

Fifty years of aperiodic crystals. Corrigendum

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Corrections to the article by Janssen [*Acta Cryst.* (2012). **A68**, 667–674] are given.

The following corrections should be made in the article by Janssen (2012):

(i) On page 671, right column, line 42, and in the caption to Fig. 3, '*n*-heptane-urea (Mariette *et al.*, 2012)' should be changed to 'nonadecane-urea' (Toudic *et al.*, 2011)'.

(ii) In the reference list, 'Mariette, C., Huard, M., Rabiller, P., Nichols, S. M. E., Colivet, C., Janssen, T., Alquist, K. E., Hollingsworth, M. D. & Toudic, B. (2012). *J. Chem. Phys.* **136**, 104505' should be changed to 'Toudic, B., Rabiller, P., Bourgeois, L., Huard, M., Ecolivet, C., McIntyre, G. J., Bourges, P., Brezewski, T. & Janssen, T. (2011). *Europhys. Lett.* **93**, 16003'.

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- Janssen, T. (2012). *Acta Cryst.* **A68**, 667–674.
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Historians often have debates about the beginning and end of a certain era. The same discussion can be had about the history of aperiodic crystals. There are reasons to claim that in 2012 one may celebrate the 50th anniversary of this field. A short description is given of the development of this branch of crystallography. It is argued that the most important point in its history is the discovery of quasicrystals, which has been recognized by awarding the Nobel Prize in Chemistry 2011 to Dan Shechtman.

1. Introduction

A hundred years ago modern crystallography started with the work of von Laue, for which he received the Nobel Prize in Physics in 1914 'for his discovery of the diffraction of X-rays by crystals'. Since that time it was the common opinion that the ground state of matter at low temperature is crystalline, having lattice periodicity. It has taken more than 50 years to discover that this is not always the case.

It is open to discussion when the first doubts about this paradigm were raised. Magnetic spin waves became known, and it was in 1960 that these were described as waves with a period different from that of the underlying lattice (Herpin *et al.*, 1960). However, there was no indication that the observed magnetic spin wave had an influence on the crystallographic structure. Therefore, one could argue that the structure and the magnetism were two independent properties.

A few years later, the situation changed when displacive waves were observed which destroyed the lattice periodicity of the crystal. Nevertheless, the structure, later called incommensurate modulated structure, showed long-range order. Such phases were found to appear in various ways and they became a subject of research in the 1960s and 1970s.

Still later, other perfectly ordered structures without lattice periodicity were found. In the following I shall give a brief description of the development of this field. Of course, this is quite a brief history of the field, with a personal view. For further reading, see *e.g.* Yamamoto (1996) and Janssen *et al.* (2007).

2. Incommensurate modulated phases

In 1963 a study appeared of the structure of NaNO_2 (Yamada *et al.*, 1963). At 437 K it shows a ferroelectric phase transition. In fact, there is a temperature range of width 1.5 K where the ferroelectric phase is modulated with a period that does not fit to the average structure. In the first publications this structure was described in terms of micro-domains. A year later, de Wolff *et al.* found satellite peaks in the diffraction pattern of

anhydrous Na_2CO_3 at room temperature (Brouns *et al.*, 1964). This could be interpreted as a periodic modulation of a basic structure such that the period of the modulation is not a period of the basic structure. Here, for the first time, it was shown that crystals are not necessarily lattice periodic. Later it was found that this incommensurate phase is an intermediate phase. Above 757 K the crystal is periodic and has hexagonal symmetry (α phase). Between 628 and 757 K it becomes monoclinic (β phase), and below 628 K it is incommensurate (γ phase). Then, at 170 K the modulation period 'locks in': it becomes commensurate (δ phase). This is quite a common situation, that the incommensurate phase is an intermediate phase between two lattice periodic phases, but there are also compounds that remain incommensurate down to the lowest temperatures.

Because of the incommensurate periodicities, the diffraction pattern consists of sharp spots on positions which need more than three integer indices. The electron density then is what is called a quasiperiodic function in mathematics. However, according to the mathematical definition, periodic functions are also quasiperiodic. That is the reason why one uses the word incommensurate to indicate that the structure does not have lattice periodicity.

Soon after many other compounds with incommensurate modulation were found. Two other systems studied in the beginning were thiourea and K_2SeO_4 . NaNO_2 could also be described as a system with incommensurate modulation. In this case the modulation is not a displacive wave. The NO_2 triangles point either to the left or to the right along the c direction. In this case the probability of finding a triangle pointing to the right is a periodic function with periodicity incommensurate with the basic structure. This is a case of occupation modulation. Incommensurate modulated crystals turned out to be not rare at all. A substantial portion of the earth's crust consists of incommensurate modulated minerals.

de Wolff found an elegant way to describe the aperiodic crystals as a restriction of a lattice periodic structure in four dimensions to the three-dimensional physical space. The fourth dimension then is the origin of the modulation wave

with respect to the basic structure. The four-dimensional periodic structure can consequently be described using a four-dimensional space group (de Wolff, 1974). Such four-dimensional space groups had been studied by Janner and Janssen as symmetry groups in space and time of electrodynamic systems. Formally these groups were identical with the groups needed for incommensurate modulated crystals (de Wolff *et al.*, 1981). Together, and with corrections by A. Yamamoto, the first list of all ‘3 + 1 superspace groups’ was produced, where 3 is the dimension of physical space and 1 the dimension of the additional ‘internal space’, time is for space–time groups and phase of the modulation is for modulated phases.

If a lattice periodic structure in four dimensions is intersected by a three-dimensional subspace, the projection of its Fourier transform is precisely the Fourier transform of the obtained three-dimensional intersection. The intersection is quasiperiodic and incommensurate if the intersecting subspace does not contain three independent translation vectors which leave the four-dimensional structure invariant. This procedure may be generalized to arbitrary dimensions. Suppose that $\rho(\mathbf{r})$ is the intersection of a lattice periodic function in n dimensions and the three-dimensional physical space. Then

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}} \hat{\rho}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}), \quad \text{with } \mathbf{k} = \sum_{i=1}^n h_i \mathbf{a}_i^*. \quad (1)$$

The minimum number of basis vectors needed to index the diffraction peaks with integers is called the *rank* of the structure, and this is equal to the *dimension* of the higher-dimensional space in which the lattice periodic structure is defined. The n basis vectors \mathbf{a}_i^* are the projection of the n basis vectors of the reciprocal lattice corresponding to the n -dimensional lattice periodic structure. On the other hand, the Fourier component in the point \mathbf{k} has the same value as the Fourier component in the n -dimensional vector of which \mathbf{k} is the projection. This determines the lattice periodic structure in n dimensions, which has as symmetry group an n -dimensional space group, the superspace group. If R is a rotation (or, more generally, an orthogonal transformation) leaving the Fourier transform in three dimensions invariant, it can be written as an n -dimensional integer matrix, on the basis \mathbf{a}_i^* . All the operations R form a finite group corresponding to an orthogonal group in n dimensions, the point group of the superspace group. For modulated phases it has the additional property that the R 's leave the lattice of main reflections invariant. For that reason the point group must be one of the crystallographic point groups in three dimensions. Of course, one does not measure the Fourier transform, but only its absolute value. Therefore, we still have a phase problem. Anyway, from the symmetry and the systematic extinctions, one gets information about the n -dimensional structure and its superspace group.

In principle, the structure determination starts with the basic structure. Considering the main reflections only, these determine a lattice periodic structure, the average structure. This is the density distribution obtained as the inverse Fourier

transform of the Fourier components of the main reflections. These are usually distributions in the unit cell from which one may obtain the atomic positions of the basis structure. The second step then is the determination of the functions $u_j(\mathbf{n}, \mathbf{r}_j)$ and $p_j(\mathbf{n}, \mathbf{r}_j)$ of the displacive and occupational modulation, respectively.

Since the first discovery, hundreds of incommensurate phases have been found and their structure has been determined. And they are by no means rare. Many minerals have been found to be incommensurately modulated. Lists of higher-dimensional superspace groups have been determined (de Wolff *et al.*, 1981; Stokes *et al.*, 2011) and computer programs have been developed to help in the structure determination. The two main examples are *JANA* by V. Petriček *et al.* and *REMOS* by A. Yamamoto. Lists of the corresponding groups for the action in reciprocal space, where translations in internal space appear as phase factors, were published by Mermin *et al.* (Rabson & Mermin, 1991; Mermin, 1992). The modulation functions have to be parametrized in order to make a determination possible. In principle, the problem is much more complex than for lattice periodic structures, where only a finite number of atomic positions have to be determined.

3. Incommensurate composites

In 1978 a new class of aperiodic crystals was discovered. The first example was ‘fool’s gold’: $\text{Hg}_{3-\delta}\text{AsF}_6$. It consists of a ‘host lattice’, consisting of AsF_6 octahedra, in the channels of which chains of mercury are positioned, in two different directions. Because the repeat distance of the mercury atoms is incommensurate with the lattice constant of the host, the system is not periodic (Pouget *et al.*, 1978). This class is called that of incommensurate composites, because the materials consist of a number of mutually incommensurate subsystems.

The subsystems have a lattice periodic basic structure, but this is modulated because of the interaction with the other subsystems. If there are m subsystems, there are at most $3m$ independent basis vectors for the whole basic structure. Generally, these $3m$ vectors may be expressed in terms of a smaller number (n) using integer indices. For example, the mercury chain compound ($m = 3$) can be indexed using four indices. The basis vectors are those of the AsF_6 subsystem plus the additional vector $(3 - \delta)\mathbf{a}^* + (1 - \delta)\mathbf{b}^*$. In general, the j th basis vector of the ν th subsystem can be expressed in terms of n new reciprocal vectors $\mathbf{a}_j^{*\nu}$ as follows:

$$\mathbf{a}_j^{*\nu} = \sum_{i=1}^n Z_{ji}^{\nu} \mathbf{a}_i^* \quad (\text{integers } Z_{ji}^{\nu}). \quad (2)$$

Then the same procedure can be used as before for the modulated phases to determine an n -dimensional lattice periodic structure which gives the real structure as an intersection with the three-dimensional physical space (Janner & Janssen, 1980*a,b*). The structure and the superspace group may be determined in the same way as before. There is one difference. Because in this case there is no obvious basic structure, and symmetry operations may map one subsystem

onto another, the 'crystallographic condition' (the requirement that the point group should be isomorphic to a three-dimensional crystallographic point group) does no longer hold.

A simple model system may show this. Consider a layered structure with identical square layers perpendicular to the c axis, the even layers having translations along the a and b axes, and the odd layers turned over 45° . Then one subsystem is tetragonal with reciprocal basis vectors \mathbf{a}_1^* , \mathbf{b}_1^* and \mathbf{c}^* , and the other one with \mathbf{a}_2^* , \mathbf{b}_2^* and \mathbf{c}^* , such that \mathbf{a}_2^* (respectively, \mathbf{b}_2^*) is \mathbf{a}_1^* (respectively, \mathbf{b}_1^*) turned over 45° . Among these, five are independent (if one limits oneself to integers). Therefore, $n = 5$ and the point group has an eightfold rotation. However, such a system has never been observed.

The simple model above is an example of an important class of incommensurate composites, the incommensurate layer or misfit structures. For many examples of such systems the structure has been determined (van Smaalen, 1991).

Another interesting subclass of incommensurate composites is that of urea-alkanes. And finally, one can use the same approach for monolayers on a substrate when these are mutually incommensurate.

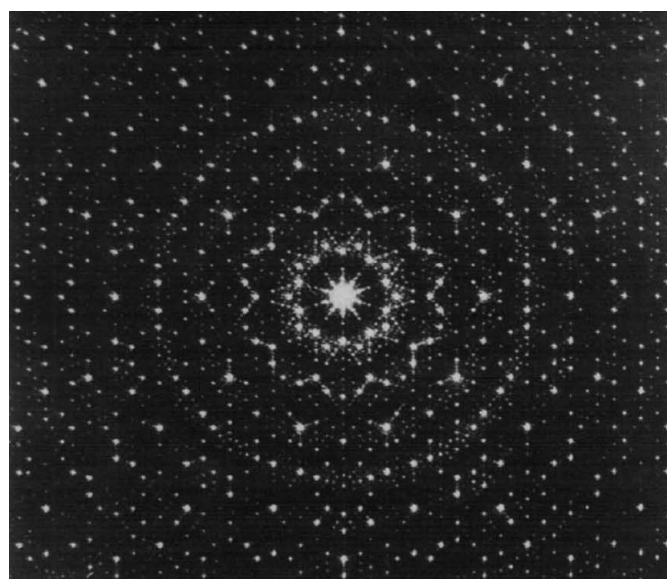
Structure determination of incommensurate composites is harder than for modulated structures, because the subsystems are, in principle, equivalent. Consider a simple example with two subsystems in parallel chains, the first with a basic structure with lattice vectors \mathbf{a} , \mathbf{b} and \mathbf{c} , the second with \mathbf{a} , \mathbf{b} and \mathbf{c}/γ . These subsystems are modulated because of the interaction between the subsystems. Then the general diffraction vector is given by $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + \ell\mathbf{c}^* + m\mathbf{q}$ with $\mathbf{q} = \gamma\mathbf{c}^*$. One may distinguish common peaks ($\ell = m = 0$), host peaks ($m = 0, \ell \neq 0$), guest peaks ($\ell = 0, m \neq 0$) and summation peaks ($m \neq 0, \ell \neq 0$). The basic positions and modulation functions have to be determined simultaneously because the modulation peaks of one subsystem coincide with the main peaks of another. The number of precise structure determinations of incommensurate composites is relatively small (Yamamoto, 1993).

4. Tilings

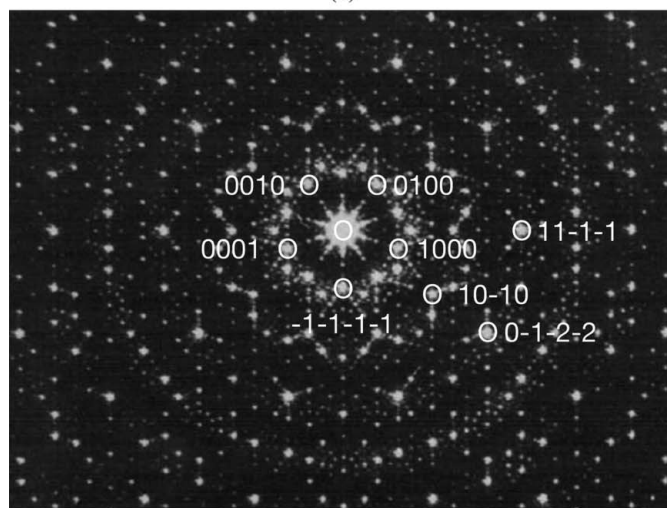
Not only in crystallography was there an intense activity on ordered structures without lattice periodicity, in mathematics one had the following 'tiling' problem. Given a finite set of tiles, can one cover the plane with copies of these tiles such that there are no gaps and no overlaps? Are there sets that force the tiling to be aperiodic? There were answers for specific sets with many different tiles. The problem of reducing the size of the set was solved by R. Penrose, who constructed a set of two tiles together with rules to put the tiles together that produced such an aperiodic tiling, later called the Penrose tiling. The tiles are rhombs, one with an angle of 36° and one with an angle of 72° . A variant of this tiling can be made with two tiles with the shape of a 'dart' and a 'kite'. (The two can easily be transformed into each other.) Many interesting properties of these tilings were proved. An algorithm to construct such a tiling was given by N. G. de Bruijn (de Bruijn,

1981). A very interesting review appeared in the January 1977 issue of *Scientific American*, written by Martin Gardner (Gardner, 1977). Many crystallographers have had the idea that there could be crystals with a comparable structure. The tilings (there are uncountably many of them) are quasi-periodic. This led A. Mackay to determine experimentally the diffraction pattern of such a tiling (Mackay, 1982). This pattern shows tenfold symmetry. So, here was an example of a perfectly ordered aperiodic structure which has a rotational symmetry that cannot occur in periodic crystals.

It is easy to index the diffraction pattern shown by Mackay (Fig. 1). One needs four integer indices. The four basis vectors are mapped on positions with integer indices under a 72° rotation. This gives a four-dimensional matrix, which on an orthogonal basis combines a two-dimensional rotation over 72° with another two-dimensional rotation over 144° . In direct space this rotation leaves a four-dimensional lattice invariant



(a)



(b)

Figure 1
(a) Diffraction pattern of a Penrose tiling (Mackay, 1982). (b) Indexing of the pattern.

for which the unit cell may be chosen. The four basis vectors have a metric tensor given by

$$g_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j = a^2 \begin{pmatrix} 2 & -0.5 & -0.5 & -0.5 \\ -0.5 & 2 & -0.5 & -0.5 \\ -0.5 & -0.5 & 2 & -0.5 \\ -0.5 & -0.5 & -0.5 & 2 \end{pmatrix}, \quad i, j = 1, \dots, 4. \quad (3)$$

For example, one may choose four four-dimensional vectors

$$[\cos(2\pi n/5), \sin(2\pi n/5), \cos(4\pi n/5), \sin(4\pi n/5)], \quad (n = 1, \dots, 4). \quad (4)$$

However, it is less simple to determine the objects in the unit cell (the ‘atomic surfaces’) which give the vertices of the tiling by intersecting with the two-dimensional ‘physical’ space. On the basis of the construction given by de Bruijn it is possible to show that there are four objects per unit cell, two-dimensional pentagons in 4-space. Contrary to most modulated structures, the higher-dimensional objects are not connected.

The tiling problem is closely related to the mathematical topic of Meyer sets or model sets. The method used to construct these special sets in a plane or a space by projection from a higher-dimensional set of points is called the cut-and-project method (for a description see Baake & Höffe, 2000). This method is equivalent with the construction of aperiodic tilings by intersection of the space with a periodic array of flat atomic surfaces.

5. Quasicrystals

For the scientists working in the field of incommensurate crystals, it was a big and pleasant surprise when on 8 April 1982 Dan Shechtman discovered quasicrystals (Shechtman *et al.*, 1984). The story has been told several times. The referees of the journal to which the paper was sent clearly did not belong to the community around aperiodic crystals, as a consequence of which publication of the paper took time. The small AlMn quasicrystals of Shechtman showed not only fivefold (or tenfold) symmetry but even icosahedral symmetry.

This asked for a generalization of the Penrose tiling to three dimensions, and this was given in Duneau & Katz (1985) and Kramer & Neri (1984). The atomic surfaces in this case are triacontahedra attached to the vertices of a six-dimensional lattice. However, for the quasicrystals the question ‘where are the atoms?’ could not be answered for quite some time. One of the problems was the quality and size of the samples. But within a couple of years much better and larger crystals could be grown. A new class of quasicrystals was found which were periodic in one direction and aperiodic in the other two: the decagonal-phase quasicrystals. Better crystals could be grown with a ternary structure (*e.g.* AlMnPd, AlCuFe), and in 2000 another class of binary quasicrystals and icosahedral symmetry was found (YbCd) (Tsai *et al.*, 2000).

Immediately after the referees were convinced and the paper had been published, a huge research activity on these materials started. Quasicrystals got much more attention than the earlier aperiodic crystals. There are several reasons for that. The incommensurate modulated and composite structures have subsystems with lattice periodic basic structure. In some sense the physical properties may often be derived from those of the subsystems. That is not fully true, because the change from unmodulated to modulated structure is often discontinuous, and for composites the subsystems could not exist as such without the presence of the other subsystems. Also the character of physical properties, like the behaviour of electrons and phonons, shows the same difference with lattice periodic structures for incommensurate phases as for quasicrystals, but usually the difference is more pronounced in the latter.

The term ‘quasicrystal’ was coined by Levine & Steinhardt (1986) soon after the first publication by Shechtman *et al.* (1984). It is supposed to stand for ‘quasiperiodic crystal’, but this choice was perhaps questionable for two reasons. First, the mathematical definition, given by Bohl, is such that every periodic function is also quasiperiodic. This would mean that conventional lattice periodic crystals are also quasiperiodic. This was the reason for calling incommensurate modulated structures ‘incommensurate’ instead of ‘quasiperiodic’. The second point is that not all (aperiodic) quasiperiodic crystals are usually considered to be quasicrystals. For example, not everyone will call γ -Na₂CO₃ a quasicrystal. The non-crystallographic symmetry (*i.e.* non-crystallographic in three dimensions, such as fivefold and the like) is considered by many as essential. However, as seen above, such non-crystallographic symmetry is in principle allowed in incommensurate composites, and an icosahedral quasicrystal may lose its non-crystallographic symmetry by a small strain of the six-dimensional structure, leading to an aperiodic structure with tetrahedral symmetry. There is still not a consensus about the definition of ‘quasicrystal’. However, only the limits of the notion are disputed. For example, everybody will agree that icosahedral AlMnPd is a quasicrystal. An unambiguous notion is the general term ‘aperiodic crystal’, which has sharp diffraction spots spanning the whole space, but is not lattice periodic.

This uncertainty about the classification applies also to mesoscopic structures with non-crystallographic symmetries. This is a rather recent development. Non-crystallographic symmetries have been found in liquid crystals and polymer systems. However, these structures with non-crystallographic symmetry are mesoscopic, their diffraction spots are fairly sharp, but probably not delta peaks, even in an ideal situation.

The general approach to quasiperiodic structures may also be applied to quasicrystals (Janssen, 1986). Choosing a basis for the diffraction pattern, one may lift this to a basis of a reciprocal lattice in n -dimensional space. From this a basis for a direct lattice can be constructed. The superspace group is, if one disregards the phase problem, determined by the symmetry of the pattern and the systematic extinctions. The parametrization is a much more complicated problem than for

the incommensurate phases. One has to determine the position and the shape of the atomic surfaces, and these are not easy to parametrize. Superspace groups for quasicrystals are listed in Janssen (1988), Rabson & Mermin (1991), and Mermin (1992). Sometimes an approximant may help, if it exists. The other way is to search for the electron-density map. With the help of modern developments, like the maximum-entropy method or the charge-flipping technique, one may find an approximate solution. Several models have been developed for icosahedral and decagonal (Steurer, 2004) quasicrystals. The first accurate structure determination of an icosahedral phase was given for the ‘Tsai-type’ CdYb quasicrystal (Takakura *et al.*, 2007).

6. Incommensurate magnetic structures

The earliest aperiodic crystals were incommensurate magnetic structures. For crystallography these were less relevant as long as the interaction between the lattice structure and the magnetic structure could not be measured. Later on, this spin–lattice interaction could be observed, which leads us back to the consideration of these structures. Generally, in the magnetic state the non-uniform magnetic structure has periodicity (Fig. 2), and by the interaction the nuclear structure becomes modulated. Then, for a simple situation, spins and atomic positions are given by

$$\mathbf{S}(\mathbf{r}) = \sum_{\mathbf{q}} \hat{\mathbf{S}}(\mathbf{q}) \exp[i\mathbf{q} \cdot (\mathbf{r})] \quad (5)$$

$$\mathbf{r}(\mathbf{n}, j) = \mathbf{n} + \mathbf{r}_j + \sum_{\mathbf{q}} \hat{\mathbf{u}}(\mathbf{q}) \exp[i\mathbf{q} \cdot (\mathbf{n} + \mathbf{r}_j)], \quad (6)$$

where \mathbf{q} is incommensurate with the reciprocal lattice of the lattice periodic structure with nodes \mathbf{n} and positions \mathbf{r}_j in the unit cell. Both structures may be embedded in a higher-dimensional superspace. Then, one gets $\mathbf{S}(\mathbf{r}, \mathbf{r}_j)$ and $\mathbf{u}_j(\mathbf{n}, \mathbf{r}_j)$.

The action of a superspace-group element g may be combined with the time reversal θ . Under the action of an element $g = \{(R, R_l), (\mathbf{v}, \mathbf{v}_l)\}$ the spin arrangement changes to

$$T_g \mathbf{S}(\mathbf{r}, \mathbf{r}_l) = \det(R) \sum_{\mathbf{q}} R \mathbf{S}(R^{-1} \mathbf{q}) \exp[i\mathbf{q} \cdot (\mathbf{r} - \mathbf{v}) + i\mathbf{q}_l \cdot (\mathbf{r}_l - \mathbf{v}_l)] \quad (7)$$

and the combination $T_g \theta$ gives the same expression with an additional minus sign. Furthermore,

$$T_g \mathbf{u}(\mathbf{r}, \mathbf{r}_l) = \sum_{\mathbf{q}} R \mathbf{u}(R^{-1} \mathbf{q}) \exp[i\mathbf{q} \cdot (\mathbf{r} - \mathbf{v}) + i\mathbf{q}_l \cdot (\mathbf{r}_l - \mathbf{v}_l)] \quad (8)$$

and $T_g \theta$ act in the same way. Then the symmetry of the nuclear structure is the superspace group leaving the nuclear structure invariant, and the magnetic superspace group consists of all

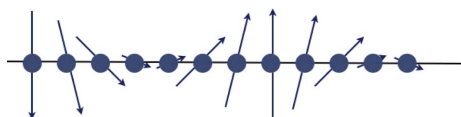


Figure 2
Incommensurate spiral spin wave.

elements leaving both the nuclear structure and the spin function invariant (Janner & Janssen, 1980a). Above the Curie temperature these two groups coincide. In particular, in systems with rare earth elements complicated spin structures and phase transitions may occur (see *e.g.* Schobinger-Papamantellos *et al.*, 2010). Recently, a number of magnetic, in particular multiferroic, compounds have been investigated with the superspace approach (Perez-Mato *et al.*, 2012). In multiferroics, the interaction of the magnetic and nuclear structures is essential. So, an incommensurate magnetic structure leads to an incommensurate nuclear structure.

Although some quasicrystals contain magnetic atoms (Co for example), long-range magnetic order has not yet been found there. However, when such a compound exists it should be described by a magnetic superspace group. In this way, incommensurate (or quasicrystalline) magnetic structures have been incorporated into the class of aperiodic crystals. That is reason to argue that this field has reached its 50th anniversary. Half the age of the field of X-ray crystallography, but still respectable.

7. Phase transitions

Aperiodic crystals are found within bounded regions of phase space. For these crystals one may distinguish two types of phase transitions.

The first is a transition where the dimension of the embedding space (which is equal to the rank of the Fourier module) changes. An example is the transition from a lattice periodic structure in three dimensions to an incommensurate modulated structure of rank 4. A frequent mechanism is that a phonon mode with incommensurate wavevector becomes unstable (a soft mode). Very often, the modulation wavevector changes with temperature and becomes commensurate at the ‘lock-in’ transition, a first-order transition from rank-4 incommensurate to rank-3 commensurate structure.

In incommensurate composites, more situations may occur. Often, one of the subsystems is liquid-like at high temperature (and the rank is 3) and shows a phase-ordering transition to a higher-rank structure. This is also a transition where the rank changes. Then the structure of one of the subsystems may change, or the relation between subsystems may become different. An example of this situation has been observed in *n*-heptane-urea (Mariette *et al.*, 2012), where in the phase diagram one may distinguish crystals of rank 3, 4 and 5 (Fig. 3).

In quasicrystals modulations have been reported. In an icosahedral phase with an icosahedral incommensurate modulation this would mean a transition from a rank-6 to a rank-12 quasicrystal.

The second type of phase transitions is that where the dimension of the superspace does not change. Among these are the centring transitions. Transitions from a primitive icosahedral to a face-centred icosahedral structure have been found. The rank here remains 6, and the point group remains the group $5\bar{3}m(5^2\bar{3}m)$, which means that the physical space transforms with the three-dimensional icosahedral (non-crystallographic) point group $5\bar{3}m$ and the perpendicular (or

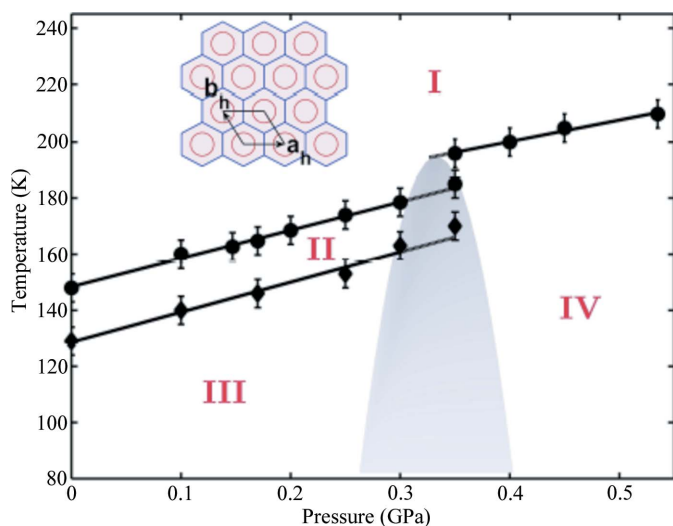


Figure 3
Phase diagram of *n*-heptane-urea (Mariette *et al.*, 2012).

internal) space with the equivalent group $5^2\bar{3}m$, such that the 72° rotation in physical space is combined with the 144° rotation in perpendicular space.

In aperiodic crystal structures one finds both first- and second-order transitions. The latter can be described using the Landau theory of phase transitions, which involves the change of symmetry from a group to a subgroup. For incommensurate crystals the n -dimensional superspace group is not a subgroup of the three-dimensional space group of the unmodulated structure. Therefore, the theory must be slightly reformulated, either by extending the space group to superspace or by considering space-dependent order parameters. Lock-in transitions and crystal–quasicrystal transitions are usually of first order.

8. Physical properties of aperiodic crystals

The discovery of aperiodic crystals, and in particular of quasicrystals, has led to interesting problems in various fields, such as crystallography, physics, chemistry and mathematics. In crystallography, the IUCr gave a new definition of ‘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. As an extension, the latter term will also include those crystals in which three-dimensional periodicity is too weak to describe significant correlations in the atomic configuration, but which can be properly described by crystallographic methods developed for actual aperiodic crystals.’ Under this definition aperiodic crystals are crystals.

In conventional rank-3 crystals physical states (electrons and phonons) are characterized by irreducible representations of the symmetry group. If the latter is the lattice translation group, states are characterized by a vector from the Brillouin zone (BZ). Aperiodic crystals only have a BZ of volume zero, unless one considers the lattice periodic structure in superspace. However, this has not yet been exploited in a conve-

nient way. Just as in rank-3 crystals, where the BZ is the region of vectors closer to the origin than to any other reciprocal-lattice point, for aperiodic crystals one has introduced a pseudo-Brillouin zone, the region closer to the origin than to any ‘strong’ diffraction vector. This may be practical, but it is arbitrary to a certain point. This means that there is not yet a rigorous classification scheme for states in aperiodic crystals.

For quasiperiodic functions and for certain classes of tilings, it has been shown that the diffraction pattern contains delta peaks. An open question still is ‘for what systems does this hold in general?’. Here, mathematicians only have partial answers (Baake *et al.*, 2003).

Electron and phonon states in aperiodic crystals have, till now, been treated in a practical way. One uses approximants, lattice periodic structures which resemble aperiodic crystals. For tiling models this can be done in a systematic way if one approaches an incommensurate value in perpendicular space by truncation of its continued fraction expansion. Using rather small approximants one gets a satisfying agreement between calculations and experiments (de Boissieu *et al.*, 2007).

However, the fundamental problem remains. One may solve the problem in superspace. Using simple models one may embed the electron or vibration states in superspace. This is feasible for low energies, but for higher energy the states no longer have a smooth character. In one-dimensional models one finds a fractal structure of the wavefunctions which means that the calculation becomes extremely complicated (Fig. 4).

All classes of aperiodic crystals share the property that the projection of the translation lattice points in superspace on internal space is a dense set. The structure of the crystal in a physical space through each of these points is the same, up to a translation. Consequently, they have the same energy. This means that small fluctuations along the internal space (phason fluctuations) have a low energy. In modulated phases these correspond to long-wavelength excitations (phasons) with a linear dispersion if the modulation function is continuous. For incommensurate composites these fluctuations correspond to a mutual motion of the subsystems. For quasicrystals the phason fluctuations may have a local or a collective character. In all cases these dynamic phasons are overdamped. For quasicrystals, this is clear, because the phasons imply finite size jumps of atoms. For composites and modulated phases with a smooth modulation function, the damping is not yet completely understood.

The stabilization of an incommensurate spin wave may be explained in simple models with first- and second-neighbour interaction, as shown by Elliott (1961) and in the ANNNI (Axial Next Nearest Neighbour Interaction) model (Selke, 1988). By adding a spin–lattice coupling this may lead to a deformation of the lattice as well (Janssen, 1991). Analogous models for the appearance of an incommensurate modulated phase have been developed as well. An example is the DIFFFOUR (Discrete Frustrated Φ^4) model (Janssen & Tjon, 1982).

For quasicrystals, tiling models were soon developed. Choosing atomic positions and interatomic interactions appropriately, one may construct stable quasicrystal struc-

tures. These were first based on the calculation of the energy and a proof that this energy is a stable minimum for the quasicrystal configuration. Later it was pointed out that a slight shift of the atomic surfaces in superspace creates phason flips, and that this could lead to a stabilization of the quasicrystal configuration by an entropy term associated with the phason flips. Phason flips lead to a random tiling model for quasicrystals (Henley, 1991) also with sharp diffraction peaks, next to a diffuse part (Baake & Höffe, 2000). Then the discussion focused on the question of whether there are

quasicrystals at low temperature. The situation is not different from that for incommensurate modulated phases. Very often, a modulated phase is an intermediate phase between a high-temperature lattice periodic structure and a low-temperature superstructure. Near the lowest phase transition the modulation often becomes discontinuous, in models. Then the structure in superspace is similar to that for quasicrystals and entropy may become important. However, there are also many incommensurate phases which remain aperiodic down to the lowest temperature. This shows that both energy and entropy play a role in the stabilization. Perhaps the question ‘energy or entropy?’ is not relevant, in general.

The special physical properties of aperiodic crystals could, in principle, be exploited for applications. Until now their number has been relatively small, but there are many potential applications (see *e.g.* Dubois, 2005).

9. Summary

In the last 50 years aperiodic crystals, to which belong incommensurate phases, incommensurate spin structures and quasicrystals, have become an important field of research. This is especially so since the discovery of quasicrystals, 30 years ago. Even quantitatively the topic is important, because there are aperiodic crystals everywhere, not only in the laboratory, but also in nature. The new materials required a new definition of the notion of a crystal. Moreover, the standard techniques for studying physical properties were, generally, only valid for lattice periodic materials. New techniques had to be developed. To mention a few, there is no longer a Brillouin zone, new methods for determining the structure had to be developed and the usual ways to calculate electron bands and lattice vibrations did not work for these materials. This has led to interesting developments in other domains of science as well.

Insight into the structure and properties of aperiodic crystals has grown enormously, but there are still fundamental questions to be solved. Some of them are: what is the character and spectrum of electrons in aperiodic crystals?; how can one characterize states by representations of the symmetry group?; and what is the fundamental reason for the stability of quasicrystals?

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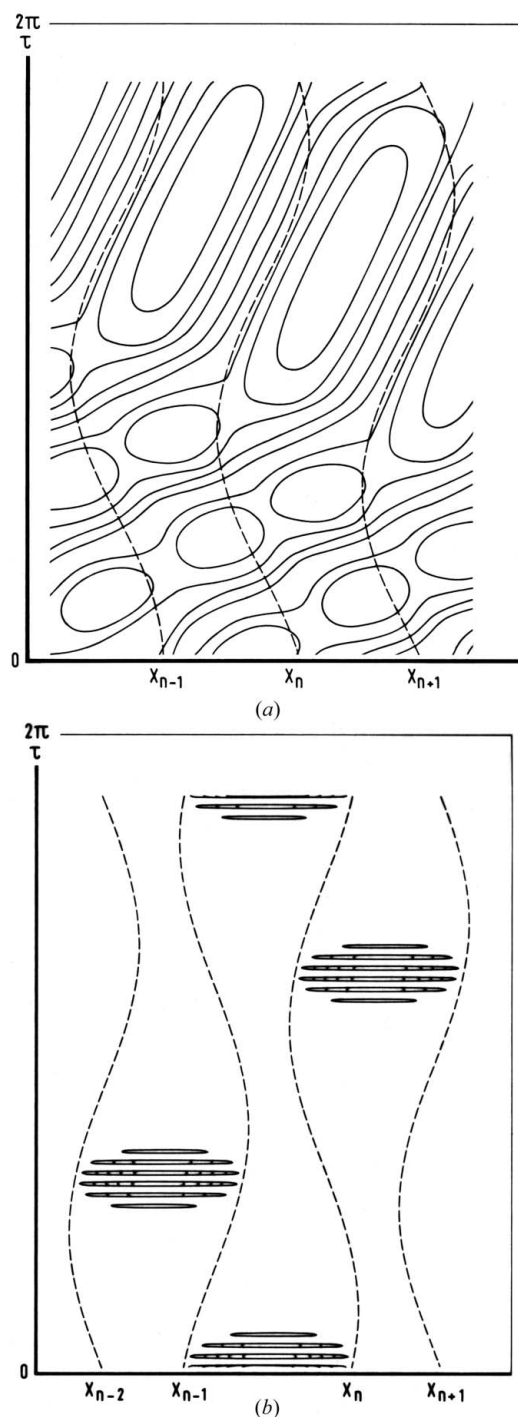


Figure 4
 Electron density in a modulated chain. (a) Low energy, (b) high energy.

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