.2. The Fourier transform

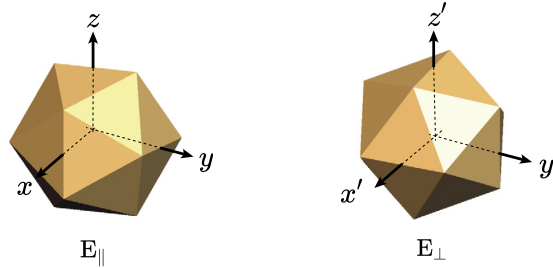
The major question posed by Shechtman's discovery [4,7] was the widely accepted fallacious idea in crystallography that diffraction patterns exhibiting Bragg spots would necessarily correspond to periodic objects. The works on incommensurate phases (displacement, chemical or magnetic order) published long before the discovery of quasicrystals are examples of this belief that they are a fallacy. But those were treated as specific structures resulting from the modulation of functions of atomic displacement, chemical or magnetic ordering that superimpose on the skeleton of a standard periodic structure. The diffraction pattern could thus be analyzed as a convolution of a host reciprocal lattice, generating the so-called *fundamental* spots with the Fourier transform of a periodic modulation function, incommensurate with the periods of the host lattice, that generates the so-called *satellite* spots. In that sense, the diffraction patterns of incommensurate phases made of sharp spots was understood as the result of more periodicities than the dimension of the space resulting in a convolution of reciprocal lattices (see Janner and Janssen [15]).

Shechtman's diffraction pattern of Fig. 2 could not be analyzed that way: there were neither host lattice with fundamental spots nor satellite spots. It was therefore very important to have an explicit calculation of the Fourier transform of the theoretical structures obtained by the cut method to get the demonstration that the diffraction pattern is indeed a set of Bragg peaks.

The complete calculation of the Fourier transform has been first given by Katz and Duneau in their original paper [12]. They achieved this calculation in following in reciprocal (Fourier) space the construction made in direct space (see Fig. 6). Enough is to say here that, because the actual structure results in a  $d$ -dimensional *cut* ( $\mathbf{E}_{\parallel}$ ) of a high  $N$ -dimensional periodic structure of lattice  $\Lambda$ , the Fourier spectrum is carried on the set of the *projection* of the nodes of the reciprocal lattice  $\Lambda^*$  on the reciprocal cut  $\mathbf{E}_{\parallel}^*$ , i.e. an enumerable set of Bragg peaks. The complete calculation shows that each projected node is weighted by an intrinsic amplitude that is the Fourier transform  $\hat{\sigma}$  along  $\mathbf{E}_{\perp}^*$  of the characteristic function  $\sigma$  – taking value



| $\langle \alpha   i \rangle$ | 1      | 2      | 3      | 4      | 5      | 6      | $\langle \bar{\alpha}   i \rangle$ | 1       | 2       | 3       | 4      | 5      | 6      |
|------------------------------|--------|--------|--------|--------|--------|--------|------------------------------------|---------|---------|---------|--------|--------|--------|
| $x$                          | 1      | $\tau$ | 0      | -1     | $\tau$ | 0      | $x'$                               | $-\tau$ | 1       | 0       | $\tau$ | 1      | 0      |
| $y$                          | $\tau$ | 0      | 1      | $\tau$ | 0      | -1     | $y'$                               | 1       | 0       | $-\tau$ | 1      | 0      | $\tau$ |
| $z$                          | 0      | 1      | $\tau$ | 0      | -1     | $\tau$ | $z'$                               | 0       | $-\tau$ | 1       | 0      | $\tau$ | 1      |



**Fig. 7.** Projections of the 6 basic unit vectors on the physical space  $E_{\parallel}$  and on the perpendicular space  $E_{\perp}$ . These two tables give the explicit expressions of the scalar products  $\langle \alpha | i \rangle$  and  $\langle \bar{\alpha} | i \rangle$  that are the matrix coefficients (up to the global normalization factor  $\kappa$ ) of the projectors  $\hat{\pi}_{\parallel}$  and  $\hat{\pi}_{\perp}$  onto, respectively,  $E_{\parallel}$  and  $E_{\perp}$ .

1 inside the atomic surface and 0 everywhere else – of the atomic surface at this node.<sup>13</sup> This weight factor  $\hat{\sigma}(q_{\perp})$  tends to zero for  $|q_{\perp}|$  tending to infinity.

This fundamental result (first presented by Katz and Duneau on 21 January 1985 at the IHES colloquium) was very important:

- it demonstrated that Bragg diffraction does also occur for objects that are *not periodic*;
- it demonstrated that in the cut model, because of the intrinsic weight factor due to the finite size of the atomic surfaces, the set of Bragg peaks with an intensity greater than any strictly positive threshold is *discrete*.

For the experimental point of view, this last property is necessary to solve the formidable problem of *unambiguously* indexing diffraction peaks out of a dense set of possible reflections.

### 2.3. The example of the icosahedral phase in the 6-dim space

Immediately after the colloquium at IHES in January 1985, Cahn, Gratias, and Shechtman were convinced that the  $N$ -dimensional approach was the only way to properly describe the atomic structures of quasicrystals as a  $N$ -dimensional object. A key issue to convince crystallographers to eventually consider quasicrystals as different from amorphous solids was to demonstrate how to embed the diffraction data of the icosahedral phase in a high-dimension space. This required performing a careful indexing [34] of the diffraction peaks.

In fact, they noticed in early 1985 that, in the electron diffraction patterns, the Bragg peaks, noted here  $q_{\parallel}$ , could be indexed in a way similar to cubic crystals, *but* in using *two* integers per cubic direction instead of one:  $q_{\parallel} \sim (h + h'\tau, k + k'\tau, \ell + \ell'\tau)$  with  $h, h', k, k', \ell, \ell' \in \mathbb{Z}$ , where  $\tau = (1 + \sqrt{5})/2$  is the golden mean (positive solution to  $x^2 - x - 1 = 0$ ).

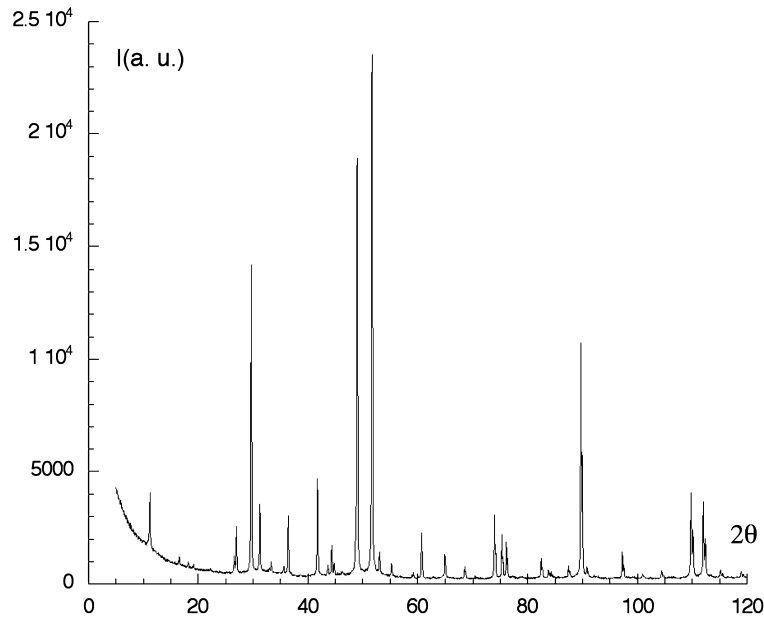
This suggested using the cut method in embedding this 3-dim object in a  $N = 3 \times 2 = 6$ -dim Euclidean space  $E^6$  to recover full periodicity. The global problem was thus to decompose the 6-dim space into two complementary and orthogonal 3-dim spaces,  $E_{\parallel}$  and  $E_{\perp}$  with  $E_{\parallel}$  being the 3D physical space and  $E_{\perp}$  a 3D internal space and designated here as perpendicular space.

It was natural, since only the orbit of the quinary axes has multiplicity 6 in the icosahedral group 235 (Hermann–Mauguin notations), to choose the quinary axes as the projections in the physical space of the six unit vectors of the 6-dimensional lattice  $\Lambda$  in  $E^6$ . Moreover, observing that the group 235 has two equivalent representations in dimension 3 that can be deduced from each other by a  $\pi/2$  rotation along the  $z$  axis, we choose  $E_{\perp}$  being defined by the projections in the perpendicular space  $E_{\perp}$  of the quinary axes after this  $\pi/2$  rotation along  $z'$ , as shown in Fig. 7.

It turned out that, using the above framework, Cahn, Shechtman, and Gratias could prove that the most intense reflections observed in the X-ray and neutron powder diffraction patterns should be located at particular wavevectors defined by  $|q_{\parallel}| \sim \sqrt{N + M\tau}$ , with  $N$  being an integer and  $M = \lfloor N\tau \rfloor$  (see appendix).

This predictive and highly not intuitive result has been of an enormous impact to validate the  $N$ -dimensional description with the cut formalism: the experimental X-ray and neutron powder diffraction patterns of the icosahedral phase  $Al_6Mn$  made at NIST and CECM followed perfectly the predicted hierarchy of intensities, as exemplified in Fig. 8, and the global

<sup>13</sup> It also shows that two locally isomorphic structures  $S$  and  $S'$  deduced from each other by a translation  $T$  in the large space have Fourier coefficients related by a trivial phase change,  $F'(q) = F(q) \exp 2i\pi q \cdot T$ . Therefore, their correlation functions to any order are identical, making them physically indistinguishable. This is the basis of an extended definition of a symmetry operation being an operation that transforms a structure into a locally isomorphic one, i.e. physically indistinguishable from the initial one.



**Fig. 8.** X-ray powder diffraction spectrum of the icosahedra phase  $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$  (CECM, CNRS, Vitry). Each peak  $q_{\parallel}$  in the physical space is characterized by two integers  $(N, M)$  such that  $|q_{\parallel}| = \kappa\sqrt{N + M\tau}$  and the most intense ones are those where  $M = \lfloor N\tau \rfloor$ ; for example, the three most intense reflections in the middle of the spectrum are labelled, from left to right,  $(18, 29)$ ,  $(20, 32)$ , and  $(52, 84)$ .

scaling factor between the calculated and the experimental pattern gave the first estimation of the unit-cell 6-dimensional parameter  $A_6$ , around 0.6–0.7 nm for the usual icosahedral phases (a detailed discussion is to be found in [34]).

This 6-dimensional indexing scheme was far more than a simple housekeeping work of crystallography; it was the necessary path to restore the 6-dimensional periodicity, the basic tool to understand these intriguing structures and describe them with a finite number of words.

Since all observed wavevectors  $q_{\parallel}$  were thus identified as the unambiguous projections in  $\mathbf{E}_{\parallel}$  of 6-dimensional vectors  $Q_6$  of  $\Lambda^*$ , the computation of the Fourier transforms could then be performed directly in the 6-dimensional space. For example, the pair correlation function – also designated as Patterson function by crystallographers – is easily displayed in  $\mathbf{E}^6$  using:

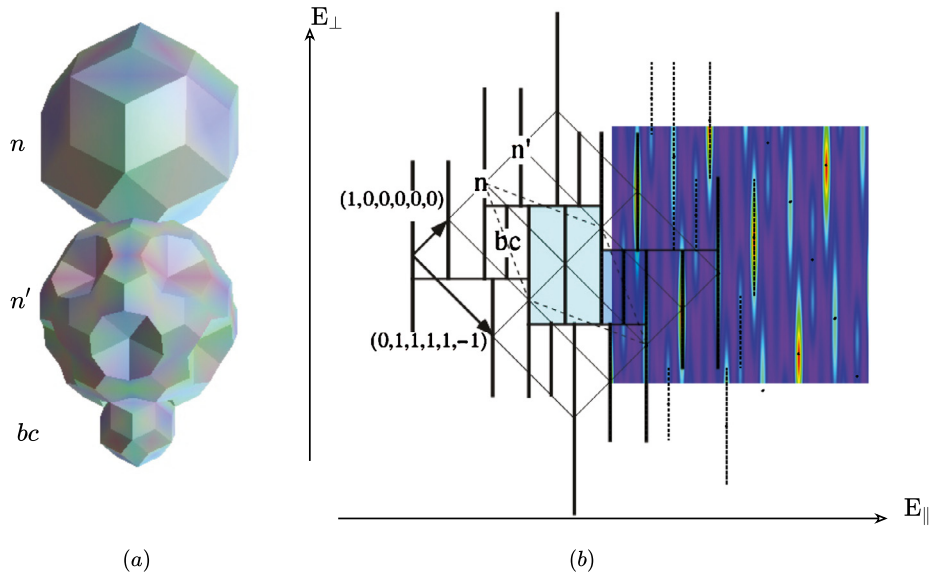
$$P(R_6) = \sum_{Q_6 \in \Lambda^*} |f(q_{\parallel})|^2 e^{2i\pi Q_6 \cdot R_6} \quad (1)$$

The second good news came at NIST at the end of 1985, when the first Fourier transforms (1) were calculated in 6-dimensional space using the experimentally observed intensities collected in powder neutron diffraction. It revealed magnificent cigar-shaped intensities elongated in the perpendicular direction giving a crude aspect of the atomic surfaces as segments parallel to  $\mathbf{E}_{\perp}$  and attached to each lattice node (see [35–37]).

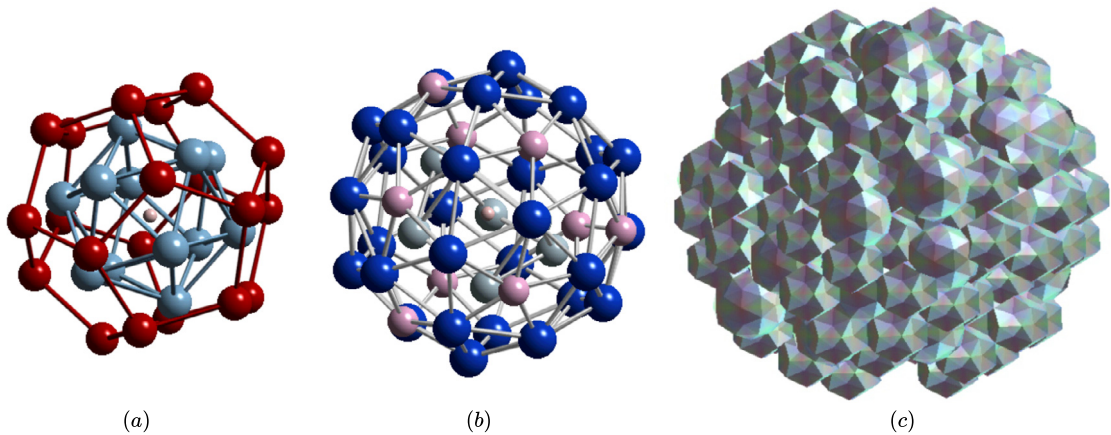
The discovery of new stable quasicrystalline phases by the group of An-Pang Tsai [23] – where large single grains could be elaborated at equilibrium by slow cooling – started the possibility of performing quantitative X-ray and neutron single-grain diffraction studies. Numerous new ternary alloys were discovered, exhibiting icosahedral and decagonal phases at equilibrium with great quasicrystalline perfection estimated by the average peak width of the strong diffraction peaks. In November 1990, Marianne Cornier-Quiquandon et al. [38] made a first structure determination of the  $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$  single-grain icosahedral phase by neutron diffraction at the “Laboratoire Léon-Brillouin” (LLB/CEA, Saclay, France). They used the cut method and devised the atomic surfaces shown in Fig. 9, inspired by previous work from Pierre Guyot and Marc Audier [39], who proposed structural units (Mackay clusters) for quasicrystals from a study of the unit cells of the crystalline phases  $\alpha$ -(AlFeSi) and  $\alpha$ -(AlMnSi). In 1992, Michel Boudard et al. [40] obtained very similar results on the alloy  $\text{Al}_{70.3}\text{Pd}_{21.4}\text{Mn}_{8.3}$  using X-ray diffraction at the European Synchrotron Radiation Facility (ESRF, Grenoble, France).

The experimental results expressed in  $\mathbf{E}^6$  were surprisingly simple: the atomic structures are made of quasiperiodic aggregations of intersecting atomic clusters like the one shown in Fig. 10. The simplest model proposed by Quiquandon et al. [41] is described by three main atomic surfaces only located at the high-symmetry special points of a face-centered 6-dimensional lattice as shown in Fig. 9(a). It is easily demonstrated that Mackay and Bergman clusters are indeed the most frequent atomic aggregates, as suggested by Guyot and Audier [39] in early 1986.

From about the 2000s, the  $N$ -dimensional aspect – that is the mathematical essence of quasiperiodicity – has finally been accepted by the crystallography community. Concerning the high-dimension symmetry groups, Louis Michel and Jan Mozyrnyas [42] published in 1988 a very synthetic work entitled *Fundamental Concepts of Crystallography* in the *Comptes*



**Fig. 9.** The first simple atomic models issued from experimental diffractions lead to define the icosahedral phase  $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$  in 6-dimensional space by a  $F(2A_6)$ -type lattice with three (main) atomic surfaces, here polyhedra, shown in (a), and located at the high-symmetry special points of the  $F$  6D-lattice ( $n = (0, 0, 0, 0, 0, 0)$ ,  $n' = (1, 0, 0, 0, 0, 0)$  and  $bc = 1/2(\bar{1}, 1, 1, 1, 1, \bar{1})$ ). These atomic surfaces are revealed by Fourier-transforming the experimental data in 6D: (b) shows the expected model on the left and the experimental Fourier map on the right in a cut along the 5-fold plane; the 5-fold direction in the physical space  $E_{\parallel}$  is along the horizontal line and the corresponding 5-fold direction in the perpendicular space  $E_{\perp}$  is along the vertical line.



**Fig. 10.** Typical atomic structure of the icosahedral phase  $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$ : (a) the Bergman cluster, (b) the Mackay cluster, and (c) the way they arrange and intersect in space.

*rendus de l'Académie des sciences* that unified all the usual crystallography concepts for any finite dimension using the usual tools of group action theory. The International Union of Crystallography changed the definition of crystals in 1992 as already mentioned above. New X-ray high-resolution investigations came out that led to very convincing and accurate descriptions of the atomic structures of stable quasicrystals in binary systems (see, for instance, the case of  $\text{YbCd}$  [43–48]). They are all described roughly as a quasiperiodic intrication of different atomic clusters with local icosahedral symmetry like those seen in Fig. 10. A detailed description of the research on quasicrystals in this recent period can be found in the special issue “Quasicrystals” of *Comptes rendus Physique* [24].

### 3. Conclusion

The existence of quasicrystals has been well and easily accepted around the world, with the exception of part of the US crystallographers led by the double Nobel Prize Linus Pauling, who rebelled strongly against this discovery. Quasiperiodicity does not exhaust, by far, all possible long-range ordering in solids: many other mathematical deterministic algorithms exist that give rise to perfectly ordered distributions of points that are neither periodic nor quasiperiodic. It is not yet known

which of these distributions could appear in nature but, because of quasicrystals, it is clear that solid-state physicists and crystallographers are now much better prepared to face these new possibilities today than in the 1980s.

#### 4. Appendix

As already noted in the text, the embedding of the actual physical 3-dimensional structure in a higher  $N$ -dimensional space is the key point in the recovering of full periodicity. Usually, the unique experimental information for a new quasicrystal is its diffraction pattern where the locations of the Bragg peaks are the irrational projections of nodes of a  $N$ -dimensional reciprocal lattice  $\Lambda^*$  with reciprocal unit vectors  $e_i^*$ . They form a so-called  $\mathbb{Z}$ -module, a dense set of peaks of the form  $q_{\parallel} = \sum_{i=1}^N n_i \hat{\pi}_{\parallel} e_i^*$ ,  $n_i \in \mathbb{Z}$ , projections of the nodes  $Q = \sum_{i=1}^N n_i e_i^*$ . Embedding the physical space in the high-dimension space consists in explicitly specifying the orientation of  $\mathbf{E}_{\parallel}$  (and thus  $\mathbf{E}_{\perp}$  as complement to  $\mathbf{E}_{\parallel}$ ) in the  $N$ -dimensional space.

We exemplify here the derivation of such an embedding (see [34]) for the case of the icosahedral phase with  $N = 6$ .

Let  $\{|i\rangle\}$  be the orthonormal basis<sup>14</sup> of  $E^6$  built on the six quinary axes defining the 6-dimensional hypercubic lattice  $\Lambda$ . Let  $\{|\alpha\rangle\}$  be the three unit vectors along  $x, y, z$  defining the standard cubic orthonormal basis of  $\mathbf{E}_{\parallel}$ , and  $\{|\bar{\alpha}\rangle\}$  the three unit vectors along  $x', y', z'$  defining the standard basis of  $\mathbf{E}_{\perp}$ .

The sum of the projectors  $\hat{\pi}_{\parallel}$  in  $\mathbf{E}_{\parallel}$  and  $\hat{\pi}_{\perp}$  in  $\mathbf{E}_{\perp}$  being the identity:

$$Id = \sum_i^6 |i\rangle\langle i| = \hat{\pi}_{\parallel} + \hat{\pi}_{\perp} = \sum_{\alpha} |\alpha\rangle\langle\alpha| + \sum_{\bar{\alpha}} |\bar{\alpha}\rangle\langle\bar{\alpha}|$$

the easiest way of characterizing these projectors is to express the basis change from  $\{|i\rangle\}$  to  $\{|\alpha\rangle, |\bar{\alpha}\rangle\}$ .

Let  $V$  be a vector of the lattice  $\Lambda$ ,  $V = \sum_i n_i |i\rangle$ ; the decomposition onto  $\mathbf{E}_{\parallel}$  and  $\mathbf{E}_{\perp}$  leads to:

$$V = \sum_i \left( \sum_{\alpha} |\alpha\rangle\langle\alpha|i\rangle + \sum_{\bar{\alpha}} |\bar{\alpha}\rangle\langle\bar{\alpha}|i\rangle \right) n_i$$

and thus, the operators  $\hat{\mathbf{R}}_{\parallel(\perp)}$ , defined by the two  $3 \times 6$  matrices:

$$(\hat{\mathbf{R}}_{\parallel})_{\alpha,i} = \langle\alpha_k|i\rangle \quad (\hat{\mathbf{R}}_{\perp})_{\bar{\alpha},i} = \langle\bar{\alpha}_{k'}|i\rangle \quad \text{for } i = 1, 6 \text{ and } k(k') = x, y, z (x', y', z')$$

transforms a vector  $V$  of  $\Lambda$  expressed on the canonical basis  $|i\rangle$  directly into its components on the basis  $\{|\alpha\rangle\}$  in  $\mathbf{E}_{\parallel}$  (respectively on the basis  $\{|\bar{\alpha}\rangle\}$  in  $\mathbf{E}_{\perp}$ ).

Hence, using the components of the 5-fold directions in  $\mathbf{E}_{\parallel}$  and  $\mathbf{E}_{\perp}$  given in the table of Fig. 7, we obtain the matrix elements of the projectors  $\hat{\mathbf{R}}_{\parallel(\perp)}$  as the scalar product of the unit vectors  $|i\rangle$  on the bases  $|\alpha\rangle$  and  $|\bar{\alpha}\rangle$  properly normalized<sup>15</sup>:

$$(\hat{\mathbf{R}}_{\parallel})_{\alpha,i} = \kappa \begin{pmatrix} 1 & \tau & 0 & -1 & \tau & 0 \\ \tau & 0 & 1 & \tau & 0 & -1 \\ 0 & 1 & \tau & 0 & -1 & \tau \end{pmatrix}, \quad (\hat{\mathbf{R}}_{\perp})_{\bar{\alpha},i} = \kappa \begin{pmatrix} -\tau & 1 & 0 & \tau & 1 & 0 \\ 1 & 0 & -\tau & 1 & 0 & \tau \\ 0 & -\tau & 1 & 0 & \tau & 1 \end{pmatrix}, \quad \kappa = A_6 \sqrt{2(2+\tau)} \quad (2)$$

The previous projectors can also be easily computed directly on  $\{|i\rangle\}$  in expressing the unit vectors of the two bases  $|\alpha\rangle$  and  $|\bar{\alpha}\rangle$  as 6-dimensional vectors in  $E^6$ ; one obtains then the  $6 \times 6$  matrices:

$$\langle i|\hat{\pi}_{\parallel}|j\rangle = \sum_{\alpha} \langle i|\alpha\rangle\langle\alpha|j\rangle = \langle i|\hat{\mathbf{R}}_{\parallel}\hat{\mathbf{R}}_{\parallel}|j\rangle; \quad \langle i|\hat{\pi}_{\perp}|j\rangle = \sum_{\bar{\alpha}} \langle i|\bar{\alpha}\rangle\langle\bar{\alpha}|j\rangle = \langle i|\hat{\mathbf{R}}_{\perp}\hat{\mathbf{R}}_{\perp}|j\rangle$$

Since the 6-dimensional lattice  $\Lambda$  is hypercubic – defined by the orthonormal basis  $\{|i\rangle\}$  – the very same relations hold in reciprocal space for labelling the Bragg reflections with respect to  $\Lambda^*$ . Thus, because of relations (2), the vector components of the form  $h + h'\tau$  in  $\mathbf{E}_{\parallel}^*$  transform into  $h' - h\tau$  in  $\mathbf{E}_{\perp}^*$ : the reflection  $q_{\parallel} = \kappa(h + h'\tau, k + k'\tau, \ell + \ell'\tau)$  in  $\mathbf{E}_{\parallel}^*$  has its counterpart in  $\mathbf{E}_{\perp}^*$ ,  $q_{\perp} = \kappa(h' - h\tau, k' - k\tau, \ell' - \ell\tau)$ .

Elementary calculations show that the length – in  $A_6^*$  unit – of the diffracting wavevectors can be parametrized using two integers  $N$  and  $M$ ; defining the 6-dimensional Bragg reflections unit,  $Q_6 = q_{\parallel} + q_{\perp}$ , one easily obtains:

$$Q_6^2 = N/2, \quad q_{\parallel}^2 = \kappa^2(N + M\tau), \quad q_{\perp}^2 = \kappa^2\tau(N\tau - M)$$

with  $N = h^2 + h'^2 + k^2 + k'^2 + \ell^2 + \ell'^2$  and  $M = h'^2 + k'^2 + \ell'^2 + 2(hh' + kk' + \ell\ell')$ .

Because  $N > 0$ ,  $q_{\parallel}^2 \leq Q^2$  and  $q_{\perp}^2 \leq Q^2$ ,  $M$  is bounded by  $-\lfloor N/\tau \rfloor \leq M \leq \lfloor N\tau \rfloor$ . Remembering that, in the cut formalism, the atoms are characterized by intrinsic shape functions (the Fourier transforms of the atomic surfaces) that modulate the intensities of the Bragg peaks, the most intense peaks, corresponding to the smallest  $|q_{\perp}|$  values, are thus found when  $M = \lfloor N\tau \rfloor$ , i.e. for peaks located in reciprocal space at  $|q_{\parallel}| = \kappa\sqrt{N + \lfloor N\tau \rfloor\tau}$ .

<sup>14</sup> We use Dirac notations in  $E^6$  with the standard Euclidean scalar product, since this makes manipulating projectors very easy.

<sup>15</sup> Designating by  $A_6$  the parameter of the elementary hypercube, one obtains the normalization of  $|\alpha\rangle$  (and  $|\bar{\alpha}\rangle$ ) using  $\langle\alpha|\alpha\rangle = \sum_{i=1}^6 \langle\alpha|i\rangle\langle i|\alpha\rangle = 1$  as being  $\kappa = A_6\sqrt{2(2+\tau)}$ .

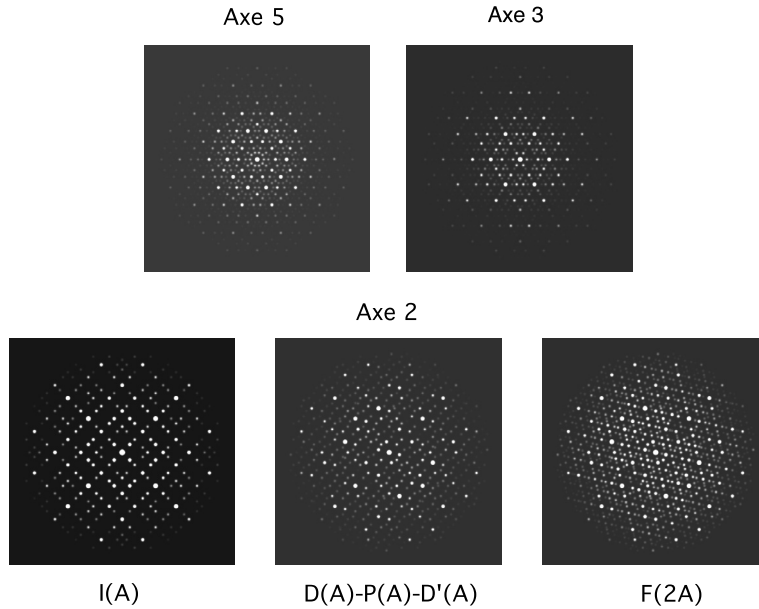


Fig. 11. The three main 6-dimensional lattices cannot be differentiated along the 5- and 3-fold axes, but are clearly distinguishable in the binary planes.

There are three main Bravais 6-dimensional lattices. Using the standard orthonormal basis with lattice parameter  $A_6$ , we have:

- the body-centered lattice  $I(A_6)$  defined by:

$$I(A_6) = \mathbb{Z}^6 + \frac{1}{2}(1, 1, 1, 1, 1, 1)\mathbb{Z}^6$$

- the primitive lattice  $P(A_6)$  defined by:

$$P(A_6) = \mathbb{Z}^6$$

- the face-centered lattice  $F(2A_6)$  defined by:

$$F(2A_6) = \mathbb{Z}^6 \text{ such that } \sum n_i = 2p$$

These three lattices are related by the very general group-subgroup relation that holds to any finite dimension:

$$I(A_6) \supset P(A_6) \supset F(2A_6)$$

of index 2 at each step. The corresponding reciprocal lattices are

$$I(A_6) \rightarrow F(2A_6^*), \quad P(A_6) \rightarrow P(A_6^*) \quad \text{and} \quad F(2A_6) \rightarrow I(A_6^*)$$

These three lattices<sup>16</sup> can be distinguished in the binary planes as shown in Fig. 11. Concerning the powder diffraction patterns where the reflections are characterized by the couples  $(N, M)$ , we have the following rules:

- for  $I(A_6)$ , reciprocal lattice  $F(2A_6^*)$ ,  $N$  and  $M$  are even;
- for  $D(A_6)$ , reciprocal lattice  $D'(A_6^*)$ ,  $M$  is even;
- for  $P(A_6)$ , reciprocal lattice  $P(A_6^*)$ ,  $N$  is even;
- for  $D'(A_6)$ , reciprocal lattice  $D(A_6^*)$ , the sum  $N + M$  is even;

<sup>16</sup> In addition to these three main lattices, two others, called  $D(A_6)$  and  $D'(A_6)$ , can be defined as:

$$D(A_6) = F(2A_6) + \frac{1}{2}(1, 1, 1, 1, 1, \bar{1})F(2A_6) \quad \text{and} \quad D'(A_6) = F(2A_6) + \frac{1}{2}(1, 1, 1, 1, 1, 1)F(2A_6)$$

Their projections in  $E_{\parallel}$  are homothetic to  $P(A_6)$  with scaling factors  $\tau$  for  $D(A_6)$  and  $\tau - 1$  for  $D'(A_6)$ . They are thus redundant with  $P(A_6)$  for crystallographic descriptions in the physical 3-dimensional space.

– for  $F(2A_6)$ , reciprocal lattice  $I(A_6^*)$ , there are no conditions on  $N$  and  $M$ .

These results concerning the description of the basic Bravais lattices in  $E^6$  (and many others, see Duneau [49]) were achieved in 1988. They formed the basic crystallographic tool to study the icosahedral phases using 6-dimensional Euclidean space.

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