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Quasicrystals / Quasicristaux

Decagonal quasicrystals – What has been achieved?



Quasicristaux décagonaux – Ce qui a été réalisé

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ABSTRACT

Where are we now, 25 years after the discovery of the first stable decagonal quasicrystal (DQC)? In this critical review, the status of research into these axial quasicrystals, which are quasiperiodic in two dimensions and periodic along the third, is discussed, and some of the open questions are addressed. We conclude that the structures of DQC are essentially known now, a few of them even as a function of temperature. Some hypotheses concerning DQC formation, growth and stability have still to be confirmed.

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R É S U M É

Cet article dresse un état des lieux de ce qui a été réalisé 25 ans après la découverte du premier quasicristal décagonal. Quasipériodiques selon deux dimensions et périodiques selon la troisième, ces quasicristaux posent encore de nombreuses questions, qui seront discutées ici. On verra que les structures atomiques de ces édifices sont globalement maintenant bien connues, y compris, pour certaines, quant à leur comportement en température. Certaines hypothèses concernant la formation, la croissance et la stabilité de ces phases méritent encore d'être confirmées.

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1. Introduction

The first quasicrystals (QC), discovered in the system Al–Mn, were metastable [1–3], and could only be obtained by rapid solidification techniques such as melt spinning or splat cooling. Since the correlation lengths of their structures was on the scale of a few hundred angstroms only, it was all but clear whether quasiperiodic structures could reach a similar degree of long-range order (*lro*) and perfection as periodic ones. However, at least the quasiperiodic-like short- and mid-range order (*sro* and *mro*) indicated by selected-area electron diffraction (SAED) patterns, could be experimentally corroborated by high-resolution electron microscopy (HRTEM) quite soon. Only in 1986, the first stable, but not perfect, icosahedral quasicrystal (IQC) could be identified in the system Al–Cu–Li [4]. It took two years more until the first stable DQC was found in the system Al–Co–Cu [5,6] and, shortly later, in the system Al–Co–Ni [7]. Subsequently, the growth of single quasicrystals big enough for quantitative single-crystal X-ray diffraction became possible, starting the almost never-ending story of quasicrystal structure analysis [8]. A detailed review of the achievements of the first twenty years of DQC structure analysis was published in 2004 [9]. Consequently, here we will focus on the progress made in the past decade as well as on the following important and still not fully answered open questions:

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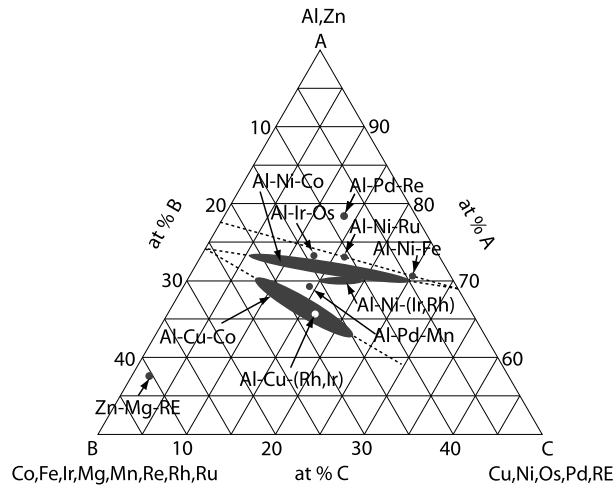


Fig. 1. Schematic representation of the compositional stability fields of DQC (adapted from [11]). Note the different ranges of the coordinates [at%]: $50 \leq A \leq 100$, $0 \leq B \leq 50$, $0 \leq C \leq 50$.

- (i) Do we know all about the structures of DQC what we want to know?
- (ii) Is there a fundamental difference in the factors leading to periodic complex intermetallics on the one hand and to quasicrystals on the other hand?
- (iii) How do quasicrystals grow, and how is the quasiperiodic *lro* achieved on atomic scale?¹
- (iv) What favors decagonal symmetry over all other theoretically possible noncrystallographic symmetries except the icosahedral one?
- (v) Energy vs. entropy – What stabilizes quasiperiodic order?

2. Do we know all about the structures of DQC what we want to know?

All stable DQC are ternary phases of the type A–B–C (Fig. 1). The majority (> 50 at%) element A corresponds to either Al or Zn. The concentration of the minority element C can be as low as ≈ 2 at% in case of C being one of the rare-earth elements (RE). In contrast to IQC, the binary DQC known so far are metastable and can only be obtained by rapid solidification methods. The stable DQC can all be assigned to either the Al–TM(1)–TM(2) (TM = transition metal) or the Zn–Mg–RE (RE = rare-earth metals) class. In the systems Al–Pd–Mn, Al–Pd–Re, and Zn–Mg–Dy, both stable DQC and IQC have been identified with slightly different stoichiometries. A further classification scheme of DQC uses the translation period along the tenfold axis, which is always a multiple n of stacks of two atomic layers. So far, stable DQC are known with $n = 1, 2, 3, 4$ (see Table 1).

There are two complimentary routes to get information on the structure of QC, imaging techniques and diffraction methods. Imaging approaches on atomic scale comprise the different electron-microscopic and surface analysis techniques. Surface sensitive techniques such as scanning tunneling microscopy (STM) can even give 3D structural information on a local scale, when applied to terraced surfaces. Electron microscopy, in particular if spherical aberration is corrected, can give local structural information with atomic resolution. However, this kind of information is averaged over the whole sample thickness of approximately 10 nm. Averaging is causing less structural ambiguities in the case of DQC than for IQC, if the projection direction is along the periodic axis.

In case of diffraction methods, single-crystal X-ray diffraction is most often used for quantitative QC structure analysis, while electron diffraction usually only serves for identifying DQC, and for deriving qualitative information about symmetry and metrics. Neutron scattering is rarely used due to the lack of large single crystals for most DQC. Powder diffraction methods cannot be employed for an unambiguous identification and characterization of QC; however, it can be quite helpful for deriving the stability ranges of QC.

While imaging methods can give direct information about the kind of *sro* and *mro* (for a recent review, see [34], for instance), diffraction methods can lead to erroneous results if not properly interpreted. What does that mean? First, Bragg reflections only contain information on the globally averaged structure. And once the Bragg-like intensity maxima are treated as true Bragg reflections and indexed on a quasiperiodic basis, the resulting structure will always be quasiperiodic. The only

¹ Roger Penrose, the creator of the quasiperiodic Penrose tiling, reminisces: "...in the late 1970s and early 80's I had often been asked to give lectures on these tiling patterns, and a question frequently posed to me after the lecture might be: "Does this not mean that there is a whole new area of crystallography opening up, with pentagonal and icosahedral symmetry allowed?" My normal response would be: "In principle yes; but how on earth would Nature do it?"... the *spontaneous* growth of large regions of such quasicrystalline five-fold symmetric substances had seemed to me virtually insurmountable" [10].

Table 1

Structure refinements of decagonal quasicrystals published so far. Listed are the number of reflections, N_{ref} , and of parameters, N_{par} , the reliability factor, R , the weighted reliability factor, wR , the year of publication and relevant references.

| Composition | N_{ref} | N_{par} | R | wR | Year | Ref. |
|--|------------------|------------------|-------|-------|------|------|
| <i>2-layer periodicity</i> | | | | | | |
| Al _{65.0} Co ₁₅ Cu ₂₀ | 259 | 11 | 0.167 | 0.098 | 1990 | [12] |
| Al _{65.0} Co _{14.6} Cu _{20.4} | 859 | 232 | 0.089 | 0.088 | 2012 | [13] |
| Al _{61.9} Rh _{19.6} Cu _{18.5} | 2174 | 245 | 0.079 | 0.086 | 2012 | [13] |
| Al _{57.6} Ir _{16.5} Cu _{25.9} | 2022 | 231 | 0.075 | 0.094 | 2012 | [13] |
| | | | | | | |
| Al ₇₀ Co ₂₀ Ni ₁₀ | 41 | 2 | 0.110 | – | 1990 | [14] |
| Al ₇₀ Co ₁₅ Ni ₁₅ | 253 | 21 | 0.091 | 0.078 | 1993 | [15] |
| Al ₇₀ Co ₁₅ Ni ₁₅ | 253 | 18 | 0.092 | 0.080 | 1995 | [16] |
| Al ₇₂ Co ₈ Ni ₂₀ | 449 | 103 | 0.063 | 0.045 | 2001 | [17] |
| Al _{70.6} Co _{6.7} Ni _{22.7} | 2767 | 750 | 0.170 | 0.060 | 2002 | [18] |
| Al _{70.6} Co _{6.7} Ni _{22.7} | 1544 | 181 | 0.103 | 0.051 | 2004 | [19] |
| Al _{70.6} Co _{6.7} Ni _{22.7} | 1544 | 105 | 0.159 | 0.086 | 2004 | [20] |
| Al ₇₂ Co ₈ Ni ₂₀ | 449 | 144 | 0.080 | 0.061 | 2008 | [21] |
| Al _{72.5} Co _{18.5} Ni _{9.0} | 957 | 112 | 0.156 | 0.123 | 2009 | [22] |
| Al _{72.5} Co _{18.5} Ni _{9.0} | 1222 | 250 | 0.186 | 0.039 | 2009 | [23] |
| Al _{70.6} Co _{6.7} Ni _{22.7} | 2767 | 106 | 0.123 | 0.062 | 2010 | [24] |
| Al _{72.0} Co _{12.4} Ni _{5.6} | 6843 | 691 | 0.348 | 0.060 | 2011 | [25] |
| <i>6-layer periodicity</i> | | | | | | |
| Al ₇₈ Mn ₂₂ (metastable) | 233 | 181 | 0.305 | 0.144 | 1991 | [26] |
| Al _{70.5} Mn _{16.5} Pd ₁₃ | 476 | 33 | 0.249 | 0.214 | 1994 | [27] |
| Al ₇₀ Mn ₁₇ Pd ₁₃ | 1311 | 72 | 0.270 | 0.186 | 1995 | [28] |
| Al _{70.5} Mn _{16.5} Pd ₁₃ | 476 | 97 | 0.084 | 0.067 | 1997 | [29] |
| Al ₇₀ Mn ₁₇ Pd ₁₃ | 1428 | 121 | 0.234 | 0.129 | 1997 | [30] |
| Al ₇₀ Mn ₁₇ Pd ₁₃ | 1428 | 217 | 0.167 | 0.119 | 1998 | [31] |
| <i>8-layer periodicity</i> | | | | | | |
| Al ₇₅ Os ₁₀ Pd ₁₅ | 1738 | 14 | – | 0.14 | 2002 | [32] |
| Al ₇₃ Os _{12.5} Ir _{14.5} | 5191 | 894 | 0.125 | – | 2007 | [33] |

signature for deviations of the actual structure from a quasiperiodic structure will be split positions, unphysical atomic displacement parameters and occupancy factors as well as rather large phasonic fluctuation factors. Consequently, it will always be beneficial if imaging methods and diffraction methods are both used in the course of a structure analysis.

The problem with QC structure analysis is that basically every structure between random tiling (covering) and perfect quasiperiodic tiling (covering) can be in thermodynamic equilibrium at a given temperature. In other words, disorder in a rhomb Penrose tiling, for instance, and in a periodic lattice has different consequences. In case of periodic structures disorder can only take place within the unit cells, while in case of quasiperiodic structures also the unit cells (tiles) can be disordered. Furthermore, in case of periodic structures only the unit cell content (*sro*) has to be determined, because the *lro* is defined by the lattice; in case of quasiperiodic structures, both *sro* and *lro* have to be determined and are prone to disorder. Since any kind of structural disorder gives rise to diffuse scattering, a full characterization of a QC includes both the analysis of Bragg reflection data as well as of diffuse diffraction intensities. Such an analysis will give the average structure as well as a distribution function of the deviations therefrom (disorder).

A list of all structure determinations of DQC published so far is given in Table 1. Their quality differs strongly; however, even the poorest analyses reflect fundamental structural features. All these structure analyses are based on X-ray single-crystal diffraction data. Structure analyses of Zn–Mg-based DQC are in progress [35]. The results of high-resolution electron-microscopic studies of DQC are summarized in another comprehensive paper published recently [36]. In summary, one can conclude that the essential features of DQC are known now, both the structure of the clusters as well as the arrangements of the clusters. More detailed structural information will be hardly available and will not be needed for understanding formation, growth, and stability of DQC.

All structures of the DQC known so far can be described by coverings based on a set of columnar clusters, which all are quite similar to each other. The underlying tilings resemble either rhomb or pentagon Penrose tilings, hexagon–boat–star (HBS) tilings or Masakova tilings [38] that are based on decagonal occupation domains (atomic surfaces). In the following, such a cluster structure will be illustrated on the example of decagonal Al–Co–Cu (Figs. 2 and 3). Its inner atomic arrangement can be described as a column of apex-sharing pentagonal bipyramids of Al atoms, with the apical Al atoms pentagonally coordinated by TM (transition element) atoms. This innermost columnar cluster shell can also be described as a cylindrically wound-up hexagonal close-packed (*hcp*) layer of Al and TM atoms. The outer columnar cluster shell can be characterized in the same way.² Both shells are linked by Al atoms. The clusters are arranged in such a way that puckered atomic layers are formed running through the structure-like lattice planes in a periodic crystal structure (Fig. 3).

² The description as cylindrically wound-up *hcp* layer applies to any structure created by the iterative action of an $N_{N/2}$ screw axis (with $N > 4$ and an even number) on an atom.

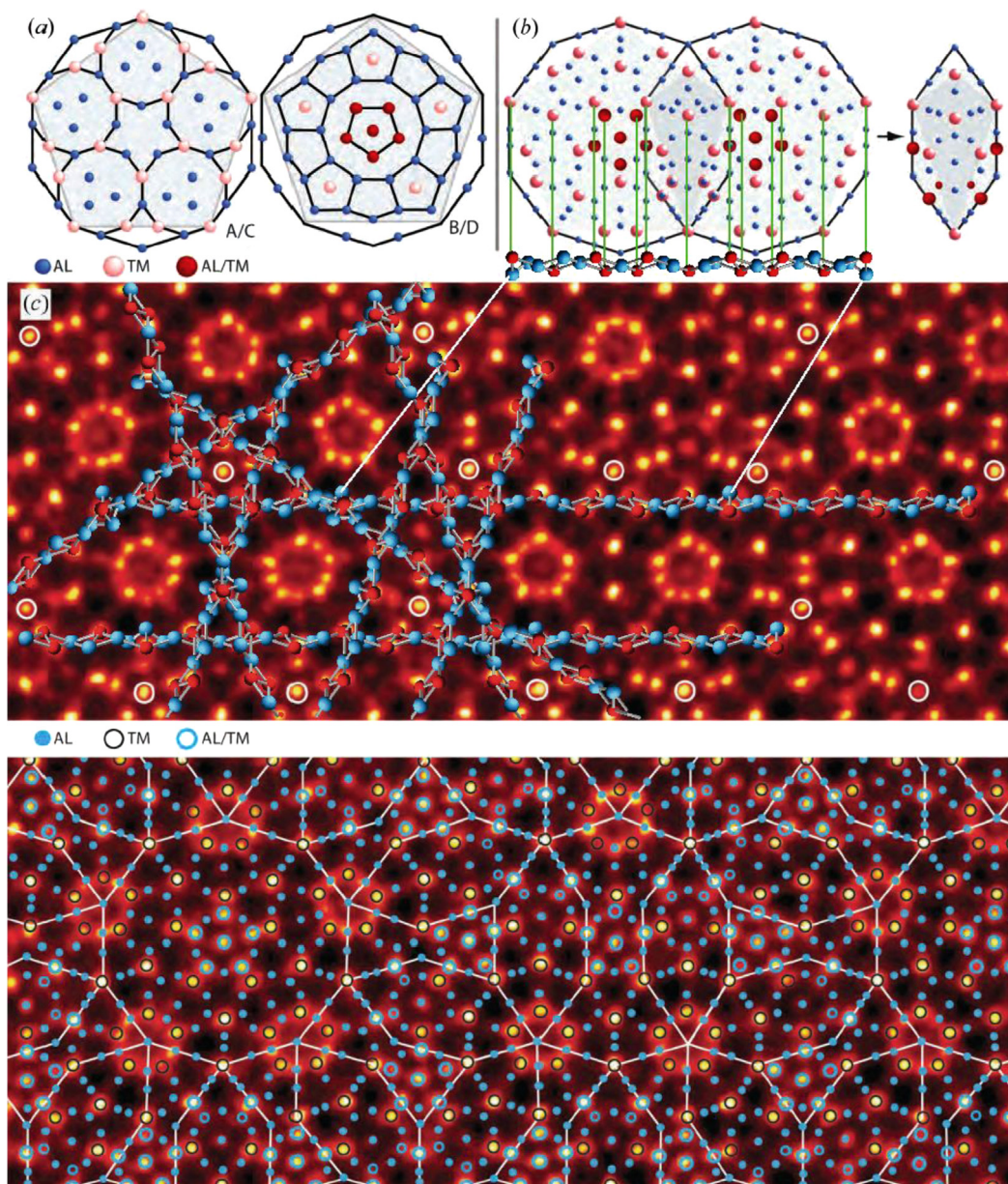


Fig. 2. (a) Atomic layers and projections of the fundamental cluster constituting decagonal $\text{Al}_{64}\text{Cu}_{22}\text{Co}_{14}$ (adapted from [36]). One puckerd atomic layer, projected onto the quasiperiodic plane, is shown in (b), a part of the network generated by them is superposed the HAADF-STEM image [37] in (c). This electron micrograph is shown without and with the cluster structure overlaid. In the upper image of (c), the cluster centers are marked by white circles.

3. Is there a fundamental difference in the factors leading to periodic complex intermetallics on the one hand and to quasicrystals on the other hand?

Many rational approximants to IQC are known, somewhat less have been identified for DQC. Rational approximants are constituted of the same kind of structural building units (short: clusters [40,41]) as the corresponding QC. Consequently, the shape of the fundamental structural subunits (building clusters) alone does not force the formation of quasiperiodic structures. Furthermore, the clusters are in quasicrystals not less distorted or disordered than in their (higher) approximants. It is rather stoichiometry that determines whether the approximant or the QC is formed. In case of a cluster-based structure, even a slight change in the chemical composition can require a different kind of *lro* resulting from a different frequency of particular cluster overlaps [42]. And changes in cluster overlaps are energetically cheaper than to create a two-phase system with phase boundaries if changing the chemical composition. So, the main driving force controlling the *lro* seems to be the constraint to keep the local chemical composition as close as possible to the overall stoichiometry. This does not differ from the structure-controlling factors in periodic complex intermetallics.

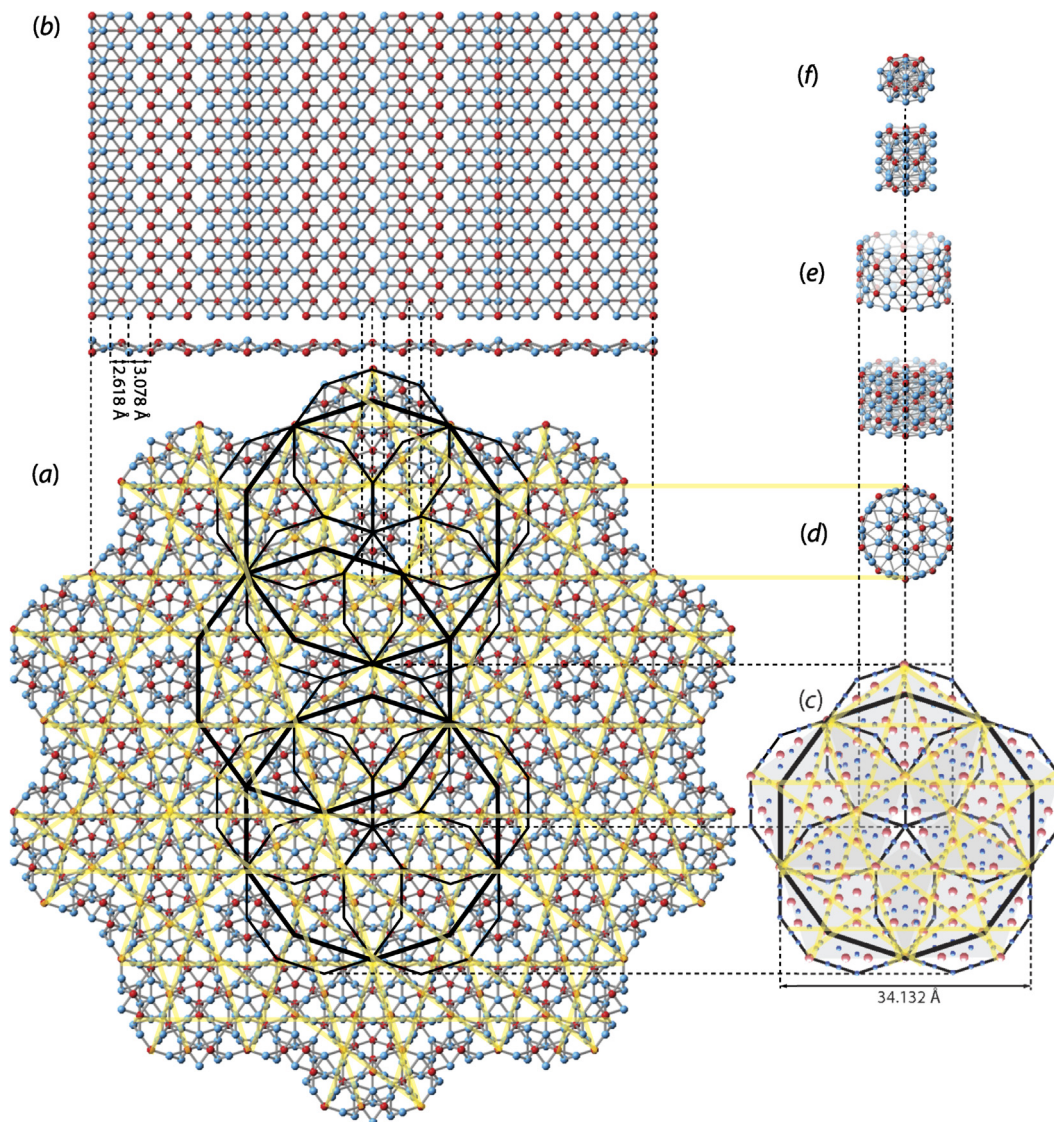


Fig. 3. (a) One supercluster [36] with the traces of the puckered atomic layers of the type shown in Fig. 2 marked by yellow lines. (b) One of these puckered atomic layers is shown on top in two orthogonal projections. Note the pseudo-hexagonal arrangement of atoms. (c) One Hiraga-supercluster [39] (outlined in black), consisting of five Deloudi clusters, is depicted together with a ≈ 14 Å subcluster (d) in different projections and exploded view. The perfectly ordered *hcp* columnar cluster shell (e) is formed by pieces of the atomic layers shown in (a), (b). So is the innermost cylindrical cluster shell. (f) Column of face-sharing pentagon dodecahedra around vertex-connected, capped pentagonal bipyramids (Al ... blue, Co/Cu ... red).

The main difference between periodic and quasiperiodic intermetallics beside their *lro* is in their physical properties (for recent reviews, see [43,44]). However, with increasing the order of rational approximants, their properties approach those of the respective quasicrystals. In case of DQC, the anisotropy of the structure-sensitive properties can be studied in both the periodic and quasiperiodic directions.

4. How do quasicrystals grow, and how is the quasiperiodic *lro* achieved on atomic scale?

There exist reasonably good models of nucleation and crystal growth for phases with simple structures. This is not the case for complex intermetallics (CI), be they periodic or quasiperiodic. Therefore, questions of the kind of how the thousandth atom finds its site in a huge unit cell or how the quasiperiodic *lro* is achieved are still not answered. In our analysis of CI (see [45], for instance), we identified so far the following three main ordering principles:

- (i) the CI can be seen as a hierarchical structure, *i.e.* repeating the same topological principles on different scales, from the arrangement of atoms to that of clusters and then to that of superclusters. This also refers to the lattice planes

of the basic structure on the lowest hierarchy level, which may survive as ‘sublattice planes’ in the actual hierarchical structure;

- (ii) the CI can be seen as a modulated structure (superstructure) of an underlying basic structure;
- (iii) the CI can be seen as the topologically best arrangement of several different atomic environment types (AET) under the constraint of chemical homogeneity. This means that the local chemical composition should be as close as possible to the global one.

There have been numerous X-ray diffraction studies of the atomic ordering in liquid alloys close to the solidification temperature or even below (supercooled liquids) – see, for instance, [46] and references therein. The experimental observations clearly point to a pronounced *sro* and, in some cases, even *mro*. This means that already in the highly dynamic liquid, local ordering (AET and cluster formation) can take place, driven by the minimization of the chemical potential under the constraint of the overall chemical composition. Consequently, by reaching the melting temperature, the growth of CI and QC takes place mainly by optimizing (with regard to packing) the shapes of the AET and clusters as well as their interactions with not so much long-range diffusion needed. A growth model, pointing out the role of flat or slightly puckered atomic layers (“quasilattice planes”), has recently been published [47].

5. What favors decagonal symmetry over all other theoretically possible noncrystallographic symmetries except the icosahedral one?

Why decagonal and not octagonal or dodecagonal or any other axial symmetry? Indeed, octagonal and dodecagonal QC have been experimentally observed in some phases; however, all of them are, perhaps with one exception, metastable and show rather short correlation lengths. One reason for their metastability may be that clusters with octagonal and dodecagonal symmetry can be well arranged on tetragonal and hexagonal lattices, respectively, while this is not the case for decagonal clusters; there may be no “need” for forming a quasiperiodic structure.

Why no QC have been discovered so far with other symmetries? One reason may lie in the existence of a periodic average structure (PAS, [49,50]), which is much better defined for quasiperiodic tilings with icosahedral symmetry or 5-, 8-, 10- and 12-fold axial symmetry, respectively, than for any other one, except the 9-fold [51]. This has the consequence that inclined netplanes [52], important for the formation and growth of QC, are also not well defined except in these cases. In the case of mesoscopic quasiperiodic structures, however, dodecagonal ordering is the most prominent one; there is also one case of 9-fold (18-fold) symmetry known [48,53].

6. Entropy vs. entropy – what stabilizes quasiperiodic order?

This exaggerated question has been discussed from the very beginning of QC research and is still not fully answered. It does not simply ask whether or not QC are high-temperature (HT) phases, it rather addresses the question whether QC structures are truly quasiperiodic or only on average, whether a quasiperiodic or a random tiling better describes the actual structure.

Electron-microscopic images of some DQC indicate almost perfect quasiperiodic ordering on the scale of many cluster diameters, some other DQC rather resemble cluster-decorated random tilings. In both cases, the clusters covering the ordered or disordered (randomized) tilings appear to be structurally rather stable entities. This means that the large configurational entropy gain by randomization of quasiperiodic tilings where only the vertices are decorated by atoms cannot be expected for realistic quasicrystal structures with clusters, which contain more than hundred atoms per repeat unit along the tenfold axis. The number of sites in such clusters allowing phason flips (atomic jumps in double-well potentials typical for quasiperiodic structures) is rather small, and (virtual) cluster flips are realized by flips of a few atoms (see, for instance, [55]). So, energy stabilization of the clusters will play a major role anyway, be it in DQC or approximants. The remaining question is whether the (at least on-average) quasiperiodic ordering of the clusters is mainly caused by entropy or a result of energy minimization.

A more realistic disordered structure model for DQC is based on the “cluster approach to random Penrose tilings” [56]. In this model, the strict overlap rules for the decagon clusters are relaxed, only a kind of minimum distance rule and specific allowed cluster orientations are maintained. The hexagon–boat–star (HBS) tiling, which was found frequently to underlie DQC structures, is a subset of the full-random Penrose pentagon ensemble, indeed.

What are the signatures of entropy stabilization that can be experimentally identified? On the one hand, the cluster distribution derived from electron-microscopic images can indicate the degree of order of the projected structure on the scale up to 100 nm, *i.e.*, approximately 50 cluster diameters. On the other hand, X-ray-diffraction-based electron density maps can clearly show the sites undergoing disorder since the actual, time-averaged structure is mapped onto an ideal quasiperiodic structure model. In case of energy stabilization, structural fluctuations around an equilibrium value (mainly phason flips) should increase with temperature and *vice versa*. At 0 K, these fluctuations would approach zero amplitudes, and the ground-state structure would be quasiperiodic. In contrast, in case of entropy stabilization, the best on-average quasiperiodic structure should exist at high temperature, because local correlated deviations from quasiperiodicity would become more and more uncorrelated. At lower temperatures, the structure should become more and more unstable towards

a distortion to an approximant structure, *i.e.*, a kind of orientationally twinned approximant nano-domain structure could result [54]. The ground-state structure would be periodic.

Recent *in situ* HT structure analyses on decagonal Al–Cu–Rh [57] revealed two things. First, the structures resulting from the *in situ* HT measurement and from the data collection on the, at the same temperature annealed and subsequently quenched, sample did not differ significantly. Second, also no significant structural variations could be observed for a data set collected at an intermediate temperature. The Debye–Waller (DW) factors follow their usual temperature dependence, while the phasonic DW factor proved to be more or less temperature independent. This means that this DQC behaves like any other intermetallic phase, and that phasons do not seem to be of crucial importance for its stability. There are no indications for the typical structural signature of entropy stabilization, *i.e.*, with increasing temperature–increasing phason fluctuations (disorder in the average structure) and with decreasing temperature–increasing local instabilities towards periodic structure formation. This does not say that this DQC can have a quasiperiodic ground-state structure. It can just be an HT-phase stabilized in the same way as any other complex intermetallic HT-phase (vibrational entropy, thermal vacancies) that do not feature phasonic excitations. A certain amount of structural disorder is always present in complex HT-phases, a signature of a structural entropic contribution.

In case of intermetallic quasicrystals, electronic stabilization (Hume–Rothery mechanism) seems to play a major role ([58,59] and references therein). However, this does not rule out that entropic contributions are essential for their stability, therewith excluding quasiperiodic order from being a ground state of solid matter. The existence of quasiperiodicity in mesoscopic structures (colloids, star-terpolymers, etc.) clearly demonstrates that electronic contributions cannot be a necessary prerequisite for quasiperiodic *lro* in general. Interactions, which can be described by particular double-well potentials seem to be the decisive factors for mesoscopic, and to some extent also intermetallic, quasicrystals. Unfortunately, the sluggish diffusion kinetics of intermetallics prohibits the experimental study of the stability of quasicrystals at low temperatures. First-principles quantum-mechanical calculations are also not yet possible due to the lack of periodicity.

7. Conclusions

The *lro* of quasicrystals, *i.e.*, the kind of tilings (quasilattices) underlying their actual structures, will always be known to some limited extent only, in contrast to periodic crystals, where the underlying tiling is always one of the 14 Bravais lattices. However, we know already what we want to know about a quasicrystal structure: the structure of the fundamental constituting clusters, their local arrangements and the average structure, which is for some Al-based DQC quite close to ordered quasiperiodic. The big open questions are how quasicrystals grow and whether they can be stable at zero K. The only way to answer these questions is by realistic simulations based on large model systems ($\gg 100\,000$ atoms) and realistic potentials. The large model size is necessary for properly taking into account the role of clusters and of netplanes, *i.e.*, the atomic layers forming the framework that guides the arrangement of clusters. One major problem for these simulations will be, however, the locally varying chemical bonding and the non-local character of the metallic bond in general. The use of pair potentials will give a first and very rough description only. It could not take into account electronic stabilization such as described by the Hume–Rothery mechanism for more complex structures. For now, it seems that geometrical factors such as optimum packing of clusters with noncrystallographic symmetry, under the constraint of maximum chemical homogeneity, are the decisive factors controlling the kind of *lro*. Of course, the geometrically best way of packing has the boundary condition of allowing the energetically and entropically most favorable interactions. The main entropic contribution seems to be provided by intracluster disorder rather than intercluster disorder.

References

- [1] D. Shechtman, et al., Metallic phase with long-range orientational order and no translational symmetry, *Phys. Rev. Lett.* 53 (1984) 1951.
- [2] L. Bendersky, Quasicrystal with one-dimensional translational symmetry and a tenfold rotation axis, *Phys. Rev. Lett.* 55 (1985) 1461.
- [3] K. Chattopadhyay, et al., Electron-microscopy of quasi-crystals in rapidly solidified Al-14-percent Mn alloys, *Scr. Metall.* 19 (1985) 767.
- [4] B. Dubost, et al., Large AlCuLi single quasi-crystals with triacontahedral solidification morphology, *Nature* 324 (1986) 48.
- [5] L.X. He, Stable Decagonal quasi-crystals with different periodicities along the tenfold axis in $\text{Al}_{65}\text{Cu}_{20}\text{Co}_{15}$, *Mater. Trans., JIM* 30 (1989) 300.
- [6] A.P. Tsai, A. Inoue, T. Masumoto, A stable decagonal quasicrystal in the Al–Cu–Co system, *Mater. Trans., JIM* 30 (1989) 300.
- [7] A.P. Tsai, A. Inoue, T. Masumoto, Stable decagonal Al–Co–Ni and Al–Co–Cu quasicrystals, *Mater. Trans., JIM* 30 (1989) 463.
- [8] W. Steurer, Quasicrystal structure analysis, a never-ending story?, *J. Non-Cryst. Solids* 334 (2004) 137.
- [9] W. Steurer, Twenty years of structure research on quasicrystals. Part 1. Pentagonal, octagonal, decagonal and dodecagonal quasicrystals, *Z. Kristallogr.* 219 (2004) 391.
- [10] R. Penrose, Tilings and quasicrystals; a non-local growth problem?, in: M.V. Jaric (Ed.), *Aperiodicity and Order*, vol. 2, Academic Press Inc. Ltd., London, 1989, p. 53.
- [11] W. Steurer, S. Deloudi, *Crystallography of Quasicrystals – Concepts, Methods and Structures*, Springer Series in Materials Science, vol. 126, Springer, Berlin, Heidelberg, 2009.
- [12] W. Steurer, K.H. Kuo, 5-dimensional structure-analysis of decagonal $\text{Al}_{65}\text{Cu}_{20}\text{Co}_{15}$, *Acta Crystallogr., Sect. B* 46 (1990) 703.
- [13] P. Kuczera, et al., Comparative structural study of decagonal quasicrystals in the systems Al–Cu–Me (Me=Co, Rh, Ir), *Acta Crystallogr., Sect. B* 68 (2012) 578.
- [14] A. Yamamoto, et al., Atomic-structure of a decagonal Al–Co–Ni quasi-crystal, *Phys. Rev. Lett.* 65 (1990) 1603.
- [15] W. Steurer, et al., The structure of decagonal $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$, *Acta Crystallogr., Sect. B* 49 (1993) 661.
- [16] L. Elcoro, J.M. Perez-Mato, Structural analysis of the decagonal quasicrystal $\text{Al}_{70}\text{Ni}_{15}\text{Co}_{15}$ using symmetry-adapted functions, *J. Phys. I* 5 (1995) 729.
- [17] H. Takakura, et al., The structure of a decagonal $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ quasicrystal, *Acta Crystallogr., Sect. A* 57 (2001) 576.

- [18] A. Cervellino, et al., Structure solution of the basic decagonal Al–Co–Ni phase by the atomic surfaces modelling method, *Acta Crystallogr., Sect. B* 58 (2002) 8.
- [19] H. Takakura, et al., Re-refinement of the basic decagonal Al–Co–Ni phase, *Ferroelectrics* 305 (2004) 257.
- [20] M. Mihalkovic, et al., Combined energy-diffraction data refinement of decagonal AlNiCo, *J. Non-Cryst. Solids* 334 (2004) 177.
- [21] J. Wolny, et al., Physical space structure refinement of decagonal quasicrystal in rhombic Penrose tiling model, *Z. Kristallogr.* 223 (2008) 847.
- [22] A. Strutz, et al., Basic Co-rich decagonal Al–Co–Ni: Average structure, *Phys. Rev. B* 80 (2009) 184102.
- [23] A. Strutz, et al., Basic Co-rich decagonal Al–Co–Ni: superstructure, *Phys. Rev. B* 82 (2010) 064107.
- [24] P. Kuczera, et al., Real space structure refinement of the basic Ni rich decagonal Al–Ni–Co phase, *J. Phys. Conf. Ser.* 226 (2010) 012001.
- [25] P. Kuczera, et al., Structure refinement of decagonal Al–Ni–Co, superstructure type I, *Philos. Mag.* 91 (2011) 2500.
- [26] W. Steurer, 5-Dimensional structure refinement of decagonal Al₇₈Mn₂₂, *J. Phys. Condens. Matter* 3 (1991) 3397.
- [27] W. Steurer, et al., The structure of decagonal Al_{70.5}Mn_{16.5}Pd₁₃, *J. Phys. Condens. Matter* 6 (1994) 613.
- [28] A. Yamamoto, et al., Structure refinement of quasicrystals, in: G. Chapuis, W. Paciorek (Eds.), *Aperiodic '94*, World Scientific, Singapore, 1995, pp. 393–398.
- [29] M. Mihalkovic, P. Mrafko, Quasicrystal structure modelling, *Mater. Sci. Eng. A* 226 (1997) 961.
- [30] S. Weber, A. Yamamoto, Application of the five-dimensional maximum-entropy method to the structure refinement of decagonal Al₇₀Mn₁₇Pd₁₃, *Philos. Mag. A* 76 (1997) 85.
- [31] S. Weber, A. Yamamoto, Noncentrosymmetric structure of decagonal Al₇₀Mn₁₇Pd₁₃ quasicrystal, *Acta Crystallogr., Sect. A* 54 (1998) 997.
- [32] A. Cervellino, Higher-dimensional modelling of decagonal quasicrystal structures, Thesis No. 14023, ETH, Zurich, Switzerland, 2002.
- [33] S. Katrych, et al., New stable decagonal quasicrystal in the system Al–Ir–Os, *J. Alloys Compd.* 428 (2007) 164.
- [34] E. Abe, Electron microscopy of quasicrystals – where are the atoms?, *Chem. Soc. Rev.* 41 (2012) 6787.
- [35] T. Oers, W. Steurer, **personal communication**.
- [36] S. Deloudi, et al., Unifying cluster-based structure models of decagonal Al–Co–Ni, Al–Co–Cu and Al–Fe–Ni, *Acta Crystallogr., Sect. B* 67 (2011) 1.
- [37] S. Taniguchi, E. Abe, Highly-perfect decagonal quasicrystalline Al₆₄Cu₂₂Co₁₄ with non-centrosymmetry, *Philos. Mag.* 88 (2008) 1949.
- [38] Z. Masakova, et al., Classification of Voronoi and Delone tiles of quasicrystals: III. Decagonal acceptance window of any size, *J. Phys. A* 38 (2005) 1947.
- [39] K. Hiraga, A large columnar cluster of atoms in an Al–Cu–Rh decagonal quasicrystal studied by atomic-scale electron microscopy observations, *Philos. Mag. Lett.* (2001) 117.
- [40] W. Steurer, Stable clusters in quasicrystals: fact or fiction?, *Philos. Mag.* 86 (2006) 1105.
- [41] C.L. Henley, et al., *Philos. Mag.* 86 (2006) 1131.
- [42] W. Steurer, S. Deloudi, Cluster packing from a higher-dimensional perspective, *J. Struct. Chem.* 23 (2012) 115.
- [43] J.-M. Dubois, Properties- and applications of quasicrystals and complex metallic alloys, *Chem. Soc. Rev.* 41 (2012) 6760.
- [44] J. Dolinšek, Electrical and thermal transport properties of icosahedral and decagonal quasicrystals, *Chem. Soc. Rev.* 41 (2012) 6730.
- [45] J. Dshemuchadse, D.Y. Jung, W. Steurer, Structural building principles of complex face-centered cubic intermetallics, *Acta Crystallogr., Sect. B* 67 (2011) 269.
- [46] O.S. Roik, V.P. Kazimirov, S.M. Galushko, The structure of the liquid Al₆₂Cu_{25.5}TM_{12.5} (TM = Mn, Ni, Fe) alloys, *Phys. Chem. Liq.* 51 (2013) 21.
- [47] W. Steurer, On a realistic growth mechanism for quasicrystals, *Z. Anorg. Allg. Chem.* 637 (2011) 1943.
- [48] W. Steurer, Why are quasicrystals quasiperiodic?, *Chem. Soc. Rev.* 41 (2012) 6719.
- [49] W. Steurer, T. Haibach, The periodic average structure of particular quasicrystals, *Acta Crystallogr., Sect. A* 55 (1999) 48.
- [50] A. Cervellino, W. Steurer, General periodic average structures of decagonal quasicrystals, *Acta Crystallogr., Sect. A* 58 (2002) 180.
- [51] S. Deloudi, W. Steurer, Higher-dimensional crystallography of *N*-fold quasiperiodic tilings, *Acta Crystallogr., Sect. A* 68 (2012) 266.
- [52] W. Steurer, A. Cervellino, Quasiperiodicity in decagonal phases forced by inclined net planes?, *Acta Crystallogr., Sect. A* 57 (2001) 333.
- [53] S. Fischer, et al., Colloidal quasicrystals with 12-fold and 18-fold diffraction symmetry, *Proc. Natl. Acad. Sci. USA* 108 (2011) 1810.
- [54] W. Steurer, The quasicrystal-to-crystal transformation. I. Geometrical principles, *Z. Kristallogr.* 215 (2000) 323.
- [55] G. Coddens, W. Steurer, Time-of-flight neutron-scattering study of phason hopping in decagonal Al–Co–Ni quasicrystals, *Phys. Rev. B* 60 (1999) 270.
- [56] P. Gummelt, C. Bandt, A cluster approach to random Penrose tilings, *Mater. Sci. Eng.* 294–296 (2000) 250, p. 250.
- [57] P. Kuczera, et al., High-temperature structural study of decagonal Al–Cu–Rh, *Acta Crystallogr., Sect. B* 69 (2013), submitted for publication.
- [58] D. Zhang, Electronic properties of stable decagonal quasicrystals, *Phys. Status Solidi A* 207 (2010) 2666.
- [59] U. Mizutani, et al., Hume–Rothery stabilization mechanism and e/a determination for RT- and MI-type 1/1–1/1–1/1 approximants studied by FLAPW-Fourier analyses, *Chem. Soc. Rev.* 41 (2012) 6799.