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Personal reflections on the history of aperiodic crystals from early days to the state of the art

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Aperiodic crystals occur as modulated, intergrowth and quasicrystal structures. Their characterization in terms of symmetries possibly requires not only a higher-dimensional description, but also non-Euclidean transformations (like scaling). These crystallographic symmetries, observed in nature, have been investigated but only partially classified. Turning points in the structure determination of aperiodic crystals are presented in historical perspective up to the present time, together with methods and programs. The WEB allows to get more information on all that, on additional tools and on databases. An attempt to present challenges towards lines of future research concludes the review.

1 Introduction

Lattice periodicity is the most important achievement of the theoretical and experimental investigations during the 19. and the 20. centuries, the golden age of crystallography. Of course only the geometric model of an ideal crystal is lattice periodic because a real crystal is always finite and has defects. It is during the second half of the last century, that the idea of *aperiodic crystal* arises. At the beginning, aperiodicity was associated with incommensurate modulation and considered by most of the people, but not by Wigner, as one of the many small deviations observed in real crystals. I remember Wigner interrupting my explanations on incommensurate modulated crystals by saying 'What you call a crystal is not a crystal. I know what a crystal is! I worked in crystallography.' It happened in Austin, 1987. For P.M. de Wolff incommensurability was based on measurements by professional crystallographers. One finds a similar attitude in Herbert Smith. In 1903 confronted with the problem of high-indices faces in the growth forms of the mineral Calaverite ($AuTe_2$) he does not speculates about possible experimental errors but concludes: 'One has to postulate the existence of five different but not independent lattices' [1]. In the same paper he also considers the possibility of 'irrational' twinning planes. Eventually, this mineral appeared to be modulated [2] and incommensurate [3,4]. For Shechtman also, the Bragg spots with icosahedral symmetry observed in 1984 represented a new fundamental phenomenon [5] and not simply the effect of a multiple twinned cubic crystal as postulated by Linus Pauling [6].

The concept of incommensurability and the relation with irrational numbers goes back to Pythagoras of Samos, in the 5. century BC. As reported in the tenth book of the Elements of Euclid, the diagonal d and the edge s of a square are incommensurate because the assumption that their ratio $d^2/s^2 = 2 = p^2/q^2$ is rational (with p, q relatively prime integers) leads to a contradiction. The difficulties felt by the scientific community in accepting incommensurability in crystals were not mathematical but due to the impressive success of the idea that a crystal is lattice periodic. In recent years, attempts have been made to give a general definition of ideal crystal which includes aperiodicity. One finds various working definitions, but a general agreement has not yet been found. The fundamental question remains: Do we really know, as Wigner claimed, what a crystal is? As I shall try to explain, the struggle is still going on.

More than an historical review what is presented is a personal view, with all the limitations implied. Missing quotations of relevant facts and persons are not simply due to lack of space but mainly to the frontiers of my knowledge and I apologize for this.

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2 Description

Fundamental for aperiodic crystals is the notion of the n independent periodicities (required for labeling the Bragg reflections h by a set of integral indices h_i) given by reciprocal basis vectors $\mathbf{a_i^*}$ generating by integral linear combinations a $\mathbb{Z}$-module M^* of rank n and dimension 3. The nature of these periodicities allows to distinguish between *modulated*, *intergrowth* and *quasicrystals*. For modulated crystals $\mathbf{a_1^*}, \mathbf{a_2^*}, \mathbf{a_3^*}$ label the main reflections of a basis (or averaged) periodic structure and the $\mathbf{a_{3+j}^*}$ (for j from 1 to d) correspond to d periodic deformation waves (modulations): displacive and/or compositional ones. In intergrowth crystals the basis structure is spanned by more than one 3-dimensional lattice only. While in these cases the symmetry of M^* is a 3-dimensional crystallographic point group, this is no more the case for quasicrystals.

All aperiodic crystals are characterized by a fairly low Euclidean symmetry in space. Their crystallographic nature is revealed by a description in a n-dimensional Euclidean space, the *superspace*. In the superspace approach the indexed reflections are interpreted as the projection of Bragg reflections at the points of a n-dimensional lattice Σ^*. The projection of Σ^* into the orthogonal complement of the 3-dimensional space defines a $\mathbb{Z}$-module M_I^*. Accordingly, the superspace V_s is the direct sum of a 3-dimensional space V (also denoted as physical, external or parallel space) and a d-dimensional space V_I (called internal or orthogonal space) [7,8]. By Euclidean duality one gets the direct lattice Σ of the symmetry translations of the aperiodic crystal embedded in the superspace and by projection in the two subspaces the $\mathbb{Z}$-modules M and M_I, respectively. These algebraic structures allow an indexing of the Bragg reflections and of the atomic positions, respectively, defined in the corresponding spaces. An indexing in direct space, usually not considered, is emphasized in the present review.

3 Symmetry

The lattice periodicity of crystals has been accepted, even before that of the existence of atoms, on the basis of the morphological restrictions imposed by the 32 crystal classes and Haüy's Law of Rational Indices and because of the simplicity of the molecular model. In 1911 a crystal is still defined by Friedel as an *homogeneous mass* and the crystal lattice is considered an hypothesis [9]. The symmetry groups of 3-dimensional lattice periodic Euclidean patterns were well known and fully classified (the 230 space groups, in particular), but without any implication for the physical nature of crystals. The situation changed dramatically in 1912 with the diffraction experiment of von Laue on ZnS, which represents the begin of the X-ray crystallography, codified in 1952 in the International Tables of the International Union for Crystallography (IUCr). At the end of the 19. and begin of the 20. centuries, as already mentioned, the morphology of the mineral Calaverite was in conflict with the Law of Rational Indices and the lattice periodicity. The phenomenon of non-indexable growth faces remained a mystery till after the discovery in 1964 of non-indexable Bragg reflections in γ-$NaCO_3$ [10], which could then be interpreted in 1972 as due to an incommensurate modulation described by a 4-dimensional space group [11]. Few years later the higher-dimensional description of Na_2CO_3 served as model for deriving the (3+1) symmetries of an one-dimensional modulated crystal depicted in the 4-dimensional space [12]. The basic idea of the superspace approach was born. The formalism based on 4-dimensional space groups was then applied to periodically distorted crystals in space and in space-time also [13]. Two years later the corresponding n-dimensional approach has been defined together with the introduction of the $(n+d)$-dimensional superspace groups [14]. The privileged role of the physical space of the crystal required a distinction from the n-dimensional crystallography, implying that the equivalence classes of the superspace groups are different from those of the space groups in the same dimension. The derivation and the classification of the crystallographic symmetries in the superspace then followed. The basic principles and the list of all (3+1) superspace groups are given in [7]. Yamamoto derived the (3+2) and (3+3) superspace groups. A full list of all these groups can be found in his home page on the WEB (www.nims.go.jp/aperiodic/yamamoto/index.html). The new conventions have been formulated by the nomenclature commission of the IUCr [15,16].

The diffraction patterns of quasicrystals show a new type of crystallographic symmetry: scaling invariance. The positions of the Bragg spots of the icosahedral quasicrystal $Al_{0.86}Mn_{0.14}$ are invariant with

respect to a radial scaling by a factor τ^3, where $\tau = (1+\sqrt{5})/2$ is the golden mean [17]. Discrete scaling invariance by a factor τ was already known to occur in the infinite Fibonacci sequence and as inflation property of the Penrose tiling [18]. In a superspace periodic embedding of dimension (1+1) and (2+2), respectively, of the corresponding $\mathbb{Z}$-modules, these scaling transformations appear as hyperbolic rotations leaving the lattice invariant. The circular and the hyperbolic rotational symmetries of a given lattice involve different invariant metrics: a positive definite and an indefinite metric, respectively. Both are taken into account by the so-called multimetrical space groups [19]. The multimetrical symmetries of the decagonal quasicrystal $Al_{78}Mn_{22}$ could be derived [20] on the basis of the 5-dimensional structure determination of Steurer [21]. Multimetrical symmetry also occurs in periodic crystals. In the case of ice, the hyperbolic symmetries have implications for the occupied Wyckoff positions of the atomic structure and, macroscopically, for the morphology of snow crystals [22]. A cubic $Al-Mg$ crystal with 3-dimensional inflation symmetry has also been found [23]. A classification of multimetrical space groups is still missing. The basis for a theory of crystal diffraction which includes scaling has been given by Steurer and Haibach [24].

Mermin and co-workers consider a symmetry characterization of aperiodic crystals in the 3-dimensional reciprocal space (in a similar way as done by Bienenstock and Ewald for periodic crystals [25]) without a higher-dimensional description [26–30]. This is also possible in the direct space when the crystallographic transformations are interpreted in a proper way. In the modulated case, for example, a translation in the internal space corresponds to a shift in space of the modulation wave. The fivefold rotation of a 2-dimensional pentagonal quasicrystal is reflected in the fivefold symmetry of the $\mathbb{Z}$-module M and the superspace glide reflection of γ-Na_2CO_3 appears in space as a reflection combined with a half-wavelength shift of the transverse modulation wave. Often a superspace symmetry corresponds in space to a local Euclidean transformation applied to part of the structure only.

Here the attention is focused to crystallographic scaling transformations S_λ with scaling factor λ. In the 3-dimensional space one distinguishes between radial, planar and linear scaling transformations. The crystallographic restriction implies that S_λ transforms a lattice Λ into itself, or to a sublattice, or to a superlattice of Λ [31]. Actually in the cases considered these transformations scale positions in space indexed by the $\mathbb{Z}$-module M. For example, the vertices of a regular pentagon are scaled by the planar S_{-1/τ^2} to those of the smaller pentagon obtained by joining the non-adjacent vertices to form a $\{5/2\}$ star pentagon, the pentagram. In the appropriate orientation the linear scaling Y_{1/τ^3}, which scales by a factor $1/\tau^3$ the y coordinate of two adjacent vertices A and B, subdivides the pentagonal edge according to the golden ratio. These scaling transformations and the fivefold rotation are crystallographic because they leave invariant the pentagonal $\mathbb{Z}$-module M generated by the basis $a = \{\mathbf{a_1}, \mathbf{a_2}, \mathbf{a_3}, \mathbf{a_4}\}$ given by the vectors $\mathbf{a_i}$ pointing from the center to four vertices of a regular pentagon. These transformations, which generate the point group of infinite order of a self-similar pentagram, appear as transformations among atomic positions of the decagonal phase of the $Al_{78}Mn_{22}$ quasicrystal, as already mentioned [20,21]. This is only the case for the ideal quasicrystal. In the real structure of $Al_{78}Mn_{22}$ both the lattice periodicities and the scaling symmetries are broken because of the finite size and of the minimal interatomic distance, respectively.

The historical development in crystallographic symmetry concepts is summarized in Table 1.

4 Crystal structures

In Table 2 one finds examples of crystal structures marking the arise of the concept of aperiodic crystal. Few comments are given in what follows.

***$AuTe_2$* (Calaverite).** Short after the discovery in the gold mines in Calaver US at the end of the 19. century, it appears that this mineral has an entangled morphology. Most of the facets could not be properly indexed. Even admitting unusually high indices larger than about 20, no single lattice allowed an interpretation of the experimental data [1]. In 1931 the international commission of Goldschmidt (Germany), Palache (US) and Peacock (Canada) charged to repeat very carefully the measurements on a fairly large number of crystals, could also not solve the enigma in a proper way [32]. Eventually this mineral was found to be incommensurate modulated [2–4] and in 1985 a 4-dimensional indexing fitted very nicely with the

experimental data of 1931 [33,34].

γ-Na_2Co_3. The Bragg reflections of the γ phase of Na_2CO_3 could not be indexed, despite (or according to de Wolff thanks to) the professional level of the Dutch crystallographers involved [10]. A temperature dependent record of the positions of the diffraction spots demonstrated a continuous variation of the satellite reflections expressed in terms of the main reflections [12]. This proved, among other symmetry considerations [11], that any rational superstructure approximation of the modulation wave was not compatible with the observations. Eventually, the structure could be solved in the harmonic approximation and in a 4-dimensional description [35]. Very recently the various phase transitions of Na_2CO_3 have been reinterpreted by Arakcheeva and Chapuis.

$(TTF)_7I_{5-x}$. The structure determination of this one-dimensional conductor by Johnson and Watson, again two highly professional crystallographers, only allowed local symmetry elements [36]. It is the first intergrowth crystal whose symmetry could be shown to have a (3+1)-dimensional superspace group symmetry. The basis structure itself, defined in terms of the two periodic subsystems of the TTF molecules and I atoms, respectively, is incommensurate and each subsystem induces in the other subsystem incommensurate satellite reflections [37].

$Fe_{1-x}S$ (Pyrrhotite). The original idea of Yamamoto has been to apply the superspace approach to a whole family of structures, to begin with the periodic case of the polytypes of SiC and ZnS [38], going on with $Fe_{1-x}O$ (wustite) and $Au_{2+x}Cd_{1-x}$. In the case of pyrrhotite the charge density modulation is highly anharmonic [39]. These pioneering works mark the beginning of still going on fruitful investigations of families of crystals where a single superspace group connects compounds having seemingly unrelated space group symmetries [40–42].

Pentaplexity. This term applies to a 2-dimensional tiling model derived by Roger Penrose for showing that two tiles only suffice for cover the whole plane in a non-periodic way [18]. As a special case one gets a fivefold rotational symmetry of the tiling. Key point in the proof of the aperiodicity is the inflation symmetry of the tiling. By optical diffraction of the Penrose tiling, Alan Mackay obtained a pattern with fivefold symmetry and sharp maxima recalling the Bragg spots of crystals [43]. At that time, fascinated by the beauty of this image, I tried to interpret the whole as a 2-dimensional crystal, without succeeding. It was too different from the aperiodic examples I knew. I could, however, transmit my interest to Peter Kramer from Tübingen, drawing his attention to the algebraic analysis of the Penrose work by de Bruijn [44]. Kramer was able to obtain fundamental results in the period preceding the experimental discovery of quasicrystals [45, 46].

***Al-Mn* (Icosahedral phase)**. The intermetallic compound ($Al-14$-at.%-Mn) obtained by Shechtman in 1984 represents the first experimental evidence of a quasicrystal [5]. The name *quasicrystal* has been introduced short after by Levine and Steinhardt [47]. Four years later followed the 6-dimensional Fourier analysis of the $Al_{73}Mn_{21}Si_6$ icosahedral phase [48]. In 1990 the number of known icosahedral structure was already so large that new classes of icosahedral crystals may be expected to be found in the future.

***Al-Mn* (Decagonal phase)**. From 1985 on there is a whole stream of theoretical and experimental results on quasicrystals. In particular, the decagonal quasicrystal has aperiodic planes perpendicular to the rotational axis [49]. These quasiperiodic planes have structures similar to the Penrose tiling, as theoretically analyzed by Ishihara and Yamamoto [50, 51]. Few years later, Steurer determined the five-dimensional structure of the decagonal $Al_{78}Mn_{22}$ [21,52]. The planar sections of Steurer's refined Fourier map allowed to identify the crystallographic scalings mentioned in the previous section as transformations of indexed atomic positions [20]. The results of twenty years of structure research on axial symmetric quasicrystal (pentagonal, octagonal, decagonal and dodecagonal ones) are reported in a recent review paper [53].

5 Structural determination: Methods and Programs

Table 3 gives a simplified overview of the methods and the programs having allowed to solve an incredible number of aperiodic crystal structures. The importance of this endeavor can hardly be overestimated. One has to be aware that at the time of de Wolff's first determination of the incommensurate structure γ-Na_2CO_3 the computer program available simply eliminated all diffraction data non obeying a space group symmetry. Yamamoto's REMOS of 1982 is the first program for incommensurate modulated structures

based on the superspace approach and played an essential role in the acceptance of a higher-dimensional crystallography [54,55]. A next step in this direction is represented by the JANA program of Petříček [56,57] with the use, in particular, of crenel functions for occupationally modulated structures. The low density elimination method by Takakura, Shiono, Sato, Yamamoto and Tsai will be the first successful method for obtaining superspace electron density from X-ray diffraction data [58]. The very recent extension of the charge flipping method to the superspace by Palatinus is a further very promising development [59]. Personally, I am looking forwards for methods and programs which will include crystallographic scaling as well.

6 Concluding remarks

Much more information on the historical development of aperiodic crystallography up to the present state of the art can be found on the WEB and in particular on the home page of the Special Interest Group on Aperiodic Crystals (SIG) as summarized in Table 4.

Here attention is focussed to two problems which are expected by the author to influence future developments.

The inverse crystallographic problem. In a crystal structure determination one implicitly starts from what one thinks is an ideal crystal structure, periodic or aperiodic, and more or less explicitly from the corresponding possible symmetry groups. Solving the structure is the final goal. Knowing where the atoms are does not mean to *understand* the structure, even at the geometrical level only. There are very often hidden structural relations not taken into account by the symmetry groups considered, which eventually can help to characterize other structures as well. This is what I call the *inverse crystallographic problem*, where one starts from a given structure and one investigates its symmetry. Typical in this respect are the non-Euclidean symmetries of a crystal.

The geometry problem. Considering a crystal as an Euclidean object implies that it is fully characterized in terms of elements of the Euclidean geometry. According to Felix Klein's Erlanger Program of 1872, a geometry consists of a set $\mathcal{S}$ defining the points of the geometry and a group $\mathbf{G}$ of transformations of the set $\mathcal{S}$. A geometrical property is a property invariant under $\mathbf{G}$ and geometrical objects are characterized by geometrical properties. In the Euclidean geometry, $\mathcal{S}$ is $\mathbb{R}^n$ and $\mathbf{G} = \mathrm{E(n)}$ is the Euclidean group generated by translations, rotations and reflections of $\mathbb{R}^n$. The *distance* d between two points A, B and the size of the *angle* φ defined by three points A, B, C are Euclidean objects. If n-dimensional scaling transformations S_λ with scaling factor λ are also admitted transformations of $\mathbb{R}^n$, one gets the similarity group $S(n)$ and the *similarity geometry*. In this geometry angles are still geometrical objects but only the ratio between two non-zero distances is geometrically defined. As scaling can occur in quasicrystals [17], in incommensurate modulated crystals [60] and even in crystals [23], one should seriously consider crystallography in the context of similarity geometry. Moreover, the fact that not all Euclidean transformations are crystallographic has implications on the geometrical level. The question then arises about the properties of a properly defined *crystallographic geometry*.

How far these two problems are relevant for the future developments is hard to say at present. In the view of the author, the properties of aperiodic crystals have consequences at the fundamental level of crystallography which go far beyond the present known implications of aperiodicity.

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Table 1. Crystallographic Symmetry Groups

Point groups	Morphology	Diffraction
32 Crystal classes (Frankenheim 1826)	Crystal forms (Kepler 1611, Haüy 1801)	von Laue ZnS (1912)
N-fold Rotations		Axial crystals and quasicrystals (Bienenstock, Ewald 1962, Mermin *et al.* 1988)
(3+1)D Rotations	Calaverite $AuTe_2$ (1895-1989)	γ-Na_2CO_3 (de Wolff 1964)
(3+3)D Rotations	Dodecahedron, ...	Icosahedral QCR (Shechtman 1984)
1D,2D,3D Scalings		Quasicrystals (Elser 1985)
		Cubic $Al-Mg$ (Donnadieu, *et al.* 1996)
Scale-rotations		(Steurer, Haibach 2001)
Space groups	**Structure**	**Diffraction**
3D (Fedorov 1885, Schoenflies 1891)	Periodic crystals	Bragg reflections
3D (Bienenstock, Ewald 1962)	Complex weights on reciprocal lattices	
3D (Mermin, *et al.* 1988)	Gauge functions on Fourier modules	
(3+n)D Superspace groups (1979)	Modulated, Intergrowth crystals	Main reflections + Satellites
(3+2)D Superspace groups + Scaling	5- 8- 10- 12-gonal quasicrystals	1D and 2D Scaling symmetry
(3+3)D Superspace groups + Scaling	Icosahedral quasicrystals	3D Scaling symmetry
Multimetrical space groups (1991)	Snow flakes (1997)	Ice crystals

Table 2. Aperiodic crystals: Examples of turning points

$AuTe_2$	1902	Non-indexable growth forms	Penfield, Ford, Smith [1]
	1931	Singular point at [5 29 -3]	Goldschmidt, Palache, Peacock [32]
	1985	4-Dimensional indexing	Dam, Janner, Donnay [33, 34]
γ-Na_2CO_3	1964	Non-indexable satellites	Brouns, Visser, de Wolff [10]
	1972	4-dimensional space group	van Aalst, de Wolff [11]
	1974	Harmonic approximation	de Wolff, *et al.* [12]
	2005	Additional phase transitions	Arakcheeva, Chapuis
$(TTF)_7I_{5-x}$	1976	Local symmetry only	Johnson, Watson [36]
	1980	Incommensurate basic structure	Janner, Janssen [37]
SiC, ZnS	1981	Polytypes as modulated crystals	Yamamoto [38]
$Fe_{1-x}S$	1982	Higher order harmonics	Yamamoto, Nakazawa [39]
$LaTi_{1-x}O_3$	2000	Family of modular structures	Elcoro, Pérez-Mato, Withers [41]
Fivefold symmetry	1974	Planar tiling with inflation symmetry	Penrose [18]
	1982	Optical diffraction of Penrose tiling	Mackay [43]
$Al-Mn$	1984	Icosahedral quasicrystal	Shechtman, Blech, Gratias, Cahn [5]
$Al_{73}Mn_{21}Si_6$	1988	6-dimensional Fourier analysis	Gratias, Cahn, Mozer [48]
Decagonal $Al-Mn$	1988	Penrose-like quasicrystal	Yamamoto, Ishihara [50, 51]
	1989	5-dimensional structure	Steurer [21, 52]
	1992	Decagrammal scaling symmetry	Janner, Steurer [20, 21]

Table 3. Methods and programs for solving aperiodic crystal structures

Superspace approach	1982	Yamamoto REMOS [54, 55]
	1985	Petříček JANA [56, 57]
Direct methods	1987	Hao, Liu, Fan, *et al.* [61, 62]
	1993	Fan, Lam, Beurskens, van Smaalen [63]
Patterson method	1987	Steurer (decagonal QCR) [52, 64]
	1988	Gratias, Cahn, Mozer (icosahedral QCR) [65]
Trial-and-error method	1988	Yamamoto, Ishihara [50, 51]
Contrast variation	1989	Janot, De Boissieu, Dubois, Pannetier [66].
Maximum entropy method	1993	Steurer, Haibach, Zhang, Kek, Lück [67]
	1997	Weber, Yamamoto [68], Haibach, Cervellino, Steurer [69].
	2003	Van Smaalen, Palatinus, Schneider [70]
Low density method	2001	Takakura, Shiono, Sato, Yamamoto, Tsai [58]
Atomic surface modeling	2002	Cervellino, Haibach, Steurer [71]
Charge flipping method	2004	Palatinus [59]

Table 4. Special Interest Group on Aperiodic Crystals (SIG)

SIG Home page	www-xray.fzu.cz/sgip/aphome.html
Superspace groups	Yamamoto home page
Software	REMOS JANA2000 Superspace tools CCP4
Links	Incommensurate structures Quasicrystals
Databases	Bilbao server Lausanne server Caracas home page
Research groups	A list of 23 research groups
References	A full list on aperiodic crystals