Quasicrystal structure and growth models: discussion of the status quo and the still open questions

Walter Steurer
Department of Materials, ETH Zurich, Leopold-Ruzicka-Weg 4, 8093 Zurich, Switzerland
E-mail: steurer@mat.ethz.ch

Abstract. Where are we now in quasicrystal (QC) research more than three decades after Dan Shechtman’s discovery? Do we fully understand the origin of quasiperiodicity, the formation, growth, thermodynamic stability, structure and properties of quasicrystals? First, I will shortly present the status quo, then I will address the still open questions, and identify potential focus areas for future research. Because of the limited space, I will focus on decagonal quasicrystals (DQCs); the status quo for research on icosahedral quasicrystals (IQCs) is comparable.

1. Introduction
More than three decades after Dan Schechtman’s discovery [1], QC research has become a mature field. This is reflected in the approximately 12,000 publications that have appeared so far (for an introduction into the area and an overview of the field see [2], for instance). That the number of QC publications per year is shrinking since the peak year 2000 (Fig. 1) does not mean that we know now more or less everything what we want to know about QCs; it is rather a consequence of the lack of important applications for intermetallic QCs and related therewith the ever decreasing funding.

While we already know many fascinating details about the yet increasing number of QC, the big picture is still showing many white spots. Even some fundamental questions are still open:

• What is the origin of quasiperiodic order?
• How is quasiperiodicity achieved during growth?
• What is the role of entropy for the stability of QCs?
• Are there many more yet unknown intermetallic systems featuring QCs?
• Why is fivefold symmetry prevalent in intermetallic QCs in contrast to twelvefold symmetry for assemblies on the meso- or macro-scale?
• Etc.

In contrast to intermetallic QCs, quasiperiodic arrangements on the mesoscale are much better understood due to the simple, well-defined pair-potentials between the interacting particles, which can be easily modeled (see, e.g., [3] and references therein). The atomic interactions in intermetallic QCs are much more complex and diverse, and they can vary significantly in the structure between covalent and metallic bonding. Furthermore, the global valence electron concentration (VEC) plays a decisive role for the stability of intermetallic QCs [4]. In the following, I will address the topics 'QC structure analysis’, 'QC stability’ and 'QC growth’, and suggest ways for tackling the open questions.
Figure 1. Number of publications on QCps per year. The arrows mark the years when International Conferences on Quasicrystals (ICQs) took place. Proceedings of these conferences appeared in most cases in the subsequent year increasing the number of papers significantly over the average value in several cases.

2. QC structure analysis

State-of-the-art structure analysis of complex intermetallic phases in general does not only comprise the quantitative determination of the atomic positions and displacement parameters but also of the chemical bonding and the electronic structure (see, e.g., [5] and references therein). Furthermore, for a full understanding of the structure also the kind of intrinsic disorder, if any, has to be determined. The method of choice for QC structure analysis is based on X-ray and/or neutron diffraction in combination with spherical-aberration (Cs) corrected electron microscopy. Needless to say that only thermally well-equilibrated homogeneous samples should be used. This method allows obtaining quantitative information on the local as well as the global arrangement of atoms and structural subunits (clusters) in a quasiperiodic structure. However, one has to be aware of the limits of this approach:

Diffraction techniques

(i) Once one identifies the observed reflection intensities as Bragg reflections, one excludes per definitionem all structure models that can only be described as decorated non-Pisot (random) tilings (see, e.g., [6]).

(ii) Applying the higher-dimensional (nD) approach automatically leads to quasiperiodic structure models.

(iii) If only Bragg reflection data are used, then the structural information is averaged over the irradiated volume of the QC modulo the nD unit cell. Only electron microscopy can show the differences between the (over the sample thickness projected) actual structure and the so obtained averaged quasiperiodic structure (for an example see, e.g., [7]).

(iv) Due to the scaling symmetry of the diffraction pattern, the choice of a proper unit cell leading to the optimum partition (large contiguous areas) of the atomic surfaces (occupation domains) is
non-trivial. This problem can be solved based on the par(allel)-space pair-correlation (Patterson) function, which allows to derive the typical intercluster distances [8, 9].

(v) If the cluster-embedding method is used, one has to keep in mind that the clusters identified in approximants (ACs) do not necessarily correspond one-to-one to the clusters in the related QC (see also [10, 11]). For instance, in the case of decagonal Al-Co-Ni and Al-Co-Cu the cluster diameters of the ACs amount to \( \approx 20 \) \( \AA \) diameter (the size is already limited by the unit cell dimensions) [12], while those of the DQCs have been found to be \( \tau \) times larger [13, 15].

(vi) Dynamical effects such as multiple diffraction can change the intensity of weak reflections drastically (see, e.g., [16] and references therein). If not taken into account it can deteriorate the quality of a refined structure model significantly.

(vii) Using improper weighting schemes for weak reflections can lead to too large phason Debye-Waller factors masking failures in the refined structure models. Reflections with large perp(endicular)-space components of the diffraction vectors have low intensities. If they are biased, it will have implications for the quality of the partitioning of the atomic surfaces, and therewith also for the determination of the kind of quasiperiodic long-range order.

**Electron microscopy**

(i) The structural information is averaged over the whole sample thickness (\( \approx 10 \) nm corresponding to 40-50 atomic layers). The imaged area may not be characteristic for the whole sample.

(ii) Whole columns of atoms (parallel to the electron beam) must flip at the same time to make a flip observable. Such events will be much rarer than single atom flips.

(iii) Contrasts due to structural disorder between different atomic layers perpendicular to the electron beam will be leveled down due to averaging and may become unobservable.

**Open questions and ways to answer them**

QC structure analysis should focus on the determination of the actual long-range order and its variation as a function of temperature. So far, it seems to have been implicitly assumed that the 2D Penrose tiling and the 3D Ammann tiling, respectively, are good model quasilattices for the actual structures of most QCs. Only in a few cases other kinds of quasiperiodic order have been explicitly suggested (see, e.g., [13]). However, while the long-range order of periodic intermetallics is already defined by the determination of the Bravais lattice, one out of 14, this is more complex for QCs. In the case of DQCs, for instance, there exists an infinite number of different quasiperiodic tilings that can underly the structure; for instance, the generalized Penrose tilings [17] or the Masakova tilings [18, 19, 20].

It is also an open question whether structural disorder mainly takes place between atoms within clusters or between clusters. Can structural disorder destroy clusters or are clusters relatively stable subunits? How does the disorder change as a function of temperature? Favorable ways to determine the actual, non averaged long-range order are, for instance:

(i) Large-scale electron microscopic studies for the determination of the cluster ordering (see, e.g., [14]).

(ii) Large-scale surface studies by scanning tunneling microscopy (STM) or atomic force microscopy (AFM) for the determination of the cluster ordering.

(iii) Repeated scans of one and the same area of a QC sample by STM/AFM at elevated temperature for identifying any changes in the quasiperiodic order (rearrangements of clusters). In contrast to electron microscopy, where whole columns of atoms must flip to be observable, single-atom flips can be detected by STM.
3. QC stability
It has been a long-lasting discussion whether QCs are energy- or entropy-stabilized, i.e., whether or not the entropic contribution is essential for their thermodynamic stability. In the case of entropy stabilization, a quasiperiodic ground state (structure at zero K) could not exist, QCs would be high-temperature (HT) phases. The crucial role of the VEC for the phase stability has been successfully used as a powerful tool for the discovery of new QCs [21]. Therefore it is hardly surprising, that intermetallic QCs and their ACs have been identified as Hume-Rothery-type phases (see, e.g., [4, 22, 23]. This supports the hypothesis of QCs being energy-stabilized. However, it does not exclude the possibility that in addition to electronic stabilization also an entropic contribution is necessary. Examples for HT Hume-Rothery phases are, for instance, the $\beta$- and $\delta$-phases in the classical system Cu-Zn.

The hypothesis of QCs as entropy-stabilized HT phases (see, e.g. [24, 25]) cannot be ruled out based on the experimental evidence collected so far. Simple low-temperature (LT) experiments are not suitable for studying the LT stability of QCs due to the sluggish diffusion in intermetallics at LT. Attempts to force diffusion by LT ball milling induced a transition to a periodic phase in decagonal Al-Co-Ni [26]. In contrast, icosahedral Cd-Yb remained quasiperiodic under similar conditions [27].

QCs and their ACs differ slightly in their stoichiometries (see, e.g., [28] and Fig. 2). There is no lock-in transition QC$\leftrightarrow$AC known that would be comparable to those found for some incommensurately modulated structures (IMSs). A devil’s staircase of ACs of increasing order does not exist either. It is also remarkable that only low-order ACs have been discovered so far. High-order ACs should have similar Gibbs free energies, $G=H-TS$, with similar $H/TS$ ratios, as the related QC; the stabilizing mechanism for such a series of phases AC$\leftrightarrow$QC with slightly varying stoichiometry should be the same, consequently.

In the case of an IMS with displacive modulation, a continuous change in the modulation wave

![Figure 2. Arrangements of columnar clusters forming decagonal Al-Cu-Rh [9]. Their chemical composition varies with increasing size and the kind of cluster overlaps. The three structures at bottom right are patches of one quasiperiodic and two periodic arrangements of clusters, respectively. They differ significantly in their chemical composition. DQC growth could start from a pentagonal cluster (bottom left), growing along quasilattice lines as indicated schematically in the quasiperiodic structure.](image-url)
vector would lead to a dense set of commensurate and incommensurate structures, all with the same stoichiometry. With temperature continuously changing wave vectors have been experimentally observed, indeed. In contrast, in the case of a substitutional modulation, the stoichiometry would have to change with the wave vector, what would need diffusion, and what would have a larger influence on the Gibbs free energy. The same is true for a devil’s staircase of ACs.

Since high-order ACs have never been experimentally observed so far, there seems to be a significant difference between their Gibbs free energies, indeed. This finding can be explained by the Hume-Rothery mechanism. Different stoichiometries lead to different valence electron concentrations and different structures. Those will be stable which allow the best possible fit of the respective Fermi surface to the Brillouin zone boundaries; the higher the symmetry is of a structure, the better the fit can be. For the series of approximants, the symmetry would always correspond to one of the 14 Bravais lattices. Consequently, the symmetry of the QC would be higher. However, the Brillouin (Jones) zone of a high AC has already the pseudo-symmetry of the QC. Only if the size of the Fermi sphere (related to the electron concentration) fits best for the QC it will be stabler than any of its high ACs.

High-order ACs would have large unit cells. However, the unit-cell dimensions of periodic intermetallics seem to be quite limited. Only approximately 2% of all intermetallics have a complex structure (> 100 atoms per primitive unit cell [5]) with larger lattice parameters. Thus, the structure stabilizing power of periodicity (Bloch waves, phonons,...) seems to work only for moderate unit cell dimensions (lattice parameters << 100 Å).

Open questions and ways to answer them
What are the main factors contributing to the stability of QCs? To which amount contribute phonons, phasons, electrons, and configurational disorder to the total entropy?

(i) Measure the entropies of a QC and its ACs in an intermetallic system by calorimetry (see, e.g., [29]. If the QC has the highest entropy it supports the hypothesis of QCs being HT phases.

(ii) Compare the variations in QC reflection intensities with high perp-space components of the diffraction vectors as a function of temperature (see, e.g. [30]). Correct the intensities for the par-space Debye-Waller factor. A decrease of the intensities with increasing temperature indicates an increase in phason fluctuations deteriorating the quasiperiodicity of the structures. An increase indicates the improvement of on average quasiperiodicity by decreasing the spontaneous local phason strains, precursor effects of a transition to the periodic state.

(iii) Perform first-principles calculations on a series of higher and higher ACs, 0/1, 1/1, 2/1, 3/2, ..., n/m. The results should explain why only low-order ACs have been found experimentally, and what changes as a function of the AC order Gibbs free energy, chemical bonding, electronic structure, etc.). The calculations should also allow to extrapolate the stability of the QC and the origin of quasiperiodic order - why are QCs quasiperiodic [31]?

4. QC growth
Not much is known about the growth of QCs on the atomic scale. This is not surprising because the growth mechanism of periodic complex intermetallic is also largely unexplored ("how does the thousandth atom find its place in a giant unit cell with thousands of atoms?"). In case of QCs, random tiling approaches [32] were quite popular in the first years of QC research, because, to say it with Roger Penrose’s words "...the spontaneous growth of large regions of such quasicrystalline five-fold symmetric substances seemed to me virtually insurmountable" [33]. There are a couple of papers reporting approaches for modeling the growth of QCs based on tilings (see, e.g., [34] and references therein), and others based on clusters. From my point of view the cluster-based approaches are more physical (see, e.g., [35] and references therein). There are also a number of papers on experimental in situ studies such as [36, 37, 38] and references therein.
Open questions and ways to answer them
How do QCs and ACs grow on atomic/cluster scale? Do QCs already grow more or less strictly quasiperiodic or is this the result of optimization processes during annealing?

(i) Develop realistic 3D growth models, i.e., starting with nucleation and growth from a melt (see, e.g., [35]). Take into account that already in the melt, close to the melting temperature, chemical short-range ordering takes place. Depending on the stoichiometry either ACs should grow or QCs.

(ii) Study the heterogenous growth of QCs on surfaces of periodic crystals by AFM/STM; for instance, the growth of decagonal A-Co-Ni on the (110) surface of cP2-Al(Co,Ni) (B2- or β-phase) (for an example see [39]).

(iii) Is it possible to grow a 2D QC on the surface of a periodic crystal?

References
[1] Shechtman D, Blech I, Gratias D and Cahn J W 1984 Phys. Rev. Lett. 53 1951-3
[2] Steurer W and Deloudi S 2009 Crystallography of Quasicrystals (Berlin: Springer)
[3] Barkan K, Engel M and Lifshitz R 2014 Phys. Rev. Lett. 113 098304
[4] Tsai A P 2004 J. Non-Cryst. Sol. 334 & 335 317-22
[5] Steurer W and Dshemuchadse J 2016 Intermetallics - Structures, Properties and Statistics (Oxford University Press)
[6] Godrèche C and Lançon F 1992 J. Phys. I France 2 207-20
[7] Ors T, Takakura H, Abe E and Steurer W 2014 Acta Crystallogr. B 70 315-30
[8] Cervellino A, Haibach T and Steurer W 1998 Phys. Rev. B 57 11223-31
[9] Kuczera P, Wolny J and Steurer W 2012 Acta Crystallogr. B 68 578-89
[10] Steurer W 2006 Philos. Mag. 86 1105-13
[11] Steurer W 2012 Struct. Chem. 23 1115-20
[12] Hovmöller S, Hovmöller Zou L, Zou X and Grushko B 2012 Phil. Trans. R. Soc. A 370 2949-59
[13] Deloudi S, Fleischer F and Steurer W 2011 Acta Crystallogr. B 67 1-17
[14] Joseph D, Ritsch S and Beeli C 1997 Phys. Rev. B 55 8175-83
[15] Hiraga K, Yasuhara A 2013 Mater. Trans. 54 720-4
[16] Fan C Z, Weber T, Deloudi S and Steurer W 2011 Philos. Mag. 91 2528-35
[17] Pavlovich A and Kléman M 1987 J. Phys. A: Math. Gen. 20 687-702
[18] Masáková Z, Patera J and Zich J 2003 J. Phys. A: Math. Gen. 36 1869-94
[19] Masáková Z, Patera J and Zich J 2003 J. Phys. A: Math. Gen. 36 1895-912
[20] Masáková Z, Patera J and Zich J 2005 J. Phys. A: Math. Gen. 38 1947-60
[21] Tsai A P 2003 Acc. Chem. Res. 36 31-8
[22] Mizutani U, Inukai M, Sato H and Zijlstra E S 2012 Chem. Soc. Rev. 41 6799-820
[23] Mizutani U, Inukai M, Sato H and Zijlstra E S, Lin Q 2014 Philos. Mag. 94 2571-94
[24] De Boissieu M 2006 Philos. Mag. 86 1115-22
[25] Kiselev A, Engel M and Trebin H R 2012 Phys. Rev. Lett. 109 225502
[26] Hassendeufel K H and Steurer W 2006 Philos. Mag. 86 355-9
[27] Krauss G, Steurer W, Ross A R and LoGrasso T A 2006 Philos. Mag. 86 505-11
[28] Ohhashi S, Hasegawa J, Takeuchi S and Tsai A P 2007 Philos. Mag. 86 3089-94
[29] Holland Moritz D, Ju I R, Wilde G, Schroers J and Grushko B 1999 J. Non-Cryst. Sol. 252 829-32
[30] Kuczera P, Wolny J and Steurer W 2014 Acta Crystallogr. B 70 306-14
[31] Steurer W 2012 Chem. Soc. Rev. 41 6719-29
[32] Joseph D and Elser V 1997 Phys. Rev. Lett. 79 1066-9
[33] Penrose R in Tilings and quasicrystals: a non-local growth problem? 1989 Jaric M V (ed.) Academic Press Inc. London Ltd. 3 53-79
[34] Hann C T, Socolar J E S and Steinhardt P J 2016 Phys. Rev. B 94 041413
[35] Kuczera P and Steurer W 2015 Phys. Rev. Lett. 115 085502
[36] Willmott P R, Schleputz C M, Herger R, Patterson B D, Hassendeufel K and Steurer W 2005 Phys. Rev. B 71 094203
[37] Gastaldi J, Reinhart G, Nguyen-Thi H, Mangelinck-Noel N, Billia B, Schenk T, Hartwig J, Grushko B, Klein H, Buffet A, Baruchel J, Jung H, Pino F and Przepiorkowskik B 2007 Philos. Mag. 87 3079-3087
[38] Nagao K, Inuzuka T, Nishimoto K and Edagawa K 2015 Phys. Rev. Lett. 115 075501
[39] Steurer W 2006 Z. Kristallogr. 221 402-11