STRUCTURAL CHARACTERIZATION OF THE d-Al-Ni-Co QUASICRYSTAL SURFACE AND XENON ADSORPTION

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ABSTRACT

Quantitative low-energy electron diffraction (LEED) was used to characterize the structure of the tenfold surface of decagonal Al-Ni-Co quasicrystal. A quasicrystal slab model was used in the LEED calculation with approximations that averaged over composition and local geometries. The results show that the surface region is a relaxed, bulk terminated structure, with the same composition of the bulk. The outermost layer is slightly contracted relative to the bulk interlayer spacing, while the next layer is expanded. Periodic models that approximate the actual local quasicrystal structure (approximants) were used in a more exact atomistic calculation and compared to the approximated calculation. The results obtained with both methods were consistent with each other and suggests that the use approximant structure models provide a simpler method for the determination of local geometries in quasicrystal structures.

LEED isobar measurements were used to characterize the adsorption and film growth of Xe onto the tenfold surface of d-Al-Ni-Co. Xe grows layer-by-layer at temperatures between 50 K and 80 K. The structure of the first layer appears to retain the symmetry of the substrate but at the onset of second-layer adsorption, the film reorders to a 6-fold structure. This 6-fold structure has domains that are aligned along the 10-fold directions of the quasicrystal, leading to a diffraction pattern having 30-spot rings. The momentum transfer of the first-order diffraction beams from Xe coincides with one of the principle momentum transfers from the quasicrystal surface, indicating that the Xe inter-row spacing is related to a principal distance on the surface. The Xe multilayer is consistent with bulk fcc(111) Xe.
Preliminary elastic and inelastic helium scattering experiments were performed on the clean graphite to characterize its surface structure and dynamics and Xe adsorption. These experiments are used as a testing ground for similar HAS experiments which will be carried out in the near future with the same apparatus on the tenfold d-Al-Ni-Co quasicrystal surface.
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Chapter 1

Introduction

The determination of the atomic structures of crystal surfaces has been one of the most active fields of Surface Science in the last thirty years. This endeavor, driven both by the improvement of surface science techniques (Ultra High Vacuum, Low Energy Electron Diffraction, Auger Electron Spectroscopy) and by the possibility to study complex surface phenomena like catalysis, has produced a large database of surface structures of most of the metals and semiconductors and for a large variety of adsorbates, from alkali metals to rare gases and small molecules like benzene. The current challenge faced by surface scientists is to apply traditional methods of surface structure characterizations to more complex systems, including biological materials and complex alloys.

Most of solid state physics is built upon the definition of crystal as being constructed by the infinite periodic repetition of identical structural units in space. The long range effect of periodicity was considered the essential reason for a discrete diffraction pattern in a solid. In this scenario, discrete diffraction spots were a direct indication of the periodicity in a solid. Whenever the translational symmetry was disrupted, the spots in the diffraction pattern would vanish. The classical definition of crystal however was deeply challenged by the discovery of metal alloys known as “quasicrystals” in 1982 by Shechtman and co-workers. The presence of a very dense set of sharp discrete diffraction peaks having 10-fold rotational symmetry could not be explained by the traditional definition of crystals, whose translational symmetry
requirement allowed only some symmetries (2, 3, 4, 6-fold), while it prohibited others (5, 8, 10, 12-fold). The long range structural order possessed by quasicrystals was however consistent with having both a diffraction pattern and a previously forbidden symmetry. A new definition of crystal was then established by the International Union of Crystallography to include “any solid with an essentially discrete diffraction pattern”\textsuperscript{5}. Although quasicrystals are formally part of this family, they retain their prefix “quasi” to underline the inherent divergence from the periodic counterparts.

Quasicrystals show peculiar macroscopic surface properties, often totally different from the closest crystal of origin. For example they have a very low surface energy, which tends to give non-stick behavior\textsuperscript{6}, good resistance to corrosion and high hardness\textsuperscript{7}. They also posses peculiar transport properties such as low thermal conductivity\textsuperscript{9}. This, in addition to a very low coefficient of friction, one order of magnitude lower than the crystalline metallic constituents or alloys and similar to the one of diamond, makes quasicrystals perfect candidate for coating and wear resistant materials. Some applications are commercially available for the consumer market (non-stick, scratch-free frying pans, razors)\textsuperscript{7}. Medical applications have also been investigated: polymeric composites of Al–Cu–Fe quasicrystal and polyethylene have been successfully tested as possible material candidates for acetabular cup/hip prosthetics\textsuperscript{10}. Quasicrystals have also shown to have interesting behavior when used as catalysts in the steam reforming of methanol: because they are equilibrium phases and stable up to high temperature (close to their melting point), they achieved the highest amount of gas generated and the lowest reaction initiation temperature\textsuperscript{11}. The low electron density of states is responsible for the presence of a pseudo-gap at the Fermi level\textsuperscript{12}, which could make quasicrystals suitable
for semiconductor applications, such as selective solar light absorbers\textsuperscript{13}. This particular band gap formation has been exploited at higher scales for acoustic 2D systems\textsuperscript{14} and recently for 2D\textsuperscript{15} and 3D\textsuperscript{16} photonic quasicrystals.

While the list of applications is most likely to increase, paradoxically the set of reliable, experimentally derived models of the surface structures is still limited. This information is of crucial importance, since it constitutes the basis for further modeling of surface interactions with other materials and it relates the macroscopic properties to the atomic structure. The determination of structural models of quasicrystal surfaces is challenged by the lack of periodicity, which does not allow an immediate use of conventional experimental and computational techniques, based on a periodic formulation. The simple idea of applying periodic boundary conditions in calculations and simulations is not permitted. For this reason new alternative and often complementary tools had to be developed and some of those are presented in this thesis. These tools comes as either approximations in the calculation process, to reduce the number of free parameters from the theoretically infinite number of the quasicrystal itself; or as “approximants”, approximate periodic crystalline models of the quasiperiodic crystal.

Stimulated by the appealing possibility of growing epitaxial films using quasicrystal surface as templates\textsuperscript{17, 18}, several transition metal adsorption experiments have been performed on quasicrystal surfaces (a comprehensive overview is given in reference 19), although the details of the chemical interaction with the substrate are yet not clear. Surprisingly not as many experiments have been performed using rare gases,
whose presumably simple interaction with the substrate would make them ideal to understand how the balance between adsorbate-adsorbate and adsorbate-substrate interaction potential determines the atomic configuration of the overlayer. For this purpose rare gases have been extensively studied on metal surfaces\textsuperscript{20}. The question of whether and how the adsorption process is influenced by the presence of a quasicrystalline substrate is not trivial and not immediately derivable from the experience with periodic substrates. The concept of commensurability of the adsorbed layer on a quasiperiodic substrate has different implications when compared to periodic structures. If the adsorbate is incommensurate with the quasiperiodic substrate (either by showing a different quasiperiodic decoration or by being periodic), the lattice mismatch may be responsible for the friction behavior\textsuperscript{8, 21, 22}. If the adsorbate grows as a commensurate film, it means that it is itself quasicrystalline. Will it retain the quasiperiodicity beyond the monolayer? Is it possible to grow three-dimensional single-component quasicrystals? If not, what is the mechanism that regulates the balance between periodicity vs. quasiperiodicity? An attempt to answer to these questions is the primary goal of this thesis.

The motivation of this thesis is two-fold. From one side, it presents detailed structural models for the ten-fold d-Al-Ni-Co quasicrystal surface. It then presents a set of thermodynamic and structural measurements of the adsorption of xenon on the quasicrystal surface. These measurements provide a description of the evolution of quasiperiodicity during adsorption. The combination of these experimental models for both the surface structure and the adsorption mechanisms serves both as an incentive and as a proving ground for simulations and calculations on these systems, as well as
complementary verification of other experiments performed with different techniques. This verification process will be useful to validate the advancement in applying conventional surface science methods to complex quasicrystal surfaces and ultimately to understand the role of conventional interaction mechanisms in the formation of quasiperiodic crystals.

This thesis is organized as follow: Chapter Two will provide the theoretical background behind this work: an introduction to real quasicrystal surfaces as a natural evolution from a simple 1D quasiperiodic model (the Fibonacci sequence) to sophisticated 3D models used in the experiments. This description will be correlated by a background theory of diffraction and how it is challenged by the quasiperiodicity. Chapter Three will describe the experimental apparatus used as well as the quasicrystal-specific techniques employed for the sample preparation and discuss some of the methods of acquisition and analysis, with particular emphasis on the optimization of those to the quasicrystals. Chapter Four will present the surface structure models of the 10-fold d-Al-Ni-Co quasicrystal surface, derived from low energy electron diffraction experiments. It will also include a measurement of the Debye temperature of the d-AlNiCo surface. Chapter Five will present and discuss detailed results of LEED experiments of xenon adsorption d-AlNiCo, including the evolution of the structure upon adsorption, isobars of adsorption, the isosteric heat of adsorption. Chapter Six will present test results with helium atom scattering on the surface of graphite: diffractions scans of the clean surface, surface Debye temperature measurements, Xe adsorption isobars and inelastic scattering measurements of surface phonons of the clean surface. These experiments were performed as a prerequisite and for testing the apparatus in view of the planned
experiments on the d-AlNiCo quasicrystal surface. This will include a detailed
description of the apparatus and the software. Finally, Chapter Seven will summarize the
results and provide a future outlook.

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Chapter 2
Quasiperiodicity and Diffraction

A periodic crystal is constructed by the infinite repetition of identical structural units in space\(^1\). The crystal lattice is defined by a set of coordinate vectors, of which linear combination provides the full lattice. Only five rotational symmetries are allowed (1, 2, 3, 4 and 6-fold) in periodic lattices due to constraints imposed by the translational symmetry, and their diffraction patterns consist of sharp Bragg peaks reflecting the crystal symmetry and the periodicity.

The “tiling” problem defined by covering a plane with two or more tiles with no overlaps\(^2\) was studied long before the discovery of quasicrystals in 1982\(^3\). It dates back to the tenth-century Arabian mathematician Mohammad Al-Buzjani and was later studied by Albrecht Dürer (1471-1528) and Johannes Kepler (1571-1630). The modern theory of tilings was described by Grunbaum and Shepard\(^4\) and that work culminated with the famous paper by Roger Penrose in 1974, “The role of aesthetics in pure and applied mathematical research”\(^5\), in which he describes how the tiling of a plane can be obtained by using two non similar rhombic tiles assembled by strict matching rules (Figure 2.1). The Penrose tiling shows definite elements of five-fold symmetry, the overall all structure being nevertheless aperiodic, or in other words, lacking a long range translational symmetry.
Quasicrystalline alloys are now available in a wide variety of compositions and several bulk and surface structural studies have been performed\textsuperscript{6}. The most commonly studied groups are icosahedral quasicrystals (such as i-Al-Pd-Mn and i-AlCu-Fe), and decagonal quasicrystals, such as d-Al-Ni-Co, which is the type investigated in this thesis.

2.1 Basic Concepts of Diffraction

Let us consider a grating of 1D array of periodically spaced slits, where the position of the $n^{th}$ slit can be expressed as function of the lattice constant $a$:

$$r_n = na$$
Assuming only single scattering events (the so called “kinematical approximation”), when illuminated by a plane wave with wave vector \( k_o \), the scattered amplitude along \( k \) is proportional to:

\[
A(\Delta k) = C(k)S_G(\Delta k)
\]

\[
S_G(\Delta k) = \sum_n f_n \exp(i\,r \cdot \Delta k) = \sum_n f_n \exp[i(na \cdot \Delta k)]
\]

where \( C(k) \) is a constant phase factor, \( \Delta k = k - k_o \) and \( f_n \) represents the amplitude of the wave scattered from a single slit. \( S_G(\Delta k) \) is called the structure factor, the Fourier transform of the distribution of scattered waves \( f_n \). The measured intensity of the total scattered wave is given by:

\[
I(\Delta k) = |A(\Delta k)|^2 \propto |S_G(\Delta k)|^2
\]

In a real diffraction experiment, the constructive and destructive interference between the waves scattered from the gratings, will give rise to the diffraction pattern, of which \( I(\Delta k) \) is the mathematical expression. In the kinematical approach, a direct comparison can be drawn between diffraction pattern and the squared modulus of the Fourier transform. This identification is useful to relate features in the diffraction pattern to the diffraction grating. Limitations to this analysis occur in presence of multiple scattering events, which occurs in the case of electron diffraction. This will be discussed later in this chapter.
2.2 The Fibonacci sequence: quasiperiodicity in its simplest form

The main requirements for an aperiodic tiling consist of a set of two (or more) non-similar tiles and a set of matching rules that describe how to assemble them. This can be easily accomplished in 1D to produce the Fibonacci sequence named after the inventor, Leonardo di Fibonacci (1175-1250). Let us consider two different segments and call them L (for Long) and S (for Short), which will be our tiles. The two matching rules in building the sequence are substitution rules (also called “inflation rules”): $L \rightarrow LS$ and $S \rightarrow L$. The resulting sequence is shown in Figure 2.2.

Several features are evident. First, the sequence is not periodic. It is self-similar, i.e. it can be recreated by rescaling the tiles: a visual inspection at different generations of the sequence shows similar patterns. If we denote $L_n$ and $S_n$ the number of long and short segments respectively per generation, we obtain:
This is typically a quasiperiodic feature: for any periodic crystal, this ratio would be a rational number. A formal explanation of the origin of the value of $\tau$ within the Fibonacci sequence can be seen using the recursive representation of the Fibonacci sequence that states: “The $n^{th}$ number of the sequence is the sum of the previous two”:

$$f_n = f_{n-1} + f_{n-2}$$  \hspace{1cm} 2.4

Approximating this to finite difference equation:

$$y'' = y + 1$$

To solve this 2$^{nd}$ order differential equation:

$$x^2 = x + 1$$

The roots for this equation are:

$$x = \frac{1 \pm \sqrt{5}}{2} = \left\{ \begin{array}{l}
\phi \\
1 - \phi
\end{array} \right. \quad \text{where : } \phi = \frac{1 + \sqrt{5}}{2} = \tau$$

The general form of equation Eq. 2.4 in terms of the parameters $a$ and $b$ is:

$$f_n = a\phi^n + b(1-\phi)^n$$

Using boundary conditions ($f_0 = 0$ and $f_1 = 1$) to determine the values of the parameters $a$ and $b$, we obtain:

$$f_n = \phi^n - \frac{(1-\phi)^n}{\sqrt{5}}$$  \hspace{1cm} 2.5
The components $f_n$ are called “Fibonacci numbers” (Figure 2.3).

$$f_5(= 8)$$

$$f_4(= 5) + f_3$$

$$f_3(= 3) + f_2 + f_2 + f_1$$

$$f_2(= 2) + f_1 + f_1 + f_0 + f_1 + f_0 + f_1$$

$$f_1 + f_0 + f_1 + f_0 + f_1 + f_0 + f_1$$

1 0 1 1 0 1 0 1 1 ⇒ golden sequence (8 components)

Figure 2.3: Construction of the Fibonacci sequence through the Fibonacci numbers

$\tau$ uniquely defines the Fibonacci sequence as a quasiperiodic structure: it can be demonstrated that $\tau$ is the only irrational number that guarantees a minimal separation between atoms in the line. Such a requisite is not satisfied for any other sequence built with two tiles with any irrational relation.

2.2.1 Diffraction pattern of the Fibonacci sequence

Normalizing the Long and Short segment to $\tau$ and 1 respectively yields to spatial positions (or atomic separations):

$$x_n = n + \left(1/\tau\right)\text{Int}\left(\frac{n+1}{\tau}\right)$$

2.6
The sequence is the sum of a first term which corresponds to a periodic spacing equal to one, while the second term increases by $\frac{1}{\tau}$ each time $n$ is increased by $\tau$. Both terms have a periodic spacing, although incommensurate with each other.

A Fourier transform of the two terms individually considered consists of components periodically spaced with period $K_1$ and $K_2$ respectively, with $K_2$ being incommensurate with respect to $K_1$. The linear combination of the two terms results is a Fourier transform that includes both the Fourier components of each term plus the components from the linear combinations of $K_1$ and $K_2$. Because the two are incommensurate, the Fourier transform consists on a dense, countable set of peaks. In a quasiperiodic diffraction pattern this means that diffraction spots are present in every point in reciprocal space, so in principle every reflection should be included to describe the structure completely.

A comparison of the diffraction pattern and the Fourier transform of the Fibonacci sequence with the ones from a periodic structure is shown in Figure 2.4. First, it is interesting to notice that the background intensity between intense peaks, which in periodic crystals is usually due to a degree of disorder in the structure, for the Fibonacci sequence (and in general for quasicrystals) is due to low intensity diffractions spots. Secondly, because of the long range translational symmetry in the periodic structure, the position of diffraction spots relative to each other is a rational number. The lack of periodicity makes it impossible for quasiperiodic structures to have the same type of rational relation for the diffraction beams, which then must be irrational (and it corresponds to $\tau$). The ratio A/B corresponds exactly to the golden mean $\tau$. 
The dense sets of diffraction spots are also clearly self-similar: diffraction patterns similar both in relative intensity and distribution can be found at different scales (Figure 2.5).
2.3 Quasiperiodicity Generated as a Projection from Higher Dimension Space

The Fibonacci sequence can also be generated from a 2D square lattice, using the projection method. Let us consider a square lattice of spacing $a$, and axes $X$ and $Y$. A line with direction $R$ is drawn from the origin at the angle $\alpha$. The lattice sites of the

![Figure 2.5: Self-similarity in the Fourier Transform of the Fibonacci sequence](image)
square lattice can be projected on to the line, to obtain a 1D set of atomic sites. For this reason $R_\parallel$ is also called physical space. If the slope of $R_\parallel$ is rational with respect to the rows of the square lattice (in this case the $X$ axis), the projected 1D structure forms a discrete periodic 1D set of sites. In case of the slope being equal to $1$ ($\alpha = \pi / 4$, Figure 2.6), the 1D array is periodic with period $a\sqrt{2}$, and the each site is the degenerate projection of an infinite number of sites from the square lattice aligned as $R_\perp$, called the perpendicular space. If the slope is a fractional number, the 1D array is still periodic, with a different period. If the slope is instead irrational, the projected 1D structure is no longer periodic, and the projected atoms along the physical space become a singularly continuous distribution. To remove this density overload, only a restricted number of sites from the square lattice is allowed to be projected on $R_\parallel$, and specifically those that are confined within a strip parallel to $R_\parallel$ and having a cross section along $R_\parallel$ equal to the square unit cell. This strip (Figure 2.7) is called “acceptance domain” and it has a width $\Delta = a(\cos \alpha + \sin \alpha)$. The reduced number of projected atoms along $R_\parallel$ consists now of two segments, $L = a \cos \alpha$ and $S = a \sin \alpha$. With the additional requirement of $\cos \alpha / \sin \alpha = \cot \alpha = \tau$, the atomic distribution along $R_\parallel$ corresponds to the Fibonacci sequence.
Figure 2.6: Periodic 1D array obtained from the projection of the square lattice: \( \cot \alpha = 1 \)

Figure 2.7: Fibonacci sequence obtained with the projection method: \( \cot \alpha = \tau \). The strip corresponds to the “acceptance domain”. 
The Fourier transform of the atomic structure along $R_∥$ can be calculated starting from the 2D square lattice. It can be demonstrated\textsuperscript{7} that the Fourier Transform of a projection is a cut (and vice versa). The Fourier transform of the projection of a square lattice into $R_∥$ (which has an irrational slope) is a cut across the full reciprocal space defined by $R_∥^*$ and $R_⊥^*$. Positions and intensities of the diffraction peaks for the projected array correspond to the intersection by $R_∥^*$ of the 2D structure factor of the square lattice, characterized by the conventional Miller indexes $h$ and $h′$. For any reciprocal vector $G^{h′h}$ of the square lattice, a diffraction peak for the 1D Fibonacci sequence has the position $Q_{∥}^{h′h}$ and intensity $I^{h′h}$:

$$Q_{∥}^{h′h} = \frac{2\pi}{a} \frac{1}{\sqrt{2 + \tau}} (h + \tau h′)$$

$$I^{h′h} \propto \left( \frac{\sin \Delta Q_{⊥}^{h′h}/2}{\Delta Q_{∥}^{h′h}/2} \right)^2$$

$$Q_{⊥}^{h′h} = \frac{2\pi}{a} \frac{1}{\sqrt{2 + \tau}} (h - \tau h′)$$

It is remarkable to note that although the Fibonacci sequence is strictly 1D, the diffraction pattern can be labeled using two indexes, $h$ and $h′$ from the original 2D square lattice. Because any $h′$ value can be associated with a given value of $h$, the complete diffraction pattern is comprised of a dense set of points. Because $Q_{∥}^{h′h}$ is invariant under multiplications of $\tau^n$, there is no restriction in the minimum separation between spots. Also this invariance results in the self-similarity of the pattern, since all diffraction spots can be rescaled by powers of $\tau$.  

\[2.7\]
2.3.1 Approximants of a quasiperiodic structure

In the projection method, the Fibonacci sequence is characterized by the requirement \( \cot \alpha = \tau \). Let us consider a different angle \( \alpha' = \cot^{-1}(\chi) \), where \( \chi \) is an arbitrary number. At this angle, a new axis \( R'_1 \) and a new acceptance domain can be used to select the points of the square lattice to project into \( R'_1 \), along the initial \( R_\perp \). Projecting along the initial \( R_\perp \) and using the same \( \Delta = a(\cos \alpha + \sin \alpha) \), allow us to obtain segments of the same length as those in the Fibonacci sequence. In Figure 2.8 three different values of \( \alpha \) are considered (\( L = a \cos \alpha \) and \( S = a \sin \alpha \)). For \( \alpha = 2 \) for example the projected sites form a periodic sequence, with period \( LSL \). Similarly for \( \alpha = 3/2 \) we obtain a periodic sequence with period \( LSLLS \). In theory we could choose any value of alpha to obtain a sequence with the same building tiles as the Fibonacci ones. However a close look at the periods just found for the two values of alpha, indicates they in fact corresponds to building generations of the Fibonacci sequence. For example when \( \alpha = 2 \), it corresponds to the second generation (see Figure 2.5) \( LSL \), while \( \alpha = 3/2 \) corresponds to the third. In general: \( \alpha_n = \frac{F_{n+1}}{F_n} \), where \( F_n \) is the nth Fibonacci number. The rational sequence derived with the projection at the angle \( \alpha_n \), represents the “n rational approximant” of the Fibonacci sequence. A \( \alpha = 3/2 \) approximant is a better approximant than \( \alpha = 2 \), but worse than for example \( \alpha = 5/3 = 1.6 \), whose period \( LSLLSLSL \) is a better approximate of the quasiperiodic Fibonacci sequence. A list of approximants for the Fibonacci sequence is given in Table 2-1.
In Figure 2.9, the Fourier transforms of the periodic approximant structures listed in Table 2-1 are shown compared to the Fibonacci sequence. Several common features can be observed. First, the modulation in intensity of the diffraction spots is the same over the different approximants. The modulation of the most intense peaks is present
already for the simplest and coarsest approximant (1/1), with period LS. Because the two periods are incommensurate with each other, the diffraction pattern is modulated with a linear combination of two sinusoidal functions with period related to L and S. Secondly, while every diffraction peak in the approximant has a counterpart in the diffraction pattern of the Fibonacci sequence, the opposite is not true. The quasiperiodic diffraction pattern is dense, so that in every point in the reciprocal space there is a diffraction spot. If a higher order approximant is considered, more fine details start to appear, as more Fourier components are included. Although a quick look at the diffraction pattern would suggest that the positions of most intense peaks are actually identical throughout the approximant, this is in fact not true. The self-similarity is a property only of the Fibonacci sequence. This means that while for the sequence itself the pattern can be rescaled by powers of \( \tau \), for the approximants, the ratios between peak position are different. This is a major complication in the process of labeling the spots in approximant diffraction patterns, because spots positions are not related to each other by the same rescaling properties. However, a sufficiently high order approximant will have a diffraction pattern extremely close, both in terms of peak density and positions to the quasiperiodic array. This is true in general when considering approximants: in principle there is no limit in the order of the approximant to consider. However, experimental and computational limitation occurs, because of the complex periodicity involving several atoms per unit cells. The tradeoff is marked experimentally by the diffraction pattern of the high order approximant being indistinguishable from the quasiperiodic structure.
Figure 2.9: Fourier transforms from rational approximants of the Fibonacci sequence, listed according to the value of \( \cot \alpha \).
**2.3.2 Approximants generated by Linear Phason Strain**

Periodic structures have vibrational excitations, phonons, where atoms oscillate about the equilibrium positions. In the quasiperiodic case, in addition to the physical space $R_{||}$, the 2D square lattice introduces new degrees of freedom in the perpendicular space $R_{\perp}$. While the phonon excitations in the physical space are still present, a new set of oscillations called “phasons” determines the oscillation along $R_{\perp}$ (Figure 2.10).

![Figure 2.10: Phason excitation: an oscillation along $R_{\perp}$ deforms the acceptance domain (as indicated by the red arrow). This results in a new sequence LSLLSLLSLLLSS, compared with the original sequence LSLLLSLLSLLS in Figure 2.7.](image)

Because of the orthogonality of these oscillations to the physical space, their only physical manifestation into the physical space corresponds to position switching of single atoms. This behavior is different from phonon excitation, which can be considered collective phenomena. A periodic vibration in the 2D square lattice determines the change in the lattices sites allowed in the acceptance domain. A few new lattice sites are
allowed and at the same time others are not. In the physical space, where those sites are projected, this means that in the sequence two tiles switch position (the “phason flip”). These can be frozen, so that they appear as defects. Phason excitations can also appear in the form of linear strain: the physical space can be forced, through the phason excitation so that a new condition \( \cot \alpha = \eta \neq \tau \) is satisfied. This determines the generation of an approximant sequence; for this reason phasons are believed to play a crucial role in the quasicrystal vs approximant formation.

2.4 Extending quasiperiodicity to higher dimensions: tiling

2.4.1 The multigrid method

By overlapping two Fibonacci sequences, one rotated with respect to the other by 90°, we obtain the Fibonacci square. All the properties of the 1D sequence, self similarity, a dense set of diffraction peaks are retained in this simple 2D case. Similarly, by using three sequences, rotated by 120° one from the other we can obtain a triangular grid (the Fibonacci triangle). The diffraction pattern shows clearly the 2-fold symmetry (as well as it would show the 3-fold for the triangle). Although those symmetries are allowed in the conventional definition of crystal, the pattern is still aperiodic, since the peaks are quasiperiodically spaced (Figure 2.11). Aperiodicity, by itself can be achieved regardless of the rotation symmetry. This process of producing quasiperiodic 2D structures from 1D Fibonacci sequences is called the multigrid method. Structures with forbidden symmetries (5-, 8- 10-fold) can be produced by overlapping a corresponding
number of sequences at symmetry angles. The most famous, the Fibonacci pentagrid, in Figure 2.12 is shown along with the corresponding laser diffraction pattern. The 10-fold symmetry in the diffraction pattern is similar to real electron diffraction patterns obtained from 10-fold quasicrystal surfaces: The spot position are similarly located, and they are related by powers of $\tau$. Pentagrids have been used as lattice templates for modeling real quasicrystal surfaces.12.

Figure 2.11: The diffraction pattern of the Fibonacci square is compared to its Fourier transform$^8,10$. 
2.4.2 The projection method in 2D: Penrose tiling

2D and 3D quasiperiodic structures and their approximants can be independently reproduced using the projection method in exactly the same way it is done in 1D. If a 2D plane is oriented along the diagonal of the 5D cube its edges will project onto the five line segments of the same length equally spaced around a circle. The full projection yields the 2D Penrose tiling, whose diffraction pattern reflects the 5-fold symmetry. Just
as the body diagonal of the 3D cube has 3-fold symmetry, similarly for the 5D cube, the diagonal (which corresponds to the physical space) has 5-fold symmetry.

The Penrose tiling consists of two rhombus tiles of different shape: the “skinny” tiles S have inner angles $\frac{4\pi}{5}, \frac{\pi}{5}$, while the “fat” ones F have angles $\frac{2\pi}{5}, \frac{3\pi}{5}$. The tiles are assembled according to specific matching rules (Figure 2.13): a) two adjacent vertices must be both be blank or black; b) two adjacent edges must both be blank or have an arrow. As for the Fibonacci sequence, where the length ratio $\frac{L}{S} = \tau$, it easy to show that the ratio of the areas of the tiles is $\tau$. Because of the self similarity in the tiling, the tiles can be inflated or deflated (Figure 2.13). The tiling is not unique: The matching rules allow severaldifferent patterns to be produced, the most common being the rhombic and pentagonal. These patterns however are related to each other by an inflation/deflation symmetry operation.

Figure 2.13: Deflation scheme of the Penrose tiling. a) first and second generation of Penrose tiles. The areas of the old fat and skinny rhombi are related by the new one by a factor of $\tau$. b) The old generation of (thick lines), can be deflated using the newer generation.
Physically the matching rules of the Penrose tiles may be interpreted as combination rules of local clusters of atoms, to reach a minimum energy configuration. This energy driven formation is however not universal for all quasicrystals. An entropy driven approach has also been suggested: In terms of the tiling, the matching rules are relaxed (or removed), so the tiles are allowed to redistribute randomly, following the entropy of the system. The defined concentration of elements in the alloy controls the occurrence frequencies and keeps them fixed. This “random tiling” approach presents topological and chemical disorder, compared to the perfect Penrose tiling, so several configurations other than the quasiperiodic one are possible, including periodic or and disordered. However the entropy is maximized only for the decagonal quasiperiodic configuration\textsuperscript{13}.

2.4.3 From tiling to covering: the “quasi-unit cell” model

The idea of looking for a possible alternative to the tiling process, yielded to a new procedure to characterize quasiperiodic structures. While the Penrose tiling requires two tiles and a set of matching rules, a unique cluster with appropriately chosen overlapping rules can instead be used as a building block. The approach is similar to the conventional use of a periodic unit cell for regular crystals, with the difference given by allowing the overlapping of those cells: for this reason they are called “quasi-unit cells”. However unlike unit cells in periodic crystals, the basis of the quasi-unit cell, called “decoration” is not identical in every cell, and exhibits no translational symmetry.
Therefore motifs in the atomic decoration differ from a quasi-unit cell to another, even if
the quasi-unit cell lattice structure is still perfectly quasiperiodically constructed.

Figure 2.14: a) the decagonal quasi-unit cell can be mapped to a Penrose tiling by
inscribing a fat Penrose rhombus in each decagon. b) the coloring of the regions of the
quasi-unit cell ensures that this mapping conforms with the matching rules of the Penrose
tiling.\textsuperscript{14,15}

Petra Gummelt has shown that the quasi-unit cell construction is isomorphic to
the Penrose tiling\textsuperscript{16} (Figure 2.14). The overlapping regions within the quasi-unit cell
provide a set of matching rules that correspond exactly to the matching rule for the
vertices of the pentagonal Penrose tiling.

2.5 Low Energy Electron Diffraction

Since its discovery in 1927\textsuperscript{17}, low energy electron diffraction (LEED) has been
extensively used for surface structure determination. A simple kinematical theory,
inspired by x-ray diffraction and based on the assumption of that electrons undergo single
scattering event, can be applied to interpret LEED diffraction patterns. The kinematical
approach, which consists on the analysis of the kinematical structure factor, provides
qualitative and quantitative information about the symmetry and the order of the surface
as well as step and terraces distributions. However this approach, which works well for
weak scatterers (x-rays, neutrons), has strong limitations when applied quantitatively to
electrons. Low energy electrons (10-600eV) strongly interact with the surface, so multi-
scattering events dominate. Dynamical LEED theory has been developed to provide a
more accurate description of the scattering.

In the dynamical LEED analysis, the scattering from the surface atoms is
calculated for model structures including the effects of multiple scattering and then
compared to the experimental data. The utility of this method depends on the complexity
of the structure under analysis and specifically on the size of the unit cell. The application
of a dynamical LEED analysis to quasicrystal surfaces is furthermore complicated by the
lack of periodicity. The methods that have been developed to overcome this limitation
will be described in this paragraph, after a brief description of both the kinematical and
dynamical LEED theories.

2.5.1 Kinematical theory

The kinematical description of diffraction from a 1D gratings presented in
paragraph 2.1, can be extended for diffraction from 3D periodic crystals. The nth-atom
can be expressed as function of the basis unit vectors $a_i$ and the relative position within
the unit cell $\tilde{r}_j$:

$$\tilde{r}_n = \sum_{i=1}^{3} m_i a_i + \tilde{r}_j$$  \hspace{1cm} 2.8
Eq. 2.1 can be modified, so that the scattered amplitude and the diffraction intensity along $\vec{k}$ are proportional to:

$$J(\Delta \vec{k}) = C(\vec{k}) S_G(\Delta \vec{k})$$

$$S_G(\Delta \vec{k}) = \sum_n f_n \exp(i \vec{r}_n \cdot \Delta \vec{k}) = S_G^A(\Delta \vec{k}) \cdot S_G^B(\Delta \vec{k})$$

$$S_G^A(\Delta \vec{k}) = \left[ \sum_j f_j \exp(i \vec{r}_j \cdot \Delta \vec{k}) \right]$$

$$S_G^B(\Delta \vec{k}) = \sum_{m_1, m_2, m_3} f_n \exp\left[ i (m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3) \cdot \Delta \vec{k} \right]$$

$$I(\Delta \vec{k}) = |J(\Delta \vec{k})|^2 = |S_G(\Delta \vec{k})|^2$$

where $C(\vec{k})$ is a constant phase factor, $\Delta \vec{k} = \vec{k} - \vec{k}_0$ and $f_n$ represents the amplitude of the wave scattered from a single atom. $S_G^A(\Delta \vec{k})$ is called geometric structure factor, and it depends on the how the atoms of the basis are displaced within the unit cell. $S_G^B(\Delta \vec{k})$ is called atomic structure factor and it depends on the lattice structure of the unit cell. If there are only few atoms in the unit cell, $S_G^A(\Delta \vec{k})$ will be either constant or slowly varying with $\Delta \vec{k}$.

The atomic positions within the unit cells can be easily derived by the correct determination of the geometric structure scattering factor\textsuperscript{18}. This description applies for diffraction techniques that employ weak scatterers. In case of strong scatterers, like electrons, the geometric scattering factor cannot be calculated within the kinematical theory, because of the complication of multiple scattering and intensity attenuation as electrons penetrates the surface.

Diffraction peaks occur whenever the Laue conditions are satisfied:
Those conditions can be visualized using the Ewald sphere construction (Figure 2.15). In the reciprocal space, diffraction occurs only when the sphere of radius $\vec{k}$ intersects a 3D reciprocal space point $\vec{G}$. Changing the magnitude of $\vec{k}$ increases the radius of the sphere, and new diffraction events occur. For a purely 2D plane, the system is periodic only along the lattice, while along its normal the period is infinite. The reciprocal lattice points along the normal are therefore infinitely dense, and in fact they can be seen as continuous rods (Figure 2.15b). Along the 2D plane, periodicity ensures that diffraction occurs if the Laue conditions are satisfied. Those conditions are relaxed with respect to the 3D case, because they apply only to the reciprocal vector corresponding to the 2D plane. Since the reciprocal space in the 2D case consists of continuous rods, diffraction events depend only by the intersection of the Ewald sphere with the rods. Changing the magnitude of $\vec{k}$, which increases the radius of the sphere, has the effect of changing the scaling of the reciprocal lattice. The rods projected to the sphere provide a diffraction pattern from which lateral surface symmetry and periodicity can be determined. Varying $\vec{k}$ has also the effect of scanning the intensity along the rods. For a perfectly two dimensional system, the intensity is constant. In the case of LEED however, because the electrons penetrate the surface by few atomic layers, the system is somewhat in between the 3D and the 2D case: the rods are not continuous but their intensity is modulated (Figure 2.15c). The more the electrons penetrate the surface the more the intensity is modulated: in fact if the penetration depth would be infinite the modulation would correspond to the set of delta functions of the 3D lattice. This modulation along the rods contains important

$$\vec{a}_i \cdot \Delta \vec{k} = 2\pi n \quad i = 1,\ldots,3$$
information about the geometrical structure factor. If electrons were to obey the
kinematical theory, a simple convolution of the geometrical structure factor as function of
the momentum $\vec{k}$ would provide the full atomic structure.

Figure 2.15: Ewald sphere construction: a) from a 3D lattice; b) from a 2D lattice; c)
modulated rods for a “thin” 3D lattice (a periodic stack of few infinite layers). By
changing $\Delta\vec{k}$ it is possible to scan the intensity modulation along the rods.

2.5.2 Dynamical LEED theory

Experimentally, intensity spectra for each diffraction spot are recorded as function
of the beam energy $E$. In the dynamical LEED method this intensity modulation along the
rods is analyzed for a set of reference structures$^{19,20}$. The calculated and experimental
$I(E)$ are compared using a reliability factor. The process is described in Figure 2.16.
The dynamical LEED calculation must include multiple scattering. The scattering wave $f_n$ from a single atom in the kinematical theory is replaced by the amplitude that includes the scattering contribution of the electron from all the different multiple paths that end at that single atom. In addition, scattered electrons undergo phase shifts, caused by the motion through region of lower potential: the validity of the point sources scattering assumption in the kinematical theory, can be conserved if those phase shifts are included in the scattered wave. Surface dipole effects and attenuation of the scattered intensity are also present in electron diffraction. The former can be included by adding an offset negative constant (called “inner potential”) to the surface potential. The latter, due to inelastic scattered electrons, is fixed by adding to the inner potential an imaginary part. This allows the scattered wave to decay exponentially with penetration depth. Temperature effects are also included in the calculation, by adding Debye-Waller factors.
into the scattered amplitudes of each atom. Those factors can be set in multiple values for layer-to-layer or atom-to-atom scattering, allowing anisotropic vibrations\textsuperscript{19}.

The calculation consists of four steps:

1. Calculation of the scattering from individual ion cores, to determine the phase shifts;
2. Calculation of the scattering from coplanar layers of atoms, including multiple scattering events;
3. Calculation of the single and multiple scattering from and between layers.
4. Structure refinements on the reference structure using a perturbation theory to calculate the effects of small changes in the structural parameter to the spectra.

In order to compare the experimental and theoretical I(E) spectra, several reliability factor are available. Since the most valuable information in the spectra consists of the modulation of the intensity along the rods, and not of the magnitude of the intensity itself, an effective reliability factor must be more sensitive to the position of the peaks in the spectra. The most commonly used is the Pendry R-factor\textsuperscript{21}: Eq. 2.10

\[ R_p = \frac{\int (Y_{\text{exp}} - Y_{\text{calc}})^2 dE}{\int (Y_{\text{exp}}^2 - Y_{\text{calc}}^2) dE} \]

where \( V_{oi} \) is the imaginary part of the inner potential. Two identical spectra have R-factor zero. Two randomly correlated spectra will have an R-factor close to zero.
While the kinematic structure factor contains information about the long-range order, symmetry and periodicity at the surface, the LEED I(E) spectra provide information about the local structure. Because of this, I(E) spectra from structures which have different long-range periodicity and symmetry but the same local geometry will have similarities. This feature is extremely helpful when applying the dynamical LEED method to quasiperiodic structures and their approximants.

### 2.5.3 Dynamical LEED theory with quasicrystal surfaces

In regular periodic crystals, the number of atoms with different scattering properties is restricted by the size of the unit cell and the number of atomic planes to consider. A lack of periodicity poses serious limitations in the feasibility of the calculation itself, since each atom has a different chemical and geometrical environment beyond its neighbors. For a quasicrystal, the calculation can be theoretically performed on a pseudo-periodic system, where the unit cell consists on a large quasicrystalline slab (an accurate description will be given in Chapter 4.1). However because of the large number of atoms that would need to be included in this slab model, a full multiple scattering calculation is not computationally possible. Gierer and co-workers developed approximations in order to reduce the number of free parameters in such a calculation. An alternative approach is use approximants as reference models, in a conventional dynamical LEED calculation. Both of these methods have been used here to characterize the surface structure of the 10-fold Al-Ni-Co quasicrystal and the results are presented later in this thesis.
2.5.3.1 Approximated calculation on the slab model

In order to reduce the number of atoms with different scattering properties, each slab is divided into atomic sub-planes each with a particular composition, density and with the assumption that all the atoms in that sub-plane have the same scattering properties. The first approximation to be applied is the *Average T-Matrix Approximation (ATA)*. Each sub-plane with its own bulk-like composition is replaced by a unique average “atom” with average scattering properties. In this approximation, the scattering matrices of each single atom in the sub-plane are replaced by an averaged scattering matrix, which depends on the averaged chemical composition of the plane. This approximation removes any information about the atomic position in the sub-plane and chemical identity.

For the calculation of the multiple scattering another approximation is used. Quasicrystals have in their structure a various number of different local atomic environments. These local environments within the sub-plane can be replaced a fixed, average geometry. With this *Average Neighbor Approximation (ANA)*, the atoms in each sub-plane are treated as if they had all the same scattering properties parallel to the surface. This approximation however removes any local geometrical information within the sub-plane. A further simplification of the scattering matrix is imposed by considering only the diagonal terms. For experiments performed with sample at normal incidence, the off-diagonal terms are generally small for highly symmetric structures\textsuperscript{24}. 
2.5.3.2 Dynamical calculation with approximants

A totally different approach exploits the sensitivity of dynamical LEED to local geometries\textsuperscript{22}. The same local geometries that are present in the quasicrystal are present in the approximant structures. Since the approximants are periodic structures, a conventional dynamical LEED calculation can be applied, with no approximation, using the experimental I(E) spectra of the quasicrystalline surface. The advantage of using approximant structures resides in a more accurate determination of local geometries than by using the approximated slab calculation, where, because of the ANA, this information is smeared out.

2.6 References


Chapter 3
Experimental Details

The strong interaction of low energy electrons with matter has some clear advantages. Because of the relatively short mean free path (less than \(10\text{Å}\) for electrons with energies between 20 and 600eV\(^1\)), which limits their penetration into the crystal, electrons have the potential to provide an invaluable amount of information about the first few layers of the surface, which are not accessible either by other diffraction probes (x-ray, atoms), or by surface imaging techniques (STM, AFM). This chapter will describe the LEED apparatus used in the experiments, and discuss the experimental challenges of studying quasicrystal surfaces with LEED, under varying temperatures and operation conditions. This will include a description of the preparation of the d-AlNiCo sample, which is different from that for periodic single crystals.

3.1 Ultra High Vacuum system

The experiments were performed in a Vacuum Generators chamber schematically shown in Figure 3.1. The base pressure of \(8 \cdot 10^{-11}\) mbar is achieved after 24 hours bake at 120° C with a turbo molecular pump and titanium sublimation pumps. The pressure can be further reduced with the liquid nitrogen trap. This is particularly useful to pump away residual Argon from sputtering and to reduce the background residual gas that forms in the chamber after the long annealing time required by the quasicrystal surface.
To reduce the magnetic field inside the chamber that would affect electron trajectory, the chamber is shielded internally with a µ-metal shell. For the same reason all metallic parts inside the vacuum chamber are degaussed using a degaussing coil before insertion.

Figure 3.1: Basic schematic of the UHV chamber used in the experiments.
The chamber is equipped with an Auger Electron Spectroscope, which is used to monitor the surface chemical composition and the presence of contaminants. A VG Quadrupole mass spectrometer monitors the residual gas. It can also be used for leak detection.

A leak valve is used to inject gases both for surface preparation (argon) and for deposition (xenon). The backpressure of the gas injected in the chamber for adsorption is measured with the same ion gauge used for monitoring the base pressure. Its distance to the sample has to be minimized to reduce pressure gradients between the sample and the gauge itself. Heavy rare gases, such as xenon and argon, are easily pumped out of the system after dosing or sputtering.

The temperature is measured with a chromel-alumel (K-type) thermocouple with its junction in contact with the sample. The thermocouple is calibrated in liquid nitrogen, and its reading is fed to a personal computer via digital-analog converter after being amplified. The temperature during annealing ($600 < T < 850\degree C$) is also monitored with an optical pyrometer (Minolta/Land Cyclops 52). This is particularly important for quasicrystal surface preparation: their low thermal conductivity produces a temperature gradient between the front and the side or the back of the sample. The pyrometer reading (obtained with emissivity 0.35 for the Al-Ni-Co sample) provides a reliable measurement of the surface temperature. The discrepancy between the thermocouple (at the back of the sample) and pyrometer reading (at the front of the sample) is about 15 to 20 degrees.

The chamber is equipped with a Janis Research Supertran cryostat, which can be operated both with liquid nitrogen (77K) and liquid helium (4K). In the former case nitrogen is directly poured into the cryostat, while in this latter case a helium transfer-
tube is used. It is mounted on a differentially pumped rotary feedthrough which allows full sample rotation while maintaining ultra-high vacuum in the chamber. The cryostat cold finger is connected to the sample holder by a copper braid: its short length and polished contact junctions are designed to maximize the heat transfer.

### 3.1.1 Sample mechanical and thermal manipulation

The sample holder is designed to allow full polar rotation and tilting. This is particularly important for dynamical LEED acquisitions, since the sample has to be at normal incidence with the incident beam. The sample holder consists of a spring loaded assembly connected to the main XYZ manipulator by a horizontal stainless steel bar. A molybdenum plate is mounted to this assembly which provides support for an alumina ceramic plate and the tungsten filament used for heating the sample. Additional ceramic spacers and rods are placed to provide electrical and thermal insulation between the sample and the holder. Thermal insulation is particularly important to maximize the sample cooling without cooling at the same time the manipulator assembly. Electrical insulation is also important to heat the sample by electron bombardment. The heater filament is heated up by a current flow: thermoelectrically emitted electrons are accelerated to the sample by the means of an external electric potential (0-500V) placed between the heater filament (at negative voltage) and the grounded sample. This results in an electron bombardment current (30 mA) which finally allows heating the sample to high temperatures (about 1000°C) in few minutes.
The sample is sandwiched between three tantalum plates; the center plate has a set of clamps that surrounds the sample with the double purpose of firmly supporting the sample and to provide adequate and homogeneous cooling to the surface of the sample. The sandwich is spot-welded in several positions to maximize the point of contact which reduces heat transfer losses; for the same reasons all the plates and both the faces of the sample are polished with diamond-based paste abrasive, the same used for sample preparation. The copper braid used for cooling is connected on top of the sandwich. Since the sandwich is thermally insulated from the sample holder, the cooling is effectively maximized on the sandwich itself. Reaching the lowest temperatures possible without losing manipulation capabilities allows adsorption of rare gases, which occurs at temperatures of about 80K or lower. In addition the reduced thermal motion improves the quality of the LEED patterns by reducing the diffusion elastic scattering contribution. This allows better discrimination of the features in the diffraction pattern.

### 3.2 Low Energy Electron Diffraction apparatus

Low energy electrons are produced inside the electron gun (Figure 3.2) by thermoionic emission from a thoria (ThO₂) coated tungsten filament that is heated by a current of about 2.5A. Those electrons are extracted by an external potential G₁, which yields an electron current of approximately 2 µA or higher. The energy of the beam is controlled by an external potential A₁ (up to 600V), which can be controlled either manually or remotely from a personal computer, thorough a digital-analog converter. The electrons are focused by positive voltage A₂ to produce a beam of about 0.25mm.
As electrons strike the surface of the sample, they are backscattered towards the so-called LEED optics. This is composed of three meshes and a hemispherical phosphor screen. The purpose of the meshes is to suppress the inelastically scattered electrons. Finally, the elastically scattered ones are further accelerated to the phosphor screen where the fluorescence is detected. The compact design of the electron gun, which is concentric
with the optics, allows the observer to observe the LEED pattern directly from behind the screen.

The sample is placed as close as possible to the center of curvature of the hemispheric phosphor screen: in this configuration the screen approximates the Ewald sphere (Paragraph 2.6). In this configuration, the conversion from incident energy to transfer momentum is simplified, because lateral distances on the screen are linear with the momentum transfer.

3.2.1 Data acquisition and analysis

High resolution, 16 bit LEED patterns are acquired using a monochromatic high luminosity CCD camera (Sony XC75) which is mounted on front of the view port of the LEED assembly, right outside the chamber. The camera is interfaced to a personal computer via a monochromatic high accuracy, low-noise and high speed frame grabber (Data Translator DT3155). The pattern acquisition, manipulation and analysis are performed using a set of programs specifically designed for the purpose. The main one is called HotLEED$^3$ and a user manual is included in this thesis in Appendix A.

LEED patterns are individually acquired together with sample temperature and acquisition conditions. To reduce the random electronic noise, a set of frames is acquired, and the average is stored. From those stored frames, different types of analysis are possible. A comprehensive description can be found in Appendix A and in previous studies$^4$. Here only a general description will be given:
*Kinematical:* The LEED patterns are examined individually for surface symmetry characterization, order, and to measure terrace size and distribution. This is done by extracting 1D line profile from the 2D pattern, usually across the diffraction peaks. The width of peaks is inversely related to the terrace sizes. Knowing the incident energy of the beam the radial distance between peaks provides a measurement of the substrate lattice constant. Line profiles are also extremely useful to evaluate the distribution of the background intensity. In well-ordered periodic crystals this is due to thermal diffuse scattering: it is linear in the radial direction from the center of the screen. Patterns from quasicrystal surfaces however have a more complicated background intensity which is a combination of both thermal diffuse scattering and low diffraction intensity from the dense diffraction pattern. In principle, the intensity from any two separate diffraction spots could be studied, but only those with a separation larger than the resolution of the LEED apparatus can be resolved. For this reason only the brighter spots are considered, while the others are treated as background intensity. The subtraction process in this case involves in this case a low-order (instead of linear) polynomial fitting.

*Dynamical LEED:* Diffraction patterns can be stored at high speed as function of the incident electron energy. From those patterns the intensity of each single diffraction spot can be extracted to obtain the I(E) spectra.

The extraction of the I(E) intensities is obtained by integrating all the pixels inside a window centered on the diffraction spot. The extraction mechanism is automatic, so once the initial and final positions of the integration window are set, the window itself “follows” the spot as it moves. This is achieved by selecting a set of integration windows
in the same number as the equivalent spots around the specular in the diffraction pattern (Figure 3.3).

![LEED patterns of the 10-fold d-AlNiCo surface at two different incident electron energies. Ten equivalent spots are chosen (one is hidden by the electron gun holder), and the integrated intensity is extracted using a circular integration window for each diffraction spot (displayed in cyan).](image)

**Figure 3.3**

Those spots are by virtue of symmetry totally equivalent, which means that they share the same I(E) spectrum. The positions of the equivalent diffraction windows at two different energies provide the scaling constant and the position of the specular in the diffraction pattern: as a result, the position of any point on the screen can be calculated for any incident energy. The same scaling is applied to the size of the integration windows: Their dimensions are rescaled as the incident energy increases, to keep constant the integration area in reciprocal space.

Background subtraction must also be applied to I(E) spectra. A primary subtraction is performed during the intensity extraction. The linear background at the
perimeter of the window is subtracted from the total integrated intensity. By keeping the integration window as small as possible, the effectiveness of the subtraction process is maximized. However in the case of quasicrystal surfaces, a significant amount of background intensity can still be observed. An additional method to enhance the peak contributions in the I(E) from the background is by subtracting a low order polynomial fit from each I(E) (Figure 3.4).

Figure 3.4: Peaks in experimental I(E) spectra (black curve) can be enhanced by subtracting a low order polynomial (red curve). Further smoothing (blue curve) reduces the amount of noise.

This enhances (and so it changes) the intensity of peak in the I(E) spectra at higher energies, without loosing any information about its position. In fact, as previously discussed, for dynamical LEED, the peak position in the I(E) spectrum mainly provides
structural information, not the intensity. Finally, the amount of experimental noise is reduced by using a 5 point smoothing.

Sample Temperature dependence of the diffraction intensity \( I(T) \): Using the intensity extraction method of the dynamical LEED, the intensity of diffraction spots can be acquired as function of the sample temperature. In this case the acquisition is simplified, because the incident energy is kept fixed and the integration window is locked in a specific position. This method finds at least two uses. For example it can be employed to monitor the diffraction intensity when a gas at fix pressure is adsorbed as the substrate is cooled. The curves obtained are called adsorption isobars. From these, the growth mode and the energy of adsorption can be extracted. Thermal vibration at the surface which is responsible for the intensity attenuation (through the Debye Waller factor) can also be monitored, and important structural parameters such as the Debye temperature can be derived. Both these methods have been extensively used, and they will be discussed in greater details in the next chapters.

3.3 Auger Electron Spectroscopy (AES)

AES is used to monitor chemical composition during sample preparation and to verify its effectiveness. It can also be used to characterize the coverage of an adsorbate or for the clean surface of an alloy to determine the percentage of the chemical constituents. The AES apparatus consists of a Perkin Elmer cylindrical mirror analyzer (CMA). Electrons are produced similarly as in the electron gun in LEED, but they are accelerated with a much higher potential (2kV). As electrons strike the surface the Auger scattered
electrons are produced and collected in the CMA, which can be adjusted to collect a narrow range of electron energies. By sweeping the analyzer voltage over the energy range of interest, an electron energy distribution is obtained; in this energy spectrum, peaks corresponding to a specific chemical identity are present. The chemical elements are identified using a look up table\(^5\). AES has been used to characterize the chemical composition of the 10-fold decagonal AlNiCo quasicrystal during the sample preparation.

### 3.4 Sample Preparation

The decagonal Al\(_{73}\)Ni\(_{10}\)Co\(_{17}\) quasicrystal used in this study was grown at Ames Laboratory using the melt decantation method\(^6\). The rod, shown in Figure 3.5 has been cut along perpendicularly to the 10-fold axis, to produce samples suitable for surface science experiments. Two of those cuts were employed in the experiments presented in this thesis.

The orientation of the sample was determined using Laue x-ray diffraction. Alignment is done by mounting the sample on a polishing bell, oriented at an angle corresponding to the misalignment from the desired crystallographic orientation. In this way the misaligned surface can be polished while preserving the orientational alignment of the 10-fold surface. The sample surface orientation is then checked again, until the correct orientation is obtained within 0.25°.
The surface is polished using a diamond-based paste, starting from a coarse 35 µm particle size down to 0.2 µm. The back of the sample is similarly polished, to improve thermal contact with the mounting plate. The sample after polishing has a shiny mirror-like look, similar to a Al(111) surface. It is also very brittle, as it was found out during the polishing process: extra care was needed to avoid cracks opening in the sample itself.

3.4.1 Surface preparation and characterization in UHV

As the sample is mounted in the UHV chamber, an AES scan reveals the composition of about 20 layers, for an incident electron energy of 2keV\(^7\) (Figure 3.6).

Figure 3.5: Al\(_{73}\)Ni\(_{10}\)Co\(_{17}\) quasicrystal: a) the rod presents a decagonal cylindrical shape, along the 10-fold axis\(^6\). b) From this rod two cuts along the quasiperiodic planes produced two samples of 4 mm tick.
The surface before cleaning exhibits a significant amount of contaminants (carbon and oxygen), from the polishing. The shape of the Al peak near 51eV is characteristic of an aluminum oxide layer rather than pure aluminum (whose peak would be near 68eV). The transition metals peaks are visible; however some overlapping between nickel and cobalt major peaks does not allow the discrimination between the two chemical identities.

Surface preparation in vacuum consists of Ar\textsuperscript{+} sputtering and annealing cycles. Although the quasicrystal hardness would suggest the use of a strong sputtering (1.0-1.5 keV) for few hours, the contrary is true instead. The contaminants and the alumina layer

Figure 3.6: AES scan of the AlNiCo sample in UHV, after polishing. No sputtering and annealing is yet performed. The major contaminants (O, C) are shown.
can be removed with three sputtering cycles at 1.0keV for 1 hour with subsequent annealing at 650°C for 3 hours. The surface does not yet show a diffraction pattern however. Repeated cycles of softer sputtering (at 0.5keV for 45 minutes) and longer annealing at higher temperatures (6 to 8 hours up to a maximum of 820°C), results in a flat surface, with terraces size of about 150-200Å, as confirmed by STM (Figure 3.7).

Figure 3.7: STM images (a: 100x100 nm²; b: 25x25 nm²) of the clean surface, after preparation in vacuum, with sample at 4K. The surface presents large terraces (average size 170-200Å) with rough edges. Larger white protrusions are also visible. Since the surface is clean and no contaminants are seen with AES, those protrusions consist of bulk material too strongly bounded to specific sites to diffuse to step edges during annealing. These images were recorded by the author at the Chemistry Department of The University of Manchester, under the supervision of Prof. Geoff Thornton.

Annealing temperatures higher than 820°C did not show any significant improvement; in addition approaching the melting temperature too closely has been considered too risky. After the annealing is complete, the system is left in a steady cooling phase. If no experiment is planned, the sample cools at the rate of 100 degrees in approximately 30 minutes. If experiments are planned, a quicker cooling is achieved
either by cooling the sample with liquid nitrogen or helium: the cooling rate improves so that the sample is at the required low temperature in approximately 30 minutes.

The resulting LEED pattern shows sharp diffraction spots over a wide energy range (from 30 to 500 eV) (Figure 3.8). At this stage the surface is ready for the experiments. The AES spectrum in such case shows the Aluminum peak, no contaminants and not very pronounced peaks from the transition metals. The chemical composition of the surface can be extracted from the intensity of the peaks in the AES spectrum, weighted with the specific sensitivity of AES to each chemical identity. According to this analysis, the average composition for a well prepared surface is $85 \pm 2\%$ aluminum and $15 \pm 2\%$ transition metals.

Figure 3.8: LEED diffraction pattern at 68eV of the clean d-AlNiCo with surface at 60K. The corresponding AES scan shows no contaminants.
After the optimal surface has been obtained, the day-to-day preparation requires only one cycle of soft sputtering (0.5keV for 20 minutes) and approximately 5-6 hours at 810C. A general rule of thumb has been developed, so that usually an average total time of 40 hours is required to prepare the surface from the polishing. This value may be initially higher, since higher amount of contaminants from the bulk may need to be removed. The optimal surface has a macroscopic matte finish, distinctively different from the mirror-like look after polish. We investigated the effects of re-polishing the sample, (when the chamber is vented usually for a technical failure), without encountering any significant difference in the required sputtering/annealing time.

The effect of sputtering and annealing on the surface composition has also been investigated. Because of the different sputtering yield, components in the quasicrystalline alloy can be preferentially sputtered, so the chemical composition of the surface may differ significantly before and after the sputtering. This is clearly shown in Figure 3.9. Aluminum composition (76%) is still higher than the bulk nominal value (73%), but significantly lower than for the annealed surface (85%). Aluminum is preferentially sputtered with respect to the transition metals. Annealing the surface induces a partial evaporation of Al at the surface. However segregation of aluminum from the bulk to the surface compensates for this loss and restores the surface composition to the value corresponding to the quasiperiodic phase.
The aluminum concentration before and after annealing is higher than both the bulk nominal values. It is also higher than the corresponding concentrations found in a previous XPS study of the same surface, which indicates an Al concentration of 50% after sputtering and 70% after annealing. Although the qualitative description of the preferential depletion of Al during sputtering and its subsequent restoration by annealing is maintained, one may argue the origin of such discrepancy. It has been shown that AES sensitivity factors for the transition metals in Al-rich quasicrystals are lower than those of the single chemical components or in periodic alloys with the same chemical components. Thus a lower concentration of transition metals and an higher concentration of aluminum is to be expected, if the standard sensitivity factors are used, as in the study presented here. For the i-Al-Pd-Mn and i-Al-Cu-Fe the use of pure element standard
sensitivity factors lead to an underestimation in the concentration of transition metals by a factor of 2.5, and an overestimation of the Al concentration by a factor of 1.2. It is not immediately possible to estimate the correct chemical concentration of the d-AlNiCo from this study, since the transition metals are different. However assuming that the normalization factor for the Al concentration is the same, the sputtered d-AlNiCo surface has concentrations of Al: 63% and TM: 37%. The annealed surface has concentrations of Al: 71% and TM: 29, which are in agreement with the previous XPS study, and near the bulk nominal values.

There may be other coexisting factors determining the higher Al composition with respect to the bulk values. Different preparation procedures can also affect the chemical composition of the surface. It has been shown\textsuperscript{10} that the Al concentration in i-Al-Pd-Mn increases with respect to the bulk with higher annealing time and temperatures; at the same time the level of surface disorder is reduced. Thus, compared to the XPS study, where stronger sputtering (up to 1.5KV) and shorter annealing at lower temperatures (1.5 hours at 430C), the study presented here may indicate that the higher Al concentration be due in part by the slight different sample preparation procedure.

3.5 References


Chapter 4
The 10-fold d-Al-Ni-Co Surface

4.1 Atomic Structure of the quasicrystalline d-Al-Ni-Co

The d-Al-Ni-Co is among the most studied decagonal quasicrystals, and the characterization of its surface structure is presented in this chapter. The stable d-Al-Ni-Co quasicrystal structure was discovered by A.P. Tsai et al. in 1989\textsuperscript{1}. The phase diagram has been mapped\textsuperscript{2}, and it is shown in Figure 4.1.

The best studied phase is the Ni-rich phase d-AlNiCo. It was suggested initially\textsuperscript{3, 4} that this phase has a 4 Å period along the 10-fold axis, while Co-rich phases I-AlNiCo have a period of approximately 8 Å. The refinements of the synchrotron x-ray diffraction data\textsuperscript{5, 6} show however that the Ni-rich phase also exhibits a 8Å periodicity, which therefore seems to be general among the d-AlNiCo quasicrystals.

The structure analyses of both phases reveal the presence of decagonal columnar clusters with 10Å radius centered in a perfect pentagonal Penrose tiling (Ni-rich phase) and with height given by the period along the 10-fold axis\textsuperscript{3, 4, 7}. The significant difference between the Ni-rich and the Co-rich phase is in the atomic decoration within the columnar clusters, which is also responsible for the slight difference in periodicity among the different phases. This difference depends on the degree of atomic corrugation within the columnar clusters, which is more accentuated in the Co-rich phase: the effect of this in the diffraction pattern is an increased contribution of diffuse scattering. The different
decorations introduce a degree of structural disorder: the tiling in the Co-rich phase is not perfectly quasiperiodic; a degree of randomness is present.\(^8\)

The 10-fold surface structure was studied using scanning tunneling microscopy (STM) from both the cleaved\(^9\) and cut/polished form\(^10,11\). The cleaved surface showed a cluster like surface, with minor changes to the composition after heat treatment. The polished 10-fold surface appears to have a flat, unreconstructed terrace structure, with terraces having an average width of at least 170Å\(^12\) and separated by round-edged steps.

Figure 4.1: Temperature dependent phase diagram for the d-Al-Ni-Co alloy\(^2\)

The 10-fold surface structure was studied using scanning tunneling microscopy (STM) from both the cleaved\(^9\) and cut/polished form\(^10,11\). The cleaved surface showed a cluster like surface, with minor changes to the composition after heat treatment. The polished 10-fold surface appears to have a flat, unreconstructed terrace structure, with terraces having an average width of at least 170Å\(^12\) and separated by round-edged steps.
of 2.2Å; each terrace has local points of 5-fold symmetry, which are mirror symmetric to the adjacent terraces. This is consistent with both the screw operation along the 10-fold axis. The points of five fold symmetry appear as pentagonal arrangements of protrusions, and the spacing between such pentagons is related by power of the golden mean.

The experimental work presented in this thesis has been carried out using a Co-rich d-Al-Ni-Co, with nominal composition Al\textsubscript{73}Ni\textsubscript{10}Co\textsubscript{17}.

### 4.1.1 Structure of the bulk quasicrystal slab model

The most accurate structural bulk model to date for the Ni-rich phase (specifically Al\textsubscript{70}Ni\textsubscript{23}Co\textsubscript{7}), has been proposed by Cervellino and coworkers\textsuperscript{5}. This model provides the bulk atomic coordinates and characterization of chemical identities. Most of the atoms in the coordinate set reside in the vertices of a rhombic Penrose tiling with edge length 2.43Å: this is related to the pentagonal Penrose tiling by an inflation symmetry operation, as described previously (Paragraph 2.4.2).

The basic structure of the bulk d-Al-Ni-Co model consists of a stack of identical or nearly identical 5-fold symmetric planes A and B, each related to the next layer by a $\pi/5$ rotation and with interlayer spacing of 2.04Å. This produces a structure having ABAB stacking and an overall 10-fold screw axis\textsuperscript{5}. Atoms can be divided into different groups, depending on the nearest neighbor distance and the chemical identity (see Table 4-1)\textsuperscript{13}. The atomic groups are shown in different colors in Figure 4.2.
In the x-ray diffraction experiment, the similar scattering properties of nickel and cobalt made it difficult to discern between the two transition metals. However with the help of an EXAFS study\(^6\) it is possible to identify the group TM-1 as cobalt atoms, and TM-2 as nickel atoms. This identification is based on the type of neighborhood of Ni and Co. The nickel coordination is bimodal, indicating that it has both Al and TM as neighbors, while cobalt has only Al neighbors. Since the TM-1 group has only Al nearest neighbors, it can be identified as Co, while TM-2 is identified as Ni.

The same structure model can be constructed using a columnar decagonal quasi-cell, of radius of 10Å and interlayer spacing 2.04Å. As previously specified, the centers of these clusters reside on the vertices of a pentagonal Penrose tiling. The quasi-unit cell for this structural model is shown in Figure 4.2 along with the atomic decoration.

### Table 4-1: Atom groups separation in the quasicrystal layer

<table>
<thead>
<tr>
<th>Group</th>
<th>Coordination</th>
<th>NN distance (Å)</th>
<th># atoms</th>
<th>% atoms</th>
<th>color</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM-1 (Co)</td>
<td>3</td>
<td>2.43</td>
<td>110</td>
<td>12</td>
<td>Red</td>
</tr>
<tr>
<td>TM-2 (Ni)</td>
<td>4-5</td>
<td>2.43</td>
<td>140</td>
<td>15</td>
<td>Black</td>
</tr>
<tr>
<td>Al-1</td>
<td>1</td>
<td>2.24</td>
<td>165</td>
<td>17</td>
<td>Green</td>
</tr>
<tr>
<td>Al-2</td>
<td>2</td>
<td>2.43</td>
<td>300</td>
<td>32</td>
<td>Blue</td>
</tr>
<tr>
<td>Al-3</td>
<td>3</td>
<td>2.43</td>
<td>145</td>
<td>15</td>
<td>Cyan</td>
</tr>
<tr>
<td>Al-4</td>
<td>4-5</td>
<td>2.43</td>
<td>85</td>
<td>9</td>
<td>Yellow</td>
</tr>
</tbody>
</table>
Figure 4.2: a) Top view of the 5-fold quasicrystal layer (45x45Å²). b) Quasi-unit cell for the quasicrystalline d-AlNiCo: the shaded regions are the only allowed overlap region allowed. Two atomic layers are represented (with open and filled circles representing the atoms in the two layers). The quasi-unit cell is also schematically represented in b): the overlapping is allowed only in the shaded region. Different colors represent different atom groups as indicated in Table 4-1.
4.1.2 Surface Quasicrystal slab model for the LEED I(E) calculation

The structure of the Ni-rich phase is not exactly the same as the Co-rich phase that is used in the experiments presented in this thesis. The differences between the two phases are believed consists of different interlayer spacings and the rumpling within each quasicrystalline layer, chemical composition and local order. Since those parameters are adjusted in the dynamical LEED calculation, any particular difference from the bulk structure should be resolved in the surface structure.

In this LEED calculation, each quasicrystal layer is separated into six atomic groups identified in Table 4-1 which are based on the nearest neighbor (NN) distance and chemical identity. The dominant NN distance is 2.43 Å since most of the atoms in the coordinate set sit on vertices of a rhombic Penrose tiling with an edge of the same length. This is in general too short for an Al-Al bond, which is 2.89 Å in bulk Al\textsuperscript{14}. To reduce the unreasonably high density of Al atoms, ATA is applied at the beginning of the calculation, with the occupancy of all atoms is set 90%, while for the Al-1 group is set at 50%. Al-1 atoms are coordinated to the same atoms in the next layer below or above it. Al-2, Al-3 and TM-1 atoms form sets of pentagons rotated by $\pi/5$ in alternating layers. Their overall structure consists of decaprismatic columnar clusters, the center of which is occupied by atoms of the Al-4 group every other layer. This separation into the six atomic groups is done for the first four of the eight layers that form the slab. The next two layers are separated only into two groups (for Al and TM atoms), but no buckling is allowed. In these two layers Ni and Co percentages for the TM group are fixed using ATA at 40% and 60% respectively, so that their composition is close to the nominal
values of the bulk. The two remaining layers are not separated. The entire slab has a
thickness of 14Å and a radius of 45Å.

In the LEED calculation, only the relaxations of different atomic groups
perpendicular to the surface, such as interlayer relaxation and intralayer rumpling are
allowed. Lateral shifts of atoms within the atom groups are not allowed. The number of
resulting free geometrical parameters in the calculation is 26, giving an energy range of
68eV per parameter\textsuperscript{15}.

4.2 Approximated Dynamical LEED Study of the Slab Model

4.2.1 Experimental I(E) spectra

The surface prepared as indicated in Paragraph 3.4 produced well defined LEED
patterns for a wide energy range from 20 eV to 480 eV\textsuperscript{13} (Figure 4.3). The Debye Waller
attenuation of the diffraction beams is reduced by cooling the sample to about 60K.
Seven non-equivalent diffraction spots were used in this analysis and their energy
dependent intensity I(E) represents (Figure 4.5) a cumulative energy range of 1760 eV\textsuperscript{16}.
In general, a larger cumulative energy range consists of more experimental data which
provides a more precise surface characterization.
4.2.2 Indexing the diffraction spots

Using the projection method, we can identify decagonal quasicrystals as the projection in the physical 3D space of the 5D hypercube: five vectors are necessary to generate a reciprocal lattice of a decagonal quasicrystal. In order to index the diffraction spots, given the lattice constants in the 5D space $a_1, ..., a_5$, we identify the reciprocal basis vectors of the 5D reciprocal periodic lattice:

Figure 4.3: LEED diffraction pattern of the clean d-AlNiCo at different incident beam energies, with surface at 60K.
The 5D reciprocal space can be projected into the 3D physical diffraction space $R^*_\parallel$:

\[
\tilde{\varepsilon}_j^* = a \begin{pmatrix}
\cos \left( \frac{2\pi}{5} \right) \\
\sin \left( \frac{2\pi}{5} \right) \\
0 \\
\cos \left( \frac{6\pi}{5} \right) \\
\sin \left( \frac{6\pi}{5} \right)
\end{pmatrix}, \quad j = 1,\ldots,4; \\
\tilde{\varepsilon}_5^* = a_5 \begin{pmatrix}
0 \\
0 \\
1 \\
0 \\
0
\end{pmatrix}
\]

4.1

where for d-AlNiCo\textsuperscript{17}: $a = |\tilde{a}_j| = 1.02\text{Å}^{-1}$ and $a_s = |\tilde{a}_s| = 0.78\text{Å}^{-1}$. The vectors $\tilde{a}_j \quad j = 1,\ldots,4$ points to the vertices of a pentagon in the $xy$ diffraction plane, while the fifth is perpendicular to that surface, parallel to the 10-fold axis. The diffraction vector in the physical space is given by:

\[
\tilde{\mathbf{Q}}_{\parallel} = \sum_{j=1}^{5} h_j \tilde{a}_j
\]

where $h_j$ are integers called “generalized Miller indexes”. A set of generalized Miller indexes $(h_1,h_2,h_3,h_4,h_5)$ is assigned to each diffraction spot. In particular, the plane corresponding to the (00001) spot has 10-fold symmetry and it correspond to the 10-fold surface. The four independent unit vectors in the diffraction pattern, have generalized
Miller indexes: (10000), (01000), (00100), (00010). The vector \( \langle \overline{1} \overline{1} \overline{1} \overline{1} \overline{1} \rangle \) the combination of the four main unit vectors (Figure 4.4).

![Diagram](image)

Figure 4.4: Use of the generalized Miller indexes to label diffraction spots

Similarly we can project the 5D reciprocal lattice in the perpendicular space \( \mathbb{R}^\perp \) to obtain the basis vectors: \( \hat{a}'_j = a \left( \cos \left( \frac{6\pi}{5} \right), \sin \left( \frac{6\pi}{5} \right) \right), \quad j = 1, ..., 5. \)

Diffraction vectors in the perpendicular space are:

\[
\vec{Q}_\perp = \sum_{j=1}^{5} h_j \vec{b}'_j
\]

The magnitude of the diffraction vectors in the perpendicular space \( |\vec{Q}_\perp| \) is associated with the brightness of the beam; in particular, the larger the magnitude, the weaker is the intensity of the diffraction spot.
4.2.3 Results

After optimization of the structure to achieve the lowest Pendry R-factor, the final surface structure is determined, and the results are shown in Table 4-2. The calculated and experimental I(E) spectra are shown in Figure 4.5.

When compared to the bulk spacing (2.04Å) the spacings of the first two layers are contracted by 10% and expanded by 5% respectively, while the remaining interlayer spacings are close to the bulk value (Table 4-2). Rumpling between atomic groups within a layer is about 0.1-0.2Å on average (Figure 4.6). The agreement given by the Pendry R-factor for the best structure (0.32) is similar to that of a conventional LEED studies for multicomponent periodic systems (such as an adsorption structure), which is about 0.25-0.35.

![LEED I(E) spectra for the clean d-Al-Ni-Co](image)

Figure 4.5: LEED I(E) spectra for the clean d-Al-Ni-Co. Solid curves represents the experimental spectra, while the dashed ones the calculated spectra. The inset shows the LEED pattern at 72eV.
The dynamical LEED analysis provides some insight about the top layer composition. The composition found in the final structure agrees with the value of the bulk (Al\textsubscript{73}TM\textsubscript{27} Pendry R-factor = 0.323). By changing the chemical composition of the top layer using ATA, it is possible to verify the effects of variations in chemical composition of the top layer from the nominal bulk value. By increasing the relative composition of transition metal atoms to the top layer up to 11\% (Al\textsubscript{63}TM\textsubscript{37}), the R-factor

<table>
<thead>
<tr>
<th>$d_{12}$</th>
<th>$d_{23}$</th>
<th>$d_{34}$</th>
<th>$d_{45}$</th>
<th>$d_{56}=d_{67}=d_{78}$</th>
<th>$d_{\text{bulk}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.84 ± 0.13 (−10 ± 6%)</td>
<td>2.14 ± 0.14 (5 ± 7%)</td>
<td>2.0 ± 0.2 (−2±10%)</td>
<td>2.1 ± 0.2</td>
<td>2.0 ± 0.2</td>
<td>2.04</td>
</tr>
</tbody>
</table>

Figure 4.6: Side view of the quasicrystal slab (first four layers) showing the surface relaxation and rumpling (exaggerated for clarity). The color scheme is the indicated in Table 2-2
increases by 5% (0.338). By increasing the relative Al atoms in the top layer up to 14% (Al\textsubscript{83}TM\textsubscript{17}), the R-factor increases by 15% (0.371). Thus, the calculation seems to be more sensitive to increases in Al concentration in the top later than increases in transition metals.

The extent and type of contraction and expansion of the first two layers is similar to most low-index metal surfaces. This can be explained by the charge smoothing present at the surface\textsuperscript{18}. This behavior suggests that the surface is indeed metallic, in agreement with the delocalized charge density deduced from photoemission studies of this surface\textsuperscript{19}. The observed layer rumplings are similar to those observed in bulk structures by x-ray diffraction\textsuperscript{5} and supported by total energy calculations\textsuperscript{20,21}. The main feature of the observed rumpling is that the atoms that form the decagonal columnar clusters (Al-2, Al-3 and TM-1) tend to protrude out from the surface. The atom density of one layer for the determined structure is 0.123 Å\textsuperscript{-1}, compared to the atom density of a similar periodic alloy crystal AlNi(110) of 0.170Å\textsuperscript{-1}.

Lateral atom position was not varied in the LEED calculation. This is partly because of the limited sensitivity of LEED to these parameters. In order to verify any possible lateral reconstruction of the surface, the structure model derived from the LEED calculation was compared to high-resolution STM images from large flat terraces of the d-AlNiCo surface. This comparison is facilitated by filtering the image using the strongest Fourier components, followed inverse transformation and unsharp-mask filters. The filtered images show an enhanced contrast (Figure 4.7).
When the top layer of the LEED structure model is superimposed on a 75x75Å² patch of the filtered STM image, a visual comparison shows that the number of electron density protrusions in the STM image is far lower than the number of atoms present in the top layer of the LEED structure model. In order to find a match between those protrusions in the STM data and the atomic model, the different atomic groups used in the LEED calculation were tried. A good match was found for the transition metals, (Figure 4.8). This match is by no means unique; many others can be found. However this close match provides important information about the surface itself: lateral distortions in the surface structure are likely to be minimal. Thus from the combination of the LEED and the STM results, the surface structure appears to be slightly relaxed, but essentially bulk terminated. Since the layered structure of the 10-fold surface of d-Al-Ni-Co has only two possible terminations A and B, which are related by mirror symmetry, the identification of the atomic position and the chemical types in one termination can be extended to describe the complete surface.

Figure 4.7: a) STM image from the d-Al-Ni-Co (18x18 nm²): clearly visible protrusions of atomic size, arranged in pentagons and decagons. b) The same image after Fourier filtering and c) after an unsharp mask filter is applied. The pentagons and circles are highlighted to assist in identifying common features during the process. The dashed square corresponds to the area shown in Figure 4.8.
Figure 4.8: Atom positions from the LEED structure model are superimposed to the filtered STM image. The match is found for the TM-1 group, which can be identified with Co atoms. The protrusions in the image associated with this group appear brighter: this is consistent with them being close to the surface. The decagon corresponds to the quasi-unit cell identified in the bulk structure (Figure 2.16).
4.3 Dynamical LEED analysis using approximant models

The LEED calculation on the “exact” slab model requires the introduction of a number of approximations to make multiple scattering calculations tractable. A different approach can be used to perform a LEED analysis of a quasicrystal surface, by using an approximate structure model. This structure contains local structures that are expected to be present in the quasicrystal surface. However, this structure is periodic instead of quasiperiodic so an exact calculation can be performed. Since the structure is well defined, this method allows the position of individual atoms to be considered in the analysis.

Periodic approximants for the d-Al-Ni-Co quasicrystal can be constructed by imposing a linear phason strain on the physical space associated with the perfect quasicrystal, as described in paragraph 2.3.2. In principle, an infinite number of approximants can be produced. However, since LEED calculations are limited by the computational power available, a limit must be set on the size of the unit cell. An online database of atomic structural coordinates of periodic quasicrystalline approximants is available\textsuperscript{22}. For the structural characterization of d-Al-Ni-Co, three bulk approximants have been considered. The selection criteria were based on: a) the local geometry portrayed within the unit cell, which involves a specific type of tiling; b) the size of the unit cell. Three approximants have been selected based on those criteria: H1, H2, and B1.
4.3.1 H1, H2 and B1 Approximants

H1 and H2 Approximants have similar local geometries: their local structures are dominated by pentagons of transition metal atoms. The H1 unit cell has 25 atoms which are split between two layers (12+13); the unit cell has mirror plane symmetry. The nominal composition of the H1 structure is Al\textsubscript{68}Ni\textsubscript{24}Co\textsubscript{8} (Al\textsubscript{68}TM\textsubscript{32} if the transition metals are combined). The H2 unit cell is twice the size of H1 (50 atoms) and no mirror symmetry is present. Similarly to H1, the atoms are confined in two layers (24+26). The nominal composition of the H2 structure is the same as for H1.

The B1 unit cell has 40 atoms, divided into two layers (21+19), with no particular symmetry relationship to H1 or H2. Mirror symmetry is present in the unit cell. The B1 local geometry, which is different from both H1 and H2, can be described by overlapping decagons of transition metals. The nominal composition of the B1 structure is Al\textsubscript{72.5}Ni\textsubscript{20}Co\textsubscript{7.5} (Al\textsubscript{72.5}TM\textsubscript{27.5} if the transition metals are combined). The top views of H1, H2 and B1 surfaces with corresponding unit cell are shown in Figure 4.9.

Both the H1 and H2 approximant surfaces can be completely filled by tiling with rhombi and pentagons, whose vertices are located at the transition metal atoms sites. This tiling is perfectly periodic and is shown in Figure 4.10. The tiling for the B1 model consists of decagons that can overlap. Both the H1/H2 and B1 tilings are locally isomorphic with the tiling of the perfect quasicrystal surface. Thus a connection between local structures of the quasicrystal model and the approximants can be drawn. In particular this tiling allows the identification of atoms in the approximant models with the same groups used in the quasiperiodic model (Table 4-1). From this comparison, it
appears that the most frequent motifs consist of pentagons of Al-2 (blue) for the H1 model and pentagons of Al-1 and Al-2 atoms for H2. The B1 model is instead dominated by decagonal “flowers”, having a cobalt atom in the center and surrounded by Al-1 and Al-2 atoms (Figure 4.10). For the three models, these local structures can be identified on the quasicrystal model layer.

Figure 4.9: Top view of the surface of the approximants H1, H2 and B1. Dashed lines show the unit cell. The color scheme is the following: Black = Ni, red = Co and yellow = Aluminum. Larger-smaller atoms belong to two different layers.
Figure 4.10: Tiling of the approximants (white solid lines), using pentagons and rhombi for H1 and H2, or overlapping decagons for B1. The combination of the two tilings is used on the quasiperiodic model to identify the chemical identities. The color scheme is the same as in Table 4-1.
4.3.2 Beam indexing correspondence between the quasiperiodic diffraction pattern and the approximant models

In order to compare the diffraction features from the d-AlNiCo with the approximant models, it is necessary to translate the 5D pseudo-pentagonal basis of the quasicrystalline d-AlNiCo $\tilde{a}_j$, $j = 1, ..., 5$ (Eq. 4.1) into the reciprocal unit vectors of the approximants. Because of the 10-fold symmetry in the diffraction pattern, for a given for a given momentum vector $\vec{Q} = (q_x, q_y)$ ten symmetry-equivalent diffraction spots are present. Each spot is characterized by its generalized Miller indices, expressed in terms of the 5D pseudo-pentagonal basis. Each approximant index corresponds to one of those 5D indices (Table 4-3). Vice versa, not all the 5D indices have their counterpart in the approximant reciprocal space, as we noted previously in the 1D case (Paragraph 2.3.1). In order to retain the 10-fold symmetry of the diffraction pattern, the approximant indices for each $\vec{Q}$ are averaged together with equal weights.
Table 4-3: Approximants indices for each symmetry-equivalent momentum vector and the corresponding 5D index.

<table>
<thead>
<tr>
<th>Momentum Vector $\mathbf{Q} \ [Å^{-1}]$</th>
<th>5D Index</th>
<th>Approximant Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>(-1,-1,-1,-1,0)</td>
<td>(2,-2,0), (0,-2,0), (-2,-1,0), (3,-1,0), (-3,0,0)</td>
</tr>
<tr>
<td>(1.94, 0)</td>
<td>(-1,-1,-2,-1,0)</td>
<td>(3,-2,0), (-1,-2,0), (-3,-1,0), (4,-1,0)</td>
</tr>
<tr>
<td>(0, 2.67)</td>
<td>(-1,-2,-2,-1,0)</td>
<td>(3,-3,0), (0,-3,0), (-3,-2,0), (5,-2,0), (-5,0,0)</td>
</tr>
<tr>
<td>(3.14, 0)</td>
<td>(0,-2,-2,-1,0)</td>
<td>(5,-3,0), (2,-3,0), (2,-4,0), (-5,-1,0), (6,-1,0)</td>
</tr>
<tr>
<td>(0.60, 3.50)</td>
<td>(-1,-2,-3,-1,0)</td>
<td>(5,-4,0), (-1,-4,0), (3,-4,0), (-3,-3,0), (6,-3,0), (-6,-1,0), (7,-1,0), (-7,2,0), (5,2,0)</td>
</tr>
<tr>
<td>(0, 4.32)</td>
<td>(-1,-3,-3,-1,0)</td>
<td>(5,-5,0), (0,-5,0), (-5,-3,0), (8,-3,0), (-8,0,0)</td>
</tr>
<tr>
<td>(0.97, 4.01)</td>
<td>(-1,-3,-3,-2,0)</td>
<td>(6,-4,0), (-2,-4,0), (2,-5,0), (3,-5,0), (-3,-4,0), (7,-4,0), (-7,-1,0), (8,-1,0), (-8,2,0), (6,2,0)</td>
</tr>
<tr>
<td>H2</td>
<td>(-1,-1,-1,-1,0)</td>
<td>(-1,-3,0), (3,-2,0), (4,0,0)</td>
</tr>
<tr>
<td>(1.94, 0)</td>
<td>(-1,-1,-2,-1,0)</td>
<td>(-3,-3,0), (0,-4,0), (4,-1,0)</td>
</tr>
<tr>
<td>(0, 2.67)</td>
<td>(-1,-2,-2,-1,0)</td>
<td>(-2,-5,0), (5,-3,0), (6,0,0)</td>
</tr>
<tr>
<td>(3.14, 0)</td>
<td>(0,-2,-2,-1,0)</td>
<td>(-4,-5,0), (0,-6,0), (7,-2,0)</td>
</tr>
<tr>
<td>(0.60, 3.50)</td>
<td>(-1,-2,-3,-1,0)</td>
<td>(-4,-6,0), (1,-7,0), (6,-5,0), (8,-1,0), (7,3,0)</td>
</tr>
<tr>
<td>(0, 4.32)</td>
<td>(-1,-3,-3,-1,0)</td>
<td>(-3,-8,0), (8,-5,0), (10,0,0)</td>
</tr>
<tr>
<td>(0.97, 4.01)</td>
<td>(-1,-3,-3,-2,0)</td>
<td>(5,-7,0), (1,-8,0), (6,-6,0), (9,-2,0), (9,3,0)</td>
</tr>
<tr>
<td>B1</td>
<td>(-1,-1,-1,-1,0)</td>
<td>(2,-3,0), (3,-2,0), (3,0,0), (0,-3,0), (2,2,0)</td>
</tr>
<tr>
<td>(1.94, 0)</td>
<td>(-1,-1,-2,-1,0)</td>
<td>(1,-4,0), (4,-1,0), (3,-3,0), (3,1,0), (-1,-3,0)</td>
</tr>
<tr>
<td>(0, 2.67)</td>
<td>(-1,-2,-2,-1,0)</td>
<td>(3,-5,0), (5,-3,0), (5,-0,0), (0,-5,0), (3,3,0)</td>
</tr>
<tr>
<td>(3.14, 0)</td>
<td>(0,-2,-2,-1,0)</td>
<td>(2,-6,0), (6,-2,0), (5,-5,0), (5,2,0), (-2,-5,0)</td>
</tr>
<tr>
<td>(0.60, 3.50)</td>
<td>(-1,-2,-3,-1,0)</td>
<td>(3,-7,0), (7,-3,0), (6,-5,0), (5,-6,0), (7,-1,0), (1,-7,0), (5,3,0), (-3,-5,0), (1,-6,0), (-6,1,0)</td>
</tr>
<tr>
<td>(0, 4.32)</td>
<td>(-1,-3,-3,-1,0)</td>
<td>(5,-8,0), (8,-5,0), (8,0,0), (0,-8,0), (5,5,0)</td>
</tr>
<tr>
<td>(0.97, 4.01)</td>
<td>(-1,-3,-3,-2,0)</td>
<td>(3,-8,0), (8,-3,0), (7,-6,0), (6,-7,0), (8,2,0), (2,-8,0), (6,3,0), (-3,-6,0), (2,7,0), (-7,2,0)</td>
</tr>
</tbody>
</table>
4.3.2.1 Results

Since the calculation is performed on approximants which have a periodic structure, a standard dynamical LEED calculation package is used, the Barbieri/Van Hove Symmetrized Automated Tensor LEED\textsuperscript{23}. The phase shifts of Al, Ni and Co are calculated using the Barbieri/Van Hove Phase Shift Package. The total energy range for the dynamical LEED calculation is 20-480eV, with the total range for the experimental data of 1835eV. As in the previous analysis only vertical relaxation and rumpling are allowed. The results of the calculation from the three different approximant models considered are presented as follows.

**H1 and H2 approximants:** Since the unit cells are composed of two layers A and B with different number of atoms each (12+13 for H1, 24+26 for H2), for each approximant, two different terminated structures must be considered, one with a top layer A and another with top layer B. The calculation shows that the level of agreement is similar for the two terminations in either approximant, with a slightly better agreement for the denser layer B. For this reason, the optimization is performed on the denser, B-terminated surface. This optimization for the H1 model is done by allowing the z-coordinate of each of the top three layers to vary. The optimization of the H2 structure is restricted to the z-coordinate of only the top layer, which is allowed to vary, while the others are kept fixed. The optimization for the H1 results in 27 free parameters (68 eV/parameter) and the H2 model yields to 26 free parameters (71 eV/parameter).

The best structures for the two models have Pendry R-factors of 0.26 and 0.36 for H1 and H2 respectively. For the H1 model the first interlayer spacing is slightly
contracted (1%) while the second and the third are expanded (3% and 2% respectively). Rumpling is present in the first two layers (about 0.1Å) while the third is basically flat. The H2 model shows a slightly compressed first interlayer spacing (2%): however the calculation restrictions mentioned above, may have influenced this result. The geometrical parameters for the favored structures are shown in Table 4-4. The I(E) spectra are shown in Figure 4.11.

Table 4-4: Average interlayer spacing and rumpling for the favored structures of H1 and H2 approximants. Quantities are expressed in Å. Negative percentages indicate a contraction with respect to bulk.

<table>
<thead>
<tr>
<th></th>
<th>$d_{12}$</th>
<th>$d_{23}$</th>
<th>$d_{34}$</th>
<th>$\Delta_1$</th>
<th>$\Delta_2$</th>
<th>$\Delta_3$</th>
<th>$d_{bulk}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>2.01±0.09 (−1±4%)</td>
<td>2.11±0.11 (3±5%)</td>
<td>2.09±0.11 (2±5%)</td>
<td>0.08±0.06</td>
<td>0.11±0.12</td>
<td>0.04±0.11</td>
<td>2.04</td>
</tr>
<tr>
<td>H2</td>
<td>2.0±0.2 (-2±10%)</td>
<td>0.1±0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.04</td>
</tr>
</tbody>
</table>
Figure 4.11: LEED I(E) spectra for the approximants H1 (top) and H2 (bottom), compared to the experimental spectra. The cumulative Pendry R-factors are 0.26 and 0.36 respectively.
**B1 Approximant:** The level of agreement in the calculation shows no preferred termination between the two terminations A (composed of 19 atoms, 12 Al, 4 Ni and 3 Co) and B (21 atoms, 16 Al, 4 Ni and 1 Co). Both terminations are considered in the optimization, in which the z-coordinates of each atom in the top two layers are allowed to relax. This yields 24 free parameters (76eV/parameter). The optimization showed that the Al-rich termination is preferred over the TM-rich with Pendry R-factors 0.27 and 0.31 respectively. The first interlayer spacing is contracted (6%) while the second is expanded (5%) relative to the bulk. The average rumpling within the top two layers is about 0.1 Å. The geometrical parameters for the best-fit structures are shown in Table 4-5. The I(E) spectra are shown in Figure 4.12.

<table>
<thead>
<tr>
<th></th>
<th>(d_{12})</th>
<th>(d_{23})</th>
<th>(\Delta_1)</th>
<th>(\Delta_2)</th>
<th>(d_{\text{bulk}})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>B1</strong></td>
<td>1.9 ± 0.2</td>
<td>2.1 ± 0.2</td>
<td>0.07 ± 0.12</td>
<td>0.1 ± 0.2</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td>(-6 ± 10%)</td>
<td>(5 ± 10%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4-5: Average interlayer spacing and rumpling for the favored structures of B1 approximants. Quantities are expressed in Å. Negative percentages indicate a contraction with respect to bulk.
Figure 4.12: LEED I(E) spectra for the approximant B1, compared to the experimental spectra. The cumulative Pendry R-factor is 0.27.
4.3.3 Comparing the structures determined using the quasicrystal slab model with those determined using the approximant models.

The geometrical parameters derived from the LEED analysis of the slab model and the approximants are compared in (Table 4-6).

Table 4-6: Summary of the geometrical parameter for the approximant models and the QC slab model. Quantities are expressed in Å. Negative percentages indicate a contraction with respect to bulk.

<table>
<thead>
<tr>
<th></th>
<th>$d_{12}$</th>
<th>$d_{23}$</th>
<th>$d_{34}$</th>
<th>$\Delta_1$</th>
<th>$\Delta_2$</th>
<th>$\Delta_3$</th>
<th>$d_{bulk}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H1$</td>
<td>2.01±0.09</td>
<td>2.11±0.11</td>
<td>2.09±0.11</td>
<td>0.08±0.06</td>
<td>0.11±0.12</td>
<td>0.04±0.11</td>
<td>2.04</td>
</tr>
<tr>
<td>$H2$</td>
<td>2.0±0.2</td>
<td></td>
<td></td>
<td>0.1±0.2</td>
<td></td>
<td></td>
<td>2.04</td>
</tr>
<tr>
<td>$B1$</td>
<td>1.9±0.1</td>
<td>2.1±0.2</td>
<td></td>
<td>0.07±0.12</td>
<td>0.1±0.2</td>
<td></td>
<td>2.03</td>
</tr>
<tr>
<td>$QC$</td>
<td>1.84±0.13</td>
<td>2.14±0.14</td>
<td>2.0±0.2</td>
<td>0.06±0.10</td>
<td>0.08±0.14</td>
<td>0.03±0.14</td>
<td>2.04</td>
</tr>
</tbody>
</table>

According to this study, the interlayer spacings for the approximant B1 are in good quantitative agreement with the slab model. The results for approximant H1 are also in agreement with both the slab model and the approximant B1: the only significant difference is in a slightly less compressed first layer and slightly expanded third layer.

The results for approximant H2 are in an overall agreement with both the other approximant and slab models. However the results of the calculation using the H2 model may be affected by the restriction to the relaxation of only the first layer. The amount of rumpling (~0.1Å) within the layers is similar for all models.
The identification of the atoms in the approximant models with the same groups used in the quasicrystal model (described in Paragraph 4.3.1), allows a comparison of the surface composition as derived from the LEED studies presented above. The percentages of each atomic group within the unit cell of the approximants are shown in Table 4-7.

Table 4-7: Percentages of atoms per atomic group. Al-1 (green) atom sites are only half occupied in the QC slab; in H1 they appear every other layer; in H2 it varies between 4 and 2 in adjacent layers.

<table>
<thead>
<tr>
<th>Group</th>
<th>QC slab</th>
<th>H1</th>
<th>H2</th>
<th>B1</th>
<th>color</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM-1 (Co)</td>
<td>12</td>
<td>8</td>
<td>8</td>
<td>10</td>
<td>Red</td>
</tr>
<tr>
<td>TM-2 (Ni)</td>
<td>15</td>
<td>24</td>
<td>24</td>
<td>20</td>
<td>Black</td>
</tr>
<tr>
<td>Al-1</td>
<td>17</td>
<td>4</td>
<td>12</td>
<td>20</td>
<td>Green</td>
</tr>
<tr>
<td>Al-2</td>
<td>32</td>
<td>40</td>
<td>32</td>
<td>20</td>
<td>Blue</td>
</tr>
<tr>
<td>Al-3</td>
<td>15</td>
<td>16</td>
<td>16</td>
<td>20</td>
<td>Cyan</td>
</tr>
<tr>
<td>Al-4</td>
<td>9</td>
<td>8</td>
<td>8</td>
<td>10</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

From this table, it appears that the overall the percentages of aluminum are similar for the H2 model and QC slab model. The Al-1 and Al-2 concentrations for the H1 model are slightly different from the H2 model and the quasicrystal slab model, while the others are identical. Differences in Ni-Co concentration do not change the actual structure as detected by LEED, so their individual concentration derived from this analysis may differ from the real value.

A further comparison can be done by measuring the average “center of mass” positions of each atom group relative to the center of mass of each layer (Table 4-8).
Table 4-8: Center of mass position for the different atomic groups within each layer, relative to the center of mass of each layer. Negative values indicate direction towards vacuum.

**First layer [Å]**

<table>
<thead>
<tr>
<th>Group</th>
<th>QC slab (0.00Å)</th>
<th>H1 (0.00Å)</th>
<th>H2 (0.00Å)</th>
<th>B1 (0.00Å)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM-1 (Co)</td>
<td>-0.08±0.03</td>
<td>-0.04±0.04</td>
<td>0.14±0.10</td>
<td>-0.08±0.06</td>
<td>Red</td>
</tr>
<tr>
<td>TM-2 (Ni)</td>
<td>0.06±0.06</td>
<td>-0.02±0.04</td>
<td>-0.02±0.12</td>
<td>-0.09±0.06</td>
<td>Black</td>
</tr>
<tr>
<td>Al-1</td>
<td>0.1±0.2</td>
<td>-0.12±0.11</td>
<td>-0.2±0.2</td>
<td>-0.09±0.12</td>
<td>Green</td>
</tr>
<tr>
<td>Al-2</td>
<td>-0.08±0.06</td>
<td>-0.01±0.09</td>
<td>0.0±0.3</td>
<td>-0.09±0.14</td>
<td>Blue</td>
</tr>
<tr>
<td>Al-3</td>
<td>-0.0±0.2</td>
<td>-0.16±0.08</td>
<td>-0.1±0.3</td>
<td>-0.04±0.12</td>
<td>Cyan</td>
</tr>
<tr>
<td>Al-4</td>
<td>0.01±0.06</td>
<td>0.10±0.10</td>
<td>0.2±0.3</td>
<td>-0.1±0.2</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

**Second layer [Å]**

<table>
<thead>
<tr>
<th>Group</th>
<th>QC slab (1.84Å)</th>
<th>H1 (1.99Å)</th>
<th>H2 (1.93Å)</th>
<th>B1 (1.93Å)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM-1 (Co)</td>
<td>0.03±0.06</td>
<td>0.09±0.06</td>
<td>-</td>
<td>0.07±0.06</td>
<td>Red</td>
</tr>
<tr>
<td>TM-2 (Ni)</td>
<td>0.07±0.07</td>
<td>-0.06±0.06</td>
<td>-</td>
<td>-0.04±0.09</td>
<td>Black</td>
</tr>
<tr>
<td>Al-1</td>
<td>-0.2±0.3</td>
<td>-</td>
<td>-</td>
<td>-0.1±0.2</td>
<td>Green</td>
</tr>
<tr>
<td>Al-2</td>
<td>-0.08±0.07</td>
<td>-0.17±0.12</td>
<td>-</td>
<td>-0.2±0.2</td>
<td>Blue</td>
</tr>
<tr>
<td>Al-3</td>
<td>0.1±0.2</td>
<td>0.1±0.2</td>
<td>-</td>
<td>-0.0±0.3</td>
<td>Cyan</td>
</tr>
<tr>
<td>Al-4</td>
<td>0.1±0.2</td>
<td>0.2±0.2</td>
<td>-</td>
<td>-0.1±0.3</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

**Third layer [Å]**

<table>
<thead>
<tr>
<th>Group</th>
<th>QC slab (3.99Å)</th>
<th>H1 (4.12Å)</th>
<th>H2</th>
<th>B1</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM-1 (Co)</td>
<td>-0.01±0.05</td>
<td>-0.01±0.08</td>
<td>-</td>
<td>-</td>
<td>Red</td>
</tr>
<tr>
<td>TM-2 (Ni)</td>
<td>0.02±0.07</td>
<td>-0.02±0.10</td>
<td>-</td>
<td>-</td>
<td>Black</td>
</tr>
<tr>
<td>Al-1</td>
<td>0.0±0.3</td>
<td>-0.1±0.2</td>
<td>-</td>
<td>-</td>
<td>Green</td>
</tr>
<tr>
<td>Al-2</td>
<td>0.00±0.06</td>
<td>-0.05±0.10</td>
<td>-</td>
<td>-</td>
<td>Blue</td>
</tr>
<tr>
<td>Al-3</td>
<td>-0.1±0.3</td>
<td>0.04±0.11</td>
<td>-</td>
<td>-</td>
<td>Cyan</td>
</tr>
<tr>
<td>Al-4</td>
<td>0.03±0.09</td>
<td>-0.02±0.12</td>
<td>-</td>
<td>-</td>
<td>Yellow</td>
</tr>
</tbody>
</table>
The H1, B1 have values for the center of mass that are in agreement with the quasicrystal slab model. The good agreement in the position of Al-2 and TM-1 atoms in both the first and the second layer suggests that the local structure corresponding to those groups provides a good description of a local geometry in the quasicrystal surface. The agreement of the H2 model, with the other models is somewhat limited. As mentioned above, this may be due to the restriction in relaxation of only the first layer.

The overall analysis shows that using the H1 and B1 approximants is a valid method to determine the structure of the quasicrystal surface. The values of rumpling and surface relaxations are qualitatively similar to the corresponding ones obtained from the calculation using the quasicrystal slab model, with small deviations from it. However local geometries common in the H1, B1 and slab model are not immediately identified based on this current atomic group separation. In addition the precisions of the position of the transition metal atoms are generally better defined than those of the Al atoms. This may suggest that the atom groups’ separation based on the nearest neighbor distance that has been chosen for Al atoms may not be appropriate to describe common local geometries among the models considered. The effect of this into the analysis is a decreased precision in the measure of the center of mass position of Al atoms.

An alternative choice for the atom group separation, based on similar geometric patterns in the models is currently under investigation. According to this scheme Al atoms are separated into three different groups depending on their local geometry, while transition metals are separated into a fourth group (Figure 4.13).
Figure 4.13: Atom group separation based on the identification of common local geometries among the quasicrystalline slab model and the H1 and B1 models. Four groups are identified. Al-A: pentagonal cluster of five Al atoms transition atoms (blue). Al-C: cluster of three Al atoms (green). Al-C: the remaining Al atoms. TM: the transition metals (black).
Preliminary results are in good agreement with those based on the previous calculation. The comparison of the results of this calculation with those done on the approximants, will ultimately provide a complete characterization of the quasicrystal slab model in terms of single local geometries which are in common with the approximant model.

4.4 Measurement of the Surface Debye Temperature

The fluctuation of atomic positions about the equilibrium position is related to the temperature of the crystal: in particular the displacement amplitude increases as the temperature increases\(^\text{24}\). The effect of this thermal motion in a diffraction experiment is the attenuation of the scattered intensity. This is related to the atomic mean square displacement \(\langle (\Delta \vec{r})^2 \rangle\) through the Debye-Waller factor, denoted here as \(\exp(-2M)\):

\[
I = I_0 \exp(-2M) = I_0 \exp\left(-\frac{1}{3} |\Delta \vec{k}|^2 \langle (\Delta \vec{r})^2 \rangle\right)
\]

where \(\Delta \vec{k}\) is the total momentum transfer. For temperatures above 100K, the Debye-Waller factor can be rewritten in terms of the temperature \(T\), the mass \(m\) and the Debye temperature \(\Theta_D\) of the sample\(^\text{25}\):

\[
\exp(-2M) = \exp\left[-\frac{3\hbar^2 |\Delta \vec{k}|^2}{mk_B \Theta_D^2} T\right] = \exp[A \cdot T]
\]

\[
A = \left[-\frac{3\hbar^2 |\Delta \vec{k}|^2}{mk_B \Theta_D^2}\right]
\]
Equation 4.2 can be rewritten as a linear relation:

$$\ln I(T) = A \cdot T + \text{const}$$  \hspace{1cm} (4.4)

By measuring the intensity of a diffraction beam as a function of the temperature of the crystal surface and at fixed incident electron energy, a direct measure of the parameter $A$ is obtained (Figure 4.14).

Figure 4.14: The logarithm of the normalized diffraction intensity as function of the sample temperature is fit to extract the value of the parameter $A$ (Eq. 4.3).

In particular from Eq. 4.3, the Debye temperature $\Theta_D$ is given by:
where the total mass is calculated from the masses of the single chemical components, weighted with the relative compositions in the quasicrystal.

A repeated set of experiments is performed at different incident energies (42 and 67 eV). The intensities of the specular beam and one diffracted beam with indices (0, 2.67) are measured as a function of sample temperature (range: 250-600K). The Debye temperatures are obtained using Eq. 4.5 and they are shown in Table 4-9.

Table 4-9: Debye temperatures for the clean d-Al-Ni-Co quasicrystal surface, measured from different LEED diffraction beams at different incident energies.

<table>
<thead>
<tr>
<th>Diffraction beam</th>
<th>Incident Energy [eV]</th>
<th>$\Theta_D$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specular</td>
<td>42</td>
<td>391 ± 26</td>
</tr>
<tr>
<td>(0, 2.67)</td>
<td>42</td>
<td>382 ± 48</td>
</tr>
<tr>
<td>Specular</td>
<td>67</td>
<td>430 ± 28</td>
</tr>
<tr>
<td>(0, 2.67)</td>
<td>67</td>
<td>416 ± 29</td>
</tr>
</tbody>
</table>

The penetration depth of electrons into the surface is related to the incident energy. At low incident energy, electrons penetrate only few layers of the quasicrystal surface. As the energy is increased, electron penetrates deeper, thus more layers are probed. The results from this work suggest that the Debye temperature increases as more layers are probed. This is consistent with previous measurements of the Debye
temperature of the top-most layer (335K, measured by helium atom scattering\textsuperscript{17}) and of the bulk (589 ± 13K obtained from a low-temperature specific heat experiment\textsuperscript{26}).

4.5 References


In LEED calculations of low order surfaces, the minimum required cumulative energy range for the experimental dataset must be at least 400eV (F. Jona, P.M. Marcus, H.D. Shih, “Determination of Surface Structure by LEED”, Ed. By P.M. Marcus and F. Jona, Plenum, New York). For a simple surface such as Cu(100), considering three layers in the calculation and only vertical relaxation, this gives about 70eV per parameter. We can assume this as the minimum value for an accurate and reliable calculation.

The actual experimental dataset has a cumulative energy range of 1835 eV. The program discards few data points at the beginning and at the end of each spectra.

H. R. Sharma, in PhD thesis, Physics (Freie University, Berlin, 2002).


Chapter 5

Xe Adsorption on the 10-fold d-Al-Ni-Co surface

Materials grown from the melt having quasicrystalline order are binary or ternary alloys. While no single-component quasicrystal has been produced from the melt, many examples have been found of pseudomorphic growth of single component systems, i.e. using quasicrystal surfaces as a template to force quasiperiodicity in the film. A complete review of these systems has been recently published\(^1\). All these systems consist of transition metals adsorbed on quasicrystal surface.

The weak interaction of rare gases with surfaces has been extensively used to probe structural properties of the surface such as topographic mapping of the surface potential; also this simple interaction allows the investigation of the effects of symmetry and morphology on the growth of thin films on many different surfaces\(^2\). These features are very appealing when trying to understand the growth of thin films on quasiperiodic surfaces in terms of adsorbate-substrate interaction potential. In this chapter the growth and the structure of Xe adsorbed on the d-Al-Ni-Co quasicrystal surface will be presented\(^3\).

5.1 Experimental details

The clean sample is obtained in vacuum following the procedure described in Paragraph 3.4. In order to characterize the growth mode, adsorption isobars are measured (Paragraph 3.2.1). Xenon is leaked into the UHV chamber, to a stable pressure varying
between $1 \times 10^{-8}$ to $1 \times 10^{-5}$ mbar. As the surface is cooled progressively down to the minimum sample temperature (60K), Xe adsorbs on the surface. During the adsorption Xe pressure is kept constant, by adjusting the Xe flow into the chamber. The cooling rate is about 1K/s, so that the Xe gas near the surface is in equilibrium with the Xe adsorbed on the surface. Similarly, desorption is achieved by a slow sample heating (rate: 3K/s), while the Xe pressure is still kept constant.

LEED patterns are acquired as function of the sample temperature for a fixed Xe partial pressure and fixed incident electron energy. The diffraction intensities of specific substrate beams are then extracted (Paragraph 3.2.1). The isobars are corrected for the Debye-Waller attenuation, by measuring the Debye-Waller factor (Eq. 4.2) of one substrate diffraction spot as the sample temperature is decreased and by dividing the measured factor from the isobars$^4$.

### 5.2 Adsorption characteristics

LEED adsorption isobars for Xe adsorption at different pressures are shown in Figure 5.1. They correspond to the intensity of the (1.94, 0) diffraction beam (shown in the inset). LEED diffraction patterns at different sample temperatures, corresponding to different phases of Xe adsorption are shown in Figure 5.2.
Figure 5.1: LEED adsorption isobars for Xe adsorption on the d-AlNiCo quasicrystal surface. The isobars consist of the integrated intensity of a substrate diffraction spot as function of the sample temperature at various Xe partial pressures and at fixed incident electron energy (55eV). The white circle in the LEED pattern in the inset shows the beam (1.94, 0), from which the intensity is extracted. The monolayer and bilayer completion points are indicated in the isobars.

Figure 5.2: LEED patterns recorded at 62eV from: a) the clean d-Al-Ni-Co surface; b) after the adsorption of one layer; c) after the adsorption of two layers; d) after adsorption of several layer of Xe. These LEED patterns correspond to the $3.2 \times 10^{-7}$ mbar isobar in Figure 5.1.
As the temperature is lowered, each isobar exhibits an initial slow decrease in intensity, followed by a larger, more vertical drop in the substrate spot intensity by 50% from the intensity of the same beam for the clean surface. The slow initial decrease in intensity may be due to adsorption at specific sites in the substrate and it shows that up to 20% Xe may initially bind at sites within the surface structure where the Xe adsorption is lower.

The round edges of the first adsorption step at high temperatures and pressures may also suggest another scenario. For very low coverage, Xe atoms may adsorb into a mobile, liquid phase. As more Xe is deposited this mobility is reduced until solidification is reached. Similar rounding effects have been observed for adsorption of liquid or disordered layers have been observed in LEED isotherms\(^5\) and constant flux adsorption measurements\(^6\).

The subsequent sharp step in the isobars corresponds to the adsorption of the monolayer. The total decrease in intensity during the first layer adsorption is similar to that observed for the first layer adsorption of Xe on Ag(111)\(^4,7\). The LEED pattern corresponding to the point in the isobar at the bottom of the first adsorption step is shown in Figure 5.2 b). As the temperature is further reduced, a second step occurs in the isobar, corresponding to the adsorption of the second layer. Similarly, after some further decrease in the intensity at lower temperatures and a third step appears, corresponding to the adsorption of the third layer. The reduction of intensity continues after the third step, but no additional steps can be easily resolved in the isobars.
When the second adsorption step occurs, new diffraction spots are visible in the LEED patterns (Figure 5.2 c)): in particular rings made of 30 spots each appear. In the inner ring, 10 of the 30 spots correspond exactly to the substrate spots with momentum transfer (0, 1.65), while the other 20 have the same momentum transfer and are aligned along directions ±12° with respect to the substrate spots. As more Xe is adsorbed, these spots increase in intensity as shown in the LEED pattern corresponding to several layers of Xe (Figure 5.2 d)).

Figure 5.3: LEED adsorption isobars corresponding to different diffraction spots for adsorption at $1.6 \times 10^{-6}$ mbar. The diffraction pattern in the inset (55eV) shows which diffraction spots were used. The spot labeled “C” is not visible in the clean surface LEED pattern. The dashed line correspond to the point where the multilayer structure is fully developed (Figure 5.2 d).
In Figure 5.3 the isobaric evolution of the intensities of the new superlattice diffraction spots that occur upon Xe adsorption are compared to the intensity of the substrate spot as in Figure 5.1 (curve B). One of these superlattice spots (curve A) is at location of an existing substrate spot beam (1.94, 0) while the other (curve C) is one of the 20 additional spots which are not at location of a substrate spot. The reduction of intensity in all three curves during monolayer adsorption is due to the attenuation of the substrate diffraction intensity by the overlayer. In particular the initial reduction seen at higher temperature for curve C is due to the reduction in background intensity of the substrate, rather than a reduction in intensity of the spot itself, since the additional diffraction spots for appear only at about 70K. The main contribution to background intensity for the quasicrystal substrate at these temperatures comes from the densely spaced weak diffraction beams rather than from diffuse elastic scattering. Thus the reduction in intensity indicates that this diffraction from the substrate is being attenuated at a greater rate than the increase in diffuse elastic scattering from the adsorbed Xe. The intensities at both locations A and C increase upon adsorption of the second layer (identified as the bilayer step in curve B), due to diffraction from ordered Xe. The maximum intensity at locations A and C is reached upon adsorption of the third layer.

5.2.1 Xe Monolayer

The Xe monolayer is either disordered or has quasicrystalline order that produces diffraction intensity only at the same position as the substrate. The fact that the intensity of substrate diffraction spots decreases upon Xe adsorption suggests that the first layer
may be ordered, because a disordered Xe layer would produce a greater degree of diffuse scattering. If the Xe monolayer is commensurate with the substrate, one might expect an increased intensity of the substrate diffraction spots, as it has been observed in quasicrystalline Sb and Bi monolayer adsorbed on the d-Al-Ni-Co surface⁸. However because of the large size and large perpendicular vibrational amplitude of Xe atoms compared to Sb and Bi, the diffraction intensity actually would be weaker upon adsorption of a commensurate Xe layer, as seen in these experiments. In principle a dynamical LEED calculation could be carried out to determine the structure. However the intensities are rather low, limiting the possibility to extract the I(V) spectra needed for the calculation. The use of more sophisticated LEED optics with electron amplification can potentially overcame this limitation.

The isosteric heat of adsorption of the first layer can be determined from the LEED adsorption isobars. The isosteric heat of adsorption is given by: Eq. 5.1

\[ q_{st} = -k_B \frac{d(\ln p)}{d(1/T)} \]

The temperature dependence of the pressure for the different coverages in the isobars is shown in an Arrhenius plot in Figure 5.4. The slopes of the curves give heats of adsorption of 220 ± 10 meV (for the full monolayer), 250 ± 10 meV (for half-monolayer), 275 ± 10 meV (0.25 monolayer) and 290 ± 10 meV (~0.20 monolayer). These values are consistent with the heats of adsorption of Xe on other metals surfaces (Table 5-1) and in particular with AlNi(110), the closest crystalline counterpart for which data are available. A recent calculation⁹ for low-density Xe adsorbed on the d-Al-Ni-Co
determined a value for the heat of adsorption of 305 meV, which is also consistent with the experimental value.

Figure 5.4: Specific points in the isobars corresponding to different coverages are plotted on a $P$-$T$ graph. The heats of adsorption are determined as described in the text. Their values are reported in Table 5-1.

Table 5-1: First layer heats of adsorption on various surfaces\textsuperscript{10}. Where several measurements were reported an average value is given.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Heat of Adsorption (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(110)</td>
<td>180</td>
</tr>
<tr>
<td>Ni(110)</td>
<td>190</td>
</tr>
<tr>
<td>Cu(110)</td>
<td>220</td>
</tr>
<tr>
<td>Ag(111)</td>
<td>225</td>
</tr>
<tr>
<td>Ni(100)</td>
<td>225</td>
</tr>
<tr>
<td>AlNi(110)</td>
<td>240</td>
</tr>
<tr>
<td>Al-Ni-Co (this study)</td>
<td>220 (1.0 ML)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(111)</td>
<td>310</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>360</td>
</tr>
</tbody>
</table>
5.2.2 Structure of multilayer Xe

The rings of 30 spots that develop during the adsorption of the second layer of Xe suggest that it consists of five rotational domains of 6-fold structures or ten domains of a 3-fold structure. The momentum transfer of the inner ring is $1.65\,\text{Å}^{-1}$, which would correspond to a nearest-neighbor distance of $4.4\,\text{Å}$ in a close-packed structure. This is consistent with the nearest neighbor distance found in bulk Xe ($4.38\,\text{Å}$) and also with the monolayer nearest-neighbor distance found on other metal surfaces ($4.22-4.80$)\textsuperscript{11}.

Figure 5.5: a) Model structure of domains of hexagonal structure having five rotational directions. b) Fourier transform of the structure model shown in a). The yellow dots denote one rotational domain in the FT, while the rhombus denotes its reciprocal unit cell. The same FT can be obtained from ten rotational domains of a three-fold structure, which would be expected if the structure comprises more than one layer of Xe(111). c) LEED pattern from the Xe multilayer at 62eV.
Figure 5.5 shows a structural model which consists of hexagonal islands oriented along five different directions, 72° apart. The Fourier transform consists of 30 spots, arising from the five different rotational domains. The diameters of the three rings are typical of an hexagonal structure, having ratios of 1: \( \sqrt{3} : 2 \) relative to the first ring diameter. This is consistent with the LEED pattern from the Xe multilayer, which is shown in Figure 5.5 c).

In the multilayer range, from the LEED pattern itself it is not clear if the multilayer consists of a stack of hexagonal layers on top of one or more disordered or quasicrystalline monolayers, or if all layers are hexagonal. A dynamical LEED analysis is performed to understand the structure of the multilayer. The diffraction intensity spectra of the spots within the three inner rings are extracted over a range 10-300eV. In this range of energies the penetration depth of electrons is about 10Å. The Xe multilayer consists of more than three layers (with interlayer spacing of approximately 4.4Å), so its total height is more than 13Å. Thus the contribution to diffraction from the substrate is negligible. One should not expect any difference in the I(V) spectra for the ten spots which coincide with the substrate ones and the twenty new ones corresponding to the superstructure. Indeed no noticeable difference is visible among the thirty spot. Thus all the thirty spots within one ring are treated as equivalent and their intensity is compared to the calculated LEED intensity. The diffraction intensity I(E) spectra are calculated for a Xe(111) surface, with no contribution from the quasicrystal substrate.

The conventional dynamical LEED calculation is performed using the symmetrized automated tensor LEED program from Barbieri-Van Hove described
previously in Paragraph 2.5.2. The total energy range of the experimental data (3 beams) is 320eV. The calculated and experimental spectra are shown in Figure 5.6.

![Figure 5.6: Comparison of the measured LEED intensity spectra from the multilayer structure and the calculated spectra for Xe(111). The beam indices are for the Xe(111).](image)

The agreement between the experimental spectra from the multilayer and the calculated ones from Xe(111) is good, especially when considering the primary peaks in the spectra. This suggests that the multilayer consists of a fcc(111) stacking of layers, with all layer being hexagonal (i.e. no layer has a quasiperiodic structure). The measured interlayer spacing is 3.61±0.09Å (compared to 3.58Å of bulk Xe).
5.2.2.1 Profile Analysis of the Multilayer

The profile of a diffraction spots in a LEED pattern provides information about the spatial distribution of terraces and domains\textsuperscript{12-14}. In particular radial and tangential profiles across diffraction spots provide a quantitative description of the shape of the beam which leads to information about anisotropic ordering and domain sizes or correlation lengths\textsuperscript{13}. The higher limit for detecting correlation lengths is given by the resolution of the apparatus, which is about 150-200Å for a conventional LEED.

Spot profile analysis is performed on selected beams from the LEED patterns of both the clean d-Al-Ni-Co surface and the Xe multilayer. Both radial and tangential profiles are measured to determine the possibility of anisotropic growth or beam splitting (Figure 5.7 and Figure 5.8).

Figure 5.7: LEED patterns (55eV) of a) the clean d-AlNiCo surface and b) the Xe multilayer. Both radial (dashed lines) and tangential profiles are acquired (Figure 5.8).
To determine the domain size of terraces, the radial profiles of the intensities is fitted with a Lorentzian. Multiple equivalent spots from the same pattern are considered to minimize the possibility of distortion in the pattern itself. The final structural parameters of the fit are averaged and the average terrace size (or correlation length) is obtained.

By comparing the radial profile of the multilayer to its tangential one renormalized to the same scale, the shape of the diffraction beam of the multilayer appear as isotropic, revealing the absence of any anisotropy of the domains, within the limits imposed by the resolution of the apparatus. From the Lorentzian fit on the radial profile (Figure 5.8 a), the domain size for the multilayer (180Å) is comparable to the average terrace size of the clean surface, 175Å (Paragraph 3.4.1). However those values are similar to the maximum correlation length that the apparatus can detect. Both Xe domains and terraces can have larger sizes. Thus the domain sizes measured here correspond to

![Figure 5.8: (a) Radial (without the factor 2π) and (b) tangential line profiles for the (0, 1.65) beam. The black profiles correspond to the clean surface while red profiles correspond to the multilayer.](image)
the lower limit of the real values. Tangential profiles (Figure 5.8 b) reveal that the
diffraction beams for the clean surface and the multilayer have similar widths, with no
sign of beam splitting.

5.2.3 Conclusions

Xe grows on the d-AlNiCo quasicrystal surface in a layer by layer mode for few layers.
The structure of the first layer is either disordered or retains the quasicrystal order of the
substrate. Although the totally disordered monolayer scenario cannot be ruled out, the
reduction in background intensity with no increase in the diffuse elastic scattering
suggests that it is likely that the monolayer to be quasiperiodically arranged. In particular,
the slow initial attenuation in the LEED diffraction intensity of the substrate spots may
suggest that Xe atoms adsorb in highly attractive sites, with quasiperiodic arrangement.
This would be justified by the quite corrugated Xe-substrate Lennard-Jones potential
calculated by Trasca et al. 9, with a gradient of 120 meV between the most attractive and
the least attractive sites. This is in fact supported by a recent Grand Canonical Monte
Carlo simulation 15-17 that uses the same Lennard-Jones potential, according to which the
Xe atoms adsorb on the most attractive sites with five fold symmetry, so that the Xe
monolayer has the same symmetry and spacing as the quasicrystal itself. Although
studies of rare gases adsorbed on metal surfaces showed low coordination sites being
preferred 18, the good agreement between these experiments and the above calculations
suggests high coordination sites. A confirmation may come with a helium atom scattering
experiment: since this technique probes only the topmost surface, it can provides information about the degree of order of the monolayer itself.

As the coverage is increased, this LEED study shows that upon formation of the second layer a hexagonal structure starts to form to reach the state of full bulk Xe(111) upon the formation of at least three layers as indicated in Figure 5.3. The Grand Canonical Monte Carlo simulation mentioned above shows a transition to a hexagonal structure before or near the formation of the second layer and that the location of this transition is temperature/pressure dependent.

5.3 References


Helium atom scattering (HAS) is a well-established surface science technique. A comparison between the main kinematical properties between the LEED and HAS is outlined in Table 6-1.

<table>
<thead>
<tr>
<th></th>
<th>Low energy electrons</th>
<th>He atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energies [eV]</td>
<td>200$^1$</td>
<td>0.02$^1$</td>
</tr>
<tr>
<td>Total gas phase scattering cross section [Å$^2$]</td>
<td>5$^1$</td>
<td>~100$^2$</td>
</tr>
<tr>
<td>Energy resolution [meV]</td>
<td>~1$^3$</td>
<td>0.2$^1$</td>
</tr>
<tr>
<td>Penetration (layers)</td>
<td>~2-3$^1$</td>
<td>0$^1$</td>
</tr>
<tr>
<td>$\hbar \omega_{\text{max}}$ [meV]</td>
<td>~200$^1$</td>
<td>~30$^1$</td>
</tr>
</tbody>
</table>

The most noticeable differences are in the energies of the beams and their cross section. Helium beam energies are three orders of magnitude lower than electron beams. This property is particularly useful to study very low energy excitation at the surface. In addition the low energy does not alter the surface structure of weakly physisorbed systems. Because of their large cross section, He atoms are unable to penetrate the surface and they are reflected at relatively large distance (about 3-4Å) from the surface.
plane. Thus the diffraction conditions for He atoms are kinematic, i.e. no multiple
scattering is involved\(^1\).

A new helium atom scattering apparatus was donated in 2003 to Penn State by
Prof. J.P. Toennies from the Max Plank Institute für Strömungsforschung in Göttingen,
Germany. In this chapter a description of the apparatus and its capabilities will be given.
In addition test results conducted on a graphite sample will be presented. Finally in light
of this test results, an outline of the future HAS experiments on quasicrystal surfaces will
be given.

6.1 HUGO II: Equipment details

A schematic drawing and a photograph of HUGO II (“Helium Untersuchungen
von Geordneten Oberflächen”, Helium Investigation of Ordered Structures) apparatus are
shown in Figure 6.1. The apparatus consists of five main parts: the source chamber where
the He beam is produced, the chopper chamber, the UHV scattering chamber, the time-
of-flight tube and the detector chamber. The various vacuum chambers operate at
different base pressures and at different pumping conditions. Table 6-2 provides an
extensive list of important operating parameters, dimensions and chamber pressures.
Figure 6.1: Top: HUGO II. Bottom: schematic representation of the apparatus\textsuperscript{1}. The pressures $P_i$ are reported in Table 6-2.
Table 6-2: Apparatus parameters for HUGO II

<table>
<thead>
<tr>
<th>Source</th>
<th>Nozzle-orifice diameter</th>
<th>15 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nozzle stagnation pressure</td>
<td>20-300 bar</td>
</tr>
<tr>
<td></td>
<td>Nozzle stagnation temperature</td>
<td>40-400 K</td>
</tr>
<tr>
<td></td>
<td>He-beam velocity</td>
<td>644-2039 m/s</td>
</tr>
<tr>
<td></td>
<td>Relative velocity spread $\Delta v/v$</td>
<td>0.01$^1$</td>
</tr>
<tr>
<td>Skimmer</td>
<td>Entrance diameter</td>
<td>0.6 mm</td>
</tr>
<tr>
<td></td>
<td>Length: entrance to base</td>
<td>37 mm</td>
</tr>
<tr>
<td></td>
<td>Nozzle orifice-to-skimmer distance</td>
<td>10-15 mm</td>
</tr>
<tr>
<td>Chopper</td>
<td>Double-slit disk, slit diameter</td>
<td>200 mm</td>
</tr>
<tr>
<td></td>
<td>Double-slit disk, slit width</td>
<td>0.1-5 mm</td>
</tr>
<tr>
<td></td>
<td>Disk rotational frequency</td>
<td>~300 Hz</td>
</tr>
<tr>
<td>Dimensions</td>
<td>Source-Target distance</td>
<td>582 mm</td>
</tr>
<tr>
<td></td>
<td>Target-Detector distance</td>
<td>1402 mm</td>
</tr>
<tr>
<td></td>
<td>Source-Target-Detector angle</td>
<td>90°</td>
</tr>
<tr>
<td>Pressures [mbar]</td>
<td>Source chamber $P_1$ total pressure</td>
<td>1 x $10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>Base</td>
<td>2 x $10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>Operation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chopper chamber $P_2$ total pressure</td>
<td>1 x $10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>Base</td>
<td>1 x $10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>Operation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Target chamber $P_5$ total pressure</td>
<td>2 x $10^{-10}$</td>
</tr>
<tr>
<td></td>
<td>Base</td>
<td>1 x $10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>Operation (unchopped)</td>
<td>2 x $10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>Operation (chopped)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Detector arm $P_7$ total pressure</td>
<td>2 x $10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>Base</td>
<td>2 x $10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>Operation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Detector chamber $P_9$ total pressure</td>
<td>8 x $10^{-11}$</td>
</tr>
<tr>
<td></td>
<td>Base</td>
<td>5 x $10^{-10}$</td>
</tr>
<tr>
<td></td>
<td>Operation</td>
<td></td>
</tr>
</tbody>
</table>
6.1.1 Source and chopper chambers

A supersonic atomic beam of ultra high purity (99.999%) $^4$He is formed by an adiabatic expansion from a high pressure, temperature controlled reservoir (1-300 bar) through a nozzle into a region of high vacuum ($P_1$ in the diagram in Figure 6.1). The nozzle is adapted from a commercial stainless steel aperture used for electron microscopy (Ladd Research Industries). During the extremely rapid expansion, collisions between He atoms transform the randomly distributed thermal velocities in the source into a motion of uniform velocity directed normal to the orifice. The velocity spread $\Delta v/v$ of the resulting beam is about 1% on average. The He beam energy after the expansion is determined by the temperature of the nozzle $T_{\text{Source}}$:

$$E_i = \frac{\hbar^2 k_i^2}{2M_{\text{He}}} = \frac{1}{2} M_{\text{He}} v_{\text{He}}^2 = \frac{5}{2} k_b T_{\text{Source}}$$  \hspace{1cm} 6.1

where $\hbar k_i$ is the momentum of helium atom, $M_{\text{He}}$ its mass $v_{\text{He}}$ its final mass and $k_b$ the Boltzmann constant\(^4\). The de Broglie wavelength of atoms is given by:

$$\lambda_i = \frac{\hbar}{\sqrt{2mE_i}} \quad \Rightarrow \quad \lambda_i [\text{Å}] = \frac{4.54}{\sqrt{E_i [\text{meV}]}}$$  \hspace{1cm} 6.2

The nozzle temperature can be adjusted from 40 to 400K by cooling the nozzle assembly through a Cu braid connected to a closed cycle He refrigerator and by warming it with a resistive heater mounted in proximity of the nozzle itself. The corresponding values for the beam energy, velocity and associated wavelength and momentum are reported in Table 6-3.
At a short, adjustable distance from the nozzle (10-15 mm), the outer part of the expanding gas is separated from the forward moving atoms by a conical skimmer (Figure 6.2). A 12000 l/s diffusion pump (Leybold DL12000) backed by a 1010 m³/s roots pump (Alcatel RSV-1000) and a rotary vane pump provide the required high vacuum in the source chamber while quickly pumping away the skimmed helium.

<table>
<thead>
<tr>
<th>Table 6-3: Helium beam characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{Source}}$ [K]</td>
</tr>
<tr>
<td>Beam energy [meV]</td>
</tr>
<tr>
<td>Atom velocity [m/s]</td>
</tr>
<tr>
<td>Wavelength [Å]</td>
</tr>
<tr>
<td>Momentum [Å⁻¹]</td>
</tr>
</tbody>
</table>

Figure 6.2: The He beam is formed as it expands from the nozzle (enclosed in the small cylinder at the center of the picture). The beam is skimmed through a conical skimmer.
As the beam enters the chopper chamber through the skimmer, it is collimated with four differentially pumped stages before entering the target chamber. For elastic scattering measurement the chopper is retracted offline. By moving the rotating chopper inline with the beam, the beam can be chopped in short pulses (~10 µs) for inelastic scattering measurements. The mechanical chopper consists on a rotating disc with two triangular slits placed in the outer rim at opposite sides (Figure 6.3); by adjusting the chopper position relative to the beam, the triangular shape of the slits allows the change in the slit width. The chopper bearings are water cooled and their temperatures monitored with a Pt100 resistive thermometer.

Figure 6.3: Chopper motor assembly (left). Schematic of the chopper disc with the two triangular slits and corresponding photocell sensor apertures (right).
The temperature of the nozzle is measured with a K-type thermocouple whose voltage is read with a digital voltmeter (Prema 5000) connected to the acquisition system.

6.1.2 Target chamber

The sample resides in the target chamber with typical base pressure of $2 \times 10^{-10}$ mbar, achieved by a turbo-molecular pump backed by a small diffusion pump and supplemented with a Ti-sublimation pump.

The sample manipulator and holder are mounted on the top flange of the chamber. The sample holder allows full azimuthal, polar and tilts rotation of the sample (Figure 6.4). Two computer operated step motors provide the polar and azimuthal rotation during the experiment, with steps as small as $0.03^\circ$.

Figure 6.4: Sample holder: Polar (P), azimuthal (A) and tilt (T) adjustments are controlled via acquisition software by step motors.
The temperature at the sample can be varied from 40 to 1100 K. The cooling is accomplished by a liquid helium cryostat whose cold finger is connected to the sample through a copper braid. The heating is accomplished by electron bombardment, similarly as in the LEED apparatus (Paragraph 3.1.1). For convenience, the heater filaments are the same for the both the LEED system and the HUGO II. The temperature is measured by two K-type thermocouples. The analog voltage is measured with a high precision digital voltmeter (HP 3440A).

The target chamber is equipped with a rear-view LEED optic (Princeton Research Instruments RVL 8-120), an ion gun (Perkin Elmer) for surface sputtering, a dosing tube for rare gases adsorption experiments and a VG Quadrupole mass spectrometer for residual gas analysis.

**6.1.3 Detector**

As He atoms are scattered off the surfaces they are detected in an in-plane scattering geometry with total scattering angle fixed at 90°. The suppression of He partial pressure in the detector chamber is achieved by using a set of five pumping stages between the target and the detector. Those pumping stages prevent too large a He pressure build up in the target chamber and in the detector, which would otherwise produce a weak molecular He beam into the detector and/or high background intensity.
The detector consists of an electron bombardment ionizer followed by a mass spectrometer to separate off ions from the residual gas Figure 6.5. For the light He ions a simple permanent magnet with radius 11 cm is used for mass selection. A pulse is then created when the He ion arrives at the channeltron (Galileo 4830G). These pulses are converted into a TTL signal by a preamplifier (Ortec VT120) and recorded through a discriminator (LeCroy 821) via a multi-channel scalar (Borer quad scalar). A CAMAC crate collects the signal as well as other parameters such as sample and source temperature and sample position. The data acquisition is performed using two custom made programs for GNU/Linux called “hugo” for data acquisition and “hiostc” for temperature control. A user manual is included in this thesis in Appendix B.

For very reflective surfaces an attenuator allows a beam intensity reduction at the detector, which limits the maximum counts to 600MHz.
6.2 Elastic helium atom scattering

For elastic scattering, in order to calculate the angles where the diffraction peaks occur, the conditions of conservation of energy and conservation of momentum must be satisfied:

\[
\frac{\hbar^2}{2m} k_i^2 = \frac{\hbar^2}{2m} k_f^2 = \frac{\hbar^2}{2m} \left[ K_j^2 + k_{\parallel}^2 \right]
\]

\[\vec{K}_i = \vec{K}_f + \vec{G}\]

\[\vec{k}_i = (\vec{K}_i,k_{iz})\] and \[\vec{k}_f = (\vec{K}_f,k_{\parallel})\] are the incident and final wave vectors respectively. \[\vec{K}_i\] and \[\vec{K}_f\] correspond to the incident and final momentum transfer parallel to the surface. \[\vec{G}\] is a reciprocal lattice vector. The diffraction pattern (which is also called “angular scan”) is obtained by changing the incident angle \[\theta_i\]. Because of the geometrical configuration of the apparatus (the total scattering angle is \[\theta_i + \theta_f = 90^\circ\]), the conservation laws and Bragg condition results in diffraction peaks at angles corresponding to:

\[\Delta K_\parallel = |\vec{K}|(\cos \theta_i - \sin \theta_i) = G\]

Geometrical information about the surface structure can be determined from the position and the width of the diffraction peaks. A diffraction pattern from the clean surface of graphite is shown in Figure 6.6.
The angular scan were measured for a HOPG crystal (ZYA grade), which consists of graphite crystallites randomly oriented in the direction parallel to the planes but all highly oriented in the perpendicular direction. The average angle of deviation of the grains’ orientation from this perpendicular axis is called Mosaic spread. By fitting the specular diffraction peak with a Lorentzian, the half width half maximum (HWHM)

Figure 6.6: Angular scans for the clean (0001) surface of highly oriented pyrolitic graphite (HOPG), acquired at two different incident beam energies. The first order diffraction peaks are located at $\pm 2.18 \, \text{Å}^{-1}$ for the black scan and $2.71 \, \text{Å}^{-1}$ for the red scan. The graphite surface is prepared by e-beam annealing at 800 K for few minutes.
distance is measured. From the angular scans in Figure 6.6, the obtained averaged value for HWHM ($\Delta K_|| = 0.503\,\text{Å}^{-1}$ which correspond to an angle $\Delta \alpha = 0.35^\circ$) is a direct measure of the Mosaic spread. This value is consistent with the nominal spread ($0.4^\circ \pm 0.1$) provided by the manufacturer. For graphite the HWHM is dominated by the mosaic spread; however for metal surfaces the HWHM can provide other information such as terrace size or domain size. The upper limit on domain size measured in this way is dictated by the experimental resolution: this usually about $\Delta K_|| = 0.015\,\text{Å}^{-1}$ (which correspond to a minimum angle of $\Delta \alpha = 0.1^\circ$).

Angular scans are used to calibrate the incident energy of the beam, which is also obtained by measuring the temperature of the nozzle (Eq. 6.1). From the angle $\theta_i$ corresponding to a diffraction peak associated to the lattice vector $\vec{G}$, Eq. 6.4 provides the value of the incident wave vector. The incident energy is given by:

$$E_i = \frac{\hbar^2 |k_i|^2}{2m} = \frac{\hbar^2}{2m} \left[ \frac{G}{(\cos \theta_i - \sin \theta_i)} \right]^2$$ \quad 6.5

The value so obtained is used to calibrate the temperature of the nozzle. The average discrepancy for these experiments was about $6 \pm 3\, \text{K}$: this calibration is used to adjust the beam energies deduced from the nozzle temperature to the correct values.

### 6.2.1 Measurement of the Surface Debye Temperature of Graphite

Thermal attenuation in the diffraction intensity is a general phenomenon for any diffraction technique. In Paragraph 4.4, the surface Debye temperature has been
measured for the clean d-Al-Ni-Co from the Debye Waller factor. Similarly the same analysis was performed with HAS on the clean graphite surface.

In Figure 6.7, the logarithm of the normalized diffraction intensity of the specular beam as function of the HOPG sample temperature is shown. A non-linear behavior characterizes the diffraction intensity as the temperature of the sample is changed. In particular the slope of the curve is increasing as the temperature is lowered. The data are

![Graph](image-url)
split into two separate datasets for low and high temperature acquisitions. Within these
two datasets the diffraction intensity is nearly linear. A linear fit provides a value of the
parameter $A$ as indicated in Eq. 4.4. The Debye temperature is finally obtained using the
equation:

$$
\Theta_D = \sqrt{-\frac{m k_B A}{3\hbar^2 |\Delta k|^2}}
$$

$$
\Theta_D [K] = \sqrt{\frac{12.109 \text{[KÅ]} \cdot A}{|\Delta k|^2}}
$$

A repeated set of experiments performed with the beam having incident energy
(65 meV) while warming or cooling the sample produced no difference in the diffraction
intensity curve. The non-linear behavior is present in all the data in the extended
temperature range 120-900K. The Debye temperatures in the two temperature regimes
are reported in Table 6-4.

<table>
<thead>
<tr>
<th>Table 6-4: Measurement of the surface Debye temperature of HOPG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low $T$: $[120, 400]$ K</td>
</tr>
<tr>
<td>$\Theta_D = 456 \pm 11$ K</td>
</tr>
</tbody>
</table>

A Debye temperature of $690\pm70$K was measured with LEED$^6$ for graphite at low
temperature (from 75 to 300K). This value is not in agreement with the HAS
measurement presented in this work. However the measurement reported here agrees
better with the value of 530K measured with HAS at low temperature by Boato et al.$^7$.
HAS measurements involves only to the Debye temperature of the top-most layer, while
the LEED measurement refers to the vibrations of the first few layers of the surface. This may account for the discrepancy since the vibrational amplitudes of surface atoms are typically larger than those in the bulk$^8$.

6.2.2 Xe adsorption isobars on the surface of Graphite.

The growth mode of an adsorbate on a crystal surface can be characterized by monitoring the intensity of a diffraction peak as the film grows. In the case of rare gases, this is usually done in isobaric regime, by changing the temperature of the sample. Xe adsorption on the d-AlNiCo quasicrystal surface studied by LEED has been described in Paragraph 5.2. In a similar experiment, the growth of Xe on the clean graphite surface was studied using HAS. The adsorption isobars are shown in Figure 6.8.

As the sample temperature is reduced, a sharp step corresponds to the adsorption of the monolayer. As the temperature is further reduced, two more steps are visible, corresponding to the adsorption of the second and third layer. This layer by layer growth is consistent with previous studies$^9,10$. The reduction intensity upon adsorption of the first layer is considerably larger than the same as seen by LEED, by six orders of magnitude. When the monolayer is adsorbed, the contribution to diffraction from the substrates is still present in the LEED, since electrons penetrate the surface. Since helium atoms are sensitive only to the top-most surface, scattering contribution from the substrate is negligible for helium atom diffraction upon adsorption of the monolayer.
Figure 6.8: HAS adsorption isobars for Xe adsorption on the clean HOPG surface. The diffraction intensity of the specular beam is recorded as the sample is cooled. The isobars are corrected for the Debye-Waller attenuation. Xe partial pressure is measured with the ion gauge and the obtained value is multiplied by the sensitivity factor of Xe (0.326). The incident beam energy is 29 meV. The isobars are vertically shifted for clarity.

Figure 6.9: Half monolayer points in the isobars are plotted on a $P-T$ graph. The heat of adsorption is determined from the slope of the linear regression, as described in paragraph 5.2.1.
By plotting the gas pressure in correspondence to the half monolayer in the isobar as function of the sample temperature (Figure 6.9), the isosteric heat of adsorption is obtained using Eq. 5.1, as described in paragraph 5.2.1. The half monolayer isosteric heat of adsorption for Xe on the clean graphite surface is 224 ± 20 meV. This value is consistent with a previous LEED measurement, 239 ± 4 meV\(^{11}\). Small systematic errors in temperature measurement can have a large effect in the calculated heat of adsorption: A deviation of 5K from the real surface temperature determines a difference in the heat of adsorption of about 25 meV (10\%).

6.3 Inelastic helium atom scattering: measuring surface phonons

During inelastic scattering, energy is transferred between He atoms and the surface. One mechanism by which energy is transferred is through creation and annihilation of surface phonons. Surface phonons are localized lattice vibrations which travel parallel to the surface and whose amplitude decay exponentially into the bulk. The total energy of the entire system (consisting of the free He atom and the whole crystal) and the total momentum parallel to the surface must be conserved:

\[
\Delta E = E_f - E_i = \frac{\hbar^2}{2m} k_f^2 - \frac{\hbar^2}{2m} k_i^2 = \hbar \omega (\mathbf{Q})
\]

\[
\Delta \mathbf{K} = \mathbf{K}_f - \mathbf{K}_i = \mathbf{Q} + \mathbf{G}
\]

\[
|\mathbf{K}_f| = k_f \sin \theta_f
\]

\[
|\mathbf{K}_i| = k_i \sin \theta_i
\]
Here $\vec{G}$ is a reciprocal lattice vector, $\hbar \omega(\vec{Q})$ is the energy of the phonon and $\vec{Q}$ is its wave vector projected onto the surface. If $\Delta E < 0$, a phonon is created with energy $\hbar \omega(\vec{Q})$. If $\Delta E > 0$, a phonon is annihilated. By combining the conservation equations (Eq. 6.7) we obtain:

$$\frac{\hbar \omega}{E_i} = \frac{\sin^2 \theta_i}{\sin^2 \theta_f} \left( 1 + \frac{\Delta K}{K_i} \right)^2 - 1 \quad 6.8$$

Eq. 6.8 represents a parabola in the $(\hbar \omega, \Delta K)$ space with origin at $(- E_i, - K_i)$ and with a curvature which depends on the angles $\theta_i$ and $\theta_f$ and the energy $E_i$. This parabola is called “scan curve”. The intersection between a single scan curve and a dispersion curve plotted in the same graph, determines the values of $\hbar \omega$ at which maxima would be expected to appear in an energy loss spectrum measured for the given angles.

In an inelastic diffraction experiment the helium beam is mechanically chopped into packets, and the time of flight (ToF) spectra from the sample to the detector is measured at different incident angles. A He atom with higher time of flight has lost energy while creating a phonon at the surface. A faster He atom has gained energy from an annihilated phonon. Since the flight path distance is known, the energy distribution of the beam can be derived from the time of flight. Thus the time of flight domain can be converted into an energy domain (Figure 6.10).
Both creation and annihilation peaks can be observed depending on the angle of incidence. These ToF scans are plotted together with the scan curve. For each creation/annihilation peak, a line is drawn down to the corresponding scan curve, giving the wave vector associated to the energy of that peak (Figure 6.11).

Figure 6.10: Time-of-flight scan for the clean HOPG surface. The incident beam energy is 22 meV, the angle of incidence is 43° from the direction normal to the surface. The dotted, dashed lines are located in correspondence of two phonons, while the dashed line is in correspondence of the elastic peak. The same spectrum is represented in the inset, in the time-of-flight domain.
Figure 6.11: ToF scans from HOPG at different incident angles. The positions of the creation/annihilation peaks are projected on the scan curves (plot at the bottom) to obtain the phonon dispersion curve. The beam energy is 22 meV.
The graphite Rayleigh mode dispersion curve from these measurements is shown in Figure 6.12. Rayleigh vibrations of atoms at the surface occur in the plane defined by the normal to the surface and the direction of the propagation of the wave.

![Rayleigh dispersion curve](image)

Figure 6.12: Rayleigh dispersion curve for HOPG, synthesized from ToF spectra from the clean HOPG.

The dispersion curve is in good agreement with previous measurements $^{12,13}$. Because the instrumental resolution for ToF is currently about 3%, the inelastic scattering results presented here for the clean surface of graphite must be considered preliminary. Work is currently done to improve the resolution to at least 1%.
6.4 Helium atom scattering from the d-Al-Ni-Co quasicrystal surface: future outlook

The test results obtained from the new helium atom scattering apparatus at Penn State, provide a roadmap for future experiments to perform on the d-Al-Ni-Co quasicrystal surface.

From the LEED characterization study of the surface structure of Xe adsorbed on the d-Al-Ni-Co surface (Paragraph 5.2.1), it was not possible to identify clearly the structure of the monolayer, which can be either disordered or having quasicrystal order. Because of the sensitivity to the top-most layer of the surface, HAS angular scans measured at different stages of adsorption can provide a more accurate description of the structure of the adsorbate compared to LEED. Since diffraction spots are produced by the adsorbate structure only, a comparison between the diffraction pattern of the adsorbate and the one corresponding to the clean surface can indicate whether the growth is epitaxial. This method has been successfully employed to identify the epitaxial growth of Sb and Bi on the d-Al-Ni-Co surface\textsuperscript{14}. The same procedure will be used to determine the order of the Xe monolayer. Similar scans at different coverages will also help determining the evolution of surface order.

Since the spatial resolution of HAS is higher relative to LEED, the size and distribution of terraces in the clean surface and of Xe domains can be measured more precisely from the position, distribution and width of diffraction peaks. The surface corrugation can also be determined from the intensity distribution of the diffraction peaks\textsuperscript{15}. For a highly corrugated surface, He atoms are scattered into diffraction peaks with large momentum transfer, so the higher order diffraction peak intensity dominate
over the specular. This feature is useful to determine any correlation between the transition from quasiperiodic (or disordered) monolayer to a hexagonal structure and the surface corrugation. This can be achieved by monitoring the distribution of intensities for the specular, compared to higher order beams as the coverage is increased. Similarly, since angular scan can be collected during any stage of the surface preparation, the surface corrugation monitored from the distribution of the diffraction intensities during sputtering and annealing will lead to a quantitative estimate of the effectiveness of the annealing to produce a high quality surface.

Low energy surface phonons for the clean d-Al-Ni-Co quasicrystal surface have been already measured by Sharma et al.\textsuperscript{16}. This result will be used as a benchmark to help for further testing of the apparatus with a quasicrystal surface. Inelastic scattering from the Xe monolayer will provide the dispersion curve for this phase. The effects on this dispersion curve will also be investigated as the coverage is increased and the transition to a hexagonal structure occurs.

6.5 References


13 J. D. White, in PhD Thesis (Penn State University, University Park, 1994).


Chapter 7

Conclusions

The work presented in this thesis aimed at the structure determination of the 10-fold d-Al-Ni-Co quasicrystal surface and at the characterization of the adsorption of xenon on this surface. In both cases new experimental approaches have been developed and adopted to overcome the limitations in studying these surfaces due to the lack of periodicity.

By using the complementary techniques of dynamical LEED and STM, the structure of the 10-fold d-Al-Ni-Co surface was established. The dynamical LEED calculation was performed on a slab model with a set of approximations in order to overcome the computational limitations imposed by the lack of translational symmetry and the large number of atoms in the slab. This calculation shows a small amount of vertical relaxation of the quasiperiodic layers, similar to what is found in metal surfaces. The lateral relaxation of atoms within the quasiperiodic layer was analyzed by comparing the structure model to a STM image. The match found shows that the atoms at the locations of atoms at the surface are the same as in the bulk, and there is no significant lateral relaxation. These combined results indicate that the surface is bulk-terminated, with a small degree of vertical relaxation.

The unique and most important feature of this combined LEED-STM study consists on the complete identification of the position and chemical type (Al or TM) of all surface atoms. Unlike in icosahedral surfaces, the structure of a decagonal surface is completely determined because there is effectively only one termination (two
terminations related to each other by a rotational symmetry). By identifying the atomic coordinates in this termination, the complete surface structure is determined. To date, the resulting structure model is the first of its kind. This model can be used for calculations of surface geometric, electronic and dynamical properties. Its application in the study of tribological properties of this surface is of particular interest. It has been predicted theoretically and recently shown experimentally, there is a direct correlation between the quasiperiodic atomic order in quasicrystals and the low coefficient of friction at the surface. By using the model structure presented here, calculation could be done in order to understand the role of aperiodicity in this peculiar tribological behavior.

This model also provides a basis for interpretation of adsorption and growth on this surface. It has already been successfully employed in calculations and simulations in the case of xenon adsorption and other rare gases on this surface. Similarly it could be used for modeling the adsorption of transition metals on the d-Al-Ni-Co substrate (Sb and Bi, Al, Ag, Au). In addition dynamical LEED studies such as the clean surface one presented in this thesis can be extended to study the surface structure of such adsorbates on the 10-fold d-Al-Ni-Co surface. Similarly the 10-fold surface of other decagonal quasicrystals (such as d-Al-Co-Cu, d-Al-Co-Pd, d-Al-Fe-Ni, d-Al-Cu-Ir and d-Zn-Mg-Dy) can be studied.

An alternative way to analyze the LEED data from of the d-Al-Ni-Co was explored in this thesis, by using periodic structure models in which their local geometry is an approximation of local geometries in the quasicrystal surface. The identification of local patterns and geometries in the approximant models which correspond to similar structures in the quasicrystal surface, allows the complete mapping of the quasicrystal
surface in terms of such local structures. A conventional LEED calculation using those approximants models can provide a reliable structure model for the quasicrystal surface. This model is consistent with the model structure found on calculation using the slab model. The advantage in using this method is the simplification of the calculation which would not required approximations. More important, by combining these results with the slab model studied previously, the distribution of local geometries may provide information about their role in the surface potential: Areas with a more attractive potential may correspond to specific local geometries. Modeling could benefit from these results, since calculation can be performed specifically in selected combinations of particular local geometries. New LEED experiments on surfaces of periodic crystals whose structure is an approximant could provide experimental data which could be used to test the validity of the comparison between approximants and quasiperiodic structures. This could be done by performing an approximated dynamical LEED analysis using the slab model on the approximant experimental data.

The layer by layer growth of xenon on the d-Al-Ni-Co quasicrystal surface has been characterized by LEED. This growth is observed for at least few layers and the structure of the film is consistent with the Xe(111) structure. In this study the atomic structure of the monolayer was not resolved. The monolayer could be either disordered or quasiperiodic. Recent calculations suggest that Xe adsorbs in locations at the surface with quasiperiodic order and a transition to a hexagonal structure appear before or near the formation of the second layer and that the location of this transition is temperature/pressure dependent. Although a transition from a disordered or quasiperiodic
to a hexagonal structure is observed in this LEED study, more can be done experimentally to determine the structure of the monolayer. Helium atom scattering experiments are currently ongoing, in order to expand our current knowledge about the xenon adsorption. These experiments will provide a set of adsorption isobars, to be compared to the LEED isobars. The evolution of the surface order will be investigated with angular scans at different coverages. In particular angular scans of the monolayer will finally resolve the issue of the order of the monolayer with respect to the substrate. Inelastic scattering will be performed to measure the surface phonons distribution at different Xe coverages. This will indicate if and how surface dynamics is affected when the Xe layer undergoes a transition from an aperiodic (and possibly quasiperiodic) to a hexagonal structure.

In conclusion, this work provides a deeper understanding of the surface structure of the d-Al-Ni-Co quasicrystal and Xe adsorption. It provides new tools that can be useful to study other quasicrystal surfaces or adsorption systems on quasicrystal surfaces. Theoreticians can benefits from the structure models and the experimental observations of the xenon adsorption. Experimentalists can benefits from novel approaches in using LEED to characterize quasicrystal surfaces.
7.1 References


Appendix A

HotLEED: Data Acquisition and Analysis Program: User Documentation

A.1 Introduction

HotLEED allows the acquisition and the analysis of low-energy electron diffraction (LEED) patterns, both statically and dynamically, as function of incident beam-energy or time. The analysis can be performed both in real time and with stored pictures. HotLEED has been designed using Borland Dephi for Microsoft Windows™.

A.1.1 Acquisition

Three are the possible types of acquisition:

1. **Static acquisition of LEED patterns**: a set of frames can be acquired and averaged to produce a high resolution LEED pattern;

2. **Dynamic acquisition I(V)**: a set of different frames is acquired as function of the incident beam energy (a compatible AD/DA card is required to control the incident energy via HotLEED). This type of acquisition is used to acquire I(V) spectra;

3. **Time acquisition I(t)**: a set of different frames is acquired as function of time; the thermocouple reading is also recorded for each single frame (a compatible AD/DA card is required to control the incident energy and the thermocouple
reading via HotLEED). This is used to acquire isobars for example, or more
generally to monitor the intensity of a specific beam over time.

A.1.2 Analysis

HotLEED provides two main tools for LEED patterns analysis:

1. **Beam Intensity extraction**: The extraction of the intensity of single diffraction
   spots can be extracted from the stored frames or in real time. HotLEED can save
   in an ASCII file the spectra of the intensity for a specific beam, as function of
   incident Energy or time.

2. **Profile Analysis**: A spot profile analysis (for conventional LEED optics only) can
   be performed. Linear, rectangular and circular profiles can be acquired.

Using a set of utilities that are distributed with HotLEED, additional analysis can
be performed. These are the programs:

1. **CurveView**: it is a general curve analysis program. Any ASCII-formatted curve
   can be smoothed, fitted, interpolated, and math operations can be performed.
   Multiple curves can be averaged, and compared using the R-Pendry factor\(^1\).

2. **Normalize**: even though HotLEED is capable to control the incident beam energy
   (if the parameters are properly set, see Preferences menu **A.2.2**), a degree of
   uncertainties is present. “Normalize” renormalizes the energy values to the correct
   ones (this feature is available also in the stand-alone program “**LEEDnorm**”).

---

“Normalize” also corrects the intensity values of the curves to positive values (this feature is available also in the stand-alone program “Xnorm”), to be compatible with Dynamical LEED calculations programs.

3. **IntTemp**: from a set of frames acquired using HotLEED (specifically I(t) acquisition), this program extracts the intensity spectra as a function of temperature. Also renormalizes the time for I(t) acquisitions to the correct value. Acquisition of Intensity vs time (or vs exposure) is possible. Previously known as “Isobars”. (Paragraph A.4.3.1)

4. **ImgConv**: HotLEED saves the frames in a dedicated format (“.img”) where the pictures are saved but also the acquisition information (time, date, temperature, comments). ImgConv allows converting “img” frames into bitmap (BMP).

5. **DifConv**: Program used to convert AES spectra acquired with PHI (Perkin Elmer) from the proprietary format “.dif” into ASCII. This program has to be used only in conjunction with PHI acquisition software, currently running in the VGLEED system.

6. **Langmuir**: quick program to determine the exposure in Langmuir, from the pressure and from the exposure time.

This information is given as a general introduction. For a more detailed description we redirect to the proper chapters.
A.1.3 Suggestions

• Before the acquisition is started, we advise to create a folder where all the pictures will be stored. Then it is good practice to start HotLEED, acquire a test frame, and save it manually in the previously created folder. In this way HotLEED will be prevented from saving the frames into a folder which is different from the one it has been created for the purpose.

• When HotLEED is first opened, it is a good practice to open the preference menu (“Edit” – “Preferences”) and check that all the parameters are set as they are supposed to. Due to unfixed bugs in the program, when it is first started it may not read the configuration file (located in: C:/Windows/HotLEED.ini) correctly.

• For the analysis, it is much quicker to access the frames if they are saved into the hard disk, instead of opening them from the CD. For this reason it is usually preferable to copy the frames from the CD back into the hard disk.

• A lab convention has been established for labeling the folders with the data. The labels usually correspond to the date of acquisition. For example if the acquisition is done October 25, 2004 the folder will be called: “102504”. Inside, the IV frames are usually named alphabetically (i.e. set a: “a1, a2, a3” etc.)
A.2 User Interface

HotLEED uses the Microsoft Windows™ GUI libraries. So the general user commands (opening and saving curves and frames, printing) are similar as in Microsoft Windows™ based programs.

The main HotLEED window is divided in five areas (Figure A.1). The area 1 is where the actual picture acquired in real time (or stored as a frame) is visualized. Below in the area 2 there is a plot chart where the acquired spectra are visualized. A scrolling bar with adjustable values between 0 and 600 eV, is used to set the incident beam energy (area 3). On the right side there is the command panel for the acquisition and analysis (area 5). Above that there is a text panel (area 4) where all the information saved for a specific frame is visualized. In the area 5, the three different tab panels can be selected:

- **Acquire** to go to the Single Frame Acquisition panel (Paragraph A.3.1),
- **Timed Acquire** to go to the I(V) or I(t) panel (Paragraph A.3.2);
- **Profile** tab brings you to the profile analysis control panel (Paragraph A.4.1).
A.2.1 The main menu

Most of the features in HotLEED can be accessed through the main menu (Figure A.2).
The menu is so structured:

- **Image**: to open, preview, save, copy and print the LEED frames.

- **Curve**: to open, save, close, cut, copy, paste and print the curves displayed in the plot area (area 2 in Figure A.1). Also available there are the **Cursor Control**, the **Zoom control**, the **R-factor** evaluation tool, and the **Curve Average control** panel. For more information about curve handling with HotLEED, Paragraph A.4.2.

- **Edit**: to access the Preference panel (Paragraph A.2.2) to input the comments which are going to be saved into the frames (**Default frame info** Figure A.3). The **Shape coordinates** and the **Enable Energy input** options are not implemented.

- **View**: the **Single Frame** or **Dual Frame** option allows deciding the screen size with respect to the plot area (Figure A.4 and Figure A.5). The **View** menu let the user enable the **Live Video** mode. When this mode is not enabled the **real-time** mode is not available both for acquisition and analysis. In the **View** menu, it is possible to **Zoom** a curve, by clicking and dragging.
• **Frame Acquire**: It is possible to set the **Acquisition window** (Paragraph A.3.1), and to enable the **Auto-Save** mode during single frame acquisition. The **Auto-Save Option** opens the panel shown in Figure A.12. The **Go!** command starts the acquisition.

![Figure A.4: Single Frame](image)

![Figure A.5: Dual Frame](image)
• **Timed Acquire:** Control the I(V) or I(t) Acquisition and Analysis. *The Open* (Save) Spot File command opens (saves) a spot file (extension .iv) with the position and the number of integration windows used for the analysis. By default when HotLEED is closed after the analysis is performed the file CurrentSpots.iv is saved in the same directory where the images are stored. The following commands have the same functions as the buttons in the I(V) acquisition panel respectively (more details in Paragraph A.3.2.1): **Options** ( ), **Set Anchor** ( ), **Set Origin** ( ), **Go!** ( ) and **Stop** ( ). The Start Sample Alignment option is not yet implemented.

• **Profile:** The following commands have the same functions as the buttons in the Profile acquisition panel respectively (Paragraph A.2.2): **Line** ( ), **Ellipse** ( ), **Box** ( ), **Go!** ( ).

• **Help:** Contents is supposed to have a help guide, which is not yet implemented (the user should refer to this document as the official guide). The About box gives information about the actual HotLEED version and the author.
A.2.2 HotLEED preference panel

HotLEED requires the preferences to be set before starting the acquisition. The preferences menu can be accessed from the menu bar Edit and Preferences. The opening window presents three different tabs:

1. **Display**: In this panel (Figure A.6), it is possible to set the preferences for the visualization screen, to control the video camera (Scale – Offset). The values indicated have been tested, and proved to be reliable. A number of different available frame buffers can be set (frame buffer count). HotLEED offers the possibility to use up to 10 buffers to store acquired pictures, without saving them. Each single Frame buffer can be accessed by the set of buttons in the main window (Figure A.7).

![Figure A.6: Preferences: Display](image)
2. **Frame Grabber**: in this panel (Figure A.8), it is possible to set the B/W parameters for the Frame Grabber (**Black level, White level, Sync Sentinel**). The values indicated have been tested and proved to be reliable.

![Frame Grabber](image)

Figure A.7: Frame buffer buttons

![Preferences: Frame Grabber](image)

Figure A.8: Preferences: Frame Grabber

3. **Hardware Configuration**: In this panel (and) it is possible to specify the hardware to use for acquisition, specifically the AD/DA card and the frame grabber card to be used. The values indicated in the two panels (for VGLEED - Figure A.9 - and for CPLEED - Figure A.10) have been tested, and proved to be reliable.
It is important to set the correct values for the LEED Energy (Scale and Offset). A wrong set of parameters for the “Scale” and “Offset” will determine a value of the real incident LEED energy different from the one recorded with HotLEED. Please refer to Chapter A.6.2 for the settings specific to each system (VGLEED or CPLEED). If those settings are used, a program called “Normalize”
is available to renormalize the energy scale saved with HotLEED to the real energy output from the LEED optics.

4. **It is also extremely important for temperature sensitive acquisitions to check the box for the “Channel 0” in the A/D Acquisition box.** If this is not set or another channel is set, the temperature measurement may not be recorded.

HotLEED saves all the important **configuration parameters** into a configuration file called **HotLEED.ini** in the main directory of Windows (usually: C:/Windows/HotLEED.ini). In particular in this file all the parameters used to control the frame acquisition as well as the analysis are saved. Since the program can be used with different LEED systems, we recommend creating and saving an individual configuration file for each system. We provide two files with this distribution:

- HotLEED VG.ini
- HotLEED CP.ini

Those files can be used immediately on demand:

1. Back up the old **HotLEED.ini** file, for example renaming it **HotLEED.bak**
2. Copy the file of interest in the main Windows directory
3. Rename the new file as HotLEED.ini
4. Start HotLEED

Check in the preference panel that the settings are correct (Figure A.9 and Figure A.10).
A.3 Acquisition

A.3.1 Single Frame Acquisition: Acquire Panel

The control panel for single frame acquisition is shown in Figure A.11.

![Single Frame Acquisition control panel](image)

Figure A.11: Single Frame Acquisition control panel

Buttons and commands:

1. **Live** button: Pushing this after the acquisition (any acquisition, Single Frame, I(V), I(T)), let you return in **real-time or live mode**. While pushing this button when the screen is already in real-time mode, HotLEED acquires a 1-frame shot (useful for calibrations) and a set of information (date, time, comments, experimental details, thermocouple reading) are displayed in the text field of area 4 (Figure A.1). It may sound stupid, but if after an acquisition nothing is changing...
while you are adjusting some experimental parameters, press this button: You may be looking at the recorded picture and not to the real-time pattern.

2. **Acquire** button: This is the main button for the **single frame acquisition**. With this command a number of frames (as many as specified in the average box) are collected and averaged to produce a picture that is then shown and a set of information (date, time, comments, experimental details, thermocouple reading) are displayed in the text field of area 4 (Figure A.1). This is an example of the experimental information displayed and saved in the frame:

File name:         a1.img
Header length:          562
Image:
Data type:         image
Beam Voltage (eV): 5
Date:              6/17/2004 12:05:08 PM
Number of frames: 5
Comment:
Frame scale max:   1279
Frame scale min: 0
x1:                0
y1:                0
x2:                639
y2:                479
Granularity:       1
Bits per pixel:    16
F-Stop:            0
Black level:       53.855
White level:       714.88
Data offset:       562
Data length:       614400
Analog input 0     0.2197265625 (thermocouple reading)

3. **Average**: number of frames acquired and averaged for each acquisition into a single frame (max 255, suggested values: 10-15-20).
4. **Granularity:** For a value of n, HotLEED saves every \( n^{th} \) pixels of every \( n^{th} \) row. Unless HotLEED is running on an old platform, the value \( n=1 \) is suggested, all pixels acquired are saved.

5. **Auto normalize:** If checked, HotLEED renormalizes the intensity of the pattern so that the maximum intensity pixel in the frame corresponds to the maximum intensity available for the pixel.

6. **Windowed acquire:** If checked, the acquisition will be performed only in the active area of the screen, which can be selected by pushing the `set window` button and by drawing the area of interest on the screen (right click on the mouse).

7. **Auto Save:** If **Enable Auto Save** is checked, HotLEED will save the acquired frame in the folder specified by clicking on the **options** button. This button will open an auto-saving panel (Figure A.12). The name of the frame will be the one specified in the field provided, plus an index number (i.e., profile1.img). To save manually the pictures, click to the menu **Image -> Save** or **save as**.

![Auto-saving options](image)

Figure A.12: Auto-saving option panel
A.3.2 I(V) and I(t) acquisition: *Timed Acquire* panel

Two possible dynamic acquisitions can be selected by using the radio button in the **Aq Type** box are (as indicated in Figure A.13): **Intensity vs Beam Incident Energy I(V)** and **Intensity vs Time I(t)**. The latter one is also used for Intensity vs sample Temperature, by converting the time domain into the temperature as measured in the thermocouple and saved in the image file. This is done using the program **IntTemp**.

![Figure A.13: Timed Acquisition type radio button](image-url)
A.3.2.1 I(V) Acquisition

To enable I(V) acquisition, select the I(V) radio button in the Aq type box (Figure A.13). The set of commands is the following:

- ![Go!]: With this button the acquisition is started.
- ![Stop]: To stop the acquisition in progress.
- ![Options]: To enter the option menu for the Acquisition Options

The standard procedure for IV acquisition can be summarized as follow:

1. Prepare the LEED experimental setup, sample preparation, and temperature stabilization.

2. Using the slider in area 3 of Figure A.1, change the incident LEED energy to check for the correct values of brightness and contrast in the screen. Sometimes the diffraction pattern from the LEED optics appears to be different in terms of brightness and contrast from the one displayed in HotLEED.

3. Select the energy range where the I(V) needs to be extracted. To do this use the provided fields Energy Control box (Figure A.14). In this case the initial energy is 1eV and the final is 600 eV, and the energy step from a frame to the next is 1eV.
4. By pushing \textcolor{red}{E1}, HotLEED will display the LEED pattern in real time mode corresponding to the initial energy selected. In the same way, pushing \textcolor{red}{E2} will display the final energy selected.

5. By using the two buttons \textcolor{red}{E}, it is possible to browse the patterns by increasing or decreasing the incident beam energy.

6. After the energy range has been selected, push \textcolor{red}{E1} to move to the initial energy pattern. Press \textcolor{red}{125} to set that as the “Anchor energy”, which is the energy HotLEED sees as the starting point.

7. Enter the Acquisition Options by clicking on \textcolor{red}{Options}. The \textbf{Acquisition option panel} (also called \textbf{IV Acquisition Setting}) is shown in Figure A.15.
8. For the Acquisition only the **Frame Acquire** tab needs to be checked.

9. Select the label which will be assigned to the set of acquired frames. The sequence will be labeled “name + (frame number of the sequence).img”. For example if the chosen name is “IVframe”, the frames are “IVframe1.img”, “IVframe2.img” and so on.

10. **Auto normalize**: If enabled, HotLEED renormalizes the intensity of the pattern so that the maximum intensity pixel in the frame corresponds to the maximum intensity available for the pixel.

11. **Frame to average**: number of frames acquired at the same energy and averaged for each acquisition into a single frame (max 255, suggested values: 10-15-20).

12. **Granularity**: For a value of n, HotLEED saves every n\(^{th}\) pixels of every n\(^{th}\) row. Unless HotLEED is running on a old platform, the value n=1 is suggested, all pixels acquired are saved.

13. **Save file as**: It allows deciding which format the frames are going to be saved as (8 or 16 bit). The suggested value is 16 bit. However if the PC has a hard disk of
limited capacity (>5MB) 8bit is preferred. In 16 bit configuration a full window frame is about 600kB.

14. **Window Acquisition:** It allows to decide whether the acquisition has to be done in the full frame (in the full area of the screen), or within an acquisition window.

To set the size of the acquisition window, enable the **Window Acquisition** checkbox and press the **Acquire** button in the single frame acquisition panel (Paragraph A.3.1).

**A.3.2.2 I(t) Acquisition**

To enable I(t) acquisition, select the I(t) radio button in the **Aq Type** box (Figure A.13). The set of commands is the following:

- **Go!** : With this button the acquisition is started.
- **Stop** : To stop the acquisition in progress.
- **Options** : To enter the option menu for the Acquisition Options

The standard procedure for I(t) acquisition can be summarized as follow:

1. Prepare the LEED experimental setup, sample preparation, and temperature stabilization.

2. Set the number of time steps in the Energy Control box for the I(V) acquisition Figure A.14 (maximum is 597). A bug in the program prevents the time steps to be controlled from the I(t) panel. As the acquisition is in progress, the energy bar
(area 3 in Figure A.1) indicates the current status of the acquisition (from 1 to 597).

3. Enter the Acquisition Options by clicking on [Options].

4. The Acquisition option panel (also called IV Acquisition Setting) is shown in Figure A.15.

5. For the Acquisition only the Acquire tab need to be checked.

6. Select the label which will be assigned to the set of acquired frames. The sequence will be labeled “name + (frame number of the sequence).img”. For example if the chosen name is “IVframe”, the frames are “IVframe1.img”, “IVframe2.img” and so on.

7. **Auto normalize**: If enabled, HotLEED renormalizes the intensity of the pattern so that the maximum intensity pixel in the frame corresponds to the maximum intensity available for the pixel.

8. **Frame to average**: number of frames acquired at the same energy and averaged for each acquisition into a single frame (max 255, suggested values: 10-15-20).

9. **Granularity**: For a value of n, HotLEED saves every $n^\text{th}$ pixels of every $n^\text{th}$ row. Unless HotLEED is running on an old platform, the value n=1 is suggested, all pixels acquired are saved.

10. **Save file as**: It allows deciding which format the frames are going to be saved as (8 or 16 bit). The suggested value is 16 bit. However if the PC has a hard disk of limited capacity (>5MB) 8bit is preferred. In 16 bit configuration a full window frame is about 600kB.
11. **Window Acquisition**: It allows to decide whether the acquisition has to be done in the full frame (in the full area of the screen), or within an acquisition window. To set the size of the acquisition window use the **Window Acquisition** checkbox and press the **Acquire** button in the single frame acquisition panel (Paragraph A.3.1).

12. **Delay Time (ms)** (accessible from the **General Settings** tab of the IV Acquisition Settings option panel, step 17 pag. 177): **Time delay** between the acquisition of a frame and the next one (suggested 3ms).

While the acquisition is in progress the slider bar (in area 3 of Figure A.1) is not indicating the energy (which is supposed to be constant in I(t) acquisition), but the progress in time.

Because of the limitation in the maximum number of frames (597), the total acquisition time cannot be directly adjusted. To overcome this limitation, it is usually convenient to set the number of averaged frames (Figure A.15) to a specific value. The higher the number of averaged frames, the longer is the total acquisition. A calibration of the total time of acquisition vs number of averaged frames is presented in Figure A.16.
Figure A.16: Total acquisition time calibration as function of the number of averaged frames.

\[ \text{Time} = 38.5 + 20.46 \times \text{Frames} \]
A.4 Data Analysis

A.4.1 Profile analysis

The profile analysis can be performed in both real-time, or onto stored or acquired pictures. If this is the case, acquire a picture first, or open a stored one. To perform real-time analysis, open the Profiles tab (shown in Figure A.17)

![Profile Control Panel](image)

Figure A.17: Profiles Control Panel

Two are the types of profiles which can be extracted:

1. **Intensity profiles**: the intensity is mapped as function of the position in the screen along a Line, Ellipse or a box (each can be selected from the profile Type box);
2. **Histograms**: The intensity is mapped in log scale as function of the number of pixels counts along a Line, an Ellipse or a box (each can be selected from the “profile type” box).

3. The width (in pixels) of the profile can be specified in the **width** box. To draw the profile line, ellipse or box, use the right click of the mouse over the area of interest.

4. Once the profile type is drawn, the profile curve is shown in the plot area (area 2 in Figure A.1). By pointing the mouse on the profile type and dragging it, it is possible to use the same profile type in different area of the frame, without redrawing it. The plot curve will be automatically redrawn, if the **Update curve while dragging** checkbox is enabled.

5. Once the desired profile curve is obtained, press ![profile](image) to read the curve from the buffer and have it displayed into the plot area, ready to be exported, modified, saved or compared to others, using the menu **Curve** (Chapter A.2.2).

6. **Auto Save**: If **Enable Auto Save** is checked, HotLEED will save the acquired profile curve in the folder specified by clicking on the **options** button. This button will open an auto save panel (Figure A.12). The name of the curve will be the one specified in the field provided, plus an incremental number (i.e. profile1.dat). The curve is saved as ASCII.
A.4.2 I(V) Analysis

The I(V) analysis control panel is essentially the same as the I(V) Timed acquire control panel (Figure A.13). The I(V) analysis can be performed with three different modes of operation, as indicated in Figure A.18:

1. **Frames**: This is the I(V) Timed acquired mode, which is used to acquire IV frames (see Paragraph A.3.2). No analysis can be performed in this mode.

2. **Curves**: In this mode I(V) analysis can be performed for real-time images.

3. **Files**: In this mode I(V) analysis can be performed for stored frames.

In order to acquire LEED I(V) curves from either a saved or a real time pattern, one of the two (Curves or Files) modes need to be selected BEFORE the analysis is started. The procedure to acquire I(V) spectra is basically the same for the two modes:

1. Select the desired mode of operation (Curves or Files) using the Mode box shown in Figure A.19.
2. As shown in Figure A.19, the control panel changes slightly, with the introduction of a **spot list**, and with a number of integration windows (windows where to collect the intensity) in the main screen (area 1 in Figure A.1).

3. If the **Files** mode is selected (analysis of stored pictures), open the menu **Image – Open** and select the first of the frames of the I(V) frame sequence. Usually if the sequence is “**IVframe1.img IVframe2.img ...**”, open the first of the frames. If the **Curve mode** is selected (for Real-Time analysis), you can skip this step;

**NOTICE:** To open a stored frame there are two possible ways: One is described in the step 3 above. In alternative it is possible to use the menu **Image – Open Preview**.
In this case the panel shown in Figure A.20 will appear, giving the possibility to browse the stored pictures while actually seeing a preview of both the frame and the associated experimental information.

Figure A.20: Stored frames browser

4. Based on the symmetry of the specimen (3-4-5-6-8-10 fold), a number of integration windows need to be chosen. To do this, press the small + button in the beam list (Figure A.21) to add as many integration windows as needed. The number of integration windows and the coordinates are saved when HotLEED is closed into a file called CurrentSpots.iv in the same directory where all the frames are saved; alternatively it can be saved manually using the command in the main menu Time Acquire – Save Spot File (Paragraph A.2.2). In order to recall a previous set of integration windows, use the main menu Time Acquire – Open Spot File to load a .iv file used in other I(V) extractions. REMEMBER to push the + button after you open the iv file.
5. If a new “spot” is added to the list, a new integration window will appear in the main acquisition screen in the position indicated (in pixel) in the first column of the beam list. Also a set of indexes can be assigned to the integration window, according to the beam indexes.

6. The position of the beams can be modified both by changing the screen coordinates (screen column) in the beam list or by dragging the integration window in the desired position. The typical arrangement of beams is presented in Figure A.22.

Figure A.21: Diffraction beam manager panel

Figure A.22: HotLEED screenshot: I(V) Analysis of stored patterns
7. Once the integration windows are positioned in correspondence to the desired beams in the first frame of the sequence, it is extremely important to push the button [+] . This will fix the center where all the integration windows will converge to, when the energy of the incident beam is increased and the diameter of the Ewald sphere will increase\(^2\). This step is extremely important to guide the integration windows in a way that they can follow the beams as the energy changes.

8. Then push the button \(\overset{\text{125}}{\text{\textbullet}}\). This will tell HotLEED that the visualized frame is the initial one, the starting point for the I(V) extraction.

9. Push the button [E2] to display the last of the recorded frames of the sequence, corresponding to the final incident energy.

10. Repeat steps 6 and 7 to have the integration window to match the spots in their final position.

11. At this stage everything is ready for the IV extraction. It may be useful to browse the frames using the buttons [E]. If the position of the integration windows needs to be modified, this can be done at intermediate energy steps. If so, remember always to press [+] after this.

12. Push the button to go to the first frame.

13. Open the Options panel with the button . The IV Acquisition Settings menu panel will open in the Curve Acquire section (Figure A.23).

![IV Acquisition Settings](image)

**Figure A.23:** I(V) Acquisition and Analysis Settings: Curve Acquire tab

14. After a set I(V) or I(t) are extracted from a set of images, when another set of images need to be processed it is strongly advised to close HotLEED and restart it. Due to a bug in the program, when a new set of images is opened, the old one is actually processed, not the new one. The button , when pressed, reopens the first set of images.

15. This Option panel is designed to set all possible combination of parameters for the I(V) extraction. These are the function of all the parameters in the Curve Acquire tab:

- Background subtraction: if enabled, the integrated intensity measured along the perimeter of the integration window will be subtracted to the
integrated intensity measured inside the integration window. For this purpose the integration window should be big enough to include the diffraction spot, but not too big to include too much of the background intensity.

- **Peak extrapolation:** It allows HotLEED to apply the compensation for saturated pixels at the center of the spot.

- **Average Count:** (suggested value: 1)

- **Size:** Specify the size in pixel of the integration windows. This can be kept fixed or it can be made function of the incident energy (if the Ref Energy Size checkbox is enabled as shown in Figure A.23). In this case the size specified is referred to the energy specified in the Ref. Energy (eV) field.

- The **Coordinate System** can be assigned as Cartesian or hexagonal, according with the nature of the specimen. This helps HotLEED determining the evolution of the LEED pattern, as function of incident energy

- The integration window can be rectangular or circular (suggested: circular).

16. Further Settings are available in the **General Settings** tab, accessible from the same **IV Acquisition Settings** panel (Figure A.24 and Figure A.25).
17. In this panel it is possible to set the type of LEED optics in use during the experiment. Specifically for conventional optics (like the VGLEED), where all the grids are hemispherical, in the LEED Screen Type box, the Curved screen option needs to be selected. In case the experiment is performed using a LEED optics with flat grids or a flat screen or a flat channeltron (as in the case of CPLEED), the Flat screen option needs to be selected. For the flat screen, a correction to the intensity of the outer beams needs to be included, having
these beams a lower intensity due to the flat nature of the screen itself. For this correction, the screen-sample position (measured in mm, not in pixels as stated in the panel) is required and a field is provided. For the Curve Screen, this distance is not required. However for the Curved Screen, we would recommend to position the sample at the center of curvature of the screen.

18. The Aspect Ratio (suggested value 1) is also adjustable. It may be important to set also the Time Delay (ms), which is the delay time between the acquisitions of one frame from the next one.

At this point the I(V) extraction can begin, by pushing . Depending on how many integration windows are in use, there will be as many I(V) curves depicted in the plot area Figure A.26.

Figure A.26: I(V) curves after the extraction from the LEED patterns
19. These curves can be exported singularly using the right click on the mouse and select save from the menu in Figure A.27:

![Figure A.27: I(V) curves handling menu](image)

20. **Only the active curve** (indicated in the list panel) is saved. To save all the extracted curves, each single one needs to be selected first from the list, or by clicking over the curve of interest. Alternatively the curves can be saved all at the same time by using in the main menu **Curve – Save All**, as indicated in Figure A.28. Curves can be also copied and pasted to external programs. Alternatively, it is good practice for equivalent beams, to use the “average curves” option (see below Figure A.30) to average the I(V) spectra from equivalent beams. This produces the averaged curve that then can be easily exported.

21. It is possible to perform some **simple manipulations** to the curves, using the same menu (accessible with the right click of the mouse over the plot) shown in Figure A.27. These are accessible also by using the main **Curve** menu, as indicated in Figure A.28.
These are the possible operations:

- **Cursor**: it enables a cursor in the active curve, to measure point by point the point values of the curve;
- **Zoom**: it allows to zoom in and out the plot to enhance some part of the curve;
- **R-Factor**: It allows to calculate the Pendry R-factor for two curves displayed.

It is quite useful to verify the alignment of the sample at normal incident, since in these conditions the agreement for all the different beams (only if equivalent beams) should be the same (The Pendry R-factor should be the same). A 3-point smooth is also available to reduce the noise while evaluating the R-factor (Figure A.29).
• **Average:** It allows to average a set of I(V) curves associated to a set of equivalent beams (Figure A.30). The averaged curve will be displayed in the plot area, along with the original curves.

Acquire profile: not in use.
A.4.2.1 Normalizing the energy scale for I(V) analysis

Even though HotLEED is capable to control the incident beam energy (if the parameters are properly set, see preferences panel A.2.2), a degree of uncertainties is present. “Normalize” renormalizes the energy values to the correct ones. “Normalize” also corrects the intensities in the curves to positive values, to be compatible with Dynamical LEED calculations programs. Finally it allows the renormalization of the energy steps in the curve (Figure A.31).

![Screenshot of “Normalize”]

The energy calibrations for both VGLEED and CPLEED have been acquired by measuring the output voltage to the LEED Optics vs the HotLEED displayed voltage. Both calibrations can be changed at any time, if new ones become available.
A.4.3 I(t) analysis

In order to extract I(t) curves, the I(t) option needs to be selected in the Aq Type box (Figure A.1, Figure A.18 and Figure A.32). Also one of the two (Curves or Files) modes needs to be selected before the analysis is started. The procedure to acquire I(t) spectra is basically the same for the two modes:

1. Select the desired mode of operation (Curves or Files) using the Mode box shown in Figure A.18.
2. As shown in Figure A.32, the control panel changes slightly, with the introduction of a **spot list**, and with some integration windows in the main screen (area 1 in Figure A.1).

3. If the Files mode is selected (analysis of stored pictures), open the menu **Image – Open** and select the first of the frames of the I(t) frame sequence. Usually if the sequence is **IVframe1.img IVframe2.img**, open the first of the frames. If the **Curve** mode is selected (for Real-Time analysis), you can skip this step;

4. Based on how many spots are considered for the I(t) extraction, a number of integration windows need to be chosen. To do this, press the small + button in the beam list to add as many integration windows (windows where to collect the intensity) as needed. The number of integration windows and the coordinates are saved when HotLEED is closed into a file called **CurrentSpots.iv** in the same directory where all the frames are saved; alternatively it can be saved manually using the command in the main menu **Time Acquire – Save Spot File** (Paragraph A.2.2). In order to recall a previous set of integration windows, use the main menu **Time Acquire – Open Spot File** to load a .iv file used in other I(t) extractions. **Remember** to push the **+** button after you open the iv file (Figure A.21).

5. The position of the beams can be modified both by changing the screen coordinates in the beam list or by dragging the integration window in the
desired position. The typical arrangement of beams is presented in Figure A.33.

![HotLEED screenshot: I(t) Analysis of stored patterns](image)

Figure A.33: HotLEED screenshot: I(t) Analysis of stored patterns

Since in I(t) acquisition, the electron incident energy is kept fixed, the position of the beams will not change. For this reason the Energy Control Panel, available for the I(V) acquisition (Figure A.14), is disabled for I(t).

6. The options parameters need to be adjusted as well. Being the parameters for the I(t) extraction identical to the one for the I(V) acquisition, we redirect the reader to the step 13 and subsequent in Paragraph A.4.2. The curve manipulation features available in HotLEED are also similar.
7. The actual I(t) spectra as they are extracted by HotLEED, they are not saved as a function of time, but as a function of the frame number. This means that the I(t) spectra is actually a Intensity vs frame number spectra. As it is, the spectrum is pretty useless. To overcome this issue, another program is available in this distribution, called **IntTemp (Ch. Error! Reference source not found.)**.

8. When the extraction is completed, select the **Acq Type** (as shown in Figure A.13) as I(V). Then press to return to the first stored frame of the sequence. Select again the **Ac Type** as I(t) to return to the I(t) analysis section. Because of an unsolved bug you may need to set again the size of the integration windows by opening the I(V) **Acquisition Settings** panel (and selecting the **Curve Acquire** tab (Figure A.24 and A.25).

9. After a set I(V) or I(t) are extracted from a set of images, when another set of images need to be processed it is strongly advised to close HotLEED and restart it. Due to a bug in the program, when a new set of images is opened, the old one is actually processed, not the new one. The button, when pressed, reopens the first set of images.
A.4.3.1 IntTemp: Intensity vs Temperature (or time)

IntTemp allows the user to use the I(t) spectra extracted using HotLEED to produce:

- **Intensity vs time** (in sec) spectra;
- **Intensity vs Exposure** (in langmuir) spectra;
- **Intensity vs Temperature** (in C or K) spectra, also called isobars (the fixed pressure is required in these measurements).

The main option menu of **IntTemp** is shown in Figure A.34.

![IntTemp main menu screen](image)

Figure A.34: IntTemp main menu screen
These are the possible options Isobars has available:

- **COLLECT temperature reading**: It collects the thermocouple readings for each single frame, and it saves it into an ASCII file.

- **Save Int(Temp) (K or C)**: Using the I(t) spectra extracted with HotLEED and the Thermocouple reading collected in step 1, IntTemp converts the TC reading into temperature (using the calibration in Figure A.35 and Figure A.36) and saves the Intensity vs temperature curve.

- **Extract Temperature only**: The Thermocouple reading is converted into temperature and then it is saved in an ASCII file. This option may be useful for noise checking in the temperature reading.

- **Quick temperature conversion**: With the input of the thermocouple reading, it displays the corresponding temperature, using the calibration in Figure A.35 and Figure A.36.

- **Save Int(Temp) (TC reading)**: Similar to step 2 but without the temperature conversion. The output is a Intensity vs Thermocouple reading (V) curve.

- **Acquisition Intensity vs Time/Exposure**: Using the time calibration in Figure A.35 and Figure A.36, this option allows to save Intensity vs time (in sec) spectra, or Intensity vs Exposure (Langmuir).

Very important: Remember to save the executable IntTemp.exe inside the folder where all the images are saved.
The time and temperature calibration parameters can be changed (using option 7) if newer calibrations are available. The current ones are presented in Figure A.16, Figure A.35 and Figure A.36.

Figure A.35: Thermocouple reading conversions for VGLEED, at low and high temperature.
A.5 Known bugs and limitations

HotLEED has been developed throughout the years, but it still presents some bugs. The following is a list of the yet unsolved bugs or/and not implemented commands:

- When HotLEED is first open, the AD/DA card is not immediately recognized. HotLEED is not reading properly the HotLEED.ini files. So it is necessary, every time HotLEED is started, to open the preferences panel (Figure A.9 and Figure A.10), and manually select the AD/DA card.

![TC calibration for CPLEED - 04/23/04](image-url)  
*Figure A.36: Thermocouple reading conversions for CPLEED*
• The **Shape coordinates** and the **Enable energy input** options in the **edit** menu (Figure A.2) are not implemented.

• The **Start Sample Alignment** option in the **Timed Acquire** menu (Figure A.2) is not yet implemented.

• After the extraction of I(t) spectra, it is possible to go back to the initial frame of the sequence by selecting the **Aq Type** as **I(V)** and by pressing ![I(t) button](image). When the **Aq Type** is selected again as **I(t)**, the size of the integration windows changes and it needs to be set again by opening the **I(V) Acquisition Settings** panel and selecting the **Curve Acquire** tab (Figure A.24 and Figure A.25).

• HotLEED freezes temporarily for 10 seconds when the **Files** mode is selected (Figure A.18).

• After the an I(V) or I(t) analysis is performed and a number of integration windows is selected, if this number is higher than 4, HotLEED does not save this beams in the Spot files correctly.

• After a set of integration windows are selected and I(V) or I(t) analysis are performed, if the position of the windows are changed with the mouse, the displayed position in the beam list (Figure A.21) has unrealistic values (negative usually).

• In the profile analysis once the profile types are drawn, they can not be dragged in different positions, so they need to be redrawn every time.
After a set $I(V)$ or $I(t)$ are extracted from a set of images, when another set of images need to be processed it is strongly advised to close HotLEED and restart it. Due to a bug in the program, when a new set of images is opened, the old one is actually processed, not the new one. The button $E_1$, when pressed, reopens the first set of images.

This list is still open.

A.6 System requirements

A.6.1 Full Installation (Acquisition + Analysis)

This is the minimum configuration required:

- PC – IBM compatible running Microsoft Windows™ 95/98/ME/NT/2000/XP
- Pentium 3/4 or AMD Athlon
- 256 MB RAM
- A full frame requires about 600kB. A total $I(V)$ acquisition requires about 597 frames. For multiple acquisitions we advise an hard disk of at least 10GB
- For the same reason a CD-RW or DVD-RW is advised.
• Frame grubber: DT-3155. Other frame grabbers (Data translation only) can be used, but HotLEED has been tested only with the DT-3155

• AD/DA card: Data Translation DT21-EZ (ISA BUS) + STP-EZ I/O connector if using Microsoft Windows™ 95/98/ME. Data Translation DT9802 (USB) or DT302 (PCI BUS) if using Microsoft Windows™ 2000/XP.

• Data Translation “DataAcq SDK” and “FG SDK” development kits need to be installed.

• A thermocouple amplifier may be useful (the TC reading is in mV). A schematic of the one used is available in Figure A.37.

Figure A.37: Schematics for a thermocouple voltage amplifier
A.6.2 Client Installation (Analysis only)

**Microsoft Windows™ 95/98/ME**

- PC – IBM compatible
- Pentium 3/4 or AMD Athlon
- 256 MB RAM
- A full frame requires about 600kB. A total I(V) acquisition requires about 597 frames. For multiple acquisitions we advise an hard disk of at least 10GB
- For the same reason a CD-RW or DVD-RW is advised.
- No frame grubber or AD/DA card are necessary. However libraries must be installed to allow HotLEED to work properly. Data Translation “DataAcq SDK” and “FG SDK” development kits for Microsoft Windows™ 95/98/ME need to be installed.

**Microsoft Windows™ 2000/XP**

- PC – IBM compatible
- Pentium 3/4 or AMD Athlon
- 256 MB RAM (512MB for optimal performance)
- A full frame requires about 600kB. A total I(V) acquisition requires about 597 frames. For multiple acquisitions we advise an hard disk of at least 10GB
- For the same reason a CD-RW or DVD-RW is advised.
- No frame grubber or AD/DA card are necessary. However libraries must be installed to allow HotLEED to work properly.
• Two are the current available methods:

1. Copy in the C:/Windows/System32/ folder, the following files (located in the folder /HotLEED package/Drivers LEED/No card setup in the HotLEED package CD):

   olaapi32.dll, olimg32.dll, olmem32.dll, olmemsup.dll, olfg32.dll

2. In alternative, install Data Translation “DataAcq SDK” and “FG SDK development kits” for Microsoft Windows™ 2000/XP. Those packages are available at DataTranslation (http://www.datatranslation.com)

A.7 HotLEED Preferences Default Settings

Frame grabber:
Black level: 53.86
White level: 714.9

Hardware configuration:
LEED Energy:
Output Channel: 0
Input Channel: 1

<table>
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<tr>
<th></th>
<th>VGLEED</th>
<th>CPLEED</th>
</tr>
</thead>
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<td>scale</td>
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<td>0.9645</td>
</tr>
<tr>
<td>offset</td>
<td>2048</td>
<td>2056.5</td>
</tr>
</tbody>
</table>

A/D Acquisition:
Channel: 0

Display:
Frame buffer: 4
Palette num.: 0
Scale: 1.1
Offset: 4
Appendix B

"Hugo-hiostc" helium atom scattering acquisition programs: user manual

HUGO/HIOS Helium Atom Scattering apparatus is controlled by two main programs:

- **hugo**: for data acquisition in various HAS conditions (angular scans, intensity vs time, source or temperature measurements, Time of flight inelastic measurements)
- **hiostc** (previously named tcont): controls and displays temperatures in different parts of the system. Hiostc must always run on top of hugo.

### B.1 Preliminary instructions: initializing the workstation

- Boot the workstation with the multimeters and the camac crate turned on.
- Press CTRL+ALT+F1 to switch to a terminal window
- Login using: login: **camac** password: **terminator**
- Open a terminal window
- Type **su** to get superuser (root) privileges.
- Type the root password
- Type: **modprobe pc2_gpib**
- Type: **gpib_config**
- Return to user camac by typing: **q**
- Run tcont program (TC reading) by typing: **hiostc**
• Run the tcont program (TC reading) by typing: `tc`

• To run the automatic temperature reading view, type “view”

The workstation is now fully initialized with a session of `hiostc` running in the background. Multiple sessions of `hiostc` can now run at the same time in user mode.

• Press CTRL+ALT+F7 to return to the Graphical User Interface (GUI)

• Login as `camac`

• In a new terminal window (in the toolbar), run `hiostc` again and in another terminal window, the main program (sample motion, acquisition) by typing: `hugo`

• To be able to access remotely the GUI through VNC remotely, open a new terminal window and type: `vncserver`. Once loaded, you can close the terminal by typing `q`.

To close `hugo` and `hiostc` in user mode:

• Close hugo by typing: `q`

• In the hiostc terminal, type `view` to stop the view display.

• To close the current hiostc panel, type `q`. Note that `hiostc` will still run in the background

To completely stop the background session of hiostc:

• Press CTRL+ALT+F1 to switch to the initial terminal window

• from the hiostc terminal, type `view` to stop the temperature display

• type `terminate`.
**B.2 Running tccont**

There are 6 different temperature modules:

1. **fcho1**: the chopper rotational frequency is reported (not the temperature).
2. **crist**: crystal temperature, measured with the HP 3440A digital voltmeter
3. **duese**: source temperature, measured with the Prema 5000 digital voltmeter
4. **Cu ring**: temperature originally measured in the sample holder. Actual temperature measured in the crystal, using the JOE_Amplifier.
5. **Duese1**: source temperature measured with the JOE_Amplifier.
6. **Adc**: not connected.

To display the panel type `sh`. Each single module can be displayed individually, with the specific details. Each module can be accessed by typing:

```
   cd 1   (or 2, 3, 4, 5, 6 for the different modules)
```

All the parameters are already set, so they do not need to be changed. If changes are needed, these commands (for the module 2) are:

- `cd 2`
- `set preamp = 0.09905` (this is just an example)
- `cd ..`
- `cd 2`
- `sh`
The preamp factor is now showing the new value. The same can be done for the other modules. The calibrated preamp factors are given in Table B-1.

Table B-1: Standard values of the pre-amplification factors in tcont

<table>
<thead>
<tr>
<th>module</th>
<th>Preamp factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – fcho1</td>
<td>0.10000</td>
</tr>
<tr>
<td>2 – crist</td>
<td>0.09800</td>
</tr>
<tr>
<td>3 – duese</td>
<td>0.9925</td>
</tr>
<tr>
<td>4 – cu-ring</td>
<td>0.09325</td>
</tr>
<tr>
<td>5 – duese1</td>
<td>0.6725</td>
</tr>
</tbody>
</table>

For advanced settings each module can be accessed individually in the AD and DA section with these commands:

- **cd da** (or **cd ad**)
- **sh**

To access each single module: **cd** 2 (or 1, 3, 4, 5, 6). Use **set** to set the parameters to the desired value. To automatically display the temperature type **view**.
<table>
<thead>
<tr>
<th>module</th>
<th>type</th>
<th>slot</th>
<th>address</th>
<th>polarity</th>
<th>status</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>BOR_1004</td>
<td>9</td>
<td>2</td>
<td>NBIT</td>
<td>IDLE</td>
</tr>
<tr>
<td>[2]</td>
<td>HP_DVM</td>
<td>5</td>
<td>14</td>
<td>BIP</td>
<td>PID1</td>
</tr>
<tr>
<td>[3]</td>
<td>PREMA_DVM</td>
<td>5</td>
<td>7</td>
<td>BIP</td>
<td>PID1</td>
</tr>
<tr>
<td>[4]</td>
<td>JOE_AMPL</td>
<td>5</td>
<td>15</td>
<td>BIP</td>
<td>IDLE</td>
</tr>
<tr>
<td>[5]</td>
<td>JOE_AMPL</td>
<td>5</td>
<td>12</td>
<td>BIP</td>
<td>IDLE</td>
</tr>
<tr>
<td>[6]</td>
<td>NONE</td>
<td>0</td>
<td>22</td>
<td>BIP</td>
<td>IDLE</td>
</tr>
</tbody>
</table>

**Table B-3: Standard settings for the Analog-to-Digital I/O**

<table>
<thead>
<tr>
<th>module</th>
<th>type</th>
<th>slot</th>
<th>address</th>
<th>polarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>JOE_DAC</td>
<td>8</td>
<td>7</td>
<td>POS_10</td>
</tr>
<tr>
<td>[2]</td>
<td>JOE_DAC</td>
<td>8</td>
<td>4</td>
<td>POS_10</td>
</tr>
<tr>
<td>[3]</td>
<td>JOE_DAC</td>
<td>8</td>
<td>6</td>
<td>POS_10</td>
</tr>
<tr>
<td>[4]</td>
<td>NONE</td>
<td>8</td>
<td>7</td>
<td>POS_10</td>
</tr>
<tr>
<td>[5]</td>
<td>NONE</td>
<td>8</td>
<td>6</td>
<td>POS_10</td>
</tr>
<tr>
<td>[6]</td>
<td>NONE</td>
<td>8</td>
<td>7</td>
<td>POS_10</td>
</tr>
</tbody>
</table>
B.3 Running hugo

The program has a hierarchical structure with menus and submenus accessible, depending on the type of experiment required. Three are the possible modes of operation:

1. **win**: for angular scans (command line: \textit{WIN}>)

2. **ivt**: Diffraction intensity as function of sample or source temperature or time.
   (command line: \textit{IVT}>)

3. **tof**: Time of flight measurements. (command line: \textit{TOF}>)

Each mode of operation can be accessed any time from the command line, while \texttt{hugo} is running. For any mode of operations several submenus are present and they are shown in Table \textbf{B-4}. Type a name of the function to enter the submenu. Type “..” to move back.

<table>
<thead>
<tr>
<th>Function</th>
<th>Command line</th>
<th>Submenus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample polar rotation</td>
<td>WIN.THETA1&gt;</td>
<td>WIN.BEAM.TEMP&gt;</td>
</tr>
<tr>
<td>Tilt position</td>
<td>WIN.TILT&gt;</td>
<td>WIN.BEAM.PRESSURE&gt;</td>
</tr>
<tr>
<td>Beam properties</td>
<td>WIN.BEAM&gt;</td>
<td>WIN.CRYST&gt;</td>
</tr>
<tr>
<td>Crystal properties</td>
<td>WIN.CRYST&gt;</td>
<td>WIN.CRYST.TEMP&gt;</td>
</tr>
<tr>
<td>Chopper</td>
<td>WIN.CHO1&gt;</td>
<td>WIN.CHO1&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WIN.CHO1.POS&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>beam temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td>beam pressure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>sample properties</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sample temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chopper properties</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chopper position</td>
</tr>
</tbody>
</table>
B.3.1 Sample position calibration

To calibrate the polar angle (thetai) as shown in hugo with the actual angle, type

- `ti` (thetai)
- `sh` (to show the current parameters)

Use the step motor to align the sample with the LEED window. The small viewport below the LEED optics should show the sample exactly at its center. To rotate the sample holder type:

- `set 100` (where 100 is any desired angle)

Proceed by small steps (0.5°) to avoid stressing the step motors and the sample holder in case of jams. Once the sample is aligned with the LEED, type:

- `gauge 118`

This will set that as the position of the sample corresponding to the LEED. The other principal positions are shown in Table B-5.

<table>
<thead>
<tr>
<th>LEED</th>
<th>118</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specular</td>
<td>0</td>
</tr>
<tr>
<td>Sputtering</td>
<td>0</td>
</tr>
</tbody>
</table>
Use the command `set X` (where X is the desired angle) to change the polar angle. The suggested range during angular scan is $+53^\circ < \text{ti} < -40^\circ$. The current polar position can be displayed anytime by using the command `sh`. The same commands apply for the `tilt` rotation.

### B.3.2 Angular scan (WIN)

The angular scan is performed under the submenu `win`. The typical commands used for angular scans are reported in Table B-6. These commands work either in `thetai` and `tilt` mode.

<table>
<thead>
<tr>
<th>Command</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>sh</strong></td>
<td>to show the main panel</td>
</tr>
<tr>
<td><strong>set astart –30</strong></td>
<td>to set the initial position of the angular scan</td>
</tr>
<tr>
<td><strong>set aend 30</strong></td>
<td>to set the final position</td>
</tr>
<tr>
<td><strong>set astep 0.01</strong></td>
<td>to set the step</td>
</tr>
<tr>
<td><strong>set 30</strong></td>
<td>to set manually the position at angle 30°</td>
</tr>
<tr>
<td><strong>start</strong></td>
<td>to run the acquisition</td>
</tr>
<tr>
<td><strong>stop</strong></td>
<td>to stop the acquisition</td>
</tr>
<tr>
<td><strong>v (or view)</strong></td>
<td>to view the plot of the acquisition</td>
</tr>
<tr>
<td><strong>save</strong></td>
<td>to save the acquisition inside the folder specified under <code>save_info</code> file (in the case of HOPG, it is saved inside: <code>u/camac/data/HOPG</code>)</td>
</tr>
</tbody>
</table>
B.3.3 Diffraction intensity versus other parameters (IVT)

The angular scan is performed under the submenu `ivt`. The typical commands used for angular scans are reported in Table B-7.

<table>
<thead>
<tr>
<th>Command</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><code>sh</code></td>
<td>to show the main panel</td>
</tr>
<tr>
<td><code>set astart</code></td>
<td>50 to set the initial position/temperature/time/energy</td>
</tr>
<tr>
<td><code>set aend</code></td>
<td>800 to set the final position/temperature/time/energy</td>
</tr>
<tr>
<td><code>set astep</code></td>
<td>1 to set the step</td>
</tr>
<tr>
<td><code>set ascan</code></td>
<td><code>t_cryst</code> to set the step intensity vs sample temperature</td>
</tr>
<tr>
<td><code>set ascan</code></td>
<td><code>e_beam</code> to set the step intensity vs source temperature</td>
</tr>
<tr>
<td><code>set ascan</code></td>
<td><code>thetai</code> to set the step intensity vs polar angle (same as WIN)</td>
</tr>
<tr>
<td><code>set ascan</code></td>
<td><code>ivt</code> to set the step intensity vs time</td>
</tr>
<tr>
<td><code>start</code></td>
<td>to run the acquisition</td>
</tr>
<tr>
<td><code>stop</code></td>
<td>to stop the acquisition</td>
</tr>
<tr>
<td><code>v (or view)</code></td>
<td>to view the plot of the acquisition</td>
</tr>
<tr>
<td><code>save</code></td>
<td>to save the acquisition inside the folder specified under <code>save_info</code> file (in the case of HOPG, it is saved inside: <code>/home/camac/data/HOPG</code>)</td>
</tr>
</tbody>
</table>
B.3.4 Time-of-Flight measurements

The schematics of the wiring connections of the chopper with the control panel are shown in Figure B.1.

- In the REFU box, set the chopper current to about 1A (knob D in Figure B.1) and increase slowly (knob C in Figure B.1) the frequency using to the desired value (optimal frequency: 300Hz, max. 500Hz). Reduce the cooling water flow with the valve shown in Figure B.2. This is done by closing the valve all the way and...
reopening it by an angle of about 135°. Monitor the temperature of the bearings
with the Pt100 thermometer (by measuring its resistance from the two red and
black banana plugs). They should not be higher than 40°C. If their temperature
goes higher, open more the cooling water valve and watch the temperature
decreasing.

Figure B.2: Flow regulator valve for cooling the chopper bearings.

- In a new console terminal run the program `refu`. The frequency set by the REFU
  should correspond to the one set manually in the REFU. The red light in the Ch1
  module in the CAMAC crate lights up.
- Type: `Refu [frequency]`  (ex. `Refu 300` for a frequency of 300Hz).
- Switch into automatic using the Auto/Man switch in the REFU box. The
  computer generates a single frequency through a feedback loop. This is just a
  locking frequency program and it should not be used to change the frequency.
- In the HUGO program type: `tof` to initiate time of flight measurements.
Move the chopper inline with the beam by typing: **cho1**, and **pos**.

<table>
<thead>
<tr>
<th>Inline position</th>
<th>set 26 (wait until it gets there) then: set 28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Offline position</td>
<td>set 1 (wait until it gets there) then: set 0</td>
</tr>
</tbody>
</table>

Different parameter can be set. By changing one of them the others will adjust consequently.

| Measurement time | set metime = 1 min  
<table>
<thead>
<tr>
<th></th>
<th>set metime = 30 sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of cycles</td>
<td>Neyc = 99</td>
</tr>
</tbody>
</table>

The chopper position needs to be adjusted in front of the beam for ToF measurements.

By selecting **start** the measurement begins. Type **sh** to view the status of the measurement (a progress digit in percentage is given). When the TOF is running, the light in the CAMAC module for the chopper (#12) lights up.

To stop the acquisition you need to reset the CAMAC module.

To view the actual data, type **v** or **view**.

At the end of the acquisition, to save the data, type: **save**.

To stop the chopper, switch the chopper Auto/Man switch to Man in the REFU controller (switch A in Figure **B.1**) and ramp down the chopper frequency to zero (knob C). Then, using knob D, turn the current of the chopper motor to zero. Turn off the main power of the REFU controller (switch E).
Table B-8: ToF acquisition: main commands

<table>
<thead>
<tr>
<th>Command</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tof (or hugo)</strong></td>
<td>Tof menu</td>
</tr>
<tr>
<td><strong>tof cho1</strong></td>
<td>View and change variables related to the chopper</td>
</tr>
<tr>
<td><strong>tof cho1 pos</strong></td>
<td>View the variables related to the actual position of the chopper, and control the step motor. Set the position to 4</td>
</tr>
<tr>
<td><strong>set 4</strong></td>
<td></td>
</tr>
<tr>
<td><strong>tof cho1 pos set motor_scale</strong></td>
<td>Set displacement per step [mm/sec]</td>
</tr>
<tr>
<td><strong>tof cho1 pos set encoder_scale</strong></td>
<td>Set displacement per digit [mm/digit]</td>
</tr>
<tr>
<td><strong>tof cho1 pos set x0</strong></td>
<td>Set the gauge position for the chopper</td>
</tr>
<tr>
<td><strong>gauge 0</strong></td>
<td></td>
</tr>
<tr>
<td><strong>tof cho1 pos set res</strong></td>
<td>Set the position resolution</td>
</tr>
<tr>
<td><strong>tof cho1 pos set xmin</strong></td>
<td>Set min/max limits for position</td>
</tr>
<tr>
<td><strong>tof cho1 pos set xmax</strong></td>
<td></td>
</tr>
<tr>
<td><strong>tof cho1 pos motor</strong></td>
<td>Set the CAMAC module parameters for the step motor controller and encoder</td>
</tr>
<tr>
<td><strong>tof cho1 pos encoder</strong></td>
<td></td>
</tr>
</tbody>
</table>

Table B-9: Chopper position calibration parameters in hugo

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>xmin</td>
<td>-1.2 mm (OUT)</td>
</tr>
<tr>
<td>xmax</td>
<td>28 mm (IN)</td>
</tr>
<tr>
<td>zero_position</td>
<td>-0.009 mm</td>
</tr>
<tr>
<td>position</td>
<td>28.0463 mm (when fully inserted)</td>
</tr>
<tr>
<td>get_scale</td>
<td>-5.8932 mm/step</td>
</tr>
<tr>
<td>set_scale</td>
<td>0.0261 mm/step</td>
</tr>
</tbody>
</table>
B.4 Additional programs

Two additional programs have been developed by the author to extend the capabilities of the main program. They are available in the workstation and for MS windows platform (for later analysis).

1. **AscConv**: This program converts the data as it is saved from the acquisition program into ASCII format. It also allows data manipulation for the Time-of-Flight measurements (Figure B.3).

![AscConv program: screenshot.](image)

2. **HAS**: this utility is used for beam energy conversion from sample temperature or from first order diffraction peak position. It is also used to calibrate the Time-of-Flight length. A light version is also available for the PalmOS PDA platform, useful in the lab environment when workstation is not immediately available (Figure B.4).
3. **ScanCurve**: Given the incident angle, the beam energy and the range in momentum transfer, this utility produces scan curves for inelastic scattering. By typing the transfer energy, the program displays the correspondent momentum transfer.

Figure B.4: HAS program: screenshots of the MS Windows/UNIX version (left) and PalmOS (right).

Figure B.5: ScanCurve: screenshot.
### B.5 Electrical connections charts

Table B-10: Heater connections for bake out. The number in bold refers to the heaters where the thermocouple is connected.

<table>
<thead>
<tr>
<th>No.</th>
<th>Description</th>
<th>Power (W)</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>HI.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HI.2</td>
<td>2.18 – <strong>2.19</strong> (windows under LEED – leak valve) – 2.20</td>
<td>250</td>
<td>CF35</td>
</tr>
<tr>
<td>HI.3</td>
<td><strong>2.14</strong> – 2.13 (blanks on manipulator) – 2.20 (subl. Pump)</td>
<td>2x130</td>
<td>CF35</td>
</tr>
<tr>
<td>HI.4</td>
<td><strong>2.2</strong> – 2.4 – 2.15 (Top manipulator and windows close to leak valve – leak valve/dosing tube)</td>
<td></td>
<td>CF35</td>
</tr>
<tr>
<td>HI.5</td>
<td>3.1 – 3.2 - <strong>3.3 – 3.4</strong> (windows target chamber)</td>
<td>4x180</td>
<td>CF63</td>
</tr>
<tr>
<td>HI.6</td>
<td></td>
<td>800</td>
<td>Tape</td>
</tr>
<tr>
<td>HI.7</td>
<td>2.3 (mass spec)- 2.9 – 2.10 – <strong>2.11</strong> (Beam line level windows)</td>
<td>4x100</td>
<td>CF35</td>
</tr>
<tr>
<td>HI.8</td>
<td>2.5 (IonGauge2)– 2.6 (inlet) – <strong>2.17</strong> (Vent)</td>
<td>380</td>
<td>CF35</td>
</tr>
</tbody>
</table>

| HII.1 | Mass Spec + Auger window                                    | -         | Tape   |
| HII.2 | Tape aroung LN2 trap, subl. pump                           | 800       | Tape   |
| HII.3 | Body main target chamber                                   | 800       | Tape   |
| HII.4 | **2.12**                                                    | -         | CF35   |
| HII.5 | Blank flange on the right of LEED window                    | -         | CF63   |
| HII.6 | **5.2** (turbopump)                                        | 400       | CF150  |
| HII.7 |                                                               | -         | Tape   |
| HII.8 |                                                               | -         | Tape   |
**Table B-11:** Power connection switches in the electric panel for the pumping units.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1) Gas Line</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP1</td>
<td></td>
<td>TP1</td>
<td></td>
</tr>
<tr>
<td><strong>2) Chopper 2</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP2</td>
<td>Pir2</td>
<td></td>
<td>TP2</td>
</tr>
<tr>
<td>LT4.2 – T6</td>
<td>C61</td>
<td>LT3.6 – (PST2)</td>
<td></td>
</tr>
<tr>
<td><strong>3) Selector</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP3</td>
<td>Pir3</td>
<td>DP3A</td>
<td>DP3B</td>
</tr>
<tr>
<td>LT3.3 – T92</td>
<td>C30</td>
<td>LT4.4 (Selk)</td>
<td>LT4.5</td>
</tr>
<tr>
<td><strong>4) Detector (UHV)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP4</td>
<td>Pir4</td>
<td>Vent4</td>
<td>DP4</td>
</tr>
<tr>
<td>LT5.1 - T143</td>
<td>C29</td>
<td>LT1.5</td>
<td>LT5.6</td>
</tr>
<tr>
<td><strong>5) Selector 2</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP5</td>
<td>Pir5</td>
<td>DP5</td>
<td>TP5</td>
</tr>
<tr>
<td>LT4.3 – T90</td>
<td>C28</td>
<td>LT4.9</td>
<td>LT4.6 – (PST3)</td>
</tr>
<tr>
<td><strong>6) He – Transfer line</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP6 – T80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>7) He - Transfer Line</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>8) Chopper 1</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP8</td>
<td>Pir8</td>
<td>DP8A</td>
<td>TP8A</td>
</tr>
<tr>
<td>LT2.3 - T133</td>
<td>C64</td>
<td>LT2.9</td>
<td>LT2.6</td>
</tr>
<tr>
<td><strong>9) Target (UHV) – Main Chamber</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP9</td>
<td>Pir9</td>
<td>Vent9</td>
<td>DP9</td>
</tr>
<tr>
<td>LT2.2 - T141</td>
<td>C58</td>
<td>LT1.6</td>
<td>LT3.7</td>
</tr>
<tr>
<td><strong>0) Source</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP0</td>
<td>Pir0A</td>
<td>Root0</td>
<td>Pir0B</td>
</tr>
<tr>
<td>LT1.3</td>
<td>LT4.1</td>
<td>LT1.1</td>
<td></td>
</tr>
</tbody>
</table>
VITA

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