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Time-resolved structural investigation of quasicrystal surfaces

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Time-resolved structural investigations of quasicrystal surfaces

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Preface

Georges Seurat

was born in Paris on December 2, 1859. Seurat's father Antoine-Chrisostome spent most his time in a cottage in Le Raincy, and his mother Ernestine Favier raised Seurat and his siblings in Paris. Seurat began to draw at an early age, and in 1875, he took a course with sculptor enrolled at the Ecole des Beaux-Arts and studied with Henri Lehmann. Seurat remained at the school for two years, during which time he discovered a book entitled Essoi sur les signes inconditionnels de l'art (Essay on the Unmistakable Signs of Art) by Humbert de Superville. This discovery of the relationship between lines and images became the inspiration for Seurat's entire career.

However, Seurat's style was unconventional, and he soon broke with the school. The Pointillism technique (see detail), in which small dots of color are grouped to create a vibrant work, painted in perfection in Les Poseuse, that Seurat introduced was adopted by his followers, the Neo-Impressionists.

He recommended the use of mathematical formulas, such as constant proportions to determine intervals between lines, angles and colors. The rule was not only applied to neighboring dots but also to axes of different sizes. Although Georges Seurat did not betray how he defined the metric of colors, maybe it also was the instinct of an gifted artist, this two rules, constant proportions and self similarity lead directly to the golden section which indeed can be found in many of his paintings (La Parade) and to the Fibonacci sequence, which seems to play an important role in the geometry of icosahedral
quasicrystals.

During the next year, Seurat worked on an immense painting entitled *Sunday Afternoon on the Island of La Grande Jatte*. The final painting was preceded by more than 200 drawings and oil studies. He completed the almost mural-sized work in 1886, and it was displayed with great interest at an Impressionist art show from May 15 to June 15, 1886.

In 1890, Seurat began to work on what became his final painting, *Le Cirque*. Although the painting was incomplete, Seurat exhibited it at the Salon des Independants. While Seurat helped organize the exhibit, he became ill due to exhaustion. Before the exhibit ended, he died on March 29, 1891, 31 years old.
Contents

Abstract 2

Zusammenfassung 3

Introduction 4

1 Experimental setup and methods 6

2 Non-periodic lattices 7
  2.1 Non-periodic diffraction spots .......................... 7
  2.1.1 Substitutional lattices ................................ 7
  2.1.2 Fibonacci sequence .................................... 8

3 Algorithm for the structure 12
  3.1 Information obtained from the secondary-electron pattern ........ 12
  3.2 Secondary-electron imaging on AlPdMn .......................... 13
    3.2.1 Mackay cluster as a building block of the structure ......... 13
    3.2.2 Enlarging the Mackay cluster to a quasicrystal with icosahedral symmetry .............................. 15
    3.2.3 Algorithm for the structure of an icosahedral quasicrystal ... 18

4 Experimental verifications 21
  4.1 Kikuchi diffraction ........................................ 21
  4.2 Stepped pentagonal surface .................................. 26

5 Phase transitions 33
  5.1 Crystalline epilayer on icosahedral AlPdMn ..................... 34
  5.2 Quasicrystalline epilayer on icosahedral AlPdMn ................ 38

6 Outlook 42

References 45

List of publications 50

Curriculum vitae 52

Dank 53
Abstract

The atomic structure of quasicrystals is neither periodic, as in crystals, nor random, as in an amorphous material, by contrast, it is aperiodic. The aperiodicity explicitly includes a long-range order like in crystals but with a wider formalism of translational symmetry. In the icosahedral quasicrystal, twofold-, threefold- and fivefold-symmetry elements are observed in the near-surface region using a real-space imaging technique based on secondary-electron emission. The observed icosahedral point-group symmetry implies the presence of atomic clusters within the analyzed region of the solid. At the same time, the surface produces pronounced Kikuchi lines, typical for well-defined crystallographic planes. In the following, a model which reconciles this dual structural nature of quasicrystals is presented. This model is constructed from an icosahedral seed followed by a concentric symmetry-preserving growth to form the macroscopic solid. The same positions for the atoms can also be obtained by stacking planes along the symmetry axes of an icosahedron. The spacing between the planes follows the Fibonacci sequence, atoms are placed at the points of intersection of the planes. Peculiarities of the structure such as steps on the surface or the interpretation of the Kikuchi lines are discussed in the light of this model.

Furthermore, two structural phase transitions at the surface of the icosahedral quasicrystal were observed. Both can be induced by changing the chemical composition by means of preferential removal of atoms at the surface. The structure of the epilayer, which is either body-centered cubic or quasicrystalline possessing a tenfold symmetry, can be chosen by holding the surface at room temperature or at 700 K during the sputtering process, respectively. The orientations of the evolving films relative to the substrate is found to be dictated by the underlying bulk. In the case of the body-centered cubic structure, two equivalent orientations, [110] or [311] aligned parallel to a fivefold-symmetry axis are observed, whereas the tenfold-symmetry axis of the decagonal phase is always aligned along the fivefold axis, which is the surface normal of the substrate. The interfaces between epilayer and substrate are investigated with respect to the proposed model. The initial bulk chemical composition and consequently the initial bulk structure at the surface is reconstructed either by temperature-induced surface segregation or external deposition of the depleted ingredients.
Zusammenfassung


Introduction

The structure of solids is divided into two groups. Solids, formed by a structure with a random atomic arrangement are called amorphous. Members belonging to the other group, the so-called crystals, possess an atomic structure which is found to follow a very strict rule. Atoms or groups of atoms are placed on the vertices of a regular lattice. Due to the regularity of the lattices, these atoms are repeated periodically in space. However, the existence of such a lattice restricts the variety of their shapes dramatically. In fact, in three dimensions only 14 different lattices are possible because a crystalline structure can only have two-, three-, four-, and sixfold-symmetry axes.

In 1984, Shechtman et al. [1] discovered in rapidly solidified Al-Mn alloys a long-range ordered icosahedral, thus non-crystallographic, symmetry. Furthermore, the specimen produced a sharp diffraction pattern. This finding was in clear antithesis to the classical crystallography. The term quasicrystal (QC) was introduced later [2] and denotes a structure with non-crystallographic symmetries and the suitability of producing sharp diffraction patterns. Till today, many different alloys having a structure with a non-crystallographic point-group symmetry with eightfold-, tenfold-, or twelvefold-rotational axes have been found.

<table>
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<th>Fivefold</th>
<th>Eightfold</th>
<th>Tenfold</th>
<th>Twelvefold</th>
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<tr>
<td>Al-Pd-Mn</td>
<td>V-Ni-Si</td>
<td>Al-Co-Ni</td>
<td>Cr-Ni</td>
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<tr>
<td>Al-Mn-Si</td>
<td>Cr-Ni-Si</td>
<td>Al-Cu-Mn</td>
<td>V-Ni</td>
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<td>Al-Li-Cu</td>
<td>Mn-Si</td>
<td>Al-Cu-Fe</td>
<td>V-Ni-Si</td>
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<td>Al-Cu-Fe</td>
<td>Mn-Si-Al</td>
<td>Al-Cu-Ni</td>
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<td>Al-Mg-Zn</td>
<td>Mn-Fe-Si</td>
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In the last fifteen years, much effort has been taken to elucidate the atomic structure of quasicrystals (QC's) or even to find rules, comparable to the periodicity in crystals, according to which the atoms in the solid are arranged. In the special case of three-dimensional icosahedral (i)-QC's only one algorithm has been proposed so far. Janot [3] based his suggestion on the relationship of the i-symmetry to the Fibonacci rule and uses its selfsimilarity to obtain a quasiperiodic model (cf. chapter 2.1.2). In each construction step, the present atomic positions are replaced by an appropriately scaled cluster with i-symmetry. An icosahedron was used as a seed for the model. Although the structure of this QC possesses the correct symmetry, there exist regions with no atoms, thus holes, which can not be observed in the experiment.

On the other hand, experimental methods such as diffraction experiments are widely used to determine the atomic position of i-QC's. Two different groups of
models are proposed: Cluster models, with an aperiodic distribution of densely packed atomic arrangements, such as Mackay clusters [4]. A. L. Mackay introduced such a densely packed cluster in which the atoms are located on centrosymmetrically arranged spherical shells having an $i$-symmetry. Instead of Mackay clusters, related forms like pseudo Mackay clusters, Bergman dodecahedron [5] or Katz and Gratias clusters [6] have been used. However, little is known about how these clusters are assembled together to form a QC of macroscopic size. Since experiments do not show any hint of a glue which stabilizes the structure, it is either of infinite small size or possesses the same symmetry as the specimen itself. An alternative structure which avoids the necessity of gluing clusters together was proposed separately by T. M. Schaub and by M. Gierer. These models are all planar constructions with a quasicrystalline distribution of atoms in layers which are stacked in a quasiperiodic way along one fivefold-symmetry axis of the structure. Scanning tunneling microscopy [7], showed two different spacings between these planes and, furthermore, the observed sequence containing eleven elements could be identified as a part of the Fibonacci sequence. Unfortunately, only scarce information is available on the exact distribution of the atoms in the individual planes.

In this work, an algorithm according to which an $i$-QC can be constructed is proposed. The algorithm can be obtained by expanding the rules for a crystalline growth, consequently, quasiperiodic structures no longer belong to the family of exotic species. The atomic positions found by applying these rules are compared with experimentally obtained data. Reversible phase transitions from quasiperiodic to periodic as well as to another quasiperiodic structure are discussed.
Chapter 1

Experimental setup and methods

All experiments presented in this work have been performed in an ultra-high vacuum chamber with a working pressure of $10^{-10}$ mbar. The surface of the samples were cleaned by sputtering with Ar$^+$ or Ne$^+$ ions at energies between 500 eV and 2000 eV, an ion-current density up to $1\mu\text{A/mm}^2$ was reached. In order to obtain information about the chemical composition in the near-surface region, Auger-electron spectroscopy (AES), for structural information low-energy electron diffraction (LEED) and secondary-electron imaging (SEI) were applied. Since AES [8, 9] and LEED [9, 10] are well established and widely used techniques, only SEI is briefly discussed. Most of the techniques that provide surface structural information rely on electron diffraction. In these experiments, the real-space information on the atomic geometry can be deduced from the position of the Bragg spots and the energy dependence of their intensities. Hence, a prerequisite for the success of this procedure not only is long-range order in the arrangement of atoms on the examined surface but also a surface temperature below approximately 700 K. In contrast, SEI allows real-time imaging of the near-surface structure in real space [11]. This method comprises the excitation of the solid surface with electrons of energy $\geq 1500$ eV, and the two-dimensional imaging of the backscattered electrons, i.e., secondary electrons. Due to the retarding potential, which acts as high-pass energy filter for these electrons, only a narrow band of wave lengths contribute to the image. These processes can be described in the following way: Primary electrons scatter at atoms at and beneath the surface. These atoms can be viewed as individual point sources which emit incoherently within the sample. The emitted secondary electrons subsequently scatter at their surrounding atoms. The part of the electrons which finally leaves the sample$^1$ is made visible on a display screen. The screen possesses the shape of a spherical segment with a 110° opening angle. Since the scattering amplitude has a significant maximum in forward direction [12, 13], the bright spots on the screen, which stand for high electron intensities, are directly connected via their polar- and azimuthal angle to the orientation of atomic rows within the investigated specimen.

$^1$An information depth of approximately 20±10 Å can be deduced from SEI patterns produced by the structure of $\text{Gd}_2\text{O}_3$ films possessing different thicknesses.
Chapter 2

Non-periodic lattices

2.1 Diffraction at non-periodic atomic arrangements

For determining symmetry properties or even obtaining exact atomic positions in a sample, diffraction methods such as X-ray diffraction or LEED are extensively used. There not only exists well established experimental techniques to investigate the structure of crystals but also various interpretation of the recorded data can be performed, which allows to obtain information about the crystal lattice, crystal basis, or the bond-lengths within the sample[14]. Since the physical effect of diffraction is equivalent to the Fourier transformation of the atomic positions in the sample, interpretation of diffraction experiments requires detailed mathematical data processing. Inspired by the discovery of quasicrystals and the development of growth techniques of monoatomic layers such as molecular-beam epitaxy [15], much interest has been attracted to the study of substitutional structures. Examples of such structures are quasiperiodic lattices which show a long-range order such that the Fourier spectrum of the lattice contains Bragg peaks [16]. From the mathematical point of view, it is clear that a non-periodic lattice can show sharp diffraction spots, however, their physical interpretation still provides an enormous challenge. This chapter describes why non-periodic lattices show sharp Bragg peaks, to simplify matters on the example of the one-dimensional Fibonacci chain, which is found to play an important role in the construction of i-QC's.

2.1.1 Substitutional lattices

Periodic lattices have a discrete atomic measure with Bragg peaks, while disordered lattices have an absolutely continuous one. Therefore, quasicrystals are the first class of structures on the way from periodic (crystalline) to random (amorphous or glassy) matter. Quasiperiodicity can easily be assembled by means of substitution rules of the general form

\[A \rightarrow A^n B^m,\]

\[B \rightarrow B^n A^m,\]

where \(n, m \in \mathbb{N}\), \(A^n = AA \ldots A\) \((n \text{ times})\)

which provides neither a periodically nor a randomly ordered sequence of A and B. An example of substitutional lattices is the Thue-Morse lattice [17, 18] for which
CHAPTER 2. NON-PERIODIC LATTICES

Figure 2.1 shows a plot of $I_N(k)$, the intensity distribution of a diffracted electron beam of $N = 1024$ atoms assorted in the Thue-Morse lattice, i.e., the distances between the atoms follow the Thue-Morse sequence. Although the plot shows sharp spots there exists a rugged background concentrated around $\phi = \frac{\pi}{8}$ and $\frac{3\pi}{8}$. Furthermore, a comparison of plots of $I_N(k)$ as a function of $N$ suggests that the sizes of different peaks scale differently with the size of the system, unlike the case of periodic and quasiperiodic systems (not shown). The Fourier spectral measure of the Thue-Morse lattice is known to be a singular continuous one (i.e., neither a discrete one nor an absolutely continuous function of the spectrum) [19], which indicates that the order of periodicity can be considered to be inbetween the order of quasiperiodic and disordered lattices. An important subgroup of the substitutional lattices are the generalized Fibonacci (GF) lattices [20]. The GF sequences are defined by the binary substitution rule $A \rightarrow A^n B^m, B \rightarrow A$. They can be divided into two classes for which $(n \geq 1, m = 1)$, with Fourier spectra containing Bragg peaks, meanwhile the Fourier spectra of the lattices $(n = 1, m \geq 1)$ belong to the quasiperiodic and disordered lattices. This second class of lattices is called aperiodic.

2.1.2 Fibonacci sequence

The Fibonacci sequence is a special case of GF sequences for which $n = m = 1$. Thus, the Fibonacci sequence is defined by the rule $L \rightarrow LS, S \rightarrow L$. The first 6 generations of the Fibonacci sequence are:
CHAPTER 2. NON-PERIODIC LATTICES

Figure 2.2: Intensity distribution of a diffracted electron beam at a one-dimensional Fibonacci chain as a function of angle.

1. L
2. LS
3. LSL
4. LSLLS
5. LSLLSLSL
6. LSLLSLSL

Note that this sequence is a special case of the random Fibonacci sequence, which is defined by \( R_n \to R_{n-1} \ast R_{n-2} \) with probability \( p \) and \( R_n \to R_{n-2} \ast R_{n-1} \) with probability \( 1-p \). The \( R_n \) symbolizes the sequence of the \( n^{th} \) generation, the asterisk defines concatenation of \( R_{n-1} \) and \( R_{n-2} \) [21]. The Fibonacci sequence is obtained when \( p = 1 \). The GF number \( F_i \) in the \( i^{th} \) generational sequence is given by the recursion relation \( F_i = nF_{i-1} + mF_{i-2} \), with initial values \( F_1 = 1, F_2 = n + m \). The characteristic value \( \tau(n,m) \), namely, the ratio of \( F_1 \) to \( F_{i-1} \) in the limit of \( i \to \infty \), is given by the positive solution of the quadratic equation \( \tau^2 - n\tau - m = 0 \). The values of \( \tau(n,m) \) for \( (n,m) = (1,1), (2,1), (3,1), (1,2), (1,3) \) and \( (2,2) \) are conventionally called golden mean, silver mean, bronze mean, copper mean, nickel mean, and mixed mean, respectively. Only the \( (1,1) \)-case, the Fibonacci numbers starting with 1, 2, 3, 5, 8, 13, 21, ... with \( \tau(1,1) =: \tau = \frac{1+\sqrt{5}}{2} = 1.618... \) will be further discussed.

Since in the limit of \( i \to \infty \), \( F_{i+1}/F_i = \tau \), \( F_i \) is proportional to an exponential function with basis \( \tau \).
CHAPTER 2. NON-PERIODIC LATTICES

Therefore

$$\lim_{n \to \infty} F_n = \alpha \tau^n$$  \hspace{1cm} (2.1)

where \(\alpha = \frac{1}{\sqrt{5}}\).

In fact, the convergence is very fast, \(\frac{F_n}{\alpha \tau^n} \approx 0.997\). Note that \(\alpha = 1\) only for \(F_1 = 1, F_2 = 3\). These numbers are called Lucas numbers. Various mathematical work has been done on the theory of the Fibonacci- and Lucas numbers, for details see M. R. Schroeder [22].

The Fibonacci chain is built by putting atoms on positions \(x_n\) in such a way that the bond lengths \(x_n - x_{n-1}\) follow the Fibonacci sequence with \(L = \tau, S = 1\). The first 5 generations of the Fibonacci chain are shown in figure 2.3.

The liaisons between Fibonacci sequence, Fibonacci chain, and Fibonacci numbers are large:

- \(G_n = G_{n-1} G_{n-2}\), where the asterisk symbolizes concatenation and \(G_n\) is the \(n^{th}\) generation of the Fibonacci chain. The Fibonacci numbers are defined analogically: \(F_n = F_{n-1} + F_{n-2}\).
- The number of bonds in the \(n^{th}\) generation is \(F_n\).
- The total length of the chain of generation \(n\) is \(F_{n-1} \tau + F_{n-2} = \tau^n\).
- The ratio between the total length of \(G_{n+1}\) and \(G_n = \tau\).

The Fibonacci chain is a self-similar arrangement. If the chain of generation \(n\) is scaled by \(\tau\), one again obtains a Fibonacci chain with \(L' = \tau \cdot L\) and \(S' = \tau \cdot S\) and all the atom sites of \(\tau G_n\) can be found in \(G_{n+1}\). Using these properties, the position \(x_n\) of the \(n^{th}\) atom in the chain can be written as \(\sum_i \tau^n\), where \(n_i\) is the segmentation of \(n\) into its Fibonacci numbers. (Example: \(x_7 = x_{5+2} = \tau^5 + \tau^2\)). Therewith, the diffraction spectrum \(I(\phi)\) of a one-dimensional chain with atoms at positions \(x_n\) can be written as:

$$I(\phi) = \left| \sum_{n_i} e^{i \phi \sin \phi x_n} \right|^2.$$  \hspace{1cm} (2.2)
A necessary characteristic of the chain to give \( \delta \)-peaks in its diffraction spectrum is, whether the condition
\[
x_n \mod 1 \to \phi \text{ for } n \to \infty
\] (2.3)
can be satisfied. This condition fixes the phase in expression (2.2) and, for a suitable value of \( \phi \), \( |e^{i k \sin \phi x_n}|^2 \to 1 \) and therefore \( I(\phi) \to \infty \). Since \( x_n \) is a sum of \( \tau^n \), \( n \in \mathbb{N} \) and according (2.1) \( \tau^n \xrightarrow{n \to \infty} \text{const} \cdot F_n \); \( F_n \in \mathbb{N} \), condition (2.3) can be satisfied. Note that the \( \mod \) in equation (2.3) comes from the fact that the argument \( x_n \) enters through complex exponentials. Figure 2.2 shows the Fourier spectrum from a one-dimensional Fibonacci sequence with \( N = 987 \) atoms. Sharp peaks with different intensities are distributed all over the spectrum.
Chapter 3

Algorithm for the construction of quasicrystals with icosahedral symmetry

3.1 Information obtained from the secondary-electron pattern

An experimentally obtained secondary-electron pattern includes several classes of information. Since the opening angle of the screen we used is about 110°, the symmetry of the pattern, which represents the symmetry of the specimen around the axis of incidence of the primary-electron beam, is evident at first glance. Due to the enhanced amplitude of the secondaries in the forward-scattering direction [12, 23], the presence of bright spots indicates the existence of rows of atoms in the specimen. Note that a symmetry axis must not necessarily result in a bright spot [24]. Diffraction processes which occur in the sample can be observed in the pattern and interpreted in form of Kikuchi bands [25] (see also chapter 4.1). The existence of Kikuchi lines and Kikuchi bands not only proves that the atoms in the specimen are arranged in layers, but also that the sequence of the layer distances is suitable for producing diffraction, i.e., they cannot be distributed in a random way. Therefore, the SEI patterns carry information which has local (short-range) as well as global (long-range) character. Apart from this rather qualitative results, also quantitative predications can be drawn from the pattern. Angles between rows of atoms, between Kikuchi bands or between two arbitrary sites in the pattern can easily be determined. This allows to distinguish between different lattice types, the identification of Kikuchi bands can be used for orienting the sample and the distance between two Kikuchi lines is related via the Bragg condition to the separation of the layer, producing the diffraction pattern. All these, together with the easy application of the method itself makes SEI an attractive tool for investigating the surface-near atomic structure.

1The lack of such a spot does not necessarily signify an unordered atomic arrangement along this direction, since the scattering process must be described as a superposition of electron wave functions, negative interference can occur. This behavior can be seen comparing the [111] direction of a bcc (spot present) to a fcc (spot not present) lattice. Knowing this difference, it is easy to distinguish between these two lattices.
3.2 Secondary-electron imaging on the icosahedral quasicrystal AlPdMn

3.2.1 Mackay cluster as a building block of the structure

Figure 3.1 shows the SEI pattern of the $\mathrm{i-Al_{70}Pd_{20}Mn_{10}}$ quasicrystal. The pattern on the left-hand side is dominated by a bright pentagon with a fivefold-symmetry axis in its center. Equilateral triangles with threefold-symmetry axes in their centers are adjacent to each pentagon side. This is more obvious on the pattern on the right-hand side, for which the sample was rotated by approximately 30°. The corners of the pentagons overlap with those of the triangles and are twofold-symmetry axes. The angles between these symmetry axes are within the experimental uncertainty equal to those of an icosahedron. Therefore, the sample possesses the icosahedral or ($\bar{5}3m$) point-group symmetry [24]. Bright spots appear along all three families of symmetry axes, i.e., along five-, three-, and twofold2. This leads to the direct conclusion, that, at least part of the structure, consists of three polyhedra possessing ($\bar{5}3m$) symmetry: the icosahedron, the dodecahedron and the icosidodecahedron. These structures have atoms at the vertices along the five-, three-, and twofold-symmetry axes, respectively. Figure 3.2 displays such an assembly which is called the Mackay cluster. The Mackay cluster possesses the correct $i$-symmetry and, considering atoms at the vertices, it is almost as closed packed as a hexagonal closed packed structure [4]. Essentially, the scattering process not only occurs in a centrosymmetrical way between a central atom and the

\footnote{If the surface is not prepared properly, the bright spots along the threefold-symmetry axes are not visible [24].}
individual shells, every atom in every shell can act as an emitter or a scatterer. Therewith, the individual radii of the three different shells gain important and can be adjusted by simulating the experimentally obtained pattern. Since a simulation which takes the wave nature of the electrons into account [26] is time-consuming and therefore not convenient to fathom this first question, a much faster but purely geometric approach was used. Every pair of atoms in the investigated structure was used to form a vector. Every vector was intersected with a sphere to simulate the enhanced intensity along two atoms observed on the screen. Because the local environment of every atom is included in this calculation, any errors either in coordination number or bond lengths have an immediately discernible effect on this central projection (cp). Thus, we obtain an accuracy of 1% for the polyhedral radii.

Figure 3.3 (left) presents the result of the described cp obtained from a Mackay cluster after adjusting the individual radii of its three shells. For comparison, the SEI pattern of the sample is displayed on the right-hand side. Even with these rudimentary assumptions of the scattering process and the geometrical structure, all main features are reproduced and the conformity is surprisingly good.
3.2.2 Enlarging the Mackay cluster to a quasicrystal with icosahedral symmetry

Additional evidences for the existence of Mackay clusters, which may serve as a building block in the structure of \(i\)-AlPdMn QC is provided by the imaging of 10 Å-diameter clusters by means of scanning tunneling microscopy [27, 28]. Yet, the question of how to construct the macroscopic solid with these building blocks, while retaining long-range orientational order (cf. chapter 4.2), remains open. A straightforward way would be to pack these clusters in a "quasi" lattice without violating either the \(i\)-symmetry or the quasiperiodicity. An elegant construction is based on packing Mackay clusters in a self-similar quasiperiodic fashion into hierarchical groups, i.e., inflation symmetry [3]. Although an \(i\)-QC can be constructed by applying this method, the structure includes widespread holes which cannot be observed experimentally and, therefore, the density of the structure is too low.

One can argue that the empty space is filled with additional atoms, some glue, the structure of this glue thus must possess the same symmetry as the sample since there is no indication in the experiment for a different symmetry. Another way to enlarge the Mackay cluster to a macroscopic QC is to add further concentric shells. This way of growth is widespread in nature [29, 30, 31] and is also a common method in crystal growth (Czochralsky process). However, there immediately are two questions to be answered: a) what are the shapes of the shells to be added in order to maintain the \(i\)-symmetry and b) how to find out their individual radii. Question b) is easy to answer by calculating the SEI pattern by means of a cp and minimizing the difference between the experimentally obtained pattern and the simulations while varying the radii. The solution to question a) requires that one recognizes the relation between icosahedron, dodecahedron, and icosidodecahedron. Icosahedron and dodecahedron are dual polyhedra, i.e., by replacing a...
face by an atom placed in its center the icosahedron (dodecahedron) transforms to a dodecahedron (icosahedron). This transformation from one polyhedron to the other can also be described in a continuous way by truncating the protruding atoms [32].

Figure 3.4: Every polyhedra with (53m) symmetry can be created starting with an icosahedron by truncating the protruding atoms. Six polyhedra with truncation ratios from 0 (icosahedron) to 1/2 (icosidodecahedron) are displayed.

Figure 3.4 displays the transformation starting with an icosahedron via four intermediate shapes to an icosidodecahedron. Note that every “truncated” shape possesses $i$-symmetry. The ratio of truncation for the truncated icosahedron, also known as C$_{60}$-cluster (top-right polyhedron in the figure), is $\frac{1}{2}$ and for the icosidodecahedron $\frac{1}{3}$. The dual polyhedron of the icosahedron, the dodecahedron, can be achieved by a truncation ratio of 1. Figure 3.4 not only illustrates the relationship between the three shells forming the Mackay cluster, but also discloses new potential candidates for an enlargement of the cluster. There is no way of neglecting the existence of e.g., a truncated icosahedron in the structure of i-QC’s. In fact, Hiraga et al. [33] found truncated icosahedra in the structure of approximants for i-AlPdMn.

Different polyhedra were generated by truncating an icosahedron or even an already truncated icosahedron and determined their individual radii by means of the cp calculation described above. By doing this, the cluster was enlarged up to a diameter of 25 Å, by enveloping a central atom with 14 individual shells having six different shapes. In principle, this procedure can be applied repeatedly to get an i-QC of arbitrary size.
Figure 3.5: Thirteen polyhedra possessing (53m) point-group symmetry which constitute the first twenty-one shells of the quasicrystalline cluster. The shell number(s) and radii (in Å) of each polyhedron are indicated.
3.2.3 Algorithm for the structure of an icosahedral quasicrystal

The described method, truncating a (53m) polyhedron and determining its radius, is not very convenient to go on with because it is difficult to generate new polyhedra which fit in the already existing structure. Problems can occur e.g., if the bond lengths between existing cluster and new shell are too short. Nevertheless, the simulation of the SEI pattern based on the structure of the cluster with a diameter of 25 Å is satisfactory. All major spots appear at their expected positions. Furthermore, a closer analysis of the cluster discloses that the atoms not only are located in centrosymmetrically arranged shells but also in planes. These planes are stacked perpendicular along five-, three-, and twofold-symmetry axes of the cluster. In addition, the stacking sequence of the planes along the i-symmetry axes exactly follows the first twelve elements of the Fibonacci sequence (see chapter 2.1.2), where \( L = \tau \cdot S \), with \( \tau \approx \frac{1 + \sqrt{5}}{2} = 1.618 \). These findings suggest a complementary way of construction an i-QC. Instead of adding shells which become more and more complicated because more atoms can be placed on spheres with growing radius while maintaining a reasonable bond length, we only make use of the i-symmetry of the sample found in the experiment and the Fibonacci sequence. In a first attempt, planes were stacked perpendicular to the twelve fivefold axes of the icosahedron. The stacking sequence of these planes follows the Fibonacci sequence, an atom is placed at the point of intersection of three planes. Although the cp calculation of the resulting structure was satisfying, the bond lengths must have been set to a unphysical low value in order to achieve a reasonable density of the structure or, equivalently, not all the possible atom sites were found. If planes not only were stacked along fivefold-, but also along threefold-symmetry axes, the missing atom sites were generated. Figure 3.5 shows thirteen polyhedra produced by applying the described algorithm. Each polyhedron possesses the (53m) point-group symmetry and constitute the first twenty-one shells of the quasicrystalline cluster. If the atomic density of the whole cluster is set to 0.046 Å\(^{-1}\), which is close to that of bulk Al, there only are two nearest neighbor distances: 2.4 Å and 2.6 Å. The cluster has a diameter of approximately 33 Å. Essentially, both methods, adding suitable shells or intersecting planes which are stacked along the symmetry axes of an icosahedron produce equivalent atomic positions. The latter is much more convenient in application, whereas the former mechanism probably is favored by nature during the growth process of i-QC's.

Figure 3.6 shows the results of a quantum mechanical scattering calculation [39] performed on this cluster. This is a more faithful representation of the secondary-electron pattern than the cp because it properly accounts for the wave nature of the electrons, based on phase-shifts computed from the superposition of neutral-atomic potentials [38]. Since SEI does not provide any chemical information, no attempt was made to determine the Al, Pd, and Mn sites. The overall chemical composition was considered by a random distribution of 70% Al and 30% Pd species in the structure.\(^4\) The agreement between the calculated and the experimental (figure

\(^3\)It is nothing extraordinary that atoms are located in planes as well as on spheres. The most simple case showing this ambiguity is a crystal structure with a cubic lattice [34].

\(^4\)The phase shifts for Al and Pd were not calculated in a self-consistent way. Due to minor influence of the structure on the shifts, the native fcc structure was used instead.
3.1) secondary-electron patterns is quite acceptable in all of the principal local and global features, indicating the suitability of the structural model. In fact, the experimental pattern agrees with the simulated pattern in figure 3.6 much better than with one based on the coordinates obtained from diffraction measurements [35, 36, 37], which overemphasize planes passing through threefold-symmetry axes, while omitting those passing through the twofold axes.

Generalization of the algorithm

Two essential remarks should be made about the described algorithm which allows to construct the atomic positions of a QC with \(i\)-symmetry:

- The Fibonacci sequence with a \(L/S\)-ratio of \(\tau\) and \(i\)- or pentagonal symmetry in three- or two dimensions are linked. The ratio appears often in a pentagon (e.g. diagonal/side) and thus also in \((53m)\) polyhedra. In fact, if just one plane is placed perpendicular to just one of the three symmetry-axes families in the icosahedron, i.e., either two-, three-, or fivefold, and atoms are put at the intersections of three of those planes, a layered structure is created, whose layers are stacked along all three symmetry families and the spacing follows the Fibonacci sequence with \(L/S = \tau\). This shows that the Fibonacci sequence is the natural stacking rule in systems with \(i\)-symmetry. In analogy, the natural stacking rule for a \((43m)\)-symmetry is a periodic sequence. In figure 3.7 (left), the algorithm is applied in two dimensions onto a fourfold symmetry. The resulting atomic arrangement is a simple quadratic, hence periodic lattice. On the right-hand side, the fourfold-symmetry is replaced by a pentagonal symmetry and the periodic sequence by the Fibonacci sequence. Here, the arrangement is a "quasi" lattice possessing fivefold symmetry. Both two-dimensional lattices are based on the same building rule,
the only parameter is the symmetry. It is self-evident that the algorithm can be applied universally to construct crystals as well as quasicrystals.

![Figure 3.7: Application of the described algorithm in two dimensions creating a fourfold- (left) and a fivefold-symmetric (right) lattice. The spacings of the lines, either periodic or aperiodic is related to the chosen symmetry.]

- In classical crystallography, the structure of a crystal can fully be described by two entities, a lattice and a basis of atoms. In the above sense, the structure is also determined by the symmetry (i.e., the stacking sequence) and the basis. Therefore, introducing a basis in our algorithm would allow to create different structures possessing the same symmetry. By this, more complex crystals, such as zincblende or wurtzite or different quasicrystals with $i$-symmetry (see table on page 4) can be produced. So far, no attempt was done to introduce a basis in the algorithm, this may be the reason, why the experimental pattern (figure 3.1) is not perfectly reproduced by the calculation (figure 3.6).
Experimental verifications of the model for icosahedral AlPdMn

4.1 Kikuchi diffraction

Kikuchi lines and Kikuchi bands appear in electron diffraction at electron energies in the high keV range [40, 41, 42]. If the specimen is thick enough the primary electron beam will produce a large number of scattered electrons which will propagate in all directions. Some of these electrons will hit the \((hkl)\) planes at an angle \(\theta_B(\lambda)\), which denotes the Bragg angle. The part of the electrons reaching the surface will leave the sample under the Bragg angle with respect to the planes at which they have been diffracted. Therefore, the width of the bands observed on the display-system is proportional to \(\sin \theta_B\), whereas the intensity distribution in a Kikuchi band is very complex [43]. However, the better a plane is defined, i.e., the more atoms are located in the plane, the more pronounced is the band. Since each Kikuchi band is assigned to a \((hkl)\) plane, the pattern can be used for orienting the sample and, in the case of a crystalline specimen, the distances \(d\) between \((hkl)\) planes can be determined by

\[
d = \frac{n \lambda R}{w} \tag{4.1}
\]

where \(w\) is the width of an axial Kikuchi band belonging to the \((hkl)\) plane on the spherical screen with radius \(R\), \(\lambda\) the wave length of the electrons, and \(n\) an integer. In the case of Al, this method is accurate up to 5% [11] (see figure 4.1).

Since Kikuchi diffraction can be explained by Bragg diffraction on periodically stacked planes in a crystal and, as shown in chapter 2.1 also aperiodic structures can show under certain condition sharp diffraction spots, one can observe Kikuchi lines and Kikuchi bands in the SEI pattern even from a quasicrystalline structure. Or vice versa, the existence of Kikuchi bands proves that the investigated structure is suitable for producing a diffraction pattern.

Figure 4.2 (left) shows the SEI pattern of an \(i\)-AlPdMn quasicrystal. The pronounced Kikuchi lines and Kikuchi bands prove the existence of planes in the sample. These lines are drawn schematically in figure 4.2 (middle). Two different families of Kikuchi bands can be identified. Dashed lines connect the fivefold axes via threefold- and twofold axes, whereas dotted ones, outlining the pentagons and
Figure 4.1: SEI pattern of crystalline Al. The sample is oriented in such a way, a fourfold-symmetry axis along [100] coincides with the angle of incidence of the primary-electron beam. Additional high-symmetry axes of the crystal as well as several Kikuchi bands are labeled. The reliability of equation 4.1 is demonstrated for the crystal planes (111), (110), and (011), referred as, \( w_1 \), \( w_2 \), and \( w_3 \), respectively.

\[
\begin{align*}
\frac{w_1}{w_2} : w_3 = 1 : 1.2 : 1.7 \\
\text{from experiment}
\end{align*}
\]

\[
\begin{align*}
\frac{w_1}{w_2} : w_3 = 1 : 1.16 : 1.64 \\
\text{from crystal data}
\end{align*}
\]

Figure 4.2: (left) SEI pattern of \( i \)-AlPdMn. The sample is oriented in such a way, a fivefold-symmetry axis of the QC coincides with the angle of incidence of the primary-electron beam. (middle) Two families of the experimentally observed Kikuchi lines are sketched. Dotted lines only connect twofold-symmetry axes, whereas dashed lines connect fivefold-, threefold-, and twofold-symmetry directions of the specimen. (right) An icosidodecahedron is used as a simplification of the structure of \( i \)-AlPdMn. The vertical lines represents the projection along the view direction of planes in the structure which produce the vertical Kikuchi band passing the center in the left pattern.
CHAPTER 4. EXPERIMENTAL VERIFICATIONS

Figure 4.3: Atomic density in planes stacked according a Fibonacci sequence with $L = 0.67 \text{Å}$ along a fivefold-symmetry axis. The average density is around 0.025 Å$^{-2}$ (dashed line). Planes which are well defined, i.e., possess a large density are stacked according a Fibonacci sequence with $L' = 1.75 \text{Å}$, which is by a factor $\tau^2$ larger than $L$.

triangles, connecting only twofold-symmetry axes. Based on the $i$-structure of the sample, Kikuchi bands crossing at fivefold-symmetry axes are due to planes stacked along the fifteen twofold-symmetry axes of the $i$-symmetry. Figure 4.2 (right) shows the icosidodecahedron along its fivefold-symmetry direction. This polyhedron is used as a simplification of the structure in order to explain in an easy way the orientation of the first family (dashed lines) of the observed Kikuchi lines, terminating the Kikuchi band. The vertical lines representing the projection along the fivefold axis of those planes, which are responsible for the formation of the vertical Kikuchi band, visible in the left panel. Not shown in the figure are the additional four sets of planes around the central fivefold axis, each stacked perpendicular to their corresponding twofold-symmetry direction. These planes from the additional bright bands observed in the experiment, which connect the fivefold-symmetry axes.

The second family of Kikuchi bands (marked with dotted lines in the middle panel), which connect twofold-symmetry axes, can be explained, knowing that their azimuthal angle is $27^\circ$ with respect to the fivefold-symmetry axes. This angle appears between twofold- and fivefold-symmetry axes in the $(5\overline{3}m)$ polyhedra. In analogy, the planes then are stacked perpendicular to the 12 fivefold-symmetry directions. Up to now, nothing can be said about the stacking sequence of the planes. The only limitation is, that the sequences must be suitable for producing a sharp diffraction pattern. However, considering figure 4.2 (right), a sequence
with two different values of separations seems to be appropriate. Since the atomic model of the $\gamma$-AlPdMn places atoms in planes which are stacked along two-, three-, and fivefold-symmetry directions, a quantitative comparison with the experiment is possible. Using equation (4.1), the spacings of the planes turns out to be $d_2 = 1.4 \, \text{Å}$, $d_5 = 1.9 \, \text{Å}$, whereas $d_2$ ($d_5$) denotes the spacings of the planes, stacked along twofold- (fivefold-) symmetry axes. Unfortunately, only the value for $d_2$ fits within 10% with the predicted value by the model. To explain the misfit of a factor 2.6 in $d_5$, one has to consider that, unlike in crystals, in this quasicrystal no periodic stacking of planes is present and furthermore, planes are not equally populated, which means that certain planes are less defined.

Figure 4.3 shows the two-dimensional atomic density in the planes, which are stacked perpendicular to a fivefold-symmetry axis as a function of stacking height. This density varies in the QC by more than a factor 2 around the average value (dashed line). However, there are planes which are well defined, i.e., which have a density well above this average. These overcrowded planes are also stacked according the Fibonacci rule, but with larger $L'_2$ and $S'_5$ values. They are found to be by a factor $r^2$ larger than $L_2$ and $S_5$. Assuming that the pronounced Kikuchi bands are due to Bragg diffraction only on these well-defined planes, the experimentally obtained values for $d_5$ differs by less than 10% compared to those obtained in the

Figure 4.4: Diffraction pattern of a periodic and an according to the Fibonacci sequence spaced one-dimensional atom chain. The spacings for the periodic chain is set to $4 \, \text{Å}$, which is equal to $L$ in the Fibonacci sequence. The first-order diffraction spots differ by 87.5%.
model.

Equation (4.1) was derived from a crystalline structure but in this case, the stacking is not periodic. A comparison of the diffraction patterns of a periodic atomic chain with only one spacing $L$ and a Fibonacci chain with spacings $LSLLS\ldots$ reveals a shift of 87% at the first order diffraction peak towards smaller values (figure 4.4). Therefore, one has to correct $d_2$ and $d_5$ by 87% which finally result in $d_2 = 1.3\,\text{Å}$ and $d_5 = 0.7\,\text{Å}$, as it is predicted by the model.
4.2 LEED-investigation on a stepped surface with pentagonal symmetry

The atomic arrangement at surfaces often is different and more complicated than the bulk structure. Reconstructions or stepped surfaces after cleaving or ion bombarding are common phenomena [44]. In the case of \( i \)-QC's, flat areas of \( \mu \)-m-size are observed by means of scanning electron microscopy after cleaving the pentagonal surface and annealing the sample at 550\(^\circ\) C for 1 hour. Other parts of the sample may show after the same treatment faceted holes, which resemble a cluster-based structure. This behavior is not linked to the surface with fivefold symmetry, it is observed for the one possessing two- as well as the threefold-symmetry. As shown in chapter 3, the structure of \( i \)-QC's can be described either by a cluster or a layer-based model. Therefore, it is not surprising to observe ambiguities in the structure of \( i \)-AlPdMn QC. In addition, when the \( i \)-QC is annealed above 420\(^\circ\) C the surface starts, in certain areas, to lose its metallic optical reflectivity and becomes dull, while in other areas the metallic appearance is maintained [28]. The irreversible disappearance of the metallic brightness as a function of temperature can be due to a roughening transition, which is analyzed systematically for the first time by Kosterlitz and Thouless [45]. Up to now, there have been no reports on experiments to detect reconstructions at the surface of \( i \)-QC's. However, computer simulations based on bulk data supply evidence for a bulk terminated surface.

In this chapter, a stepped surface along the pentagonal axis is analyzed by means of LEED investigations. Two different step heights \( L \) and \( S \) exist, which follow the Fibonacci sequence. These findings are correlated with the model of the atomic structure proposed in chapter 3.

Figure 4.5 (left) shows the LEED pattern obtained from the pentagonal surface of the \( i \)-AlPdMn QC at a primary-electron energy of 93 eV. Impurities have been removed by Ar\(^+\)-ion bombarding followed by an annealing phase at 600\(^\circ\) C for
30 minutes. The fivefold symmetry is clearly visible and the sharp diffraction spots imply a clean, flat surface [46]. On the right panel, this LEED pattern is superposed on the SEI picture, which was taken at the same sample position to clarify the orientation of the specimen. Bright lines connecting twofold-symmetry directions outline the prominent pentagon in an upright position. One threefold-(twofold-) symmetry axis is located vertically below (above) the fivefold-symmetry axis. Note the simple determination of the orientation of the sample with SEI compared to using LEED patterns.

![Figure 4.6: Schematic view of a one-dimensional stepped chain.](image)

The shape of diffraction spots change if the investigated surface is not flat on a lengthscale comparable to the wavelength of the electrons used for the diffraction experiment. Randomly distributed step heights broaden the spots, whereas a periodicity produces an energy-dependent splitting [47]. Consider the scattering at only the top layer atoms in a kinematical approximation and assuming a finite number of steps $S$, the following expression for the scattered intensity $I$ at an angle $\phi$ is derived:

$$I(\phi) \propto \sum_{s=1}^{S} \sum_{n=1}^{N} e^{ik(s(x_N+g)\sin\phi+t_n(1+\cos\phi)+x_n\sin\phi)}$$  \hspace{1cm} (4.2)

where $k = 2\pi/\lambda$, $\lambda$ is the wavelength of the electron beam, $N$ the number of atoms at a position $x_n$ in the terrace at a height $t_n$. The individual terraces of width $x_N$ are shifted horizontally by a distance $g$ compared with the adjacent step (see Figure 4.6).
Figure 4.7: a) Calculated diffraction pattern in kinematical approximation from an atomic arrangement shown in figure 4.6. Sharp diffraction spots appear at 0°, ±15°, and ±28° due to the atomic distribution in the terraces, no splitting occurs for the 00 beam. The primary-electron energy was set to 150 eV. b) Same as a) but at primary-electron energy of 120 eV. For this image the 00 spot is split into two spots with equally distributed intensities. This splitting is due to the steps.
CHAPTER 4. EXPERIMENTAL VERIFICATIONS

The second sum of equation (4.2) is due to the finite number of atoms on a single terrace and equals to the expression for the intensity distribution for a grating with \( N + 1 \) slits. The sum over \( s \) considers the steps. Figure 4.7a shows the calculated intensity distribution \( I(\phi) \) at an energy of 150 eV for the one-dimensional stepped chain displayed in figure 4.6. The step heights \( t_s \) as well as the arrangements of the atoms in the terraces \( x_n \) are distributed according the Fibonacci sequence. Sharp, pronounced peaks or pair of peaks can be observed at angles around \( 0^\circ, \pm 15^\circ, \) and \( \pm 28^\circ \). The energy is chosen in such a way that the 00 specular beam is not split. The peaks around \( \pm 15^\circ, \) and \( \pm 28^\circ \) are split, which is caused by the steps. The intensity of the two maxima of each diffraction spot is generally not distributed equally, the asymmetry is due to the positive slope \( \alpha \). Obviously, this splitting would completely disappear in the limit of a flat surface \( (t_s \to 0) \). The same calculation was performed at an energy of 120 eV, for which the 00 spot is split into two maxima with balanced intensity (figure 4.7b).

Figure 4.8: Same as figure 4.5 at a primary-electron energy of 75 eV but the heating process was replaced by only a flash annealing at 600\(^\circ\)C. Most of the diffracted spots are split perpendicular to the height of the pentagon, indicating a stepped surface.

Figure 4.8 (left) shows the LEED pattern from the same sample at a primary-electron energy of 75 eV. The heating duration of 30 minutes after sputtering the surface was replaced by only a rapid heating to 600\(^\circ\)C. The diffraction spots are as sharp as in figure 4.5, but they are split into two or three individual spots. On the right panel of figure 4.8, the LEED pattern was superposed on the faded SEI picture in order to determine the step-edge orientation. Obviously, the separation of the spots (dashed line) is perpendicular to a height of the prominent pentagon. However, there are pairs of spots (one of it is marked by an arrow), which are not aligned along this general direction. Nevertheless, the angular displacement of those spots is \( n \cdot 72^\circ \), considering the pentagonal symmetry of the surface, this value is not surprising. Consequently, the slope of the terraces is aligned along a twofold-symmetry axis (figure 4.9).

By varying the energy of the electrons, the angular distance between two coupled spots changes by approximately 4\(^\circ\). A rough estimation of the width of the terraces can be given using the approximation of a periodic distribution of the atoms in the planes. Following \([47]\), \( x_N \) is determined to be around 30±10 \( \AA \).
Figure 4.9: Schematic drawing of the atomic arrangement at the surface. The orientation of the steps is along a twofold-symmetry axis of the i-symmetry.

Considering only the 00 peak ($\phi = 0$), equation (4.2) reduces to

\[ I(0) \propto \left| \sum_{s=1}^{S} e^{2\pi i s} \right|^2. \]  

(4.3)

In this special case, the arrangement of the atoms in the individual terraces $\alpha_n$, which is not exactly known for Al$_{70}$Pd$_{20}$Mn$_{10}$, has no influence on $I(0)$. Therefore, the analysis of the specular beam is best suited for obtaining information about the step height $t_s$.

Figure 4.10 shows the measured full width at half maximum in the direction of the splitting ($\Gamma_{1/2}$) of the specular beam as a function of the primary-electron energy between 50 and 210 eV. An overall decreasing spot size coupled with an oscillating behavior with three minima (no split spots) and three maxima (maximum split spots) can be observed. Inspired by the model of the $i$-QC, which is based on a stacking of planes following the Fibonacci sequence, and the knowledge that this sequence is suitable for producing sharp diffraction peaks (see chapter 2.1), $I(0)$ is calculated for different energies and different $L$'s ($L$ is the larger unit in the Fibonacci sequence.)

Figure 4.11 shows a calculated density plot of the intensity distribution at 0° as a function of primary-electron energy and $L$ using equation 4.3. The distribution
Figure 4.10: Measured full width at half maximum of the 00 beam as a function of the electron energy. The oscillating behavior can be explained by the stepped surface.

of the step heights is according the Fibonacci sequence. Dark areas signify low intention, i.e., a split spot, whereas bright parts represent one single spot. Comparing the appropriate energies of the appearance of the maxima (solid vertical lines) and minima (dashed vertical lines) in figure 4.10 with figure 4.11, a value of approximately 1.85 Å can be obtained for $L$ (bold horizontal line).

According to the atomic model of the investigated $r-$Al$_70$Pd$_30$Mn$_{10}$ [50], not all planes are equally populated (compare chapter 4.1, figure 4.3). The atomic density in each plane perpendicular to the fivefold-symmetry axis varies by ±80% around the average value. As shown in figure 4.3, planes with a population well above this average also obey a Fibonacci sequence with $L' = 1.75$ Å and $S' = 1.1$ Å, which is $\tau^2$ times larger than the basic values of 0.67 Å and 0.41 Å given by the model. These values are in fairly good agreement with those obtained from figure 4.11. The reason why the basic values cannot be observed may be explained similarly as in chapter 4.1. There, it was shown that the diffraction at those planes inside the sample is not strong enough to produce a diffraction pattern, hence no splitting of the spots can be observed. It may also be argued, that planes with a high atomic density are more resistant against removing away during the sputtering process. This would leave behind a surface, which is packed almost as dense as in the case of a crystal.

After heating the sample at 500°C for 5 minutes, some regions of the surface showed no splitting of the LEED spots any more. These regions can be enlarged by an annealing process at 600°C till a LEED pattern as in figure 4.5 is obtained and the flat surface is restored.
Figure 4.11: Density plot of the intensity distribution of the 00 beam, diffracted at a stepped surface as a function of primary-electron energy and \( L \). The sequence of the steps follows the Fibonacci sequence. Solid (dashed) lines represent energies at which in the experiment (non) split spots occur.
Chapter 5

Phase transitions at the surface of icosahedral AlPdMn

Quasicrystals only exist in a narrow region of their phase diagrams, therefore, if the chemical composition is changed, the atomic structure may change, too. So, only considering the ternary system Al-Pd-Mn, many crystalline and quasicrystalline phases are known [54, 55]. Actually, shortly after their discovery, changes in the bulk structure due to fast-particle irradiation, which causes defects in the sample were observed [56, 57, 58, 59, 60]. In particular, since the chemical composition at the surface can be different from that of the bulk, and can be changed continuously, e.g., by surface segregation, deposition, or the preferential removal of atoms, the surface structure can differ from the bulk and may even be manipulated by external conditions.

Many experiments demonstrated that $\beta$-AlPdMn has an affinity to a cubic structure, which was mentioned by Zurkirch et al. for the first time [61]. By comparing the results of local electronic structure obtained by X-ray photoelectron spectroscopy and electron-energy-loss spectroscopy, it has been found that the properties of crystalline AlPd and quasicrystalline Al$_{70}$Pd$_{20}$Mn$_{10}$ are remarkably similar. It was concluded that the local structural and chemical environment for Pd atoms are correspondingly similar in these two materials even though the macroscopic crystal structures are substantially different. In fact, during bombarding the sample with Ar$^+$ ions, the chemical composition at the surface changes due to preferential removing of Al atoms [65] and a stable crystalline overlayer which covers the whole sample establishes. There are several experimental works which show that the structure of the overlayer is body-centered cubic (bcc) and that the orientation of a [110] axis of the bcc is aligned along a pentagonal axis of the underlying $\beta$-QC. The strong structural affinity between bcc and $\beta$-QC was theoretically demonstrated by Dimitrineko and Astaf'ev who constructed three-dimensional $\beta$-QC's starting with a CsCl unit as a seed [63]$^1$. Accordingly, the bcc structure is the very basic element of the $\beta$-QC's, indeed, almost all the quasicrystalline phase-forming systems known so far, also exhibit a closely related approximant phase in the bcc structure.

Beeli et al. [64] detected a decagonal phase in the AlPdMn system to be formed only after an extensive annealing process at 900°C for several hours is performed.

$^1$The orientation of the cube inside the dodecahedron is not the one observed in the experiment.
although, the resulting decagonal samples could only be grown in a submillimeter size. On the other hand, a thin decagonal layer, covering the whole substrate of approximately 1 cm² surface area can be grown on the i-sample by maintaining the surface at an elevated temperature during the sputtering process [62]. This decagonal surface is orientated in such a way, that the tenfold-symmetry direction lies parallel to the pentagonal axis of the substrate. Both transformations can be reversed by annealing the sample to induce the surface segregation of Al atoms, which restores the original chemical composition and structure.

5.1 Crystalline epilayer on the icosahedral quasicrystal

The chemical composition dictates the atomic structure in solids or, vice versa, the structure can be changed by varying the stoichiometry. This can be achieved by e.g. preferential sputtering or by external deposition of ingredients. Sputtering the pentagonal surface of Al₅₀Pd₆₀Mn₁₀ for 30 minutes modifies the composition to Al₄₈Pd₁₂Mn₁₀ and produces a dramatic change in the surface structure [66, 67, 68]. Figures 5.1a and b display the growth of a cubic superstructure whose

![Figure 5.1: Secondary-electron patterns from the pentagonal surface after sputtering. The fivefold-symmetry axis of the quasicrystalline substrate is parallel either to a [110] (a and b) or to a [311] (c) direction of the cubic overlayer. Patterns shown in (a) and (b) are rotated by 72° with respect to each other along [110].](image)

orientation relative to one of the fivefold-symmetry axes of the substrate is parallel to a [110] direction of the cubic overlayer. Since the angles between two- and threefold-symmetry axes in a cubic structure are close to the angles between five- and twofold-symmetry axes in the i-structure, the observed orientation of the superstructure matches with the substrate. It is further plausible that there exist, due to the pentagonal symmetry at the surface, five equivalent orientation of the cube which are rotated by 72° relative to each other like those shown in figures 5.1a or b. It is remarkable that the cubic superstructure grows perfectly on the QC in the sense that LEED spots can be observed (see figure 5.2). Spots belonging to the (110) orientation are marked by arrows, and one corresponding (110) unit cell of the reciprocal lattice is highlighted. Yet,
several spots in the pattern cannot be explained assuming that they belong to the reciprocal (110) lattice. A closer analysis divulges that they match with a (311) lattice, thus, the LEED pattern contains, due to the extended electron-beam focus, a mixture of both configurations. Different from the SEI pattern, where the pure (110) orientation is clearly visible, the additional (311) spots in the LEED pattern disappear only after a mild annealing. This was reported earlier by M. W. Heinzig et al. [69], however, they could not identify or find an explanation for those additional spots. Similarly as in the (110)-orientation, the angular difference between fivefold- and twofold-symmetry directions of the QC and between [311] and [111] axes of the cubic structure is only 2.2°. This shows the close relationship of the two structures, i.e., the fivefold-symmetry axis can be parallel to either [110] or [311]. Figure 5.1c presents the SEI pattern of the cubic overlayer in its (311) orientation for which the threefold [111] axis (bright patch on the right-hand side) is arranged along one twofold-symmetry axis of the substrate. In order to demonstrate the correspondence between the symmetry directions of the cubic structure and those of the ı-phase, the SEI pattern is represented by a cp of atoms located at different vertices (figure 5.3). On the right-hand side, the cp pattern based on a Mackay cluster (see figure 3.3) is displayed and the cp pattern from a bcc lattice is shown on the left panel. The structures are oriented with the twofold [110] and the threefold [111] symmetry direction of the bcc aligned with a fivefold- and a threefold-symmetry axis of the ı-QC, respectively. This is equivalent to the orientation of the patterns shown in figure 5.1a or b and 3.1(left). According to figure 5.3, another [111] direction coincides with a twofold- and a [311]- corresponds to another fivefold-symmetry direction. This presentation explains why the orientation of the bcc superstructure with respect to the ı-QC
Figure 5.3: (left) A cp based on a body-centered lattice and a cp from a Mackay cluster (right). The structures are oriented in such a way as to simulate the experiment (cf. figure 5.1).

is independent whether the fivefold-symmetry axis is parallel to [110] or to [311].

Figure 5.4: An atomic model of the interface between the pentagonal surface of the i-quasicrystal Al$_{70}$Pd$_{20}$Mn$_{10}$ (larger circles) and the (110) surface of a bcc structure. The interatomic distances are drawn to scale, several pentagons and rectangles are marked.
An investigation based on the atomic model presented in chapter 3 for the interface between the (110) surface of the bcc and the pentagonal phase of the \( i \)-QC reveals that the atomic positions in the two phases almost completely coincide (cf. figure 5.4). The interatomic distance along [100] corresponds to the Al-Al bond length of 3.0 Å. The length of the pentagon sides are 4.13 Å, which is to compare with \( \sqrt{2} \cdot 3.0 = 4.24 \) Å. The mismatch between \( i \)-QC and bcc only is 3%, the average displacement is less than 0.6 Å per atom. Thus, not only angles between high-symmetry directions of both structures are similar but also the atomic positions themselves are comparable despite the different symmetry of substrate and overlayer. By increasing the temperature at the surface to 600° C at a rate of 5° C per minute, the surface structure as well as the chemical composition is completely restored to icosahedral. Figure 5.5 illustrates the trend of composition during this heating process. Regions in which cubic, icosahedral, or a mixture of both phases exist are indicated. Note, that the QC may not have been in thermal equilibrium, but each composition belongs to a certain structure. After this procedure, a sharp LEED pattern showing a fivefold symmetry is observed. Subsequent sputtering may form a cubic superstructure which is oriented in a still different way with respect to the substrate. In a separate experiment, the Al depletion at the sputtered surface is compensated by deposition of Al from an atomic-beam source. Then, the restoration of the quasicrystalline structure occurs at a temperature as low as 150° C. This temperature is apparently high enough to activate the kinetics to reassemble the quasicrystal.

\[\text{Figure 5.5: The chemical composition was monitored during the annealing process. The bcc phase disappeared at a composition of about Al}_{65}\text{Pd}_{25}\text{Mn}_{10}, \text{which was reached at approximately } 200° \text{C. Above } 300° \text{C, SEI revealed no further changes in the pattern.}\]

\(^{2}\text{The transformation back to the } i \text{-phase has been recorded in a separate run with different incident angles of primary electrons to obtain information originating from different depths. Thus, a transformation rate from the bulk to the surface at a constant temperature of } 350° \text{C of approximately } 3 \text{ Å/min could be observed.}\]
5.2 Quasicrystalline epilayer on the icosahedral quasicrystal

Shortly after the discovery of the i-QC in 1984, Bendersky [70] managed to synthesize a quasicrystal with a decagonal symmetry. In contrast to the i-AlPdMn, this AlCoNi compound only is quasiperiodic in two dimensions and periodic in the third dimension, i.e., along the tenfold-symmetry axis. Nowadays, several decagonal quasicrystals having many different phases and superstructures are known, but all of them have a periodic stacking of planes along the tenfold-symmetry axis. This observation suggests that the periodic stacking is a fundamental rule in the construction of decagonal QC's [71, 72, 73, 74, 75]. Similar to the forgoing discussions, the bulk-decagonal Al70Co15Ni15 undergoes a structural phase transition at the surface which can be induced by ion bombarding. Again, a bcc structure establishes with the [110] axis aligned along the tenfold-symmetry axis [76]. This transformation can be repeated reproducibly, the reversion occurs upon annealing. The purpose of this chapter is to present the “missing” structural transformation from the i- to the decagonal symmetry. This transformation could be observed by means of SEI at the surface of Al70Pd20Mn10 and is discussed regarding to models describing both, substrate and epilayer. At the same time, a link from i-QC to quasicrystals with a decagonal symmetry will be pointed out.

Figures 5.6a and b show two SEI patterns obtained from the FQC after removing surface contaminations. To show the principal components of the structure which lie away from the surface normal, the sample is tilted by 20° such that the pentagonal axis appears as a bright patch below the central part of the pattern in figure b. The sharp definition of the patterns and their spatial orientation persist over the entire surface, indicating that the sample consists of a single icosahedral domain.

The surface segregation of alloy components in i-QC’s follows an Arrhenius law [77], whereas the sputter rate is independent of the surface temperature. Therefore, ion-bombarding the sample at an elevated temperature can produce different chemical compositions. Figure 5.6c and d display two SEI patterns obtained from the quasicrystalline sample after bombarding its surface with Ar⁺ for 30 minutes at 400°C and cooled down to room temperature. It is apparent from figure 5.6c that the surface now has tenfold symmetry and that its symmetry axis is aligned with the fivefold-symmetry axis of the initial surface. In SEI, tenfold-symmetric pattern can be generated not only by a decagonal quasicrystal, but also by twined pentagonal surfaces or by five bcc structures oriented along the (110) direction, but rotated by 72° increments [67, 68]. The pattern from the tilted sample in figure 5.6d allows these possibilities to be differentiated and only elements of decagonal symmetry are found to be consistent with this pattern. Stabilized by the substrate, the decagonal epilayer covers the whole surface of the sample and its thickness can be estimated to be at least 1.5-2 nm, which is the escape depth of the 2-keV electrons used to generate the SEI pattern [78]. The patterns in figure 5.6c and d are essentially indistinguishable from the SEI pattern produced from a bulk decagonal Al70Co15Ni15 without removing the surface impurities, i.e., both patterns show

A similar, but irreversible transition of the pentagonal surface was reported as a consequence of heating to 750°C [68]. A fragmentation of the sample into several twined pentagonal domains was observed.
identical features: Two sets of patches arranged on decagonal rings with opening angles of 18° and 31°, separated by a dark circular band. In contrast, the pattern obtained from a cleaned AlCoNi surface displays the bright lines (see pattern 5.6d) better defined. An attempt to clean the decagonal epilayer by sputtering fails; instead of the tenfold structure a bcc structure evolves. Furthermore, annealing the sample induces surface segregation of Al atoms and, therefore, the $i$-symmetry reestablishes. The sequence of SEI patterns in figure 5.7 shows the evolution of the pentagonal symmetry starting from the decagonal structure during annealing at 600°C. The pattern in figure 5.7a was taken just before the transition started, each successive pattern was recorded after annealing for additional 2-min increments. Measuring the chemical composition during this transformation reveals a similar behavior like in figure 5.5 only that the composition of the decagonal phase is $\text{Al}_{122}\text{Pd}_{56}\text{Mn}_{22}$. 

Figure 5.6: Secondary-electron patterns obtained from the pentagonal surface of a single $i$-$\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ quasicrystal at a primary-electron energy of 2 keV (a,b) and the surface of this quasicrystal after bombardment with $\text{Ar}^+$ ions at 400°C (c,d). In (a) and (c), the surface normal coincides with the axis of the display unit, while in (b) and (d), the sample is tilted such that the high-symmetry axes appear below the electron gun.
Figure 5.7: Secondary-electron patterns obtained from the decagonal surface during annealing at 600° C. The patterns are taken at 2-minute intervals. In (a) the surface normal coincides with the decagonal- and in (f) with the pentagonal-symmetry axis.
The continuous transformation between the two different phases suggests that the similarity of the different crystalline and quasicrystalline structures of Al-Pd-Mn can be explained by different stacking sequences of atomic planes. Considering the ten bright patches forming the outer bright ring with $\theta \approx 31^\circ$, in figure 5.7a. These features split radially during the transformation to form either patches with opening angles of $\theta = 27^\circ, 31.5^\circ$, or $37^\circ$ of the pentagonal phase in figure 5.7f. To show this, coordinates representing the pentagonal phase were modified in such a way, that the stacking sequence along one of the fivefold-symmetry axes is changed from quasiperiodic to periodic. A cp calculation then was performed and the resulting picture reproduced all the features (figure 5.8 (left)). Moreover, every pair of planes stacked parallel to the fivefold-symmetry axis in the $i$-QC possesses different atomic arrangements, i.e., there doesn't exist two planes in which the atoms are located the same way. After the rearrangement, this variety of different distributions of atoms in the planes is restricted to only two possibilities, which are drawn in figure 5.8 (right).

Figure 5.8: (left) cp calculation of the $i$-QC structure but with a periodic stacking of planes along one of the fivefold-symmetry axes. The pattern then is tenfold symmetric along the former fivefold-symmetry axis. (right) The rearrangement of the planes produces only two different configurations of atoms in the planes along the tenfold-symmetry axis. The assembly of these planes then follows in the decagonal QC a simple ABAB... sequence.

\footnote{This can be done without changing the density of the structure.}
Chapter 6

Conclusions and Outlook

Till this day, the structure of quasicrystals are regarded to be a separate group positioned between crystals and amorphous materials. In other words, their structures cannot be described using techniques based on classical crystallography such as the theory of Bravais lattices. Consequently, the obstacles of determining reasonable atomic positions in a quasiperiodic structure are immense. Nonetheless, many techniques developed for investigating periodic structures such as diffraction methods can be applied to non-periodic arrangements, too, and provide a powerful tool towards the experimental determination of the atomic positions in quasicrystals. On the other hand, just a few systematic approaches to the explanation of the structure of quasiperiodic systems are made [2, 3, 81, 82, 83], whereas the "simple" indication of the atomic coordinates of a certain material has the lions share. This work described one algorithm how a generalized lattice possessing a given symmetry can be produced. In particular, this rule is successfully applied for the Al\textsubscript{70}Pd\textsubscript{20}Mn\textsubscript{10} alloy forming an i-QC. It explains experimentally obtained data, such as SEI patterns, structural phase transitions and different properties of the surface.

This knowledge can further be used for making predictions of structures which have not yet been encountered, e.g., quasicrystals possessing sevenfold-symmetry elements. In order to apply our algorithm, two inputs are needed:

a) A three-dimensional object which possesses the required heptagonal symmetry. (For the (5\text{bm}) symmetry this is the icosahedron or dodecahedron.)

b) A sequence which belongs to the heptagonal symmetry. (For the (5\text{bm}) symmetry this is the Fibonacci sequence.)

The procedure then is straightforward. Planes have to be stacked along the sevenfold-symmetry directions given in a) following the sequence given in b). Atoms are placed wherever three planes intersect. The solution for b) can be found in the work by Garcia [84]. In similarity to chapter 2.1.1 the following substitutional lattice is given:

\[ U \rightarrow UVW \quad V \rightarrow UV \quad W \rightarrow U \]

This rule produces a sequence starting with \textit{UVWUVUVWUVWUVW...}. If the segment lengths were chosen as \textit{l}_U/\textit{l}_W = \beta = 1 + 2\cos(2\pi/7), \textit{l}_V/\textit{l}_W = \beta^2 - \beta - 1 =
2\cos(\pi/7), a selfsimilar one-dimensional tiling is obtained with scaling factor $\beta$ satisfying the equation $\beta^3 = 2\beta^2 + 3 - 1$. Note that the ratios of $l_V : l_V : l_V = 1 : 1.801 : 2.247$ can be found in a regular heptagon.

The solution for a) is more sophisticated. Although the highest rotational symmetry in a regular three-dimensional polyhedra is five (icosahedron or dodecahedron), a polyhedra with sevenfold-symmetry elements can be generated in the same way. Let us consider a dodecahedron. Starting with five pentagons arranged in the plane around a central pentagon with which they share one edge. The upper part of a dodecahedron can be generated if the pentagons were bent around the common edges in such a way that they touch each other. An analogous procedure cannot be performed if the five pentagons are replaced by seven heptagons because the heptagons already overlap with each other. However, the heptagons can be bent around the common edges till the smaller diagonals touch each other. The resulting structure is shown in figure 6.1(left). It consists of two regular heptagons (top and bottom) and 14 trapezes, each of which can be inscribed in a regular heptagon (one is shown in the figure).

Similar to Figure 3.7, the quasicrystal possessing sevenfold symmetry shows the ambiguity of clusters and planes. The distribution of atoms perpendicular to a sevenfold-symmetry axis is shown in figure 6.1(right). Atoms are located on the corners of heptagons, thus centrosymmetrically, but they are also forming lines. In figure 6.2, the simulated SEI pattern of a quasicrystal possessing sevenfold-symmetry elements is shown. Pattern on the left shows the quasicrystal along a sevenfold-symmetry axis. Bands forming a heptagon at an opening angle of approximately $45^\circ$ can be made out. Additional patches are located in the middle.

$^1$This angle is $63.43^\circ$.
$^2$The smaller diagonal is equivalent to $l_V$. 

Figure 6.1: (left) The building block for a three-dimensional quasicrystal possessing sevenfold-symmetry elements. The longer sides of the trapezes are equal to the short diagonal of the heptagon defining top and bottom. (right) Distribution of the atoms in a plane perpendicular to a sevenfold-symmetry axis. Several heptagons which also produce rows are visible.
Figure 6.2: Simulation of SEI patterns produced from a quasicrystal possessing sevenfold symmetry. The overall heptagonal symmetry is clearly visible. For the left panel, the quasicrystal is orientated along a sevenfold symmetry axis, on the right-hand side, this axis is rotated by $20^\circ$ out of center.

of each heptagon side at an opening angle of $43^\circ$. Seven bright spots at $31^\circ$ and seven dimmer patches at $23^\circ$, rotated by $\frac{2\pi}{7}/2$ complete the pattern. For the left panel of figure 6.2, the sample was rotated by $20^\circ$. Additional features appear at angles more than $60^\circ$ (the total opening angle in the panels) away from the sevenfold-symmetry axis.

Although nobody can verify whether this structure is the one nature would chose, because there is no sample possessing sevenfold symmetry, the equivalence to known structures such as crystals or $i$-QC is obvious. However, the discovery of new structures will not only lead to new knowledge but they will certainly also appeal to the human mind.
Bibliography


List of publications

*Local structure and symmetry elements of the decagonal quasicrystal Al$_{70}$Co$_{15}$Ni$_{15}$*

*Crystal structure of Ru complex sensitizers of TiO$_2$ anatase nanopowders*

*Surface structural transformation on the icosahedral quasicrystal Al$_{70}$Pd$_{30}$Mn$_{10}$*

*The structure of Fe on Al(001)*

*Quasicrystalline related phase transitions at the surface of Al$_5$Pd*

*Structural transformations at the surface of the decagonal quasicrystal Al$_{70}$Co$_{15}$Ni$_{15}$*

*Surface structural transitions on Al$_5$Pd*

*Symmetry changes at the surface of Al$_{70}$Pd$_{30}$Mn$_{10}$*

*Structural transformations at the surface of icosahedral Al$_{70}$Pd$_{30}$Mn$_{10}$*
Decagonal epilayers on the icosahedral quasicrystal $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$

"Ästhetische Quasikristalle"
B. Bolliger, M. Erbudak, Neue Zürcher Zeitung, Forschung und Technik, 238 (13. 10. 1999).

Planar and cluster structure of icosahedral quasicrystals

Symmetry changes at the surface of $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$

On the electronic origin of the structural changes at the surface of a bulk quasicrystal, $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$

Structure of the anatase $\text{TiO}_2$ (101) and (001) surfaces

"Çevremizdeki doğal ve yapay beşli simetriler"

Local atomic structure of the icosahedral quasicrystal $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$

"Pentepistemology" of biological structures and quasicrystals
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53