Structure, Morphology, and Dynamics of Quasicrystal Surfaces

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Contents

Abstract 5								
In	trod	uction		7				
1	Qua	asicrys	crystals					
	1.1	Basic	Concepts	12				
		1.1.1	Basic Types of Quasicrystalline Lattices	12				
		1.1.2	Higher Dimensional Concept	14				
		1.1.3	Phasons and Approximants	17				
	1.2	Stabil	ity and Structural Models	19				
	1.3	Decag	onal Quasicrystals	22				
		1.3.1	Indexing of the Diffraction Pattern	25				
		1.3.2	Superstructure in <i>d</i> -Al-Ni-Co	27				
		1.3.3	Atomic Structure of <i>d</i> -Al-Ni-Co	28				
2	Exp	perime	ntal Methods	35				
	2.1	Heliur	n Atom Scattering	37				
		2.1.1	Theoretical Aspects of Elastic Scattering	37				
		2.1.2	Theoretical Aspects of Inelastic Scattering	43				
		2.1.3	Surface Phonons and Time-of-flight Technique	46				
		2.1.4	Experimental Setup	47				
	2.2	Spot I	Profile Analyzing Low Energy Electron Diffraction	52				
	2.3	Scann	ing Tunneling Microscopy	55				

3	The	10-fold <i>d</i> -Al-Ni-Co Surface	57			
	3.1	Spot Profile Analyzing Low Energy Electron Diffraction	58			
	3.2	Helium Atom Scattering	68			
	3.3	Scanning Tunneling Microscopy	73			
4	The 2-fold <i>d</i> -Al-Ni-Co Surfaces					
	4.1	The 2-fold <i>d</i> -Al-Ni-Co(10000) Surface \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots	81			
		4.1.1 Spot Profile Analyzing Low Energy Electron Diffraction	81			
		4.1.2 Helium Atom Scattering	87			
	4.2	The 2-fold d -Al-Ni-Co(001 $\overline{1}$ 0) Surface \ldots	92			
5	Surf	face Phonons of the 10-fold <i>d</i> -Al-Ni-Co	99			
	5.1	$Time-of-flight\ Spectra\ \ldots\ \ldots\$	101			
	5.2	Dispersion Relation	105			
	5.3	Phonon Peak Width	109			
6	The 5-fold <i>i</i> -Al-Pd-Mn Surface					
	6.1	Characterization of the Clean Surface	115			
	6.2	Surface Phonons	117			
Sυ	mma	ary and Conclusions	121			
Bi	bliog	raphy	125			
\mathbf{Li}	st of	Figures	134			
Li	st of	Tables	137			

Abstract

Aside from their fascinating structure with aperiodic long range order and conventionally forbidden rotational symmetries, quasicrystals possess outstanding surface properties. It is of great interest to learn whether or not surface phenomena observed in periodic crystals are relevant in these new class of material. To investigate this, high symmetry surfaces of two distinct types of quasicrystals were examined by various surface sensitive techniques capable of providing information in both real and reciprocal space. The investigated surfaces are the 10-fold and two inequivalent 2-fold surfaces of decagonal (d) Al_{71.8}Ni_{14.8}Co_{13.4} and the 5-fold surface of icosahedral (i) Al_{71.5}Pd₂₁Mn_{8.5}. The techniques employed are highly surface sensitive He atom scattering (both elastic and inelastic), high resolution spot profile analyzing low energy electron diffraction, and low temperature (6 K) scanning tunneling microscopy. The investigations focus on structure, morphology, and dynamics (phonons).

It is found that the surfaces can be prepared with high structural quality suitable for He diffraction. Both He and electron diffraction show that the topmost surface layer of the surfaces retains the full symmetry extrapolated from their respective bulk. The diffraction spots are very sharp and their positions are related by the golden mean revealing a perfect long range, quasicrystalline order. The observed diffraction patterns can be fully explained by the respective bulk reciprocal basis vectors.

Helium diffraction from the 10-fold d-Al-Ni-Co surface reveals an average terrace width on the order of 100 Å and a predominant step height of 2 Å. Scanning tunneling microscopy confirms this step morphology by showing a high density of rough 2 Å-steps. Terraces are found to be atomically flat, having a variety of 5-fold symmetric motives, and possessing a quasiperiodic long range order. In agreement with the bulk structure model, a rhombic tiling of a large surface region is identified.

The 2-fold surfaces of the *d*-Al-Ni-Co show a weak 16 Å periodicity in addition to the main 8 Å periodicity. The 2-fold $(001\overline{1}0)$ surface is found to develop facets of (10000)-equivalent orientation due to a lower surface energy of the (10000)- compared to the as-cut $(001\overline{1}0)$ -surface.

The first result of surface phonons on quasicrystals is presented. The 10-fold d-Al-Ni-Co and 5-fold i-Al-Pd-Mn surfaces are found to possess well-defined Rayleigh modes with isotropic sound velocity of about 3750 m/s and 3250 m/s, respectively. The observed sound velocities are in good agreement with calculations based on the respective bulk data.

Introduction

Since their discovery in 1984 [1], quasicrystals (QCs) have become an interesting topic for theoretical and experimental investigations because of their intriguing structure and fascinating properties. Quasicrystals possess long range order without translational symmetry and often show conventionally forbidden rotational symmetries such as 5-fold, 8-fold, 10-fold, and 12fold, distinguishing them from other known forms of solid matter. In addition to their unique structural features, QCs exhibit many unusual physical properties compared with their metallic constituents and alloys such as a very low electrical conductivity and negative temperature coefficient of electrical resistivity [2].

Although the quasicrystalline structure first observed in a rapidly solidified Al-Mn alloy was metastable, there has been a rapid success to grow many different types of QCs in thermodynamically stable phases [3, and find references therein]. Many binary and ternary alloys of metals possess quasicrystalline phases in very narrow regions of their phase diagram. The polygonal and icosahedral are the two main types of quasicrystals discovered so far. The polygonal QCs are two-dimensional QCs exhibiting a periodicity only along the third dimension, while icosahedral QCs show quasicrystalline structure in all three dimensions. In addition, a few 1D QCs have been found which exhibit a quasiperiodic arrangement of diffraction spots along one direction and periodic arrangements of spots on the planes perpendicular to the quasiperiodic direction [4].

While significant progress has been made in the determination of physical properties of QCs [2], the problem of determining their atomic structure has not been completely solved yet. Questions regarding the physical origin of quasicrystalline structure and the cause behind the unusual physical properties are also still under debate. Atomic clusters are believed to be the main structural building blocks of the QCs [5] and many physical properties have been described

in terms of this cluster approach.

There are several reasons motivating the study of QC surfaces. First of all, it is important to determine how the surface features observed on QC will differ from those of periodic crystals. Secondly, it would be interesting to learn whether or not the aperiodic long range order of the bulk is extended up to the surface preserving bulk structural properties. Thirdly, QC surfaces possess interesting properties like a low coefficient of friction and a non-sticking behavior [6] and the potential applications of quasicrystals as coating materials, thin films etc., are related to these surface phenomena.

With the availability of mm-size single-grain samples, surface investigations by various experimental techniques have become possible. There is an increasing number of studies on the structure and physical properties of the surfaces. So far, the clean surface of decagonal (d)Al-Ni-Co and icosahedral (i) Al-Pd-Mn has been studied intensively by employing different experimental techniques, mainly low energy electron diffraction (LEED) [7-10], scanning tunneling microscopy (STM) [11-20], and X-ray photoelectron diffraction (XPD) [21].

Almost all investigations reported so far show that surfaces prepared by sputtering and annealing are bulk terminated. However, the surface termination is extremely sensitive to the preparation conditions due to the preferential sputtering of light atoms and different diffusion rates of the atomic constituents [6, 22-27]. Nevertheless, sputter-annealing is the most established method to clean the surface as in the case of normal metal surfaces. Surfaces obtained by UHV (ultra high vacuum) cleavage were found not to be sufficiently smooth for most studies. STM measurements on the cleaved 5-fold and 2-fold surfaces of i-Al-Pd-Mn show a very rough termination with an aggregation of atomic clusters in agreement with the bulk structure [14, 15].

In addition to these clean surface studies, there has been a great effort to grow a single element quasicrystalline thin film [28-33], which may be helpful to separate the influence of alloy composition and quasicrystalline structure on their intriguing characteristics.

The present work involves experimental investigations on the structure, morphology, and dynamics of high symmetry surface(s) of d-Al_{71.8}Ni_{14.8}Co_{13.4} and i-Al_{71.5}Pd₂₁Mn_{8.5} with the application of highly surface-sensitive He atom scattering (HAS), high resolution spot profile low energy electron diffraction (SPA-LEED), and low temperature scanning tunneling microscopy (LT-STM). The main focus of the investigation is on the high symmetry surfaces of d-Al-Ni-Co, while only a few measurements on i-Al-Pd-Mn are included.

He diffraction from the surfaces prepared by sputtering and annealing has been successfully measured. Due to the extreme sensitivity of He diffraction to all kinds of defects (adatoms, vacancies, steps, etc), the fact that diffraction is observed at all from the quasicrystals is evidence that their surfaces have high structural quality and contain only a modest amount of defects. The observed diffraction patterns reveal that the topmost surface layer maintains a long range, quasicrystalline order compatible with bulk terminated surfaces. In agreement with bulk models, a rhombic tiling has been identified in STM images of the 10-fold *d*-Al-Ni-Co surface.

In addition to these structural investigations, surface phonons (Rayleigh mode) of the 10-fold surface of d-Al-Ni-Co and the 5-fold surface of i-Al-Pd-Mn have been measured and constitute the first surface phonon dispersions measured on quasicrystal surfaces. The sound velocities of the Rayleigh modes are found to be in excellent agreement with bulk phonons data.

This dissertation is organized as follows: Basic concepts of QCs as well as a theoretical structure model of d-Al-Ni-Co are discussed in Chapter 1. Chapter 2 reports details about experimental techniques. Experimental results on the structure and morphology of the 10-fold and 2-fold surfaces of d-Al-Ni-Co are presented in Chapter 3 and 4, respectively, while surface phonons of the 10-fold d-Al-Ni-Co are described in Chapter 5. Chapter 6 contains results from the 5-fold i-Al-Pd-Mn surface. Finally, a summary and conclusions of the present investigation are given.

Chapter 1

Quasicrystals

The discovery of a quasicrystalline phase in a rapidly cooled Al-Mn alloy [1] broke the fundamental concept of crystallography because the diffraction of the alloy had a sharp diffraction pattern with a rotational symmetry incompatible with periodicity. This new finding forced a reconsideration of the traditional definition of a crystal as *a periodic arrangement of identical unit cells.* In 1992, the International Union of Crystallography redefined crystals as *any solid having an essentially discrete diffraction diagram* [34].

Periodic crystals are formed by a periodic repetition of a single building block the so-called unit cell exhibiting a long range translational and orientational symmetry. Only 2-, 3-, 4-, and 6-fold non-trivial rotational symmetries are allowed in the periodic crystals and their diffraction patterns give sharp Bragg peaks reflecting the symmetry and long range order.

In contrast to periodic crystals, quasicrystals exhibit a long range order in spite of their lack of translational symmetry and often possess n-fold (n = 5 and > 6) rotational symmetries. Most of the quasicrystalline structures can be described by using quasiperiodic tiling models [35, 36], where two or more different 'unit cells' (tiles) are used as the building blocks of the structure. An alternative model is a covering model, where a single, overlapping tile acts as unit cell [37].

The diffraction pattern of quasicrystals shows a dense set of Bragg peaks with their positions related by the irrational number $\tau = 1.618... = 2\cos\frac{\pi}{5}$, the so-called golden mean, which is related to the geometry of pentagonal and decagonal symmetries. In contrast to periodic crystals, where three integer indices are sufficient to characterize the diffraction of a 3D structure, ninteger indices (n > 3) are required to generate the diffraction vectors of aperiodic crystals indicating that the spots could be related to a nD periodic lattice. In fact, quasicrystals of all kinds can be explained by periodic lattices in higher dimensional space.

This chapter includes a discussion about the basic concepts, stability and structure models of quasicrystals followed by structural details of d-Al-Ni-Co.

1.1 Basic Concepts

1.1.1 Basic Types of Quasicrystalline Lattices

Fibonacci Sequence

The Fibonacci sequence is a fundamental and a well-known example of a 1D quasiperiodic structure exhibiting aperiodic long range order. Although it does not feature orientational symmetry, the Fibonacci sequence illustrates many important properties of quasicrystals, which can be generalized to 2D and 3D quasicrystals. The Fibonacci sequence is built from two elements 'L' (large) and 'S' (small). The sequence can be generated by a substitution rule $L \rightarrow LS$ and $S \rightarrow L$. The resulting sequence is as follows:

Generation	Fibonacci Sequence	Fibonacci Number
1^{st}	\mathbf{L}	1
2^{nd}	LS	2
3^{rd}	LSL	3
4^{th}	LSLLS	5
5^{th}	LSLLSLSL	8
6^{th}	LSLLSLSLLSLLS	13
•••	so on	

The frequencies of 'L' and 'S' in each sequence and the ratio of successive Fibonacci number (number of line segments in each generation) is τ (the golden mean) in the limit of infinite sequence length. The sequence is self-similar. This implies that inflation or deflation of a Fibonacci sequence yields another Fibonacci sequences with different length segment. The sequences can be generated by taking a single line segment and applying the deflation rule $(L_n \rightarrow L_{n+1}S_{n+1}$ and $S_n \rightarrow L_{n+1}$, *n* denotes number of generations) with an additional constraint that the ratio of line segments in each generation is equal to the golden mean i.e. $\frac{L_n}{S_n} = \tau$. Furthermore, the



Figure 1.1: A rhombic Penrose pattern (right panel) generated by two rhombi (left upper panel). The lower left panel shows the deflating scheme.

diffraction of the Fibonacci sequence gives sharp Bragg peaks with many interesting features, which will be discussed in the next section.

Penrose Tiling: A 2D Quasicrystalline Lattice

In 1974 the British mathematician Roger Penrose found that the 2D plane can be covered in a non-periodic fashion with two types of rhombi with equal edge length [38]. The importance of the Penrose tiling in solid state physics was realized only after the discovery of quasicrystals in 1984. Indeed, the Penrose pattern gives a diffraction pattern very similar to the diffraction observed from decagonal QCs [39].

Figure 1.1 shows a 2D rhombic Penrose pattern generated by two types of rhombi, one with an angle of 36° (skinny rhombus) and another with an angle of 72° (fat rhombus) (also see Figure 1.9). A perfect quasiperiodic pattern can be obtained only if the tiles are packed with a specific matching rule. The rule is simple, two rhombi are allowed to join if the arrows in their common edge match [38].

The Penrose pattern possesses many interesting features. Both areas and frequencies of skinny and fat rhombi in the pattern are of a ratio $1 : \tau$. The pattern consists of five sets

of tile-edges each parallel to the sides of a regular pentagon. The edges belonging to each set are orientated along a Fibonacci grid (a Fibonacci grid is a set of parallel lines separated by distances forming a Fibonacci sequence). This gives evidence of the long range order of the Penrose pattern. Furthermore, the local 5-fold and 10-fold rotational symmetries can be observed in the pattern. Some of decagonal and pentagonal features are highlighted in Figure 1.9.

Another important feature of the tiling is its self-similarity. A Penrose pattern can be transformed to another Penrose pattern by deflating/inflating the skinny and fat rhombi. Figure 1.1 (left lower panel) shows the deflating scheme, where the fat and skinny rhombi are divided into smaller fat and skinny rhombi. The fat rhombus is divided into two fat and one skinny rhombus, while the skinny rhombus is divided into one fat and one skinny rhombus. The area of the new fat and skinny rhombi is smaller than the respective old rhombi by a factor of τ^2 . Starting from a single rhombus, an arbitrarily large section of a Penrose tiling can be produced by continuously applying the deflation rule. There are some other 2D quasicrystalline tilings such as the pentagonal Penrose tiling (Figure 1.9) and the octagonal Penrose tiling, which explain the diffraction pattern of other polygonal QCs [40]. The idea of space filling is extended to 3D space, where two kinds of rhombohedrons are needed to fill the 3D space aperiodically [41]. The Fourier transform of the 3D Penrose tiling explains the diffraction pattern observed in icosahedral QCs [42, 43].

1.1.2 Higher Dimensional Concept

Higher dimensional crystallography was first introduced by de Wolff in 1974 [44]. Many quasiperiodic structures can be considered as a physical space projection or irrational cut of a higher dimensional periodic lattice. For instance, 2D and 3D Penrose tilings can be obtained from 4D and 6D periodic space, respectively [45]. Rotational symmetries incompatible with 3D periodicity are allowed in suitable nD (n > 3) periodic space. The body diagonal of a hypercubic lattice in nD space, for example is an n-fold rotational axis.

In this section, a method to generate 1D and 2D quasicrystalline lattices is presented. There are two procedures to derive quasicrystalline lattices from higher dimension: (a) the projection method, and (b) the section or embedding method, also called the cut method. The section method is dealt in the following because it provides a convenient way to obtain the diffrac-

tion pattern and the quasicrystalline structure can be explained in term of symmetry, lattice parameter and unit cell distributions in higher dimensional periodic space.

Fibonacci Sequence Generated from the 2D Square Lattice by the Section Method

Let us consider a 2D square lattice (lattice constant a) with a set of axes X_{\perp} and X_{\parallel} rotated by an angle α with respect to the axes of the square lattice (Figure 1.2(a)). The lattice is decorated with line segments A_{\perp} of length $\Delta = a(\cos \alpha + \sin \alpha)$ with the orientation along the X_{\perp} -axis. The point of intersection of the A_{\perp} with the X_{\parallel} -axis yields a Fibonacci lattice if the slope of X_{\parallel} -axis is the reciprocal of the golden mean, i.e., $\cot \alpha = \tau$. This process of getting quasicrystalline structures from higher dimension periodic decorated lattices is called the section method. The line segment used to decorate the higher dimensional lattice is called the atomic surface or occupation domain or hyperatom. The X_{\parallel} -axis locating the quasicrystalline lattice is called parallel space or physical space or external space, while its perpendicular counterpart along which the atomic surface is situated is called internal or perpendicular space.

The diffraction pattern of the Fibonacci sequence is calculated now. The distribution of lattice points in a 2D square lattice can be expressed by,

$$\rho(\mathbf{r}) = \sum_{m,n} \delta(\mathbf{r} - ma\mathbf{e}_x - na\mathbf{e}_y).$$
(1.1)

The Fourier transform of $\rho(\mathbf{r})$ is a square lattice with lattice spacing of $\frac{2\pi}{a}$. It can be written as,

$$F(\mathbf{Q}) = \frac{1}{a^2} \sum_{hh'} \delta(\mathbf{Q} - \mathbf{Q}^{hh'}), \qquad (1.2)$$

where $\mathbf{Q}^{hh'}$ are vectors of the reciprocal lattice, which have two components $\frac{2\pi}{a}h$ and $\frac{2\pi}{a}h'$ along X*- and Y*-axes (X* and Y* are the reciprocal space axes associated with the real space axes X and Y, respectively). The $\mathbf{Q}^{hh'}$ can be decomposed into the parallel and perpendicular space components, i.e. $\mathbf{Q}^{hh'} = (Q_{\parallel}^{hh'}, Q_{\perp}^{hh'})$ with,

$$Q_{\parallel}^{hh'} = \frac{2\pi}{a} \sqrt{\frac{\tau^2}{\tau^2 + 1}} (h + \frac{h'}{\tau}), \qquad (1.3)$$

and

$$Q_{\perp}^{hh'} = \frac{2\pi}{a} \sqrt{\frac{\tau^2}{\tau^2 + 1}} (h' - \frac{h}{\tau}).$$
(1.4)



Figure 1.2: (a) The section method generating a Fibonacci sequence from a 2D square lattice decorated with line segments.

The density distribution of the decorated periodic lattice $\rho'(\mathbf{r})$ is the convolution product of $\rho(\mathbf{r})$ with A_{\perp} , i.e.,

$$\rho' = \rho * \mathcal{A}_{\perp}. \tag{1.5}$$

The Fourier transform of $\rho'(\mathbf{r})$ is given by the product of the Fourier transforms of ρ and A_{\perp} ,

$$F'(\mathbf{Q}) = \left[\frac{1}{a^2} \sum_{hh'} \delta(\mathbf{Q} - \mathbf{Q}^{hh'})\right] G(Q_{\perp}),$$
(1.6)

where $G(Q_{\perp})$ is the Fourier transform of A_{\perp} and given by,

$$G(Q_{\perp}) = \Delta \frac{\sin(Q_{\perp}\Delta/2)}{(Q_{\perp}\Delta/2)}.$$
(1.7)

The main idea of the section method is that the cut operation is performed in real space, while the projection is carried out in the reciprocal space. This method uses the fact that the Fourier transform of a projection is a cut and vice versa. Thus, the density distribution of the Fibonacci lattice $\rho(r_{\parallel})$ is obtained by the cut of $\rho'(\mathbf{r})$ by X_{\parallel} , while its Fourier components are evaluated by the projection $F'(\mathbf{Q})$ on X_{\parallel}^* . The Fourier components of the Fibonacci lattice thus can be written as,

$$F'(Q_{\parallel}) = \frac{1}{a^2} \sum_{hh'} [\delta(Q_{\parallel} - Q_{\parallel}^{hh'}) G(Q_{\perp}^{hh'})], \qquad (1.8)$$

The presence of the δ -term implies that the diffraction pattern of the Fibonacci lattice exhibits sharp Bragg peaks. The intensity of the diffraction peaks associated with (h, h') is given by,

$$I_{hh'} = |G(Q_{\perp}^{hh'})|^2 = \Delta^2 \frac{\sin^2(Q_{\perp}^{hh'}\Delta/2)}{(Q_{\perp}^{hh'}\Delta/2)^2},$$
(1.9)

Many features important for quasicrystals can be extracted from the diffraction vector $Q_{\parallel}^{hh'}$ of the Fibonacci lattice (Equation 1.3). Firstly, the diffraction peaks are indexable with two indices h and h' (which are the Miller indices of the 2D square lattice) even though the structure is 1D. Secondly, the diffraction vector produces an aperiodic reciprocal lattice because of an irrational coefficient of h'. Thirdly, since $Q_{\parallel}^{hh'}$ is invariant under multiplication of τ^n , there is no restriction of minimum separation between the diffraction spots. (The invariance can be illustrated by taking an arbitrary value of n, say n = 1 for simplicity, then $Q_{\parallel}^{hh'} \times \tau = \frac{2\pi}{a}\sqrt{\frac{\tau^2}{\tau^2+1}}(h + \frac{h'}{\tau}) \times \tau = \frac{2\pi}{a}\sqrt{\frac{\tau^2}{\tau^2+1}}(h\tau + h') = \frac{2\pi}{a}\sqrt{\frac{\tau^2}{\tau^2+1}}(h(\frac{1}{\tau}+1) + h') = \frac{2\pi}{a}\sqrt{\frac{\tau^2}{\tau^2+1}}(h + h' + \frac{h}{\tau}) = \frac{2\pi}{a}\sqrt{\frac{\tau^2}{\tau^2+1}}(\tilde{h} + \frac{h}{\tau}) = Q_{\parallel}^{h\tilde{h}}$ with $\tilde{h} = h + h'$).

Penrose Tiling Generated from 4D Space

A 2D rhombic Penrose tiling can be obtained from 4D periodic space, which can be decomposed into a 2D physical space V^{\parallel} and a 2D perpendicular space V^{\perp} . The unit cell of the 4D lattice is decorated with five types of pentagonal atomic surfaces [39, 45] orientated parallel to V^{\perp} . The atomic surfaces intersect V^{\parallel} at points generating the vertices of the rhombic Penrose tiling. The Penrose patterns of other variants are obtained by taking different types of atomic surfaces. For example, a pentagonal Penrose pattern is obtained by a single decagonal atomic surface. The section method to generate a periodic stacking of the pentagonal and rhombic Penrose tilings from a 5D space will be discussed later in Section 1.3.3.

1.1.3 Phasons and Approximants

The higher dimensional description of the quasicrystals introduces additional degrees of freedom related to perpendicular space. The ordinary elastic excitation in quasicrystals is characterized by phonons, which involves the translation of atoms in physical space. In contrast, the elastic excitation associated with the new degrees of freedom corresponds to the translation of the atomic surfaces along the perpendicular space. The associated elementary excitations are called phasons. Since the perpendicular space does not exist in reality, only the effects of phason excitation in the physical space are relevant in practice. The phason excitations cause atomic jumps in the physical space in contrast to the phonon excitations which result in a collective



Figure 1.3: An illustration of phason-disorder (a) and approximants of a Fibonacci sequence generated by employing uniform phason strain rotating the physical space X_{\parallel} .

continuous motion of atoms. A very simple example illustrating how phasons influence the structure in the physical space is presented below.

Consider once again the section method generating a Fibonacci sequence (Figure 1.3(a)). Assume the atomic surfaces are displaced along X_{\perp} due to the phasonic excitations and the displacement is defined by a sinusoidal function (for the sake of simplicity, the physical space is sliced by a curve represented by the sinusoidal function in the figure). The displacement of atomic surfaces results in a new sequence LLSLSLLSLLSLSLS..., where some of the tiles (written in bold characters) have been rearranged as compared to the original sequence LLSLLSLSLS.... The rearrangement of tiles in real quasicrystals corresponds to atomic jumps between different positions, which are normally referred to as phason-flips. Indeed, the atomic jumps has been experimentally observed by transmission electron microscopy [46]. At low temperatures, the phason-flips are trapped as defects (phason disorder).

Both phonon and phason disorder influence the diffraction pattern. While the presence of phonons decreases the diffraction intensities via the conventional Debye-Waller factor yielding background intensity, the phasons decrease the intensities via a phasonic Debye-Waller factor [47]. The phonon and phason Debye-Waller factors are dependent on Q_{\parallel} and Q_{\perp} , respectively. The phonons constitute small displacements of the atoms from their equilibrium position and

the average structure maintains a long range order. In contrast, phasons may break down the long range order and thus result not only in decreased intensities but also broaden the peaks, or even shift the peak position depending upon the nature of phason disorders (see Ref. [48, 49]).

Phasons are believed to play an important role in the formation of quasicrystals and in the phase transition between crystalline and quasicrystalline phases of an alloy. Let us present a simple example illustrating a transformation of a quasicrystalline structure into a periodic structure via a special phason strain. Consider the physical space rotated due to a phason strain such that the new slope is a rational number, which approximates the initial slope $1/\tau$ (Figure 1.3 (b)). The new slope may be 1/1, 1/2, 2/3, 3/5, or 5/8 ... (ratio of successive Fibonacci numbers). The intersection of the rotated physical space with the atomic surfaces results in a periodic sequence. For example, an X_{\parallel} -axis with a slope of 2/3 cuts the atomic surfaces yielding the sequence LSLLSLSLSLSL..., which has a periodic repetition of **LSLLS.** The resulting sequence is known as the 3/2 rational approximant of the Fibonacci sequence. Similarly, 1/1, 2/1, 5/3, and 8/5 rational approximants of the Fibonacci sequence repeating unit cells LS, LSL, and LSLLSLSL, respectively, revealing that the higher the order of the approximant the more similar it is to the corresponding quasicrystalline structure. The approximants are useful to model the local structure and to determine the physical properties of quasicrystals (see Ref. [50] for a review).

1.2 Stability and Structural Models

One and a half decades have passed since the discovery of quasicrystals with a tremendous effort to find a cause behind the physical origin of quasicrystals. There are two distinct approaches proposed so far to explain the stability of quasicrystals. The first approach is based on an energetic stabilization, the second on an entropic stabilization [49]. Depending on the specific quasicrystalline phase, one of these approaches reflects the dominant mechanism of stability. Similarly, different structural models have been proposed to explain the unique properties of quasicrystals.

Energetic and Entropic Stabilization

The energetic stabilization of quasicrystals can be interpreted in terms of a perfect Penrose tiling picture. The key idea is that the edge-matching rules of the Penrose tiling could reflect local rules to attain a minimal binding energy. However, many quasicrystals are stable only at high temperature and convert into crystalline phases at low temperature [51, 52]. One should thus expect that entropy may be responsible for stabilizing the quasicrystalline phases. The entropic stabilization can be described in terms of random tilings. The basic idea of the random tilings is that the edge-matching rules of the Penrose tiling are completely discarded and the tiles are allowed to join randomly to fill the space without gaps. The randomness induces topological disorder (topological entropy) in the system. The randomization of tilings may not be the only source of entropy. The entropy can be induced by chemical disorder (chemical entropy). If the chemical entropy is dominant, the structure can be topologically ordered even at high temperature. Joseph *et al.* have shown theoretically that Ni-rich *d*-Al-Ni-Co with a perfect tiling is stable only above 800 °C [53], which is also confirmed experimentally [54, 55].

Electronic Stabilization

An alternative possibility to explain the energetic stability of quasicrystals may be electronic stabilization. Electronic properties and stoichiometry observed in many quasicrystals indicate that a Hume-Rothery type mechanism of intermetallic compounds may play an important role in the stability of quasicrystals [3, 56]. The Hume-Rothery mechanism states that a specific structure of alloy is formed for a fixed effective density of valence electrons (e/a, electron-peratom ratio) in such a way that the Fermi surface matches the Brillouin zone boundary opening a pseudo gap [57, 58], which lowers the energy of the system.

In fact, almost all stable icosahedral quasicrystals are found to have a specific value of e/a(~ 2.1 for the Zn-Mg-Al class and ~ 1.75 for the Al-TM class, where TM refers to transition metals) [3] satisfying the condition of gap opening at Fermi level, i.e., $Q = 2k_F$ (where Q is the magnitude of reciprocal lattice vector and k_F the radius of the Fermi sphere) [3, and find references therein]. In many quasicrystals, a pseudogap at the Fermi level has been observed theoretically and experimentally [2, and find references therein] supporting the Hume-Rothery type mechanism for many icosahedral phases. Although the value of e/a is fixed for icosahedral quasicrystals, it varies in a significant wide range for decagonal quasicrystals [3].

Perfect Quasiperiodic Tiling Model

Geometrically constructed quasiperiodic tilings show many features similar to those observed in quasicrystals such as non-crystallographic orientational symmetry and perfect long range. The tiling is a suitable starting point in modeling the structure of quasicrystals. In a structural model based on a rhombic Penrose tiling, atoms are organized into two distinct clusters or tiles, the skinny and fat rhombi. The edge-matching rules of the Penrose tiling could be enforced by the energetic preference of parts of clusters to properly match across tiling edges.

Random Tiling Model

In the random tiling model, two different types of tiles are considered as basic building blocks as in the perfect tiling model. But unlike in the perfect tiling model, where a strict edge-matching rule is followed, the random tiling model allows the tiles to join their edges randomly, keeping the occurrence frequencies fixed due to fixed concentration of elements in the alloy. Obviously, randomness allows to form several degenerate states (configurations) including ones that are periodic and disordered. Henley has shown that the state (configuration) having maximum entropy has an average decagonal symmetry and a long range quasiperiodic order [59].

Most quasicrystals exhibit some degrees of disorder. Extremely few quasicrystals, in particular the Ni-rich phase of *d*-Al-Ni-Co, are known to reveal almost a perfect quasiperiodic ordering [54, 60, 61]. Therefore, the random tiling model is appropriate for the majority of quasicrystalline phases. This model also accounts for the experimentally observed diffuse scattering, as the diffraction pattern of the random tilings have sharp Bragg peaks in addition to some diffuse background [47].

Cluster Model

An alternative picture of quasicrystals is the covering picture. A single repeating cluster can be used to cover the space in quasiperiodic order, provided that the clusters can overlap or neighboring clusters can share the atoms (first introduced by Burkov in 1991) [62]. In the cluster model, the formation of quasicrystals can be explained in a similar fashion as the periodic crystal in the sense that only a single type of low energy cluster is used to close-pack a macroscopic structure. The cluster is analogous to the unit cell in a periodic crystal, hence termed 'quasi-unit cell' and the cluster model is sometimes called quasi-unit cell model.

Indeed, clusters of decagonal shape have been observed in high-resolution transmission electron microscopy (HRTEM) in many decagonal phases [63, and find references therein], and most of the theoretical structural models of the decagonal quasicrystals are also based on a single decagonal overlapping cluster [55, 62, 64-69]. Similarly, icosahedral quasicrystals are believed to be made up of Mackay clusters [63]. Scanning tunneling microscopy of 2-fold and 5-fold surfaces of *i*-Al-Pd-Mn shows the aggregation of Mackay-type clusters [14, 15]. Furthermore, the cluster approach is suitable to interpret some physical properties of quasicrystals, especially the dynamical properties of *i*-Al-Pd-Mn and *d*-Al-Ni-Co measured by Neutron scattering [70-72] and electrical and thermal properties [73, and find references therein].

The cluster picture of decagonal quasicrystals is very closely related to the Penrose tiling picture. It has been shown that a rhombic Penrose tiling can be equivalently produced by using a single decagonal tile with an overlapping rule, instead of edge-matching rule [37, 74, 75]. Further developments have been made by H. C. Jeong and P. J. Steinhardt in this respect [37, 75]. They have shown that a perfect Penrose tiling can be uniquely produced by maximizing the density of some suitably chosen atomic clusters having minimum energy configuration, discarding the overlapping rules. These clusters are in a one-to-one correspondence with the decagonal cluster. This new approach is physically relevant to explain the formation of quasicrystals because the constraint of cluster overlapping rules or the constraint of atomic decoration of the clusters does not have to be considered.

The concept of random tiling can be introduced also in the cluster approach. Some constraints of the cluster overlapping rules of the perfect quasiperiodic covering are abandoned to yield a randomly ordered quasiperiodic structure (refer to [76] for details). The resulting structure is entropically stabilized similarly as the random tilings.

1.3 Decagonal Quasicrystals

Soon after the discovery of icosahedral quasicrystals, varieties of 2D quasicrystals were found (see [3, 77] for review). The 2D quasicrystals have periodic ordering along one direction and qua-



Figure 1.4: A macroscopic view of decagonal quasicrystal, which is formed by a periodic staking of quasiperiodic planes along the 10fold axis. Two inequivalent 2-fold planes perpendicular to the 10-fold planes are shaded.

sicrystalline ordering in the plane perpendicular to the periodic direction. The quasicrystalline plane can possess pentagonal, octagonal, decagonal, or dodecagonal symmetry. The influence of both quasicrystalline and crystalline ordering on the physical properties of quasicrystals can be investigated in a single sample of the 2D quasicrystals, which is not possible in case of icosahedral quasicrystals exhibiting quasicrystalline ordering in all directions. In fact, some physical properties of decagonal quasicrystals show a strong anisotropy along the periodic and quasicrystalline directions [73].

Decagonal quasicrystals, which possess a unique 10-fold rotational axis along the periodic direction and two inequivalent sets of 2-fold axis perpendicular to the 10-fold axis (see Figure 1.4), are the most studied 2D quasicrystals because of the availability of thermodynamically stable, large, and high quality samples. A variety of periodicities has been observed along the 10-fold axis. Mainly, three groups of decagonal quasicrystals with a basic periodicity of 4 Å (Al-Co-Cu type), 12 Å (Al-Mn type), and 16 Å (Al-Fe-Pd type) have been found [77]. Decagonal Al-Ni-Co, the structure of which is discussed in this thesis, consists of two sets of quasicrystalline planes stacked alternatingly along the 10-fold axis. The distance between the planes is approximately 2 Å yielding a basic 4 Å periodicity [40, 64].

Al-Ni-Co alloys have attracted much attention due to the existence of various types of quasicrystalline and approximant structures observed in a wide composition range. They possess at least eight different types of quasicrystalline phases, namely basic Ni-rich (bNi), type I superstructure (I), S1 superstructure (S1), type II superstructure (II), basic Co-rich (bCo), one dimensional quasicrystal (1D), pentagonal (5f), and pentagonal with superstructure (5f_{HT}) (abbreviation after Ref. [78]). A cut through the phase diagram is shown in Figure 1.5. A brief

States	Periodicity	Tiling	Tiling Type
Basic Ni-rich	4 Å	pentagonal	$\operatorname{perfect}$
S1 superstructure	8 Å	pentagonal	random
Type I superstructure	8 Å	rhombic	random
Type II superstructure	8 Å	pentagonal and rhombic	random
Basic Co-rich	8 Å	pentagonal	random
One dimensional	8 Å	pentagonal and rhombic	random
Pentagonal	8 Å	pentagonal	random
Pentagonal with superstructure	8 Å	rhombic	random

Table 1.1: Different phases of Al-Ni-Co with their periodicities and tiling.

explanation of some of these phases is presented here (refer to Ref. [78] for details).

Among the eight states listed, the first five show a diffraction pattern of 10-fold symmetry perpendicular to the periodic direction, while the pentagonal states possess a 5-fold symmetric diffraction pattern. The quasicrystalline ordering along one direction within the 10-fold plane transforms to crystalline ordering, forming a one dimensional quasicrystal state. As such, the 1D state is an intermediate state between the quasicrystalline and approximant phases. Both pentagonal and one dimensional states are closely related to the decagonal phases.

The HRTEM of the Ni-rich basic structure reveals that clusters of 20 Å diameter are located at the vertices of a perfect pentagonal Penrose tiling [54, 60, 61], while the clusters show some chemical disorder. In contrast, the cluster centers of the other phases form a random rhombic (Penrose) tiling of different variants and the clusters are chemically ordered.

Diffraction patterns of all phases except the basic Ni-rich structure show diffuse layers underneath the Bragg planes perpendicular to the periodic direction as well as half-way in between these planes, corresponding to an 8 Å periodicity [52, 79-84]. These diffuse layers are due to positional and orientational disorder of the columnar clusters [80, 85]. Other decagonal quasicrystals also exhibit such diffuse scattering [81, 86]. The intensity of the 8 Å periodic layers increases with increasing Co content and finally converts into sharp spots with quasicrystalline ordering. Different phases with their periodicities and tiling for the cluster centers are summarized in Table 1.1.



Figure 1.5: Phase diagram of Al-Ni-Co alloy from Ritsch *et al.* [78].

1.3.1 Indexing of the Diffraction Pattern

Five basis vectors are needed to generate a reciprocal lattice of decagonal quasicrystals. The diffraction vector \mathbf{H}^{\parallel} can be obtained by,

$$\mathbf{H}^{\parallel} = \sum_{j=1}^{5} h_j \mathbf{b}_j, \qquad (1.10)$$

where h_j are integers, $\mathbf{b}_j = b(\cos \frac{2\pi j}{5}, \sin \frac{2\pi j}{5}, 0)$ for j = 1, ..., 4 and $\mathbf{b}_5 = b_5(0, 0, 1)$ with $b = |\mathbf{b}_j|$ (j = 1, ..., 4) and $b_5 = |\mathbf{b}_5|$. The vectors \mathbf{b}_j (j = 1, ..., 4) are the in-plane vectors pointing from the center to four vertices of a regular pentagon, while \mathbf{b}_5 is along the periodic direction (Figure 1.6).

A set of five indices $(h_1h_2h_3h_4h_5)$ is assigned to each diffraction spot. The set $(h_1h_2h_3h_4h_5)$ is called generalized Miller indices, which are used to label the orientation of lattice planes as in



Figure 1.6: The projection of the 5D reciprocal basis vectors into the physical space (left) and perpendicular space (right).



Figure 1.7: The indexing scheme of a decagonal quasicrystal. The circles denote the position of diffraction spots generated by $\mathbf{H}^{\parallel} = \sum_{j=1}^{5} h_j \mathbf{b}_j$. The four of the five independent vectors $\mathbf{b}_j = b(\cos\frac{2\pi j}{5}, \sin\frac{2\pi j}{5}, 0)$ (j = 1, ..., 4) shown by solid lines with arrow head are the in-plane basic vectors, while the fifth vector (00001) is along the periodic direction (here, perpendicular to the plane of the paper). The vector ($\overline{11}\overline{11}\overline{10}$) is sum of the four vectors \mathbf{b}_j (j = 1, ..., 4) and not an independent basis vector.

the case of periodic crystals. The plane perpendicular to the vector [00001] has 10-fold symmetry and is referred as the (00001) plane. Similarly, the two inequivalent 2-fold planes perpendicular the vectors [10000] and [10110] are referred as (10000) and (10110) planes, respectively (see Figure 1.7). The vectors \mathbf{b}_j (j = 1, ..., 5) can be regarded as the physical space projections of the reciprocal basis vectors \mathbf{d}_j^* (j = 1, ..., 5) of a 5D periodic lattice given by,

$$\mathbf{d}_{j}^{*} = b \begin{pmatrix} \cos \frac{2\pi j}{5} \\ \sin \frac{2\pi j}{5} \\ 0 \\ \cos \frac{6\pi j}{5} \\ \sin \frac{6\pi j}{5} \end{pmatrix}, j = 1, \dots, 4; \qquad \mathbf{d}_{5}^{*} = b_{5} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \qquad (1.11)$$

where b and b_5 are the lattice constants of the 5D space. The physical and perpendicular space projections of $\mathbf{d}_i^* = (\mathbf{b}_j, \mathbf{b}_j')$ are shown in Figure 1.6.

1.3.2 Superstructure in *d*-Al-Ni-Co

As in periodic crystals, superstructure reflections in quasicrystals appear with weak intensity as compared to the intensity of main reflection. They are not indexable with integer indices with respect to the basis vectors of the main reflections. Several types of superstructures have been identified in both decagonal [87-89] and icosahedral quasicrystals [90]. Decagonal Al-Ni-Co phases exhibit three different types of superstructures: S1, type I, and type II. Decagonal $Al_{71.8}Ni_{14.8}Co_{13.4}$, which was investigated in this study, possesses the type I superstructure at room temperature.

For the type I superstructure, the physical space components \mathbf{s}_j of the reciprocal basis vectors of the 5D superlattice are rotated by $\frac{\pi}{10}$ and contracted by a factor 2 cos $\frac{\pi}{10}$ with respect to the physical space components of the normal basis vectors. They can be related by $\mathbf{b}_j = \sum_i S_{ij} \mathbf{s}_i$ with,

$$S = \begin{bmatrix} 1 & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & -1 & 0 \\ 1 & 1 & 2 & 1 & 0 \\ -1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}.$$
 (1.12)

Since the determinant of the matrix S is 5, the reciprocal lattice spanned by \mathbf{s}_j , $\mathbf{H}^{\parallel} = \sum_j h_j^s \mathbf{s}_j$



Figure 1.8: The physical space components of the normal and superstructure basis vectors of *d*-Al-Ni-Co.

can be divided into five sublattices satisfying the conditions $\sum_j h_j^s = 0$, $\sum_j h_j^s = \pm 1$, and $\sum_j h_j^s = \pm 2$. The sublattice with $\sum_j h_j^s = 0$ corresponds to the main reflections, while $\sum_j h_j^s = \pm 1$ and $\sum_j h_j^s = \pm 2$ represent superlattice reflections named S1 (first order) and S2 (second order) spots, respectively.

The type I superstructure phase exhibits both S1 and S2 spots, while the S1 superstructure state shows S1 spots and possibly much weaker S2 spots. The S1 spots appear around all strong reflections forming a decagon. Both S1 and S2 superstructure spots take $\frac{1}{5}$ -integer indices with respect to the basis vectors of the normal phase. At high temperature, the type I superstructure state undergoes a phase transition to the S1 superstructure state (see Figure 1.5).

Another type of superstructure observed in *d*-Al-Ni-Co is the so-called type II superstructure [89]. In this type, strong reflections are surrounded by a ring of pentagons. The pentagon is formed by five superstructure spots (new type, neither S1 nor S2) at the corners and a S1 spot at the center. The new spots are indexable with $\frac{1}{2}$ -integer indices with respect to the normal basis vectors.

1.3.3 Atomic Structure of *d*-Al-Ni-Co

The main building blocks of the *d*-Al-Ni-Co quasicrystals are columnar clusters. The cluster centers are located at the vertices of a periodic stacking of Penrose tilings. These cluster centers can be generated by decorating the unit cell of the 5D periodic lattice by atomic surfaces and taking the appropriate 3D cut.



Figure 1.9: Penrose pattern generated by the section method, (a) Rhombic Penrose pattern and (b) Pentagonal Penrose pattern. Atomic surfaces of corresponding Penrose pattern are shown on the top of each pattern. Among the four pentagonal atomic surfaces, the smaller 1st and 4th have an equal radius of $\lambda_{1,4} = \frac{2}{5\tau^2 b}$. The radius of large pentagons (2nd and 3rd) is τ times larger than $\lambda_{1,4}$, i.e. $\lambda_{2,3} = \frac{2}{5\tau b}$. The 1st and 3rd pentagons have similar orientation and are related to the 2nd and 4th by inversion symmetry.

A model determining the structure of *d*-Al-Ni-Co proposed by Yamamoto *et al.* [66] is presented here, what successfully explains the observed superstructure (Type I). The model is based on the fact that clusters of 20 Å diameter are located at the vertices of a rhombic Penrose pattern of 20 Å edge length [66].

A rhombic Penrose pattern of edge length 20 Å can be generated by four types of pentagonal atomic surfaces (see Figure 1.9) located at the points $\pm(i,i,i,i,1.25)/5$ (i = 1, 2) of the 5D unit cell. The 5D basis vectors are given by,

$$\mathbf{d}_{j} = \frac{2}{5b} \begin{pmatrix} \cos\frac{2\pi j}{5} - 1\\ \sin\frac{2\pi j}{5}\\ 0\\ \cos\frac{6\pi j}{5} - 1\\ \sin\frac{6\pi j}{5} \end{pmatrix}, j = 1, \dots, 4; \qquad \mathbf{d}_{5} = \frac{1}{b_{5}} \begin{pmatrix} 0\\ 0\\ 1\\ 0\\ 0 \end{pmatrix},$$
(1.13)



Figure 1.10: Atomic structure of *d*-Al-Ni-Co projected along the periodic direction obtained by the 5D superstructure model [66]. The clusters of 20 Å diameter are located at the vertices of a rhombic Penrose pattern of edge length 20 Å (solid lines). Dark and gray solid circles denote transition metals and Al, receptively. The large circles represent the atoms in the layer at z = 0 and the small circles at z = c/2.

where b^{-1} (= 11.67 Å) and b_5^{-1} (= 4.081 Å) are the lattice constants of the 5D lattice. The corresponding reciprocal basis vectors of \mathbf{d}_j are \mathbf{d}_j^* given by Equation 1.11.

The atom positions around the vertices of the Penrose tiling are generated by placing two independent occupation domains at 20 different points of the 5D unit cell (see Ref. [66] for details about occupation domains and their coordinates). The resulting atomic structure projected along the 10-fold axis is shown in Figure 1.10.

The structure is made up of two types of atomic layers with stacking sequences AB (A represents the layer at z = 0 and B the layer at c/2, with c = 4 Å (lattice constant along the periodic direction). The cluster in each layer has pentagonal symmetry. The cluster in the

layer A is rotated by 36° with respect to the cluster in the layer B yielding an overall decagonal symmetry.

One of the columnar clusters projected along the 10-fold axis is marked by full circles in Figure 1.10. It consists of ten rings surrounding the inner wheel-like atomic arrangement. The neighboring two clusters overlap in two ways. First, they share the outer two rings (C and D) if the center-to-center distance is equal to the edge length of the Penrose pattern (L = 20 Å). Secondly, they share some of the atoms of the inner wheel (E and F) if the center-to-center distance is equal to the skinny rhombus (S = $L/\tau = 12.36$ Å)

In the normal phase of *d*-Al-Ni-Co, the clusters are located at the vertices of a pentagonal Penrose tiling of 20 Å edge length [66, and find references therein], while the atomic distribution in the cluster is the same for both phases. The pentagonal Penrose tiling can be generated from the 5D space decorated with a single decagonal atomic surface per unit cell as opposed to four pentagons for the case of the rhombic tiling [40]. The atomic positions of the normal phase are generated by two independent occupation domains, placed at 20 points of the 5D unit cell (refer to [66] for details).

The Diffraction Pattern

To calculate the diffraction patterns of the structures presented in the preceding section, a starting point is to evaluate the diffraction of the rhombic (and pentagonal) Penrose pattern. It can be obtained via the Fourier transform of the density distribution $\rho(\mathbf{r})$ of the 5D lattice decorated with pentagonal (and decagonal) atomic surfaces. The Fourier components of the 5D lattice can be separated into the product terms depending on the 3D physical space components and 2D perpendicular space components of the 5D reciprocal lattice vector. The physical space component contains the information of the usual atomic scattering factor and the temperature factor, while the perpendicular space components involve the Fourier transform of the atomic surfaces and the term describing the phason fluctuation.

The structure factor $F(\mathbf{H})$ is the Fourier transform of $\rho(\mathbf{r})$ and is expressed as [5],

$$F(\mathbf{H}) = \int_{UC} \rho(\mathbf{r}) e^{2\pi i \mathbf{H} \mathbf{r}} d\mathbf{r} = \sum_{k=1}^{n} T_k(\mathbf{H}) f_k(\|\mathbf{H}\|) e^{2\pi i \mathbf{H} \mathbf{r}_k}, \qquad (1.14)$$

where the factor $f_k(||\mathbf{H}||)$ can be decomposed into the atomic scattering factor $f_k(||\mathbf{H}|||)$ and the Fourier transform of the atomic surface $g_k(\mathbf{H}^{\perp})$ (k denotes the atomic surface and runs from 1 to

The dotted- and

Figure 1.11: Fourier amplitude

dashed-curves represent the Fourier amplitudes along the high symmetry directions of the decagonal atomic surface, the solid curve is the envelop function. $||\mathbf{H}_{\perp}||$ is normalized by a lattice parameter b.

versus $\|\mathbf{H}^{\perp}\|$.



$$F(\mathbf{H}) = \sum_{k=1}^{n} T_k(\mathbf{H}^{\parallel}, \mathbf{H}^{\perp}) f_k(\|\mathbf{H}^{\parallel}\|) g_k(\mathbf{H}^{\perp}) e^{2\pi i \mathbf{H} \mathbf{r}_k}, \qquad (1.15)$$

with

$$T_k(\mathbf{H}^{\parallel}, \mathbf{H}^{\perp}) = e^{-2\pi^2 \mathbf{H}^{\parallel T} \mathbf{B}^{\parallel} \mathbf{H}^{\parallel}} \times e^{-2\pi^2 \mathbf{H}^{\perp T} \mathbf{B}^{\perp} \mathbf{H}^{\perp}}, \qquad (1.16)$$

(**B** is the mean-square-displacement matrix), and

$$g_k(\mathbf{H}^{\perp}) = \frac{1}{A_{UC}^{\perp}} \int_{A_k} e^{2\pi \mathbf{H}^{\perp} \mathbf{r}^{\perp}} d\mathbf{r}^{\perp}, \qquad (1.17)$$

 $(A_k \text{ is the area of } k^{th} \text{ atomic surface and } A_{UC}^{\perp} \text{ is the area of the 5D unit cell projected onto perpendicular space}). A_{UC}^{\perp} \text{ is calculated by,}$

$$A_{UC}^{\perp} = \frac{4}{25b^2} [(7+\tau)\sin\frac{2\pi}{5} + (2+\tau)\sin\frac{4\pi}{5}].$$
 (1.18)

The Fourier transform of the pentagonal (or decagonal) atomic surface can be obtained by summing the Fourier transform of five (or ten) triangles forming the pentagon (or decagon).



Using the standard formula of the Fourier transform of a triangle, $g_k(\mathbf{H}^{\perp})$ can be obtained by,

$$g_k(\mathbf{H}^{\perp}) = \frac{1}{A_{UC}^{\perp}} \sin \frac{2\pi}{5} \sum_{j=0}^m \frac{A_j(e^{iA_{j+1}\lambda_k} - 1) - A_{j+1}(e^{iA_j\lambda_k} - 1)}{A_jA_{j+1}(A_j - A_{j+1})}$$
(1.19)

where j runs over 5 (and 10) triangles of the pentagon (and decagon) and $A_j = 2\pi \mathbf{H}^{\perp} \mathbf{e}_j$ with,

$$\mathbf{H}^{\perp} = b \sum_{j}^{m} h_{j} \begin{pmatrix} 0\\0\\0\\\cos\frac{6\pi i}{5}\\\sin\frac{6\pi i}{5} \end{pmatrix}$$
(1.20)

In the simplified case which excludes the effect of temperature and considers the identical atomic scattering factor, $f_k(||\mathbf{H}^{||}||)=1$, the intensity (I) depends only upon the Fourier transform of the atomic surfaces,

$$I \propto |g_k(\mathbf{H}^\perp)|^2 \tag{1.21}$$

The Fourier amplitudes of the decagonal atomic surface along the two high symmetry directions are shown in Figure 1.11. The envelope function of the Fourier amplitudes gives the average damping with \mathbf{H}^{\perp} . In principle, Fourier amplitudes corresponding to all \mathbf{H}^{\perp} contribute to the diffraction intensities and fill the reciprocal space infinitely densely. But the diffraction intensities for larger \mathbf{H}^{\perp} are extremely weak and are not experimentally detectable, which makes it possible to distinguish individual spots.

Until now, the diffraction pattern of the cluster centers is discussed without taking account of individual atoms in the cluster. To include the contribution of individual atoms, Fourier amplitudes of 20 occupation domains have to be considered, which modulate the intensity of diffraction spots but do not change their position.

The diffraction pattern obtained by the 5D superstructure model includes main, S1 and S2 spots (one can refer to Ref. [66] for the diffraction pattern). The intensity of the S2 spots is weaker than that of the S1 spots [91]. X-ray diffraction also shows that S2 spots are relatively weak [88].

Summary

Fundamental examples of quasiperiodic structure, the Fibonacci sequence and the Penrose pattern, were presented. The Fibonacci sequence illustrates quasiperiodic structure in 1D, the Penrose tiling in 2D. These basic structures show discrete diffractions pattern without having periodicity demonstrating a long range order. The diffraction pattern of the Penrose pattern is very similar to the diffraction pattern observed in 2D quasicrystals. The section method to derive a quasicrystalline structure in physical space from higher dimensional periodic lattice was discussed. A simple example illustrating the generation of a Fibonacci sequence from a 2D periodic lattice was given. In addition, different models for the structure and the stability of quasicrystals were briefly discussed.

The phase diagram of Al-Ni-Co alloys was illustrated. Depending on temperature and exact alloy composition, Al-Ni-Co exhibits several different decagonal phases. Decagonal phases are 2D quasicrystals consisting of a periodic staking of quasicrystalline planes along the 10-fold axis. The samples used in this work belong to the type I superstructure phase. As revealed by transmission electron microscopy, the structure of this phase can be explained in terms of a random tiling. Its diffraction pattern shows S1 and S2 superstructure spots. The atomic structure can be derived from a 5D decorated lattice and exhibits 20 Å diameter clusters located at the vertices of a rhombic Penrose tiling of 20 Å edge length.

The presented indexing scheme and other properties of the diffraction pattern of decagonal quasicrystals play an important role in the discussion of the experimental results of electron and He diffraction of the 10-fold d-Al-Ni-Co surface in Chapter 3. The tilings and clusters will be illustrated in scanning tunneling microscopy images of the same surface. The discussed features of the diffraction pattern of the Fibonacci lattice are reflected in the diffraction of the 2-fold d-Al-Ni-Co(10000) surface given in Chapter 4.

Chapter 2

Experimental Methods

In this chapter, theoretical aspects and the experimental set up of He atom scattering (HAS), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM) are discussed. All three techniques are capable of determining the structure of single crystal surfaces. The diffraction experiments determine the symmetry and dimension of unit cell as well as the scattering centers in the unit cell via the angular and intensity distributions of diffraction beams. Tunneling microscopy, on the other hand, directly probes the surface in real space and provides information on local morphology in atomic scale in contrast to diffraction, which relies on long range order of the surface.

Helium atom scattering is a powerful tool to investigate exclusively the topmost surface layer. In this technique, the surface is probed by neutral He atoms with a very low kinetic energy (10-65 meV). Helium atoms in this energy range have a de Broglie wave length comparable to the lattice spacing. Scattered He atoms thus exhibit interference effects. Due to the very low kinetic energy of the He atoms, the surface is probed nondestructively. Furthermore, HAS is a useful technique to investigate imperfections on the surfaces. Because of the large He atom scattering cross section of all kinds of defects like adatoms, vacancies, etc., their presence on the surface causes a significant decrease in the intensity of the reflected He atom beam. This technique is also capable of providing information on step heights and terrace widths. Apart from these investigations by elastic He scattering, low energy surface vibrations can be studied by inelastic He scattering.

Low energy electron diffraction is the most common technique used in single crystal surface



Figure 2.1: A schematic diagram elucidating the different nature of He atoms and electron scattering from the crystal surfaces. Electrons penetrate several Angstroms into the surface and undergo multiple scattering, whereas He atoms are reflected well above the surface [93].

investigations. In LEED electrons of energy 50-200 eV are used as a probe. In contrast to the He atoms reflecting well above the surface (2-3 Å) [92] due to the repulsive force of the electron cloud of the surface atoms, electrons penetrate a few atomic layers into the sample before being scattered from the atom potentials (see Figure 2.1), therefore yielding information about a few topmost monolayers.

Scanning tunneling microscopy was developed by G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel [94] in the eighties. This technique is based on the principle of quantum mechanical tunneling of electrons between a sharp tip and a surface, where the tunneling starts at a tipsurface separation of a few Angstroms. While scanning the tip across the sample surface, the tunneling current is measured, mapping the local electron density of the surface. STM and HAS can be considered as complementary techniques in the sense that the former gives information of the topmost layer in real space and the latter in reciprocal space.

There are many books and review articles published on all three techniques. References [95-97] deal with theoretical and experimental aspects of He atom scattering, while the recent article by Farías *et al.* [92] gives a review of the diffractive phenomena on surfaces studied by He diffraction. One can refer to Ref. [98, 99] for details about low energy electron diffraction. The fundamental principle and application of scanning tunneling microscopy is cited in Ref. [100].
2.1 Helium Atom Scattering

2.1.1 Theoretical Aspects of Elastic Scattering

Atom-Surface Potential

In describing atom scattering from surfaces, an atom-surface potential has to be established. The atom-surface potential can be divided into two parts, a long range attractive potential due to Van der Waals forces dominating at large separation and a short range repulsive potential arising from the exchange force (the Pauli principle), when the electron cloud of the atom overlaps with the valence electron density extending out of the solid. A qualitative picture of the atom-solid potential can be obtained by summing over the binary interaction potential between the incoming atom and individual atoms of the solid. Figure 2.2 shows the resulting atom-surface potential. The classical turning points of atoms impinging on a surface atom (B) are farther out compared to that of atoms coming in between them (A). This is reflected in a periodic modulation of the repulsive potential. The classical turning points form an equipotential surface described by the corrugation function $\zeta(\mathbf{R})$, where **R** denotes the vector in the surface plane.

The periodic modulation of the repulsive potential reflects the density of valence electrons



Figure 2.2: A schematic diagram illustrating the interaction of neutral atoms with a solid surface. The left shows the equipotential lines in term of depth of potential well (D) and the right displays the potential versus z, the direction perpendicular to the surface plane [101].



Figure 2.3: Definition of scattering geometry. For the in-plane scattering configuration, $\phi_i = \phi_f$.

of the surface atoms. For He atoms with energies less than 100 meV, a good approximation to the repulsive potential (V_{rep}) is [102]

$$V_{rep} = \alpha \rho(\mathbf{r}), \tag{2.1}$$

with $\rho(\mathbf{r})$ the electron density and α constant. In fact, alkali halides surfaces, which have highly localized valence electrons are experimentally found to have a high corrugation, while the metallic surfaces, where the valence electrons are smeared out parallel to the surface, have a very low corrugation (see for example [92]).

Diffraction Conditions

Consider a beam of He atoms with mass m and energy E_i impinging on a surface at an angle θ_i with surface normal. The de Broglie wavelength (λ_i) of atoms with energy E_i is given by,

$$\lambda_i = \frac{h}{\sqrt{2mE_i}}, \quad \lambda_i/\text{\AA} = \frac{4.57}{\sqrt{E_i/\text{meV}}}, \quad (2.2)$$

h being Planck's constant. In diffraction experiments, He atoms with energy 10-65 meV are used so that λ_i ranges from 1.4 Å to 0.6 Å, which is comparable to the lattice spacing. The wave vector \mathbf{k}_i of the impinging atoms relates to the wavelength λ_i by,

$$k_i = |\mathbf{k}_i| = \frac{2\pi}{\lambda_i}.\tag{2.3}$$

For in-plane scattering ($\phi_i = \phi_f$, see scattering geometry in Figure 2.3), the incident wave vector \mathbf{k}_i can be decomposed into parallel and perpendicular components as,

$$\mathbf{k}_{i} = (\mathbf{K}_{i}, k_{iz}) \quad \text{with} \quad |\mathbf{K}_{i}| = k_{i} \sin \theta_{i}, \ k_{iz} = -k_{i} \cos \theta_{i}, \tag{2.4}$$



Figure 2.4: Ewald construction for elastic scattering from the 2D surface lattice. The point of intersection of the Ewald sphere (here circle) with the vertical rods determines the final wave vector \mathbf{k}_{f} . (a) for the scattering geometry with fixed θ_i and variable θ_f and (b) for fixed $\theta_i + \theta_f$, where both θ_i and θ_f are varied (see text in Section 2.2 for details).

z being perpendicular to the surface plane.

Two conditions have to be fulfilled for elastic scattering, the energy conservation,

$$k_i^2 = k_f^2 = K_f^2 + k_{fz}^2, (2.5)$$

and the parallel momentum conservation,

$$\mathbf{K}_i + \mathbf{G} = \mathbf{K}_f, \tag{2.6}$$

where $\mathbf{k}_f = (\mathbf{K}_f, k_{fz})$, with $|\mathbf{K}_f| = k_f \sin \theta_f$, $k_{fz} = -k_f \cos \theta_f$, is the wave vector of outgoing atom and $\mathbf{G} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2$ (n_1 , n_2 are integers) is a surface reciprocal lattice vector, which is related to the unit cell vectors \mathbf{a}_1 and \mathbf{a}_2 by

$$\mathbf{a}_{i}.\mathbf{b}_{j} = 2\pi\delta_{ij}, \ (i, j = 1, 2).$$
 (2.7)

Equation 2.6 is the Bragg condition in two dimensions. The conditions given by Equations 2.5 and 2.6 can be represented graphically by the Ewald construction as shown in Figure 2.4.

Experimentally, the parallel momentum transfer (Δk_{\parallel}) is probed either by varying θ_f keeping θ_i fixed or by varying both θ_f and θ_i keeping $\theta_f + \theta_i$ fixed. For either case,

$$\Delta k_{\parallel} = k_i (\sin \theta_f - \sin \theta_i). \tag{2.8}$$

The value of the lattice constant a is determined from the n^{th} order diffraction peak by

$$\Delta k_{\parallel} = k_i (\sin \theta_f - \sin \theta_i) = \frac{2\pi}{a} n.$$
(2.9)

Calculation of Diffraction Intensity

Once the atom-surface model potential V(r) is established, the scattering amplitudes or intensities can be evaluated by solving the Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r).$$
 (2.10)

The exact solution of the Schrödinger equation for a rigid periodic potential can be obtained by various methods (refer to [103] for a review). Here, some approximation methods, which are relevant to determining a corrugation function from diffraction data, are presented.

Hard Corrugated Wall (HCW) Method

The most convenient and physically plausible approximation method is the Hard Corrugated Wall (HCW), which was first introduced by Garibaldi *et al.* [104] in 1975. This method assumes the surface is an infinitely hard corrugated wall with the atom-surface potential expressed as,

$$V(\mathbf{R}, z) = \begin{cases} 0 & \text{for } z > \zeta(\mathbf{R}) \\ \infty & \text{for } z \le \zeta(\mathbf{R}) \end{cases}.$$
 (2.11)

The following assumptions about the atom-surface interaction potential are made in this method: (a) The attractive part of the potential is neglected. This assumption is reasonable if the energy of the incoming atoms is much larger than the attractive well depth $(E_i \gg D)$. For He surface potentials, the value of D is normally between 5-10 meV [92], which is much less than the energy of He atoms in a room temperature (~ 60 meV). Hence, a room temperature He atoms beam satisfies the condition. For $E_i \sim D$, the attractive part can no longer be neglected because this case leads to the resonant scattering or selective adsorption (see Ref. [96] for selective adsorption), which will strongly influence the diffraction intensities. However, if selective adsorption does not play a major role, the HCW method can be still used to calculate the diffraction intensities by employing a simple correction in θ_i and k_i [92, and find references therein],

$$\sin \theta_i' = \frac{|\mathbf{k}_i|}{|\mathbf{k}_i'|} \sin \theta_i = \frac{\sin \theta_i}{\sqrt{1 + \frac{D}{E_i}}}.$$
(2.12)

Further assumptions are:

- (b) The slope of the steeply rising part of the potential is assumed to be infinite.
- (c) Lattice vibrations are neglected i.e. surface atoms are considered to be at rest.

Based on the HCW approach, several methods have been developed to calculate the diffraction intensities (for review see [96]).

Rayleigh Approximation

Consider a wave function $\psi(\mathbf{r})$ as proposed by Rayleigh [105], which assumes the incoming and outgoing waves are plane waves up to the surface. The total wave function is the wave function of incoming atoms plus the sum of plane waves of diffracted atoms,

$$\psi(\mathbf{R}, z) = e^{i[\mathbf{K}_i \cdot \mathbf{R} + k_{iz} z]} + \sum_{\mathbf{G}} A_{\mathbf{G}} e^{i[(\mathbf{K}_i + \mathbf{G}) \cdot \mathbf{R} + k_{fz}(\mathbf{G}) z]},$$
(2.13)

where $A_{\mathbf{G}}$ is the scattering amplitude and the summation extends over a finite set of \mathbf{G} vectors corresponding to a finite number of propagating waves (for which k_{fz} is real, i.e., $k_{fz}^2 = k_i^2 - |\mathbf{K} + \mathbf{G}|^2 > 0$) and a infinite number of exponentially decaying waves (for imaginary k_{fz} i.e. $k_{fz}^2 = k_i^2 - |\mathbf{K} + \mathbf{G}|^2 < 0$). The intensity $P_{\mathbf{G}}$ of the propagating waves is calculated from the scattering amplitude by,

$$P_{\mathbf{G}} = \frac{|k_{fz}|}{|k_{iz}|} |A_{\mathbf{G}}|^2.$$
(2.14)

The intensities satisfy the unitary condition,

$$\sum_{\mathbf{G}} P_{\mathbf{G}} = 1. \tag{2.15}$$

To determine $A_{\mathbf{G}}$, the boundary condition $\psi(\mathbf{R}, z = \zeta(\mathbf{R})) = 0$ is used in Equation 2.13, which gives,

$$0 = e^{ik_{iz}\zeta(\mathbf{R})} + \sum_{\mathbf{G}} A_{\mathbf{G}} e^{i[\mathbf{G}\cdot\mathbf{R} + k_{fz}(\mathbf{G})\zeta(\mathbf{R})]}.$$
(2.16)

Multiplication of Equation 2.16 by $e^{-ik_{iz}\zeta(\mathbf{R})}$ leads to,

$$\sum_{\mathbf{G}} A_{\mathbf{G}} M_{\mathbf{G},\mathbf{R}} = -1, \qquad (2.17)$$

with

$$M_{\mathbf{G},\mathbf{R}} = e^{i[\mathbf{G},\mathbf{R}+(k_{fz}(\mathbf{G})-k_{iz})\zeta(\mathbf{R})]}.$$
(2.18)

 $A_{\mathbf{G}}$ can be obtained by solving Equation 2.17. Different methods can be employed to solve the equation. Among them the GR method and the eikonal approximation are widely used.

The GR Method: The GR method was first proposed by García [106]. The idea of the GR method is that Equation 2.17 can be solved numerically by taking certain discrete values of **R** distributed uniformly in the surface unit cell and the same number of **G** vectors uniformly distributed in reciprocal space so that the equation converts into a finite number of linear equations, which can be solved by matrix inversion. This method gives convergent solutions only for certain conditions. For instance, it is convergent for a 1D sinusoidal corrugation function of period a, $\zeta(x) = \frac{\zeta_m}{2} \sin \frac{2\pi x}{a}$, (ζ_m is the maximum corrugation amplitude) if $\zeta_m \leq 0.14 a$.

Eikonal Approximation: An alternative method to solve Equation 2.16 is the eikonal approximation, which is based on the assumption that for small \mathbf{G} $(G < k_i)$, the term $e^{ik_{fz}(\mathbf{G})\zeta(\mathbf{R})}$ is a slowly varying function of \mathbf{G} and can be taken out from the summation. Under this assumption, Equation 2.16 takes the form

$$\sum_{\mathbf{G}} A_{\mathbf{G}} e^{i\mathbf{G}.\mathbf{R}} = -e^{\left[(k_{iz}-k_{fz})\zeta(\mathbf{R})\right]},$$
(2.19)

and $A_{\mathbf{G}}$ can be evaluated,

$$A_{\mathbf{G}} = -\frac{1}{S} \int_{u.c.} e^{-i\mathbf{G}.\mathbf{R}} e^{i[(k_{iz}-k_{fz})\zeta(\mathbf{R})]} d\mathbf{R}, \qquad (2.20)$$

(S denotes the area of unit cell). $A_{\mathbf{G}}$ is simply the Fourier transform of a phase factor whose argument is the product of the known corrugation function and the perpendicular momentum transfer. For simple corrugation profiles Equation 2.20 can be solved analytically.

The eikonal approximation excludes multiple scattering and does not satisfy the unitary condition (Equation 2.15). However, the intensities calculated by this method can be very close to the exact calculation for suitable systems. Reasonable results can be obtained for $\zeta_m < 0.1 a$ and $\theta_i < 45^{\circ}$ [96].

The methods to calculate diffraction intensities explained so far consider the atoms at rest. In reality, thermal vibrations and the quantum mechanical zero-point motion of surface atoms leads to inelastic scattering reducing the diffraction intensities without changing the peak profiles. The influence of inelastic scattering is accounted for by multiplying the intensity (Equation 2.14) by a Debye-Waller factor,

$$F_{DW} = e^{-2W}$$
 with $W = \frac{1}{2} \langle (\mathbf{u} \cdot \Delta \mathbf{k})^2 \rangle,$ (2.21)

where $\Delta \mathbf{k} = \mathbf{k}_f - \mathbf{k}_i$, \mathbf{u} is the displacement of atoms from their equilibrium position, and $\langle \ldots \rangle$ denotes thermal averaging.

The GR and eikonal approximation methods give procedures to get diffraction intensities from a given corrugation function. In practice, the corrugation has to be determined from the experimental diffraction intensities. The direct inversion of experimental data is not possible because the phase information is lost in the measured intensities. Therefore, one has to follow a trial and error method. The Fourier amplitudes of $\zeta(\mathbf{R})$, which best fit the calculated and experimental data can be searched by monitoring the reliability factor,

$$R = \frac{1}{N} \sqrt{\sum_{\mathbf{G}} (P_{\mathbf{G}}^{Cal} - P_{\mathbf{G}}^{Exp})^2}.$$
 (2.22)

2.1.2 Theoretical Aspects of Inelastic Scattering

Kinematics

During the phonon inelastic scattering of atoms from a periodic surface, the parallel momentum and the energy exchange takes place between the system and the incoming atoms due to phonon creation and annihilation. The dynamical theory requires the conservations of parallel momentum and the energy of the entire system. With energy and parallel momentum transfers ΔE and $\Delta \mathbf{K}$, respectively, energy and the momentum conservation can be expressed as,

$$\Delta E = E_f - E_i = \frac{\hbar^2 k_f^2}{2m} - \frac{\hbar^2 k_i^2}{2m} = \hbar \omega(\mathbf{Q}), \qquad (2.23)$$

and

$$\Delta \mathbf{K} = \mathbf{K}_f - \mathbf{K}_i = \mathbf{Q} + \mathbf{G}, \quad \text{with} \quad |\mathbf{K}_f| = k_f \sin \theta_f, \ |\mathbf{K}_i| = k_i \sin \theta_i, \tag{2.24}$$

where $\omega(\mathbf{Q})$ is the phonon frequency and \mathbf{Q} is the phonon momentum. A negative value of $\hbar\omega(\mathbf{Q})$ ($\Delta E < 0$) corresponds to phonon creation and a positive value ($\Delta E > 0$) to phonon



Figure 2.5: A set of scan curves for He scattering with fixed $\theta_i + \theta_f = 90^\circ$ (dashed curves) and a possible Rayleigh mode dispersion curve (solid curve) in an extended zone plot.

annihilation. Similarly, a negative value of ΔK is referred to "backward-directed phonons" and a positive value to "forward-directed" phonons. Combination of Equations 2.23 and 2.24 yields

$$\frac{\Delta E}{E_i} = \left(\frac{\sin\theta_i + \Delta K/k_i}{\sin\theta_f}\right)^2 - 1.$$
(2.25)

The plot of ΔE versus ΔK is a parabola with origin at $(-E_i, -K_i)$ and the curvature of the parabola depends on k_i , θ_i and θ_f (see Figure 2.5). The plot is called scan curve, which is very useful to explain some important features of phonon excitations.

The intersections of the scan curve with the dispersion curves determine the values of ΔE at which the maxima are expected in the energy loss (or gain) spectra. As can be seen from Figure 2.5, a single scan curve in general intersects the dispersion curve in more than one point. This implies that it is possible to observe phonon creation/annihilation with backwarddirected/forward-directed peaks in a single spectrum. The width of the phonon peak depends on the angle of intersection of the scan curve and the dispersion curve in addition to intrinsic width and broadening due to other experimental parameters. The spectra taken at particular angles θ_i have phonon peaks with optimum resolution if the scan curves corresponding to those θ_i intersect the dispersion curve at a right angle. The peaks are very broad at critical angles (θ_i^c) at which the two curves intersect tangentially (indicated by arrows in the figure). A small change in θ_i from θ_i^c either causes the disappearance of peaks or generates two overlapping peaks. This mechanism is called kinematical focusing (first introduced in Ref. [107]). Furthermore, the scan curves passing through the first Brillouin zone cut the dispersion curves more steeply in the annihilation-backward or creation-forward quadrants, therefore probing the dispersion curve in these regions normally gives more pronounced phonon peaks.

Diffraction Intensity

Experimentally observed inelastic intensities due to single phonon scattering can be compared with the differential reflection coefficient $d^2 R/dE_f d\Omega_f$, which is defined as the probability that a particle impinging on the surface is scattered with final energy E_f into the solid angle Ω_f . The differential reflection coefficient calculated with a potential obtained by a summation of pairwise interaction between the impinging particle and the surface atoms is given by [103, 108, 109],

$$\frac{d^2 R}{dE_f d\Omega_f} = \frac{L^4}{(2\pi\hbar)^3} \frac{m^2 |\mathbf{k}_f|}{k_{iz}} \frac{2\pi S_{u.c.}}{\hbar} |v_0 \langle k_{fz}| e^{-\beta z} |k_{iz} \rangle|^2 e^{-\frac{Q^2}{Q_c^2}} e^{-2W}$$

$$\cdot \sum_{\alpha\alpha'}^3 q_\alpha q_{\alpha'}^* [\rho^{\alpha,\alpha'}(-\mathbf{Q},\omega)n^+(\mathbf{Q},\omega) + \rho^{\alpha,\alpha'}(\mathbf{Q},\omega)n^-(\mathbf{Q},\omega)], \qquad (2.26)$$

where $\rho^{\alpha,\alpha_{t}}(\pm \mathbf{Q},\omega)$ is the phonon spectral density, $v_{0}e^{-\beta z}$ is the repulsive part of the atomic pair potential (Born-Mayer potential), and $\mathbf{q} = (i\mathbf{Q},\beta)$.

The term $e^{-\frac{Q^2}{Q_c^2}}$ represents the "cut-off factor". Single phonon excitation by He atoms is limited to certain values of frequencies and momentums ("cut-off" effect) because He atoms, which are rather heavy and slow as compared to other probes like electrons, cannot excite phonons with high energy and short wavelength. Quantum mechanically, the cut-off is not absolute but characterized by a rapid decay of single phonon intensity. The cut-off frequency Q_c and the cut-off momentum $\hbar\omega_c$ for He scattering are typically $Q_c = 2$ Å and $\hbar\omega_c = 30 - 50$ meV [110]. The term ω_c is accounted for in the spectral density term $\rho^{\alpha,\alpha'}(\pm \mathbf{Q},\omega)$.

The temperature dependence of inelastic intensity is reflected by two terms, the Bose factor [93],

$$n^{\pm}(\mathbf{Q},\omega) = \frac{1}{2} [\cot h \frac{\hbar\omega}{2k_B T} \pm 1], \qquad (2.27)$$

(+ and - denote phonon creation and annihilation, k_B is the Boltzmann constant), and the Debye-Waller factor,

$$2W = 24 \frac{m}{M} \frac{E_{iz}}{k_B \theta_D} \frac{T}{\theta_D},$$
(2.28)

where θ_D is the surface Debye-temperature, E_{iz} the energy corresponding to the z-component of the incident wavevector, T the surface temperature, and M the mass of surface atoms. Single phonon scattering is dominant over multiple phonons if 2W < 1 [111].

2.1.3 Surface Phonons and Time-of-flight Technique

Since surface atoms have fewer neighbors than the bulk atoms, the restoring forces of surface atoms are different from those of bulk atoms. One should thus normally expect the vibration of surface atoms to have different frequencies than those of bulk atoms. The surface vibration states lie either in the surface-projected bulk band-gap or are degenerate with the bulk states. Different vibration modes have been identified on crystal surfaces (see [112] for review). One of them is the Rayleigh mode. The Rayleigh waves propagate along the surface with the polarization vector (direction of displacement of atoms) lying in the sagittal plane (the plane defined by the surface normal and propagation direction of the wave). In the Rayleigh mode, the displacement of atoms decays exponentially with distance from the surface into the bulk. At the long wave length limit, the frequency of Rayleigh waves propagating along a given direction is proportional to the length of its 2D wave vector in the surface plane. The Rayleigh mode was first predicted



Figure2.6:Aschematicdiagramof a surface phonon mea-surement using inelasticHe scattering with timeof flight analysis.

by Lord Rayleigh in 1887 on a semi-infinite, isotropic, elastic medium [113].

Since the Rayleigh modes are well separated from the bulk modes and the energy and momentum of these modes match those of He atoms, study of these modes by inelastic He scattering is possible. The time-of-flight (TOF) technique is used to measure the surface phonon dispersion. A schematic diagram of the TOF setup is shown in Figure 2.6. A highly monochromatic He beam is pulsed by a mechanical chopper and scattered from the sample surface. The inelastically scattered He atoms gain (or lose) energy due to phonon annihilation (or creation) and cause time-shifted peaks at the detector. The energy and parallel momentum exchanges (ΔE and ΔK) corresponding to inelastic phonon peaks is calculated from the time shift $\Delta t = t - t_e$ (t_e being the chopper-to-detector elastic flight time) and other experimental parameters. ΔE and ΔK can be expressed as,

$$\Delta E = E_i [(1 + \frac{d_{cd}\Delta t}{d_{td}t_e})^{-2} - 1], \qquad (2.29)$$

and

$$\Delta K = k_i \left[\left(1 + \frac{d_{cd}\Delta t}{d_{td}t_e} \right)^{-1} \sin \theta_f - \sin \theta_i \right], \tag{2.30}$$

where d_{cd} is the chopper-to-detector distance and d_{td} is the target-to-detector distance. A full set of points in $(\Delta E, \Delta K)$ space (a dispersion curve) is obtained by taking a set of spectra at different scattering angles θ_i and/or different He energies E_i .

The measured TOF spectra (intensity versus flight time) sometimes have to be converted into energy spectra (intensity versus energy exchange). The conversion always distorts the shape of the spectra because of the nonlinear relation of t and ΔE (see Equation 2.29). The creation peaks are more pronounced than annihilation peaks in the energy spectra (see [93, 114] for the derivation of scaling factors).

2.1.4 Experimental Setup

A schematic view of the experimental chamber used for the present work is shown in Figure 2.7 and important parameters of the apparatus are listed in Table 2.1. A He beam generated in the source chamber is directed towards the scattering chamber (SC) and the beam scattered from the surface of the sample is detected by a mass spectrometer. The angle between the incoming and outgoing beam is fixed at 90° and the parallel momentum transfer is probed by rotating the sample normal to the scattering plane. A brief description of the three main parts, the source



Α drawing of experimental chamber for He diffraction (B1 expansion chamber, chopper chamber, SC : scattering chamber, DI-DII : detector

chamber, the scattering chamber, and the detector chamber is presented below.

Source Chamber: A highly monochromatic He beam is produced by supersonic free jet expansion from a high pressure (10-100 bar) He gas through a tiny nozzle with a diameter 5 μ m. During expansion, the randomly distributed velocities of atoms are converted into a uniform velocity v_s directed radially outward from the nozzle. The energy of the beam is determined by the nozzle temperature T_0 ,

$$\frac{1}{2}mv_s^2 = \frac{5}{2}k_B T_0. (2.31)$$

The typical experimental range of T_0 is 30-300 K ($v_s = 600-1800$ m/s, $\lambda_i = 1.4-0.6$ Å). The lower temperature is achieved by a He refrigerator attached to the source. The full-width at half-maxima (FWHM) of the velocity distribution centered at v_s is determined by a characteristic speed ratio S defined by,

$$S = \frac{\frac{1}{2}mv_s^2}{k_BT} = \sqrt{\frac{5T_0}{2T}},$$
(2.32)

where T is the temperature of thermal motion of the atoms in the beam, which ideally turns to zero due to the supersonic expansion. The FWHM (Δv) is related to S by [115],

$$\frac{\Delta v}{v_s} \sim \frac{1.65}{S}.\tag{2.33}$$



Figure 2.8: A schematic drawing of the vacuum system used in the He diffraction chamber shown in Figure 2.7. (T : turbo pump, D : diffusion pump, S : sublimation pump, RT : root pump, and R : rotary pump).

The value of S depends on the stagnation pressure P_0 and nozzle diameter d. Therefore, for an optimal velocity resolution, a system with a suitable combination of pressure, nozzle diameter and pumping speed is needed. The value of $\Delta v/v_s$ with the experimental parameters listed in Table 2.1 is ~ 2%.

The monochromatic beam is collimated by a skimmer and then passed though an aperture (normally 0.6 mm) to achieve the angular resolution. The beam is then passed though the differential pumping units, which further reduces the undesired components of helium. For the time of flight measurements, the collimated beam is pulsed by a chopper before entering into the scattering chamber (chopper chamber: BII in Figure 2.7).

The He beam produced by this method has a disadvantage. Its velocity distribution contains a broad [93, 114], very low intensity tail with Maxwellian distribution, which creates a problem in the phonon measurements. The He atoms from the tail yield elastic diffraction peaks which appear in the TOF spectra as additional peaks. These peaks are called deceptons [93, 114]. Since the intensity of these peaks is often comparable to that of the phonon peaks, it is difficult to distinguish them from the true phonon peaks without calculation. With the known experimental parameters, these peaks can be explicitly evaluated (see [93, 114]).

Scattering Chamber: The scattering chamber is equipped with the devices necessary to prepare and characterize the surface, such as LEED and a sputter gun. An ultra high vacuum is maintained (base pressure 2×10^{-10} mbar) in the chamber with high speed pumps and the residual gas is monitored by a mass spectrometer. The chamber is fitted with a manipulator which has three rotational degrees of freedom (θ , ϕ , and tilt) and three translation degrees of freedom (x, y, and z). The sample can be mounted on the manipulator through a load lock. The use of the load lock avoids the need to bake the chamber each time after mounting a new sample.

Detector Chamber: The detector chamber consists of three differential pumping stages. The differential pumping stages are used to reduce the He partial pressure. The detector chamber provides a longer flight path for the scattered atoms yielding a better energy resolution of the time of flight spectra. The scattered He atoms are ionized by an electron bombardment ionizer prior to entering into the mass spectrometer. The mass spectrometer signal is amplified by an electron multiplier and is fed to the computer.

Transfer Width and Time-of-flight Resolution

In diffraction experiments, the width of diffraction peaks is limited by the transfer width (W) of the apparatus. For the scattering geometry shown in Figure 2.3, W can be expressed as [95, 116],

$$W = \frac{\lambda}{\sqrt{(\Delta_{\theta} \cdot \theta_f)^2 \cos^2 \theta_f + (\sin \theta_i - \sin \theta_f)^2 \frac{(\Delta E)^2}{E^2}}},$$
(2.34)

where Δ_{θ} is the angular spread due to the source and the detector and $(\Delta E)^2$ is the energy spread. For the specular beam $(\theta_i = \theta_f)$, the energy spread term vanishes such that it does not contribute in the broadening of the specular peak. With the experimental parameters listed in Table 2.1, the transfer width of our instrument is ~ 100 Å.

In a time-of-flight measurement, the total flight time t_{tof} is the sum of the contributions coming from four different parts of the apparatus,

$$t_{tof} = t_{chop} + t_{ct} + t_{td} + t_{ion}, (2.35)$$

Source	Nozzle diameter	$5 \ \mu m$		
	Nozzle pressure	$\leq 100 \text{ bar}$		
	Nozzle temperature	30-300 K		
	He beam energy	$10-65 \mathrm{meV}$		
	He beam velocity	600-1800 m/s		
	Relative velocity spread $(\Delta v/v_s)$	$\sim 2\%$		
Chopper	Slit diameter	15-17 cm		
	Slit width	0.5 mm		
	Disk rotational frequency	$\sim 80 \text{ Hz}$		
	Shutter function	$\sim 12 \ \mu s$		
	Number of slits	8		
Dimensions	Source-target distance	$\sim 50 \text{ cm}$		
	Target-detector distance	79.8 cm		
	Chopper-target distance	$35.8 {\pm} 0.2$		
	Source-target-detector angle (fixed)	$90{\pm}0.25^{\circ}$		
Detector	Ionization volume	$15 \times 7.5 \times 11 \text{ mm}^3$		
	Channel width MCA	$1 \mu { m s}$		
	Dynamic range	$\sim 5 \times 10^5$		
Resolution	Polar angle	$\sim 0.25^{\circ}$		
	Energy resolution	$\sim \pm 0.2 \text{ meV}$		
	Transfer width	\sim 100 Å		
Pressure	Source (expansion) chamber (BI)	10^{-7} mbar (without helium)		
		10^{-4} mbar (with helium)		
	Chopper chamber (BII)	10^{-8} mbar (without helium)		
		10^{-6} mbar (with helium)		
	Scattering chamber (PC)	10^{-10} mbar (without helium)		
		10^{-9} mbar (with helium)		
	Detector chamber (DI-DIII)	10^{-10} mbar (without helium)		
		10^{-10} mbar (with helium)		

 Table 2.1: A list of important experimental parameters.

where the first term is a finite opening time of the chopper slit, t_{CT} the flight time from chopper to target, t_{td} the flight time from target to detector, and the last term is the time lapses by He atoms in the ionizer before detection. All four terms contribute in the broadening of phonon peaks. The overall spread in time can be calculated by [93],

$$\Delta t_{tof} = \sqrt{\Delta t_{chop}^2 + \Delta t_{ct}^2 + \Delta t_{td}^2 + \Delta t_{ion}^2}.$$
(2.36)

All terms except the third one can be simply calculated from the dimensions of the apparatus. The third term is associated with energy and angular spread (refer to [93, 110, 117] for detail). From the total time spread Δt_{tof} , the total energy width can be obtained by,

$$\delta(\Delta E) = \frac{\partial \Delta E}{\partial t_{tof}} \Delta t_{tof} = -2E_i (1 + \frac{\Delta E}{E_i})^{3/2} \frac{\Delta t_{tof}}{t_{cd}^e}.$$
(2.37)

This implies that the energy width of phonon peaks in a spectrum is narrower for the creation peaks ($\Delta E < 0$) than the annihilation peaks ($\Delta E > 0$) provided that Δt_{tof} is similar for $\Delta E < 0$ and $\Delta E < 0$.

2.2 Spot Profile Analyzing Low Energy Electron Diffraction

Kinematics Approximation of Low Energy Electron Diffraction

The de Broglie wave length of electrons is related to the incident energy E_i by

$$\lambda_i/\text{\AA} = \sqrt{\frac{150.4}{E_i/\text{eV}}}.$$
(2.38)

In diffraction experiments, normally electrons with energies of 50-200 eV ($\lambda_i = 1.7 - 0.8$ Å) are used. The mean free path of the electrons in this energy range is a few Angstroms, such that the electrons penetrate a few atomic layers into the solid and undergo multiple scattering (see Figure 2.1). Therefore, one has to consider these multiple scattering events explicitly to evaluate the diffraction intensities. The kinematic approximation, which considers only single scattering, yields part of the information of the LEED pattern, namely the size and symmetry of the unit cell [118, 119].

Consider electrons with initial wave vector \mathbf{k}_i scattered from the surface with final wave vector \mathbf{k}_f . Assuming the incoming and outgoing electrons as plane waves, the diffraction from

the surface is normally described by a sum of scattered wave functions by all surface atoms at position \mathbf{r}_n [120],

$$\psi(\mathbf{k}, \mathbf{k}_i) = \sum_n f_n(\mathbf{k}, \mathbf{k}_i) e^{i\mathbf{k}\mathbf{r}_n}, \qquad (2.39)$$

where $\mathbf{k} = \mathbf{k}_i - \mathbf{k}_f$ is the scattering vector and $f_n(\mathbf{k}, \mathbf{k}_i)$ is the structure factor, which combines the electron waves coming from the surface atom at \mathbf{r}_n and all atoms of the underlying column.

The diffraction intensity is calculated by,

$$I(\mathbf{k}, \mathbf{k}_i) = |\psi(\mathbf{k}, \mathbf{k}_i)|^2 = \sum_{n,m} f_m(\mathbf{k}, \mathbf{k}_i) f_n^*(\mathbf{k}, \mathbf{k}_i) e^{i\mathbf{k}(\mathbf{r}_n - \mathbf{r}_m)}.$$
(2.40)

Within the kinematic approximation, all structure factors $f_n(\mathbf{k}, \mathbf{k}_i)$ are replaced by an identical structure factor $f(\mathbf{k}, \mathbf{k}_i)$ so that these factors can be taken out of the summation. Then, the intensity $I(\mathbf{k}, \mathbf{k}_i)$ simply splits up into two factors

$$I(\mathbf{k}, \mathbf{k}_i) = F(\mathbf{k}, \mathbf{k}_i)G(\mathbf{k}), \qquad (2.41)$$

with the dynamical form factor

$$F(\mathbf{k}, \mathbf{k}_i) = |f(\mathbf{k}, \mathbf{k}_i)|^2, \qquad (2.42)$$

and the lattice factor or interference factor,

$$G(\mathbf{k}) = \sum_{n,m} e^{i\mathbf{k}(\mathbf{r}_n - \mathbf{r}_m)}.$$
(2.43)

The dynamical form factor $F(\mathbf{k}, \mathbf{k}_i)$ contains the information of the arrangement of atoms within the unit cell and multiple scattering events of all kinds, whereas the lattice factor $G(\mathbf{k})$ includes the information on arrangement of unit cells. Since the lattice factor $G(\mathbf{k})$ depends only on the scattering vectors \mathbf{k} and the position vectors \mathbf{r}_n , it can be easily calculated. Thus, the kinematic approximation is sufficient to determine the arrangement of scattering units.

Experimental Details of Spot Profile Analyzing Low Energy Electron Diffraction

An instrument for quantitative spot profile analysis of low energy electron diffraction (SPA-LEED) was developed by Scheithauer *et al.* in 1986 [121]. A schematic view of a SPA-LEED is shown in Figure 2.9. An electron beam generated by an electron gun is scattered from the sample surface and detected by a Channeltron single electron detector. The incident angle of the electron beam is varied by using an electrostatic deflection unit, as opposed to rotating the



Figure 2.9: A schematic drawing of spot profile analyzing low electron diffraction instrument.

sample or detector. The geometrical angle between the electron gun and the detector is fixed at 4°. The instrument is also equipped with a florescent screen as in the case of conventional LEED apparatus.

The SPA-LEED instrument has many advantages over conventional LEED. A dynamic range of 10^6 is achieved by the use of a Channeltron. Employing an electrostatic field, the angle of incidence can be varied more smoothly than in the case of mechanical rotation of the sample or detector. A determination of the lattice parameter with an accuracy of up to 0.02 Å is possible. Because of the large transfer width of the instrument, morphological features can be determined up to a scale of 2000 Å [120]. Since the scattering geometry fixes the angle between incident and final wave vectors, variation of the incident angle rotates the Ewald sphere around the origin of the reciprocal space. The radius of the modified Ewald sphere (sphere with solid boundary line in Figure 2.4(b)) is twice the radius of the Ewald sphere. The larger diameter of the modified Ewald sphere, in principle, offers a larger area of reciprocal space accessible to the measurements.

For the present work, a commercial Omicron SPA-LEED (transfer width larger than 1000 Å, angular spread at 95 eV of 0.08° and energy resolution of 0.1 eV) was used.

2.3 Scanning Tunneling Microscopy

Technical Basic

The scanning tunneling microscope uses an atomically sharp, normally metallic tip. The tip is mounted on a system of piezoelectric drives, which allows controlled movements in three directions with an accuracy on an atomic scale and is brought very close to the surface under investigation. At a separation of a few Angstroms, the electronic states close to the Fermi level of the sample and of the tip overlap. Upon application of a small bias voltage (V) between the tip and the sample, electrons start to tunnel though the vacuum barrier due to the quantum mechanical tunneling effect. The tunneling current I_T depends exponentially on the tip-surface separation d. For a small bias voltage and low temperature, I_T is

$$I_T \propto \frac{V}{d} e^{-2kd},\tag{2.44}$$

where $2k/\text{Å}^{-1} = 1.025\sqrt{\phi/eV}$, with ϕ the average work function of sample and tip [100]. The exponential dependence implies that the tunneling current is extremely sensitive to the tip-sample separation, which provides a high resolution perpendicular to the surface (up to hundredths of an Ångstrom).

The scanning tunneling microscope can be operated in two modes, the constant current mode and the constant height mode. In constant current mode, the tip is scanned across the surface with constant tunneling current. The constant current is maintained during scanning by using an electronic feedback loop, which adjusts the vertical distance between the tip and the surface with a feedback voltage. The feedback voltages is plotted as a function of the lateral scan position in a computer, mapping the surface morphology. In constant height mode, the tip is moved in a horizontal plane above the surface and the tunneling current is recorded. This mode of scan is faster than the constant current mode providing an opportunity to study dynamical processes on the surface. However, this mode is only applicable for atomically flat surfaces because scanning with constant height on rough surfaces crashes the tip.

Theoretical Basis

The tunneling current can be evaluated within Bardeen's formalism [100],

$$I_T = \frac{2\pi e}{\hbar} \sum_{\mu\nu} [f(E_\mu)\{1 - f(E_\nu + eV)\} - f(E_\nu + eV)\{1 - f(E_\mu)\}] |M_{\mu\nu}|^2 \delta(E_\mu - E_\nu), \quad (2.45)$$

where f(E) is the Fermi function, V sample bias voltage, $M_{\mu\nu}$ the tunneling matrix element between the unperturbed electronic states of the tip ψ_{μ} and those of the sample ψ_{ν} , and E_{μ} (E_{ν}) the energy of the state ψ_{μ} (ψ_{ν}). The matrix element $M_{\mu\nu}$ can be obtained as

$$M_{\mu\nu} = \frac{\hbar^2}{2m} \int (\psi^*_{\mu} \Delta \psi_{\nu} - \psi_{\nu} \Delta \psi^*_{\mu}) \cdot d\mathbf{S}.$$
(2.46)

The matrix element can be derived explicitly if the wave functions of tip and the surface are known. But, the shape of the tip is unknown in practice. Therefore, a model wave function of the tip has to be assumed. Further explanations of the model tip wave functions and the derivation of the tunneling current are given in Ref. [100].

Chapter 3

The 10-fold *d*-Al-Ni-Co Surface

This chapter begins with a short review on investigations of clean surfaces. Then, the results of our experiments on the 10-fold d-Al_{71.8}Ni_{14.8}Co_{13.4} surface by three different techniques, spot profile analyzing low energy electron diffraction (SPA-LEED), He atom scattering (HAS), and Scanning tunneling microscopy (STM) are discussed.

Early work in the field of quasicrystal surfaces mainly focused on surface preparation, determination of surface composition, and characterization of clean surfaces of *i*-Al-Pd-Mn (see [6, 20] for a review). Recently, there have been several reports on decagonal quasicrystal surfaces, especially on the 10-fold surface of *d*-Al-Ni-Co. These investigations reveal that the surfaces obtained strongly depend on the specific preparation methods. As in periodic crystals, sputter-annealing and cleaving in UHV have been employed to prepare quasicrystal surfaces. Sputter-annealing can produce high quality surfaces suitable for various surface sensitive techniques including the extremely surface sensitive He atom scattering [19, 33, 122]. The surfaces prepared by this method often show terrace-step structures. Scanning tunneling microscopy of these surfaces reveals a typical corrugation of several tenths of an Angstrom and terrace widths up to several hundred Angstroms [6, and find references therein]. Diffraction techniques like X-ray photoelectron diffraction (XPD), low energy electron diffraction, and He atom scattering show that terraces possess a perfect long range, quasicrystalline order. The terraces closely reflect the structure of underlying bulk [6, also see Sections 3.1, 3.2, and Chapter 4].

There has been a great effort to resolve atomic structures of sputter-annealed surfaces by scanning tunneling microscopy. The first experiments were reported by Kortan *et al.* in 1990.

They investigated the 10-fold surface of d-Al-Cu-Co [16, 17] and observed atomically flat, wide terraces separated by steps of bulk expected height. The observed structure within the terraces was explained in terms of tiling models. Schaub *et al.* reported the first STM study of icosahedral quasicrystals. They found that the 5-fold surface of *i*-Al-Pd-Mn exhibits flat terraces with some pentagonal holes and stars. The steps are of two different heights forming a part of a Fibonacci sequence.

Recent reports on the 5-fold surface of *i*-Al-Pd-Mn by Barbier *et al.* [19], on the 5-fold surface of *i*-Al-Cu-Fe by Cai *et al.* [123], the 10-fold surface of *d*-Al-Ni-Co by McGrath *et al.* [20] and the 10-fold and 2-fold surfaces of *d*-Al-Ni-Co by Kishida *et al.* [18] also show very flat surfaces with 5-fold and/or 10-fold motives. However, atomic resolution of the images of these surfaces is not far better than previous results. Barbier *et al.* [19] found three different step heights scaled with each others by τ in contrast to the previous observation of two different heights. Kishida *et al.* [18] have detected a very low density of interlayer phason defects on the 2-fold *d*-Al-Ni-Co surface. In the present investigations of the 10-fold *d*-Al-Ni-Co surface by low temperature STM, a random (Penrose) tiling is identified on a large area of the surface (see Section 3.3).

3.1 Spot Profile Analyzing Low Energy Electron Diffraction

Surface Preparation and Measurement Conditions

A large grain d-Al_{71.8}Ni_{14.8}Co_{13.4} sample grown by the Czochralski method [124] was cut perpendicular to the 10-fold axis. After polishing the surface by diamond paste, the sample was attached directly on a resistive heater by using tantalum foil and mounted in the experimental chamber (base pressure 1×10^{-10} mbar after bake out). The surface was prepared by several cycles of sputtering and annealing. The sample was sputtered (Ne⁺, 1.5 kV and 6 μ A) for 30 minutes and subsequently annealed for 15-25 minutes at 600-650 °C. The sample was cooled to 95 K during measurements to reduce inelastic scattering (Debye Waller attenuation).

SPA-LEED images of the clean surface were taken at different electron energies. Sharp electron diffraction patterns at the above described sputter-annealing conditions were obtained in a energy range of 40-80 eV. As-measured SPA-LEED images are distorted at large k-values due to non-linearities of the deflection unit used in the SPA-LEED apparatus [120]. The asmeasured images are re-scaled using the known k-values of the diffraction spots obtained in He diffraction. All SPA-LEED images presented here are after re-scaling.

Results and Discussion

A SPA-LEED image recorded at 65 eV electron energy is shown in Figure 3.1, top. The spatial and intensity distribution of the diffraction spots reveals a perfect 10-fold symmetry. The spots which are equidistant from the specular spot (the central brightest spot) have an equal intensity and lie on the corners of a regular decagon. Thus the rotation of the diffraction pattern by $2\pi/10$ around the axis perpendicular to the plane of paper and passing through the specular spot (i.e., the 10-fold axis) transforms it into itself revealing a 10-fold symmetry. The diffraction pattern contains two sets of inequivalent 2-fold axes perpendicular to the 10-fold axis, which appear alternatingly at every 18°. Detailed studies of the surfaces perpendicular to these two inequivalent 2-fold axes will be presented in the next chapter.

Apart from these 10-fold and 2-fold symmetries, the SPA-LEED image exhibits self-similar patterns. For example, distributions of spots forming pentagons A-A', B-B', and C-C' are selfsimilar (Figure 3.2). Proper scaling of each pattern produces another. The scaling factor is related by the golden mean τ , which is related to the pentagonal symmetry (the ratio between the center-to-vertex-distance and center-to-midedge-distance of a regular pentagon is equal to $\tau/2$). The areas of the pentagons A, B, C, A', B', and C' have the ratio $\tau^4 : \tau^3 : \tau^2 : \tau^2 : \tau^1 : \tau^0$.

The SPA-LEED images (Figures 3.1 and 3.2) display densely distributed spots. The appearance of dense spots is a special feature of quasicrystals. More than 500 diffraction spots have been observed in the range of $\mathbf{k}_{||} < 3$ Å⁻¹. Diffraction patterns of non-reconstructed surfaces of periodic crystals would show much fewer spots (only around 20) in this range.

An additional sharp spot is observed very close to the specular (marked by a black square in Figure 3.4). This is the specular spot of a secondary grain present in the sample and not related to the diffraction from the main grain. Few diffraction spots associated with the secondary grain have been observed close to the strong diffraction spots of the main grain.

The diffraction patterns display very sharp spots. The spots are as sharp as those observed in the diffraction patterns of periodic crystal surfaces. The full-width at half-maxima (FWHM) of the specular spot is ~ 0.02 Å⁻¹. The corresponding real space dimension of the FWHM is around 300 Å, which is in the same order of magnitude of the transfer width of the SPA-LEED



Figure 3.1: A SPA-LEED image (logarithmic gray scale of electron intensity) of the 10-fold surface of d-Al_{71.8}Ni_{14.8}Co_{13.4} recorded at 65 eV electron energy (top). The position of strong spots are shown by circles (bottom). The bulk reciprocal basis vectors $\mathbf{b}_j = b \left(\cos \frac{2\pi j}{5}, \sin \frac{2\pi j}{5}, 0\right)$ $(j = 1, \ldots, 4 \text{ and } b = 1.02 \text{ Å}^{-1})$ are used to index the diffraction pattern. The fifth vector $(\bar{1}\bar{1}\bar{1}\bar{1}\bar{1}0)$ is sum of the four vectors \mathbf{b}_j $(j = 1, \ldots, 4)$ and not an independent basis vector.



Figure 3.2: A SPA-LEED image (gray scale) of the 10-fold surface of d-Al_{71.8}Ni_{14.8}Co_{13.4} recorded at 75 eV electron energy (left) and the calculated diffraction pattern (right). The pentagons demonstrate self-similar patterns.

instrument. The sharpness of the diffraction spots is evidence of a long range order in the surface region.

Positions of diffraction spots are related by the golden mean, revealing a perfect quasicrystalline ordering. The diffraction vectors of individual spots will be presented later. For the moment, consider the positions of the strong spots marked by circles in Figure 3.1, bottom. The strong spots are on the circles with radii of 0.63 Å⁻¹, 1.02 Å⁻¹, 1.65 Å⁻¹, 1.95 Å⁻¹, 2.67 Å⁻¹, and 3.15 Å⁻¹. The radii are related to each other by $\tau^{-1} : \tau^0 : \tau^1 : \tau\chi : \tau^2 : \tau^2\chi$, where χ is an irrational number and given by $\chi = 2 \sin \frac{\pi}{5} = \sqrt{3 - \tau} = 1.1755...$ As the golden mean, the constant χ is related to the pentagonal geometry. It is equal to edge-to-radius ratio of a regular pentagon.

Five independent vectors \mathbf{b}_j (j = 1, ..., 5) are needed to index the bulk diffraction pattern [40, 64]. Among these five, the four vectors $\mathbf{b}_j = b \left(\cos \frac{2\pi j}{5}, \sin \frac{2\pi j}{5}, 0\right)$ (j = 1, ..., 4 and $b = 1.02 \text{ Å}^{-1}$) are within the quasiperiodic plane and form the basis vector of the reciprocal lattice of the surface. The fifth vector $\mathbf{b}_5 = b_5(0, 0, 1)$ $(b_5 = 0.78 \text{ Å}^{-1})$ is along the periodic direction (here perpendicular to the plane of paper in the figures) and can be neglected in the discussion of diffraction from the 10-fold surface.

Spots	1	2	3	4	5	6
$(h_1h_2h_3h_4)$	(1001)	$(\bar{1}\bar{1}\bar{1}\bar{1}\bar{1})$	$(0\overline{1}\overline{1}0)$	$(\bar{1}\bar{2}\bar{2}\bar{1})$	$(100\overline{1})$	$(11\overline{1}\overline{1})$
H^x_{\parallel}/b	τ^{-1}	1	τ	$ au^2$	0	0
$H^y_{\parallel}/b\chi$	0	0	0	0	au	$ au^2$
H_{\parallel}/b	τ^{-1}	1	au	$ au^2$	$ au\chi$	$ au^2\chi$
H_{\parallel}	0.63	1.02	1.65	2.67	1.94	3.14
H_{\perp}^{x}/b	τ	1	$-\tau^{-1}$	τ^{-2}	0	0
$H_{\perp}^y/b\chi$	0	0	0	0	-1	τ^{-1}
H_{\perp}/b	τ	1	τ^{-1}	τ^{-2}	χ	$\tau^{-1}\chi$
H_{\perp}	1.65	1.02	0.63	0.39	1.2	0.74

Table 3.1: A list of diffraction vectors and Miller indices $(h_1h_2h_3h_4)$ of some strong spots. Spot numbers (S. N.) are given in Figure 3.1. The \mathbf{H}_{\parallel} and \mathbf{H}_{\perp} are decomposed as $\mathbf{H}_{\parallel} = (H_{\parallel}^x, H_{\parallel}^y, 0)$ and $\mathbf{H}_{\perp} = (H_{\perp}^x, H_{\perp}^y)$.

Almost all diffraction spots can be indexed by using the four basis vectors \mathbf{b}_j (j = 1, ..., 4). The four basis vectors are pointing from the center to four of the five corners of a regular pentagon. Since the pentagonal geometry involves the golden mean, the diffraction vectors obtained by linear combination of these basis vectors are related by the golden mean. The diffraction vectors $\mathbf{H}_{\parallel} = \sum_{j=1}^{4} h_j \mathbf{b}_j$ and the Miller indices $(h_1 h_2 h_3 h_4)$ of some strong spots are given in Table 3.1. The table demonstrates the τ -relation of diffraction vectors.

In a higher dimension description of decagonal quasicrystals, the basis vectors \mathbf{b}_j (j = 1, ..., 5) are considered as physical space projection of the 5D reciprocal basis vectors. The perpendicular space components of the 5D basis are given by $\mathbf{b}'_j = b \left(\cos \frac{6\pi j}{5}, \sin \frac{6\pi j}{5}\right) (j = 1, ..., 4)$. The diffraction vectors associated with \mathbf{b}'_j can be calculated by $\mathbf{H}_{\perp} = \sum_{j=1}^4 h_j \mathbf{b}'_j$. Values of \mathbf{H}_{\perp} of some strong spots are shown in Table 3.1. The relation of diffraction intensity with H_{\perp} (= $|\mathbf{H}_{\perp}|$) can be realized from these values. One can see that spots having larger H_{\perp} are weaker or vice versa. For example, the brightest among the observed spots (say the $(10\overline{1}\overline{1})$ spot numbered '4' in Figure 3.1, bottom) have the lowest value of H_{\perp} . This is a very important feature of quasicrystal diffraction patterns, which makes it possible to observe distinct spots as the intensity of spots having very large H_{\perp} are experimentally undetectable.

It is worthwhile to note that there exist other spots brighter than the $(10\overline{1}\overline{1})$ at larger \mathbf{H}_{\parallel} .

The position of these spots can be obtained by adding the diffraction vectors of the observed brightest spots. For example, addition of the diffraction vectors of the spots $(0\bar{1}\bar{2}\bar{1})$ (spot '9') and $(\bar{1}\bar{2}\bar{1}0)$ (spot '11') gives the position of the spot $(\bar{1}\bar{3}\bar{3}\bar{1})$, which has $H_{\perp} = b \tau^{-3} = 0.245$ Å⁻¹ and $H_{\parallel} = = b \tau^3 = 4.32$ Å⁻¹. The H_{\perp} value is lower than that hat of $(110\bar{1})$ or $(0\bar{1}\bar{2}\bar{1})$, and hence should have higher intensity. The H_{\parallel} value is τ times larger than that of $(110\bar{1})$ or $(0\bar{1}\bar{2}\bar{1})$. In principle, a continuous addition of diffraction vectors of brighter spots yields the positions of the maximum possible brightest spots with $H_{\perp} \rightarrow 0$ and very large H_{\parallel} .

Discussed in Section 1.3, clusters of 20 Å diameter are located at the vertices of a pentagonal Penrose pattern pattern of 20 Å edge length in the normal phase of the d-Al-Ni-Co, while in the superstructure phase the clusters are located at the vertices of a rhombic Penrose of the same edge length [40, 64, 66]. The diffraction pattern of the pentagonal (or rhombic) tiling can be calculated via Fourier transform of the decagonal (or pentagonal) atomic surfaces [5]. The normal phase diffraction pattern is calculated by using the Fourier transform of the decagonal atomic surfaces. The Fourier amplitude versus H_{\perp} is an oscillating function (see Figure 1.11). An envelope function is used to calculate the diffraction pattern in order to avoid the extinction of selected diffraction spots, as the present interest is to find the distribution of all possible diffraction peaks in a general decagonal structure. The resulting diffraction pattern is shown in Figure 3.2, right. A quantitative comparison between the calculated and experimental intensities would not be meaningful because the calculation excludes many factors such as the contribution of individual atoms, multiple scattering, and temperature. However, the calculated diffraction pattern reflects the symmetry of the measured diffraction pattern and provides spot positions. The calculated diffraction pattern superposed on the experimental SPA-LEED data is shown in Figure 3.3. It reveals that almost all diffraction spots are at positions expected from the bulk. Representative of those peaks that cannot be obtained by using the basis \mathbf{b}_j are marked by white circles.

The weak spots marked by white circles in Figure 3.3, 3.5, and 3.6 are identified as superstructure spots. These spots appear around strong diffraction spots forming a decagon (Figure 3.5). The superstructure basis vectors \mathbf{s}_j (j = 1, ..., 4) are rotated by $\frac{\pi}{10}$ with respect to the normal basis vectors \mathbf{b}_j (Figure 3.4). The length *s* of the superstructure basis vectors is 0.53 Å⁻¹, which is smaller than *b* by a factor of $2 \cos \frac{\pi}{10} = \tau \chi$.

The diffraction pattern can be indexed by using the superstructure basis vectors. The



Figure 3.3: A comparison between the calculated and experimental data. SPA-LEED images recorded at 65 eV (left) and 75 eV (right) electron energy. Black circles reflect calculated normal intensities. The area of the circles is proportional to the log of the calculated diffraction intensity. Superstructure spots are encircled by large white circles and the area of the circles is not scaled with intensity.



Figure 3.4: SPA-LEED images with magnified scale (left at electron energy of 65 eV and right at 75 eV). The normal structure and the superstructure basis vectors \mathbf{b}_j and \mathbf{s}_j of length 1.02 Å⁻¹ and 0.53 Å⁻¹ are shown as solid and dotted arrows, respectively. The superstructure basis is rotated by $\frac{\pi}{10}$ with respect to the normal basis. The spot very close to the specular (marked by a square) is the specular spot of the secondary grain present in the sample.



Figure 3.5: Superstructure spots (marked by white circles) appearing around the $10\overline{1}\overline{1}$ spot, one of the strong spots of the normal phase, forming a decagon.

diffraction vectors with respect to the superstructure basis vectors are $\mathbf{H}_{\parallel} = \Sigma_{j=1}^4 h_j^s \mathbf{s}_j$ with $\mathbf{s}_j = s(\cos \frac{2\pi j}{5}, \sin \frac{2\pi j}{5}, 0)$ and $s = b/(\tau \chi) = 0.53$ Å⁻¹. The perpendicular space components corresponding to these diffraction vectors can be calculated by $\mathbf{H}_{\perp} = \Sigma_{j=1}^4 h_j^s \mathbf{s}'_j$ with $\mathbf{s}_j = s'(\cos \frac{6\pi j}{5}, \sin \frac{6\pi j}{5}, 0)$ and $s' = b/2 \cos \frac{3\pi}{10} = b/\chi = s\tau$ [88]. Values of H_{\parallel} , H_{\perp} , and Miller indices $(h_1^s h_2^s h_3^s h_4^s)$ of some spots are presented in Table 3.2.

The type of a diffraction spot is given by the sum $n = \sum_i h_i^s$. Spots with n a multiple of 5 are normal structure spots, while those with $n = 5m \pm 1$ and $n = 5m \pm 2$, with integer m are referred to as S1 and S2, respectively. All detected superstructure spots satisfy $\sum_i h_i^s = 5m \pm 1$ (see Table 3.2), and hence are identified as S1 spots.

The bulk structure of d-Al_{71.8}Ni_{14.8}Co_{13.4} possesses type I superstructure at room temperature. Thus, one should expect both S1 and S2 spots in the diffraction pattern of the bulk terminated surface. However, only S1 spots were observed. This may not be so surprising. As predicted by theoretical calculations [91] and also revealed by X-ray diffraction data [88], S2 spots are even weaker than the S1 spots. The observed S1 spots are already extremely weak. Therefore, the intensities of S2 spots are likely below detection limit.

The position of the $(0\overline{2}\overline{3}\overline{2})$ spot, which is one of the S2 spots, is marked by white square in Figure 3.6. No intensity has been observed at this position even though it is one of the brighter S2 spots as expected from its H_{\perp} value. The H_{\perp} value of the spot is 0.20 Å⁻¹, which is much lower than that of the observed brightest normal spots.

The superstructure spots take fractional indices with respect to the normal basis vectors.



Figure 3.6: Indexing of diffraction spots by using the superstructure basis. The spots with $n = \sum_i h_i^s$ a multiple of 5 are normal structure spots, while those with $n = 5m \pm 1$, with integer m are the S1 spots. Position of a S2 spot satisfying $n = 5m \pm 2$ is marked by a white square.

The superstructure basis can be obtained from the normal basis by $\mathbf{s}_j = \sum_i S_{ij}^{-1} \mathbf{b}_i$ with,

$$S^{-1} = \frac{1}{5} \begin{bmatrix} 2 & -1 & 1 & -2 \\ 2 & 4 & 1 & 3 \\ -3 & -1 & 1 & -2 \\ 2 & -1 & 1 & 3 \end{bmatrix}.$$
 (3.1)

Because of the presence of the $\frac{1}{5}$ fraction term in the matrix, the superstructure spots indexed with respect to normal basis vectors take $\frac{1}{5}$ -integer indices (see Table 3.2).

Line scans along the [10000] and [001 $\overline{10}$] directions at electron energies of 65 eV and 75 eV are shown in Figure 3.7. For scans along the [10000]-azimuth, the peaks are at 0.39 Å⁻¹, 0.63 Å⁻¹, 1.02 Å⁻¹, 1.26 Å⁻¹, 1.40 Å⁻¹, 1.65 Å⁻¹, 2.04 Å⁻¹, 2.28 Å⁻¹, and 2.67 Å⁻¹. The peak positions can be obtained by $\Delta k_{\parallel} = k_0 (m + n\tau)$, with $k_0 = 1.02$ Å⁻¹ and $(m, n) = (2, \overline{1})$, $(\overline{1}, 1)$, $(1,0), (\overline{2}, 2), (3, \overline{1}), (0,1), (2,0), (\overline{1}, 2), \text{ and } (1,1)$, respectively. Similarly, for scans along the [001 $\overline{10}$]-azimuth, the peak positions are related by $\Delta k_{\parallel} = k_0 \chi \tau (m + n\tau) = 1.94(m + n\tau)$ Å⁻¹ with $(m, n) = (\overline{1}, 1)$ and (1,0), respectively. The superstructure peaks are at 0.53 Å⁻¹ and 1.7 Å⁻¹ and related by $\Delta k_{\parallel} = (k_0/\chi \tau)(m + n\tau) = 0.53 (m + n\tau)$ Å⁻¹ with (m, n) = (1,0) and

Spots	$(h_1h_2h_3h_4)$	$(h_{1}^{s}h_{2}^{s}h_{3}^{s}h_{4}^{s})$	$n = \Sigma_i h_i^s \pm 5m$	Туре	$ \mathbf{H}_{\parallel} /\mathrm{\AA}^{-1}$	$ \mathbf{H}_{\perp} /\mathrm{\AA}^{-1}$
7	$(00\overline{1}0)$	$(\bar{1}\bar{1}\bar{2}\bar{1})$	0	Ν	1.02	1.02
8	$(0\overline{1}\overline{1}\overline{1}\overline{1})$	$(0ar{2}ar{2}ar{1})$	0	Ν	1.65	0.63
9	$(0ar{1}ar{2}ar{1})$	$(\bar{1}\bar{3}\bar{4}\bar{2})$	0	Ν	2.67	0.39
12	$\frac{1}{5}(31\overline{1}2)$	$(00\overline{1}0)$	-1	S1	0.53	0.87
13	$rac{1}{5}(ar{2}ar{4}ar{6}ar{6})$	$(0ar{2}ar{2}ar{2})$	-1	S1	1.73	1.07
14	$rac{1}{5}(ar{3}ar{4}ar{6}ar{3})$	$(0ar{2}ar{3}ar{1})$	-1	S1	2.16	0.71
15	$rac{1}{5}(31ar{6}ar{3})$	$(0ar{1}ar{3}ar{2})$	-1	S1	2.16	0.71
16	$rac{1}{5}(1ar{3}ar{7}ar{6})$	$(0ar{2}ar{3}ar{2})$	-2	S2	2.27	0.20

Table 3.2: List of diffraction vectors and Miller indices: $(h_1^s h_2^s h_3^s h_4^s)$ are the Miller indices with respect to the superstructure basis, while $(h_1 h_2 h_3 h_4)$ with respect to the normal basis. (N: normal spots, S1: S1 superstructure spots, and S2: S2 superstructure spots. See Figure 3.6 for spot numbering.)



Figure 3.7: Line scans along the [10000] (a) and [001 $\overline{1}0$] (b) azimuth. The position of strong spots along [10000] show a ratio of τ^{-2} : τ^{-1} : τ^{0} : τ^{1} : τ^{2} . The peak numbers correspond to the diffraction spots numbered in Figure 3.1. The superstructure peaks are indicated by arrows.

(0,2). The fact that the positions of the superstructure peaks are related by the golden mean indicates a quasicrystalline superlattice ordering in the surface region. The superstructure spots are found to broaden. The FWHM of the spots is almost five times larger than that of the specular peak and three times that of the higher order diffraction peaks. This indicates a short range correlation of atoms associated with the superstructure ordering.

A comparison of line scans at 65 eV and 75 eV shows a strong variation in diffraction intensity over a relatively small energy range. For example, clearly observed superstructure peaks at 0.53 \AA^{-1} at 75 eV cannot be seen at 65 eV.

3.2 Helium Atom Scattering

Surface Preparation

Again, the surface was prepared by sputtering and annealing. A suitable sputter-annealing condition was obtained after several trials. It was found that the surface prepared by two or three cycles of sputtering (Ne⁺, 1 keV, 3 μ A, for 30 minutes) and annealing (600-850 °C for 30 minutes) is clean enough for the first observation of LEED. However, further cleaning cycles are needed to observe He diffraction with intense peaks because the extreme surface sensitivity of He atom scattering necessitates a high perfection of the surface. The quality of the surface was examined after each sputter-annealing cycle by monitoring the He specular intensity. The cleaning processes were repeated until an optimum He specular intensity was obtained. The clean surface was found to contaminate within a few hours at the prevailing UHV conditions with a base pressure of 2×10^{10} mbar. Annealing the contaminated surface at 600-850 °C for a few minutes recovers the surface quality to within a few percent in the specular intensity.

Results and Discussion

The two inequivalent high symmetry directions of the 10-fold surface can be represented by [10000] and $[001\overline{1}0]$ (see Figure 3.3). Helium diffraction from the clean surface was measured along these high symmetry directions at different beam energies from 9 meV to 44 meV. The spectra for selected beam energies are shown in Figure 3.8. The specular intensity is dominant for all energies. Its intensity of 10^5 c/s is comparable to the specular intensity of high quality cleaved surfaces of e.g., MgO(001) [125] and GaAs(110) [126]. Due to their high scattering cross



Figure 3.8: He diffraction along [10000] (left) and $[001\overline{1}0]$ (right) at different beam energies. Superstructure peaks are indicated by arrows.

section, adsorbates and vacancies can be detected in the 0.001 monolayer range by a significant reduction of the specular He atom intensity [92]. The observation of such a high specular intensity therefore indicates an extremely low density of defects.

The surface corrugation can be determined from the intensity distribution of the diffraction spots [92]. A higher corrugation causes more He atoms to be scattered into diffraction peaks at higher momentum transfer. As the specular peak in the observed spectra dominates the diffraction pattern (other diffraction peaks have two orders of magnitude lower intensity) a very low corrugation can be inferred.

HAS and SPA-LEED of the 10-fold surface are compared in Figure 3.9. HAS and SPA-LEED have different surface sensitivity. While HAS gives exclusive information of the topmost surface layer as the electron density extending out of the solid reflects the He atoms well above the surface [92]. In contrast, electrons penetrate several Angstroms into the surface before being scattered from the atom potential and hence provides information from a few topmost layers (refer to Chapter 2 for a more detail explanation). The comparison shows identical peak



Figure 3.9: A comparison between HAS and SPA-LEED along [10000] (left) and $[001\overline{1}0]$ (right). Spectrum 'A' is He diffraction and 'B' and 'C' are SPA-LEED at 65 eV and 75 eV, respectively. The indexing follows Section 3.1.

positions in He diffraction and SPA-LEED. As the spot positions of SPA-LEED can be explained by the bulk reciprocal basis vectors (see previous section), the observation of the identical peak positions in HAS and SPA-LEED reveals that the topmost surface layer has an identical order as the bulk.

As observed in SPA-LEED, He diffraction also shows only S1 spots with very weak intensity (see comparison in Figure 3.9, right). The appearance of these peaks is very sensitive to sample alignment and the quality of the surface due to the extremely weak intensity.

Helium diffraction from the surface prepared under different conditions is compared in Figure 3.10. The lower spectrum was from the surface annealed at 600-650 °C. The sample was mounted on an Ohmic heater. In contrast, the upper spectrum was taken from the surface annealed by using an electron beam (e-beam) heater. With this e-beam heater, the sample could be annealed at higher temperatures. For the particular spectrum shown in the figure, the sample



Figure 3.10: A comparison of He diffraction along [10000] from differently prepared surfaces. The upper and spectra were taken from the surface annealed at 800-850 °C and 600-650 °C (sputtering: 5-20 μ A, 30 minutes in both case), respectively. The intensity of the lower spectrum has been multiplied by a factor of 1.5.

was annealed at 800-850 $^{\circ}$ C. A difference between the two heating systems is that the cooling rate of the sample after annealing stopped is slower in the case of the Ohmic heater as compared to the e-beam heater.

As seen in the figure, the two spectra are qualitatively different (note that the intensity of the lower spectrum has been multiplied by a factor of 1.5 to equalize the background intensity of the two spectra. The asymmetric distribution of the intensity to the left and right of the specular is due to the sample alignment). In the case of higher annealing temperature, more peaks are resolved (for example, peaks at 0.24 Å^{-1} and 1.26 Å^{-1} , marked by arrows, are visible only in the upper spectrum) and the observed peaks are more intense. Despite these differences, the peak width is limited by the instrumental resolution in both cases. The width is a measure of a correlation length of quasicrystalline order of the atoms. The sharp peaks imply a long range order in the surface within the length scale of the instrumental transfer width. These observations demonstrate that a quasiperiodic long range order is achieved even with the lower annealing temperature. However, to get a highly ordered surface the higher annealing temperature is needed.

With this superior high temperature preparation, surface phonons have been successfully measured, which will be presented in Chapter 5. Attempts to measure phonons from the surface prepared at lower annealing temperature with the Ohmic heater were unsuccessful. In additional to the structure, the surface morphology is also found to be different for the two surface preparations.

The surface morphology was studied by recording the specular intensity as a function of





Figure 3.11: He specular intensity as a function of momentum transfer (top: surface prepared with slow cooling; and bottom: surface prepared with fast cooling). The right panel shows a sketch of scattering from two adjacent terraces.

beam energy. Since the parallel momentum transfer during scattering is zero for the specular peak, changes in the beam energy varies only the perpendicular momentum transfer. Note that the parallel momentum transfer Δk_{\parallel} is given by $\Delta k_{\parallel} = k_i(\sin\theta_f - \sin\theta_i)$ with $k_i/\text{Å}^{-1} =$ $1.39\sqrt{E_i/meV}$ and E_i the He beam kinetic energy. For the specular peak, θ_i is equal to θ_f which yields $\Delta k_{\parallel} = 0$. The specular intensity variation with beam energy thus reflects the vertical roughness of the surface.

Figure 3.11 shows the specular intensity as a function of wavevector k_i . The upper spectrum shows an oscillation due to constructive and destructive interference of the wave scattering from adjacent terraces (see the right panel of the figure). The oscillating period is $\delta k = 2.15 \pm 0.06$ Å⁻¹. From this period, the step height h is calculated to be $h = 2.06 \pm 0.06$ Å by applying a simple formula $2h \sin \theta_i = 2\pi/\delta k$. The observed height corresponds to the distance between the quasiperiodic planes [64, 66].

The ratio of in-phase and out-of-phase intensity is related to the ratio of the average terrace width and the transfer width of the apparatus [127]. The strong oscillation of the specular intensity is possible only when the terrace width is in the order of the transfer width of the apparatus (about 100 Å) or less. This morphological information is confirmed by low temperature STM results given in the next section.

The upper and lower spectra in Figure 3.11 were taken from the surface prepared under
different conditions (the preparation condition is identical to that explained above). The lower spectrum is from the surface obtained by higher temperature e-beam heating based preparation, while the upper was annealed with the Ohmic heater. The lower spectrum shows much weaker oscillations implying that the terrace widths are significantly larger. STM investigation of d-Al₇₂Ni₁₁Co₁₇ also show wider terraces on the surface prepared at higher annealing temperature than in the surface annealed at lower temperature [20].

3.3 Scanning Tunneling Microscopy

Experiment

With a better understanding of surface preparation and surface structure gained from the diffraction data, the surface was investigated by low temperature scanning tunneling microscopy (LT-STM). Measurements were performed in a home-built LT-STM (see Ref. [128] for a description of apparative details). Since the microscope is completely surrounded by a radiation shield at 4 K, the residual gases of the chamber are trapped on it providing an excellent low background pressure reducing the rate of surface contamination by several orders of magnitude compared to the HAS and SPA-LEED experiments. Once a clean surface was attained the experiments could be continued for three weeks without any significant degradation of surface quality.

All STM images presented here were taken in constant current mode at 6 K. The surface was prepared by sputtering (1.5 kV, 4-10 μ A, for 15-30 minutes) and annealing (650 °C, for 15-20 minutes followed by 700 °C for a few seconds, Ohmic heater).

Results and Discussion

A large scale STM image of the clean surface is shown in Figure 3.12 demonstrating a high density of 2 Å high steps. From various scanned images, an average terrace width of about 100 Å is determined. The terraces are atomically flat with a corrugation of a few tenths of an Angstrom. The steps height and terraces width are in good agreement with the previous observation by HAS. Steps are found to be very rough and are not orientated along any preferential direction. Other decagonal systems (for example, d-Al-Cu-Co [17] and d-Al-Ni-Co with different composition than our sample [18]) also show rough steps.

As shown in Figure 3.13 two types of surface terminations are apparent on a single terrace.



Figure 3.12: A STM image demonstrating a high density of steps (A = $2110 \times 2110 \text{ Å}^2$, V = 1.46 V and I = 0.55 nA). Terraces are of approx. 100 Å and rough steps are observed.

With the same tip and sample condition, some portions of the terrace display more resolved structure (a fine structure) than the other part of the terrace (a coarse structure). The fine structure is imaged slightly lower (0.2-0.3 Å) with respect to the coarse structure. The observation of the two types of structure in a single terrace gives further evidence for the dependence of surface termination on preparation and annealing temperature. Since the coarse structure is dominating the observed data, it will be analysed in more detail in the following.

As introduced in Section 1.3.3, *d*-Al-Ni-Co consists of an alternating stacking of two types of quasiperiodic planes (A and B). The clusters, main building blocks of the system, in each layer have 5-fold symmetry and have the same orientation in a single layer (details about the clusters are discussed later in this section). The orientation of the clusters in layers 'A' and 'B' are related by inversion symmetry. This is demonstrated by the STM image of two adjacent terraces in



Figure 3.13: A STM image showing two different surface terminations within a single terrace (A = 290×200 Å², V = 0.06 V and I = 1.4 nA).



Figure 3.14: A STM image of two adjacent terraces (a) (A = $316 \times 316 \text{ Å}^2$, V = 0.73 V and I = 1.5 nA). High resolution images of the areas marked by frames (b and c) (A = $157 \times 157 \text{ Å}^2$, V = 0.73 V and I = 1.5 nA). The dotted and full circles marked the two different types of pentagonal-shape feature.



Figure 3.15: A gray scale image of the Fourier transform of the STM image shown in Figure 3.14(a) displaying a 10-fold symmetry with sharp spots. Some of the spots are marked by white circles. Superimposed is a SPA-LEED image taken at 65 eV electron energy.

Figure 3.14(a). High resolution images of the upper and lower terrace are also displayed in Figure 3.14(b-c). The terraces shows two different types of pentagonal-shape features indicated by full and dashed circles. The pentagonal features have the same orientation in a single terrace, but they are in opposite orientation with respect to those in the adjacent terrace.

Gray scale image of the Fourier transform of the image shown in Figure 3.14(a) have a 10fold symmetry (Figure 3.15). The spots are sharp and are on five rings of radii 1.02 Å⁻¹, 1.2 Å⁻¹, 1.35 Å⁻¹, 1.65 Å⁻¹, and 1.95 Å⁻¹ within experimental errors. The radii have ratios of 1 : χ : $3(\tau - \chi)$: τ : $\chi\tau$. The position of the spots reveals a long range, quasiperiodic order. The real space value corresponding to the wavevector of the outermost spot (k = 1.95 Å⁻¹) is ~ 3 Å, which is larger than the length scale expected in an atomically resolved images. The



Figure 3.16: A high resolution STM image (a) (A = 150×115 Å², V = 0.025 V and I = 5 nA) with a tiling overlaid (b).

observed resolution is similar to previous reports on the 10-fold surface of *d*-Al-Ni-Co [18] and *d*-Al-Co-Cu [17]. A portion of a SPA-LEED image is superimposed on the the gray scale image demonstrating that the Fourier transform of the STM image agrees with the SPA-LEED results.

In addition to information about the steps and terraces, more insight of the atomic structure of the surface has been gained. Theoretical structure models of d-Al-Ni-Co are based on 20 Å diameter clusters located at the vertices of a rhombic tiling [64, 66]. In agreement with these bulk structural models, a high resolution image of a portion of a terrace can be overlaid by a rhombic tiling of 20 Å edge length (Figure 3.16(b)). The vertices of the tiling are located at the centers of cluster indicated by circles in the figure. It should be mentioned that to identify the vertices of the tiling in STM images is not as easy as in the case of transmission electron microscopy (TEM) giving an image of projected structure. In TEM images, the 10-fold symmetric contrast of the columnar clusters are apparent while the STM images (where only the topmost layer is imaged) lack these clear features (see Figure 3.17 for the atoms in the topmost layer of bulk terminated surface and compare it to the projected structure in Figure 1.10). By a careful and intensive search, a tiling was found in one selected high resolution STM image.

Magnified sections of this image are shown in Figure 3.18, left, displaying the two different tiles observed. These are the skinny (with an angle of 36°) and fat (with an angle of 72°) rhombi



Figure 3.17: The atomic structure on the topmost layer of the bulk terminated surface perpendicular to the 10-fold axis [66]. The dark and gray circles represent transition metals and Al, respectively. For the stacking of the first and second layer of the same area see Figure 1.10.

of a Penrose pattern (Section 1.1.1). The neighboring two clusters are packed in two ways in these rhombi. In one case, they overlap with each other such that the center-to-center distance S is equal to the shorter diagonal of the skinny rhombus. In the second case, they touch head-to-head with center-to-center distance equal to the edge length of the rhombi (L = S $\tau \sim 20$ Å).

The overlaid tiling of Figure 3.16(b) is illustrated in Figure 3.18, right. The tiling does not



Figure 3.18: Selected magnified sections of the image showing the two different tiles (a) and the observed tiling (b).



Figure 3.19: A comparison between the observed and theoretical cluster. The observed cluster (left) (the displayed is the magnified cluster marked by bold circle in Figure 3.16(b) and slightly rotated with respect to the original position) and the cluster of theoretical model proposed by Yamamoto *et al.* [66] (middle). Transition metals of the topmost layer in inner first and second rings are indicated by pentagons with the atomic distance of the theoretical model (right).

reflect a section of a perfect rhombic Penrose tiling but is randomized. (Note that the tiling is slightly distorted to accommodate the slight distortion in the STM imaging). A few examples of local arrangements of tiles which are not allowed in a perfect rhombic Penrose tiling are indicated by bold edges in Figure 3.16(d). As outlined in Section 1.3, transmission electron microscopy (TEM) shows that the atomic structure of the type I superstructure phase of Al-Ni-Co can be explained in terms of a random tiling. Since our sample belongs to this phase, the observed tiling thus agrees with the TEM results. A random tiling is believed to be responsible for an entropic stabilization of quasicrystal (Section 1.2). The randomness can be viewed as phason disorder.

The atomic distribution in a cluster of the bulk terminated surface is shown in Figure 3.19. The large and small solid circles represent atoms of the topmost and the second layer, while the dark and gray circles denote transition metals and Al, respectively. The atoms in each layer are arranged in a pentagonal symmetry and the whole atomic arrangement of the first layer is rotated by 36° with respect to that of second layer giving an overall 10-fold symmetry. Agreeing with the bulk terminated surface, the observed clusters show pentagonal symmetry (see an individual cluster in Figure 3.19, left). The dark areas in the cluster (where the tip approaches the sample

to keep the tunneling current constant) seem to be correlated to transition metal sites in the top layer (marked by large dark circles in the cluster), while brighter parts are related to Al. However, the center part of the cluster does not agree with the theoretical model. The observed cluster suggests extra Al atoms to be at the cluster center.

Summary

To summarize this chapter, SPA-LEED images of the surface show very sharp diffraction spots revealing a perfect long range order in the surface region. With the high resolution and high dynamic range of the SPA-LEED apparatus, the observation of nearly 500 diffraction spots in the k-vector range up to 3 $Å^{-1}$ is possible. The diffraction spots can be indexed by using the bulk decagonal reciprocal basis vectors which implies that the surface preserves the perfect quasicrystalline order of the bulk.

The He specular intensity is comparable to the specular intensity of high quality cleaved surfaces of crystalline systems revealing an extremely low density of defects. He diffraction shows a very low corrugation as the specular intensity dominates the diffraction peaks. A comparison of He diffraction with electron diffraction shows the diffraction peaks are equally observed in both cases giving evidence that the topmost surface layer also retains the perfect quasicrystalline order of the bulk.

Aside from the bulk derived symmetry and order, the surface shows the superstructure of the bulk. The d-Al_{71.8}Ni_{14.8}Co_{13.4} is a type I superstructure phase possessing bulk S1 and S2 superstructure spots. Both He and electron diffraction show very weak S1 spots. The S2 spots are not detected most likely due to their extremely low intensity.

In addition to the structural information, insights into the surface morphology were gained. The specular intensity as a function of momentum transfer shows an oscillation with a period corresponding to a 2 Å step height. This step height corresponds to the interlayer distance of d-Al-Ni-Co. The average terrace width is estimated to be on the order of 100 Å.

Low temperature STM (6 K) shows a high density of steps with monoatomic 2 Å height confirming the morphological features observed in He diffraction. The steps are found to be very rough. Terraces are atomically flat with an average width of 100 Å. The terraces show 5-fold symmetric motives, which have identical orientation in a single terrace but are oppositely oriented in successive terraces confirming the alternating stacking of two types of quasiperiodic planes. Fourier transforms of the structure on single terraces yield sharp spots with a 10-fold symmetry demonstrating the long range quasiperiodic order. The Fourier transform is in good agreement with the SPA-LEED images of the same surface.

Clusters of 20 Å diameter located at the vertices of a rhombic tiling have been identified. The tiling deviates from a perfect rhombic Penrose tiling in agreement with the transmission electron microscopy of the type I superstructure phase, which found the structure of this phase characterized by a random rhombic tiling.

Comparing different surface preparations, a dependence of surface termination and morphology on the annealing temperature was observed. Helium diffraction from the surface prepared at higher annealing temperature shows more intense peaks as compared to the surface prepared at lower annealing temperature. This demonstrates that annealing at higher temperature yields a more ordered structure. This observation is confirmed by low temperature STM. The STM images of the surface prepared at lower annealing temperature show two types of terminations (the fine and coarse structures) on a single terrace. Since the tip condition is unchanged during imaging of the surface, observation of two types of terminations reveal that the surface has not fully equilibrated at lower annealing temperature.

Chapter 4

The 2-fold *d*-Al-Ni-Co Surfaces

The high symmetry surfaces of a decagonal quasicrystal include the 10-fold and two inequivalent 2-fold surfaces. The 10-fold axis is along the periodic direction, while two inequivalent sets of 2-fold axes exist perpendicular to the 10-fold axis. These 2-fold axes appear alternatingly at 18° yielding a decagonal symmetry.

To introduce the surfaces, the bulk decagonal basis vectors shown in Figure 1.7 are reillustrated in Figure 4.1. The 10-fold axis runs along [00001], which is perpendicular to the plane of paper. The two inequivalent sets of 2-fold axes can be represented by [10000] and [001 $\overline{10}$]. The high symmetry directions of the (10000) surface are thus the periodic [00001] and the quasiperiodic [001 $\overline{10}$]. Similarly, the high symmetry directions of the (001 $\overline{10}$) surface are the periodic [00001] and the quasiperiodic [10000] ones. In this chapter investigations of the 2-fold *d*-Al_{71.8}Ni_{14.8}Co_{13.4}(10000) surface by SPA-LEED and HAS and the 2-fold *d*-Al_{71.8}Ni_{14.8}Co_{13.4}(001 $\overline{10}$) surface by HAS are presented.

4.1 The 2-fold *d*-Al-Ni-Co(10000) Surface

4.1.1 Spot Profile Analyzing Low Energy Electron Diffraction

A large single grain d-Al_{71.8}Ni_{14.8}Co_{13.4} sample was cut along the (10000) plane. The surface was mechanically polished and transferred into the UHV chamber (base pressure 1×10^{-10} mbar). The surface was cleaned by repeated sputtering (Ne⁺ of 1-3 kV, 4-10 μ A, for 20-30 minutes)



Figure 4.1: Reillustration of bulk decagonal basis vectors shown in Figure 1.7. The two inequivalent sets of 2-fold axes, represented by [10000] and $[001\overline{1}0]$ appear alternatingly at 18° .

and annealing cycles (600-650 $^{\circ}$ C).

SPA-LEED images of the clean surface recorded at different electron energies are shown in Figure 4.2. The SPA-LEED images display sharp diffraction spots revealing a perfect long range order of the surface. The sharpness of spots is comparable to that of diffraction spots observed in the 10-fold d-Al_{71.8}Ni_{14.8}Co_{13.4} surface (Section 3.1).

The horizontal and vertical in the images are the periodic [00001] and the quasiperiodic [00110] direction, respectively. The density of spots along the quasiperiodic direction is very high (average 5 spots per Å⁻¹), which is not unusual for quasicrystals. The distribution of the diffraction spots along the [00110]-azimuth is shown by line scans in Figure 4.3. The peak positions are related by the golden mean reflecting a perfect quasicrystalline order in the surface region. The peak positions can be obtained by $\Delta k_{\parallel} = k_0(m + n\tau)$, with $k_0 = 0.60$ Å⁻¹ and (m, n) integers. The values of Δk_{\parallel} and (m, n) of each peak are listed in Table 4.1.

The observed peak positions are identical to the surface projection of the bulk reciprocal lattice structure. As introduced in Section 3.1, the bulk reciprocal vectors of d-Al_{71.8}Ni_{14.8}Co_{13.4} are $\mathbf{b}_j = 1.02(\cos \frac{2\pi j}{5}, \sin \frac{2\pi j}{5}, 0)$ Å⁻¹ (j = 1, ..., 4) and $\mathbf{b}_5 = 0.78(0, 0, 1)$ Å⁻¹ (Figure 3.1), where \mathbf{b}_j (j = 1, ..., 4) are within the quasiperiodic planes and \mathbf{b}_5 is along the periodic direction. The projection of \mathbf{b}_j (j = 1, ..., 4) onto the quasicrystalline [00110]-direction yields $P_{[00110]}(\mathbf{b}_1) = 0$,



Figure 4.2: SPA-LEED images of the 2-fold d-Al_{71.8}Ni_{14.8}Co_{13.4}(10000) surface taken at 160 eV (a), 110 eV (b), and 80 eV (c) electron energy displaying a periodic ordering along [00001] and quasiperiodic ordering along [001 $\overline{10}$].

 $P_{[001\bar{1}0]}(\mathbf{b}_2) = b \sin \frac{2\pi}{5} = b\tau \sin \frac{\pi}{5}, P_{[001\bar{1}0]}(\mathbf{b}_3) = b \sin \frac{\pi}{5}, \text{ and } P_{[001\bar{1}0]}(\mathbf{b}_4) = -b \sin \frac{\pi}{5}$ (refer to Figure 4.4). The projection of any arbitrary vector in the quasicrystalline plane therefore results in $P_{[001\bar{1}0]}(\Sigma_{j=1}^4 n_j \mathbf{b}_j) = b \sin(\frac{\pi}{5})(m+n\tau) = k_0(m+n\tau)$, which agrees perfectly with the observed diffraction pattern.

The k-vectors of the vertical columns of diffraction spots are nb_5 , with $n = 0, \pm 1, \pm 2, \pm 3$,



Figure 4.3: Line scans along the quasicrystalline $[001\overline{1}0]$ direction. (Intensity in logarithmic scale).

and ± 4 , and $b_5 = 0.78$ Å⁻¹. This corresponds to an 8 Å periodicity along the periodic [00001] direction reflecting a doubling of the minimum periodicity of the decagonal system given by two layers with an interlayer distance of 2.04 Å. The observed 8 Å periodicity is in agreement with the bulk reciprocal lattice structure [64, 80].

In addition to the 8 Å periodicity, very weak streaks (shown by arrows in Figure 4.2) corresponding to a 16 Å periodicity also appear in the SPA-LEED images (see also in line scan in Figure 4.9). So far, no evidence of a 16 Å periodicity is reported in the *d*-Al-Ni-Co system. As revealed by He diffraction, the topmost layer of the surface also preserves the weak 16 Å periodicity (see Section 4.1.2). Furthermore, He diffraction of the other inequivalent 2-fold surface of d-Al_{71.8}Ni_{14.8}Co_{13.4} also shows a weak 16 Å periodicity. Since the 16 Å periodicity is observed in both inequivalent 2-fold surfaces and the intensity of the 16 Å peaks associated with the topmost layer (HAS) does not significantly differ from that resulting from the few mono-



Figure 4.4: The projection of the in-plane bulk decagonal basis vectors \mathbf{b}_j (j = 1, ..., 4) onto [10000] and [001 $\overline{1}$ 0], the two inequivalent 2-fold axes.

layers (SPA-LEED), the new periodicity is most likely a bulk feature and not due to a surface reconstruction.

The SPA-LEED images display an identical distribution of the spots (both position and intensity) in all even columns. The width of the spots along the periodic and quasiperiodic directions is isotropic within the error of SPA-LEED electron optics. The distribution of the spots on the odd columns is qualitatively different compared to that on the even columns. In contrast to the isotropic width of the spots in the even columns, the spots in the odd columns are broadened along the quasiperiodic direction, while they exhibit only instrumental broadening along the periodic direction. The FWHM of the spots along the quasiperiodic direction is about 0.08 Å^{-1} , which is 3-4 times larger than that along the periodic direction. This indicates a short range lateral correlation of atoms in the layers corresponding to the 8 Å periodicity.

In addition to these structural investigations, the surface morphology was studied. Information on vertical roughness of surfaces such as step distribution and orientation of facets can be achieved by measuring LEED intensities as a function of vertical scattering vector k_{\perp} . The intensity profiles of the measured diffraction spots reflect the surface morphology [120].

Figure 4.5 shows the measured LEED intensity $I(\mathbf{k}_{\parallel}, \mathbf{k}_{\perp})$ in gray scale representation with k_{\perp} along [10000] and \mathbf{k}_{\parallel} along [001 $\overline{1}$ 0]. The vertical rods (m, n) present the intensity variations of diffraction spots at $\Delta k_{\parallel} = k_0 (m + n\tau)$, with $k_0 = 0.60$ Å⁻¹ and (m, n) = (0, 0), $\pm (2, \overline{1})$, $\pm (\overline{1}, 1)$,



Figure 4.5: A gray scale plot of LEED intensity $I(k_{\parallel}, k_{\perp})$ with k_{\perp} along [10000] (vertical) and k_{\parallel} along [001 $\overline{1}0$] (horizontal). Left: 0^{th} order spots (spots on the 0^{th} column of SPA-LEED image, Figure 4.2) and right: 2^{nd} order spots (spots on the 2^{nd} column).

 $\pm(1,0), \pm(2,\bar{2}), \pm(0,1), \pm(2,0), \pm(1,\bar{2}), \pm(1,1), \pm(3,0), \pm(0,2), \pm(2,1), \pm(4,0), \text{ and } \pm(1,2).$ Hence, the rods are separated by distances forming a sequence LSLSLLSLLSLS. The diffraction intensities are observable for a large electron energy range, revealing a highly ordered structure up to a significant depth from the topmost surface layer. The 0th order spots (spots on the 0th column of the SPA-LEED image in Figure 4.2) are detectable with sufficient intensity from 50 eV to 330 eV ($k_{\perp} = 7.25 - 18.6 \text{ Å}^{-1}$, where $k_{\perp}/\text{Å}^{-1} = \sqrt{E/0.95 \text{eV}}$, while the 2nd order spots (spots on the 2nd column) were measurable from 50 eV to 240 eV ($k_{\perp} = 7.25 - 15.9 \text{ Å}^{-1}$). No remarkable changes in spot profiles such as splitting and broadening have been observed for any energy.

The strong spots represented by $\pm(1,0)$, $\pm(0,1)$, $\pm(1,1)$, $\pm(2,1)$, and $\pm(1,2)$ are observed for almost the entire energy range, while the remaining weaker spots are detected only up to around 250 eV ($k_{\perp} \sim 16 \text{ Å}^{-1}$). However, the intensity ratio of the strong and the weak spots remains similar for all energies.

Some interesting features of a Fibonacci sequence can be realized in the observed diffraction pattern. The separation between consecutive spots has one of two values, large L and short S forming a sequence LSLSLLSLLSLLSLSLSLS, with $L/S = \tau$ and L = 0.23 Å⁻¹ = $\tau^{-2}k_0$ (refer to the line scan at 100 eV ($k_{\perp} \sim 10.7$ Å⁻¹) in Figure 4.7). This sequence is a part of a Fibonacci sequence LSLLSLLSLLSLLSLLSLLSLLSLLSLLSLLS... (bold: observed sequence). The deflation of the sequence by $LS \rightarrow L_2$ and $L \rightarrow S_2$ ($L_2 = L + S = 0.37$ Å⁻¹ and $S_3 = L = 0.23$ Å⁻¹ = L_2/τ) produces another sequence $L_2S_2L_2S_2L_2L_2S_2L_2L_2S_2L_2$ which describes the positions of the strong spots. Similarly, the third generation $L_3S_3L_3L_3S_3...$ (LSL $\rightarrow L_2S_2 \rightarrow L_3$ and SL $\rightarrow L_2$ $\rightarrow S_3$ with $L_3 = L + S + L = 0.60$ Å⁻¹ and $S_3 = S + L = 0.37$ Å⁻¹ = L_3/τ) of the deflation corresponds to the positions of the stronger spots (the spots detected only at higher electron energy, refer to Figure 4.5). The indexing of the diffraction spots also reflects the symmetry of a Fibonacci sequence. This fact will be illustrated in a discussion of He diffraction in the following section.

4.1.2 Helium Atom Scattering

As in the SPA-LEED experiments, the surface was prepared by sputtering (Ne⁺, 1 keV, 3 μ A, for 30 minutes) and annealing (600-650 °C, for 30 minutes). In the usual manner, the surface quality is monitored after each cycle by the He specular intensity. Helium diffraction from the clean surface was recorded along the two high symmetry directions, the periodic [00001] and quasiperiodic [00110].

Helium diffraction along the quasiperiodic $[001\overline{1}0]$ direction at selected beam energies are shown in Figure 4.6. The intensity distribution of the diffraction peaks is beam energy dependent. With increasing He atom kinetic energy, the ratio of the specular intensity to the intensity



Figure 4.6: He diffraction along the quasicrystalline $[001\overline{1}0]$ direction at different beam energies from 12 meV to 38 meV.

of the higher order diffraction peaks decreases. For the strongest diffraction peak at 2.54 Å⁻¹, the ratio varies from a factor of 5 to 1 for energy varying from 12 meV to 38 meV. The strong beam energy dependence is attributed to the high corrugation of the surface.

A comparison of He diffraction with SPA-LEED (Figure 4.7) reveals identical peak positions. The peaks which are strong in He diffraction also appear as stronger peaks in electron diffraction. However, two of the weak peaks represented by $\pm(2,1)$ and $\pm(2,2)$ are stronger in electron diffraction. The stronger spots of He diffraction thus break the Fibonacci sequence. They follow a sequence $L_3S_3L_3S_3L_3S_3L_3$, which has a repeating unit of L_3S_3 .

Peaks	(m,n)	Δk^j_{\parallel} /Å ⁻¹	δk		$\delta k^{'}$		$\delta k^{''}$		$(m,n)^{\star}$	$(m,n)^\dagger$	$(m,n)^{\ddagger}$
1	$(2,ar{1})$	0.23	0.23	L					$(\bar{1},1)$	$(1,\!0)$	(0,1)
2	$(\overline{1},1)$	0.37	0.14	S					$(1,\!0)$	(0, 1)	(1,1)
3	(1,0)	0.60	0.23	L	0.60	L_3	0.60	L_3	(0,1)	(1,1)	(1, 2)
4	$(2,ar{2})$	0.74	0.14	S					(2,0)	(0,2)	(2,2)
5	(0 , 1)	0.97	0.23	L	0.37	S_3	0.37	S_3	(1,1)	(1, 2)	(2,3)
6	(2,0)	1.21	0.24	L					(0,2)	(2,2)	(2,4)
7	$(1,ar{2})$	1.34	0.13	S					(2,1)	(1,3)	(3, 4)
8	(1 , 1)	1.57	0.23	L	0.60	L_3	0.60	L_3	(1,2)	(2,3)	(3, 5)
9	$(3,\!0)$	1.80	0.23	L					(0,3)	(3,3)	$(3,\!6)$
10	$(0,\!2)$	1.94	0.14	S	0.37	S_3			$(2,\!2)$	(2, 4)	$(4,\!6)$
11^{b}	(2,1)	2.17	0.13	L			0.60	L_3	(1,3)	(3, 4)	(4,7)
12	(4,0)	2.40	0.13	S					(0,4)	(4, 4)	(4,8)
13	$(1,\!2)$	2.54	0.24	L	0.60	L_3	0.37	S_3	$(2,\!3)$	(3,5)	(5,8)
14	(3,1)	2.77	0.23	L					(1,4)	(4,5)	(5,9)
15	$(0,\!3)$	2.91	0.14	S	0.37	S_3			(3,3)	$(3,\!6)$	(6,9)
16^{b}	$(2,\!2)$	3.14	0.23	L			0.60	L_3	(2,4)	(4, 6)	(6, 10)
17	(4,1)	3.37	0.23	S					$(1,\!5)$	$(5,\!6)$	(6, 11)
18	$(1,\!3)$	3.51	0.14	L	0.37	L_3			(3, 4)	(4,7)	(7, 11)
19^a	$(3,\!2)$	3.74	0.23	L					(2,5)	(5,7)	(7, 12)
20^a	(0,4)	3.88	0.14	S					(4, 4)	(4, 8)	(8, 12)
21^a	(2,3)	4.11	0.23	L					(3,5)	(5,8)	(8, 13)
22^a	(4,2)	4.34	0.23	L					(2,6)	$(6,\!8)$	so on
23^a	(1, 4)	4.49	0.15	S					(4,5)	(5, 9)	

Table 4.1: The diffraction vectors of 2-fold d-Al_{71.8}Ni_{14.8}Co_{13.4}(10000) surface along the quasicrystalline [00110] direction. δk : difference between the vectors of two successive peaks. $\delta k'$ ($\delta k''$): difference between the vectors of two successive strong peaks of He diffraction (electron diffraction). Diffraction vectors of strong peaks and the Fibonacci pairs are written in bold characters. (^adetected only in He diffraction, ^bappears as stronger spot only in electron diffraction. $(m, n)^*$, $(m, n)^{\dagger}$, and $(m, n)^{\ddagger}$ are values for i = -1, -2, and -3, respectively).



Figure 4.7: A comparison between HAS and SPA-LEED along the quasicrystalline $[001\overline{1}0]$ direction (upper curve: HAS at 25 meV beam energy and lower curve: SPA-LEED at 110 eV electron energy. The peak positions can be obtained by $\Delta k_{\parallel} = 0.60(m + n\tau)$ Å⁻¹. The values of (m, n) are shown next to the corresponding peaks.

As outlined in the previous section, diffraction exhibits many features already encountered in the diffraction pattern of a 1D Fibonacci lattice. Two indices are needed to index the diffraction spots of the Fibonacci lattice and stronger peaks take those indices, which are the two successive Fibonacci numbers or the ratio of which is the two successive Fibonacci numbers (refer to Section 1.1.2). The Fibonacci numbers are 0, 1, 1, 2, 3, 5, 8, ..., where the nth term is the sum of the previous two terms. The diffraction peaks at 0.97 Å⁻¹, 1.57 Å⁻¹, and 2.54 Å⁻¹ (peaks 5, 8, and 13 in Figure 4.7) are stronger and take the Fibonacci numbers (0,1), (1,1) and (1,2) with respect to the basis vectors $k_0 = 0.60$ Å⁻¹ and $k_1 = \tau k_0$. Another strong peak at 1.94 Å⁻¹ (peak 10) takes the indices (0,2), which have the ratio (0,1), the first two Fibonacci numbers.



Figure 4.8: He diffraction along the periodic [00001] direction at different beam energies from 12 meV to 33 meV.

This property can be illustrated also by taking new basis vectors which are τ^i multiples of k_0 and k_1 , with *i* integers. The peak positions with respect to these new basis vectors can be obtained by $\Delta k_{\parallel} = k_0 \tau^i (m + n\tau)$. The values of (m, n) for i = -1, -2, and -3 are given in Table 4.1. One can see many stronger peaks take the two successive Fibonacci numbers with respect to smaller basis vectors.

Helium diffraction along the periodic [00001] direction for different beam energies from 12 meV to 33 meV are shown in Figure 4.8. Intensity of diffraction peaks strongly depends on beam energy. With increasing beam energy, the intensity of the diffraction peaks increases with



Figure 4.9: A comparison between HAS and SPA-LEED along the periodic [00001] direction (upper: He diffraction at 20 meV beam energy and lower: Electron diffraction at 110 eV electron energy). Weak peaks indicated by arrows correspond to a 16 Å periodicity.

respect to the specular intensity. The ratio of the specular intensity to the intensity of the peak at 1.56 Å⁻¹ varies from a factor of 5 to 0.25 for beam energy ranging from 12 meV to 33 meV.

A comparison of He diffraction with electron diffraction along the periodic [00001] direction is shown in Figure 4.9. Peak positions are identical at ± 0.39 Å⁻¹, ± 0.78 Å⁻¹, ± 1.16 Å⁻¹, and ± 1.56 Å⁻¹. The peaks at ± 0.78 Å⁻¹ correspond to the main 8 Å periodicity, while the weak peaks at ± 0.39 Å⁻¹ (indicated by arrows) to a 16 Å periodicity. The 16 Å periodic peaks are weak in both He and electron diffraction.

4.2 The 2-fold d-Al-Ni-Co(001 $\overline{1}0$) Surface

In this section, He diffraction from the 2-fold d-Al_{71.8}Ni_{14.8}Co_{13.4}(001 $\overline{10}$) surface along the quasicrystalline [10000] direction is discussed. Diffraction along the periodic [00001] direction reveals the 8 Å bulk periodicity. The diffraction data are very similar to those observed along the periodic [00001] direction of the 2-fold d-Al_{71.8}Ni_{14.8}Co_{13.4}(10000) surface (Section 4.1.2) including



Figure 4.10: He diffraction spectrum from the 2-fold d-Al_{71.8}Ni_{14.8}Co_{13.4}(001 $\overline{1}$ 0) surface along the quasicrystalline [10000]-direction at 21 meV He atom kinetic energy. The peaks are at $\Delta k_{\parallel} = 0.51(m + n\tau)$ Å⁻¹, with *m* and *n* integers. Values of *m* and *n* are shown above the peaks.

the extremely weak peaks corresponding to the 16 Å periodicity.

Figure 4.10 shows He diffraction from the surface after several cycles of Ne⁺ sputtering (3 kV, 15-20 minutes, 6 μ A) and annealing at 600-650 °C. The surface was cleaned and its quality was monitored by the same procedures employed for the (10000) surface (Section 4.1.2). As can be seen in the spectrum, the intensity of the diffraction peaks is comparable to that of the specular direction, revealing a high corrugation of the topmost surface layer. A similar corrugation is observed on the 2-fold (10000) surface (Section 4.1.2). In contrast, the 10-fold surface has a very low corrugation (Section 3.2).

The peaks at 0.19 Å⁻¹, 0.31 Å⁻¹, 0.51 Å⁻¹, 0.63 Å⁻¹, 0.83 Å⁻¹, 1.14 Å⁻¹, and 1.53 Å⁻¹ correspond to $\Delta k_{||} = (k_0/\chi)(m + n\tau)$, $k_0/\chi = 0.51$ Å⁻¹, with $(m,n) = (2,\bar{1})$, $(\bar{1},1)$, (1,0), $(\bar{2},2)$, (0,1), $(\bar{1},2)$, and (3,0), respectively. These peak positions can be compared to the surface projection of the bulk reciprocal lattice structure. Projection of the bulk reciprocal vectors \mathbf{b}_j (j $= 1, \ldots, 4)$ onto the quasicrystalline [10000]-direction of the $(001\bar{1}0)$ -surface yields $P_{[10000]}(\mathbf{b}_1) =$ $b, P_{[10000]}(\mathbf{b}_2) = b \cos \frac{2\pi}{5} = b(\tau - 1)/2$ and $P_{[10000]}(\mathbf{b}_3) = P_{[10000]}(\mathbf{b}_4) = -b \cos \frac{\pi}{5} = -b\tau/2$ (refer



Figure 4.11: Angular distribution of He diffraction along the quasicrystalline direction for different energies (A: 21.5 meV, B: 18.2 meV and C: 9.5 meV). The peaks at $\theta_i = 27^{\circ}$ and 63° are reflections from the facets inclined by 18°.

to Figure 4.4). The projection of any arbitrary vector in the quasicrystalline plane therefore results in $P_{[10000]}(\Sigma_{j=1}^4 n_j \mathbf{b}_j) = b(m + n\tau)/2 = (k_0/\chi)(m + n\tau)$ in perfect agreement with the observed diffraction pattern.

Figure 4.11 shows the angular distribution in He diffraction along the quasicrystalline direction at different beam energies. All diffraction peaks except those at $\theta_i = 27^{\circ}$ and 63° shift with incident beam energy as expected. The fixed peaks (marked by dotted lines) are 18° off from the specular peak of the original or cut surface and are identified as the specular peaks of facets inclined by 18° with respect to the original surface. These facets have (10000)-equivalent surfaces, as (10000) and ($001\overline{1}0$) form an angle of 90° , which is equal to 18° plus 72° , the rotation angle of the 5-fold symmetry (see Figure 4.1).

Expected diffraction peak positions from the facets based on the bulk structure can be obtained by a projection of the basis vectors onto the quasiperiodic $[001\overline{1}0]$ -direction of the



Figure 4.12: Region around $\theta_i = 63^{\circ}$ of the top spectrum in Figure 4.11. (m, n) and $(m, n)^*$ label diffraction from the original surface and facets, respectively. Δk_{\parallel} is the parallel momentum transfer in scattering from the facets

(10000)-surface. The projections yield $P_{[001\bar{1}0]}(\mathbf{b}_1) = 0$, $P_{[001\bar{1}0]}(\mathbf{b}_2) = b \sin \frac{2\pi}{5} = b\tau \sin \frac{\pi}{5}$, and $P_{[001\bar{1}0]}(\mathbf{b}_3) = P_{[001\bar{1}0]}(\mathbf{b}_4) = -b \sin \frac{\pi}{5}$ (refer to Figure 4.4). Therefore, the diffraction peaks from the facets are expected at $\Delta k_{||}^* = P_{[001\bar{1}0]}(\Sigma_{j=1}^4 n_j \mathbf{b}_j) = b \sin \frac{\pi}{5}(m + n\tau) = k_0(m + n\tau)$, with $k_0 = 0.60 \text{ Å}^{-1}$. The parallel momentum transfer in scattering from the facets can be calculated by $\Delta k_{||}^* = \sqrt{2mE_i/\hbar^2}(\cos \theta_i^* - \sin \theta_i^*)$, where θ_i^* is the angle of incident beam with respect to the facet normal and given by $\theta_i^* = \theta_i \pm 18^o$. Figure 4.12 is a close up view of the top spectrum in Figure 4.11 around the facet specular. The peaks labeled with $(m, n)^*$ are found at the positions expected from the $P_{[001\bar{1}0]}$ -projected basis vectors, hence identified as diffraction peaks from the facets.

In fact, the diffraction peaks from the facets appear at the identical position of peaks observed in the 2-fold d-Al_{71.8}Ni_{14.8}Co_{13.4}(10000) surface along the quasiperiodic [001 $\overline{1}$ 0] direction, which is demonstrated by comparing the diffraction from the facets and the 2-fold (10000) surface in Figure 4.13. In contrast to the spectra from the 2-fold (10000) surface, the intensities of facet diffraction peaks are not symmetric on the left and the right of the specular. This arises from the alignment of sample with respect to the surface normal, not to facet normal.

In addition to the comparison of angular distribution in diffraction from the facet planes



Figure 4.13: A comparison of He diffraction from the 2-fold (10000) surface along [00110] (upper) and from the facets (lower).

and the 2-fold (10000) surface, their morphological features have been compared by measuring the specular intensity as a function of beam energy or momentum transfer. The variation of specular intensity with perpendicular momentum transfer reflects the vertical roughness of the surface (Section 3.2). Figure 4.14 shows the specular intensity variation for the facet plane and the 2-fold (10000) surface. The specular intensity varies in a similar fashion for both cases indicating the similar morphological feature of the facet planes and the 2-fold (10000) surface within a length equal to the transfer width of the instrument.

As the facets develop during normal surface preparation and do not have to be induced by a severe surface treatment, one likely explanation for the formation of the facets is a lower surface energy of the (10000) facet surface compared to that of the as-cut (001 $\overline{10}$) surface. The shape of as-grown crystals supports the argument based on surface energy. The *d*-Al_{71.8}Ni_{14.8}Co_{13.4} single crystals grow as decagonal rods with growth faces of (10000)-orientation. Assuming the cross section parallel to the quasicrystalline plane reflects the equilibrium shape, this would indicate that the (10000) surface has indeed a lower surface energy than the (001 $\overline{10}$) surface.

The size of the facets can be estimated from the FWHM of the facet specular peak, which is about 0.06 Å⁻¹. It is limited by the instrumental resolution. Therefore, it is concluded that the



Figure 4.14: He specular intensity as a function of momentum transfer from the 2-fold (10000) surface (upper) and the facets (lower).

width of the facets along the quasiperiodic direction is in the order of 100 Å or larger. Similarly, the area covered by the facets can be calculated from the intensity of the main and facet specular peaks. The specular intensity of the as-cut surface is roughly twice the specular intensity of each of the facets inclined at either of $\pm 18^{\circ}$. The total specular intensity of the facets inclined in both directions is thus equal to the specular intensity of the as-cut surface. This shows that the faceted total area is approximately equal to the remaining non-facetted surface area.

Faceting is frequently observed in periodic systems and faceted surfaces are found to be technologically useful. They can be used to grow large-scale arrays of nanostructures, tilted superlattices, etc., because faceted surfaces exhibit selective adsorption planes [129]. Faceting in quasicrystals is very rarely observed. In fact, this is the first observation of faceting in quasicrystals with the exception of development of facets near the edge of a sample observed in 2-fold surface of *i*-Al-Pd-Mn [26].

The surface prepared by different sputtering and annealing conditions was investigated to learn the influences of preparation conditions on the developments of facets. The surface was sputtered at various temperatures varying from room temperature to around 800 °C (each step 10-30 minutes) and annealed up to 800 °C (10-30 minutes). Helium diffraction was recorded after each sputter-annealing cycle (not shown here). All spectra are found to possess diffraction peaks related to facets. The profile of these peaks was not changed.

Summary

A very high corrugation of both 2-fold (10000) and (001 $\overline{1}0$) surfaces is inferred from the intensity distribution of the He diffraction. The observed SPA-LEED and HAS data reveal that the topmost surface layer retains a quasicrystalline order and the diffraction peaks are at positions expected from the bulk. The (10000) surface shows a hierarchy of diffraction spots, which can be explained on the basis of a 1D Fibonacci lattice.

As discussed, the (10000) and (00110) surfaces have a common high symmetry direction along the 10-fold axis. The diffraction from both surfaces along the 10-fold axis shows the bulk expected 8 Å periodicity and a new periodicity of 16 Å. The intensity of the diffraction spots corresponding to the 16 Å periodicity is very weak and not particularly surface sensitive. This suggests that the 16 Å spots are related to the bulk and are not due to a surface reconstruction.

The $(001\overline{1}0)$ surface is found to develop facets of (10000)-equivalent orientation. The facet planes are identical to those observed in crystal growth, suggesting that their formation is due to a lower surface energy of the (10000)-compared to the as cut $(001\overline{1}0)$ -surface. The size of the facets is estimated to be 100 Å or larger. The area covered by the faceted planes is approximately 50 % of the total surface area. These results represent the first observation of facet formation in quasicrystals.

Chapter 5

Surface Phonons of the 10-fold d-Al-Ni-Co

Before discussing the results of our investigations, a brief review on bulk phonons of quasicrystals is presented. Phonons in periodic crystals have well-defined energy and wavevector due to the lattice periodicity. A 3D periodic crystal having N atoms per unit cell has 3N modes with three acoustic and 3(N-1) optical modes. All of these modes can be characterized by using wavevectors confined to the first Brillouin zone [130].

Because of the lack of periodicity, and hence absence of a proper Brillouin zone, the wavevector cannot be a good quantum number to describe the phonon modes of quasicrystals and the concepts of periodic crystals outlined above cannot be directly employed. It has been thus of great interest to determine the vibrational properties of quasicrystals from the very beginning of their discovery. Many theoretical and experimental studies of bulk phonons and elastic properties have been carried out [73, and find references therein].

Like other properties, theoretical investigations of dynamical properties of quasicrystals began with the 1D Fibonacci sequence [131-133] and were followed by studies of Penrose tilings [134]. Dynamics of 3D quasicrystals with realistic atomic models were determined by using their higher order approximants (Refs. [135] for *i*-Al-Cu-Li, [136, 137] for *i*-Al-Zn-Mg, and [138] for *d*-Al-Mn, and [139] for a review). All of these investigations show that quasicrystals, as periodic crystals, exhibit well defined acoustic modes in the continuum limit (the long wavelength limit). The dispersion curves originate from the Bragg peaks, follow a linear relation up to a certain wavevector, and finally become dispersionless. Since the Bragg peaks fill the reciprocal space densely, the acoustic branches in principle originate almost everywhere in k-space. However, only those phonons which are associated to the acoustic branches originating from the stronger Bragg peaks have significant intensities.

Although a Brillouin zone cannot be properly defined in quasicrystals, the positions of the stronger Bragg peaks can be considered as quasi-Brillouin-zone (QBZ) centers [140, 141]. The QBZ boundaries are packed hierarchically around the zone centers. Most of the theoretical work predicts that the acoustic branches become dispersionless at the QBZ boundaries with gaps opening. The width of the gap depends on the strength of the Bragg peaks. The calculations also show a large number of dispersionless optical branches and their density increases at higher frequencies [136].

Experimentally, the dynamics of different icosahedral and decagonal quasicrystals have been investigated by employing inelastic neutron scattering (Refs. [71, 142, 143] for *i*-Al-Pd-Mn, [144, 145] for *i*-Al-Li-Cu, [146, 147] for *i*-Al-Fe-Cu, and [72] for *d*-Al-Ni-Co) and inelastic Xray scattering [148]. Almost all measurements confirm the theoretically predicted linear and isotropic dispersion relation. QBZ boundaries have been identified in all systems. A unique feature observed in all quasicrystals is that the phonon line width is limited by the instrumental resolution up to a certain wavevector and increases rapidly for larger wavevectors. Phonon peak broadening is thus considered as a signature of quasicrystaline ordering differing from the periodic crystals. It is believed that the continuum of dispersionless modes present in (ω, k) space for larger energies is responsible for the peak broadening. The measured acoustic phonon peaks beyond a certain energy are just then an accumulation of contributions coming from the continuum of dispersionless modes.

The value of both k-vector and line width at which the phonon peaks start to broaden correspond to a length scale which is on the order of the size of the cluster from which the quasicrystals are made up. For example, peak broadening of transverse modes starts at around 0.40 Å⁻¹ [71] and 0.30 Å⁻¹ [72] in *i*-Al-Pd-Mn and *d*-Al-Ni-Co, respectively. The real space values of these numbers (2π divided by wavevector) are roughly equal to the size of the Mackay cluster (diameter = 12 Å) and the columnar cluster (diameter = 20 Å), the main building block of *i*-Al-Pd-Mn and *d*-Al-Ni-Co, respectively.

Experimental attempts to detect the theoretically predicted band gaps have not been suc-

cessful so for. Although two acoustic branches cross at the QBZ boundaries in some systems (for example see Ref. [71] for *i*-Al-Pd-Mn) where the gap is expected, no gap opening has been found. One likely reason of this may be that the gap, if present, is narrow compared to the instrumental resolution. Optical modes have been experimentally detected, particularly in *i*-Al-Pd-Mn [71, 142, 143]. The dispersionless optical modes have been observed at different energies from 8 meV to 23 meV [143].

Although the nature of the bulk phonons as discussed above have been determined, investigations of surface phonons have only just started. We have succeeded in measuring Rayleigh modes on the 10-fold surface of d-Al_{71.8}Ni_{14.8}Co_{13.4} and the 5-fold surface of i-Al_{71.5}Pd₂₁Mn_{8.5} by inelastic He atom scattering. Detail investigations on the surface phonons of the 10-fold d-Al-Ni-Co surface is carried out, which is presented in this chapter, while a brief study of the surface phonons of the 5-fold i-Al-Pd-Mn surface is given in the next chapter.

5.1 Time-of-flight Spectra

The surface phonons are measured by inelastic He atom scattering in a time-of-flight (TOF) setup. Details of the TOF technique and the experimental chamber are discussed in Chapter 2. The key idea is that the He atom beam is scattered from the surface and the time-of-flight of inelastically scattered He atoms with respect to the elastically scattered He atoms is measured (see Section 2.1.3 for details).

The surface was prepared by sputtering and annealing. The preparation conditions and quality monitoring procedures have been presented in Section 3.2. The TOF spectra were recorded at an elevated sample temperature. This has a two-fold advantage: first one is somewhat technical. The surface at room temperature contaminates very fast due to the adsorption of residual gases present in the experimental chamber. But, due to the low intensity of inelastically scattered He atoms, the measurement time of each TOF spectrum has to be fairly long (at least an hour) to observe pronounced phonon peaks. Keeping the sample at elevated temperature, the quality of surface can be maintained for a longer time, which avoids the frequent surface cleaning tasks. The second advantage is related to the thermal population of the surface phonons. At higher temperature, the population of the phonons is higher. This results in a larger probability of phonon annihilation during scattering, increasing the amplitudes of annihilation peaks. However, at very high temperature the multiphonons are dominant over single phonons. An appropriate temperature is found at around 150-200 °C. TOF spectra were taken along the two high symmetry directions of the surface at different beam energies from 10 to 33 meV and for a large set of angles of incidence θ_i .

Two representative TOF spectra recorded at $\theta_i = 46.5^{\circ}$ and 42.7° are shown in Figures 5.1(ab). They consist of a central elastic peak, phonon annihilation and creation peaks, and a broad background. The elastic peak is due to the diffuse scattering from defects. The annihilation peaks appear at lower flight time than the elastic peak due to the gain of energy during the scattering (Figure 5.1(a)). Similarly, He atoms which loose energy appear as creation peaks at higher flight time (Figure 5.1(b)). The energy and parallel momentum transfer of the phonons are calculated from the flight time, beam energy, and angle of incidence including other experimental parameters (see Section 2 for the formula).

The intensities as a function energy transfer are shown in Figures 5.1(c-d). The data were fitted by a sum of Gaussian and Lorenzian line shape for all contributions (the phonon and diffuse elastic peak and the background). The fitting was carried out by minimizing the χ^2 value ($\chi^2 = \frac{1}{N} \sum_{N} \left[\frac{(X_N^{Exp} - X_N^{fit})^2}{\sigma_N^2} \right]$). The total fit as well as the individual elastic, inelastic, and background parts are shown in the figure. The annihilation peak at 1.8 meV has a momentum transfer $\Delta K = -0.05$ Å⁻¹, while the creation peak at -2.5 meV has $\Delta K = 0.1$ Å⁻¹. The fullwidth at half-Maxima (FWHM) of these peaks is about 1.2 meV, which mainly reflects the instrumental broadening.

The presence of well-defined inelastic peaks indicates that the inelastic collisions have a significant single phonon contribution. However, a non-negligible contribution from multiphonon scattering is also expected. Single phonon scattering is dominant over multiple phonons if 2W < 1, where W is the surface Debye Waller factor and given by $2W = 24(m/M)(E_{iz}/k_B\theta_D)(T/\theta_D)$, with θ_D the Debye-temperature, E_{iz} the energy corresponding to the z-component of the incident wave vector, and T the surface temperature (refer Section 2.1.2 for details). Since the surface is bulk terminated (see discussion in Section 3.3), the major contribution is expected from Al (bulk Debye temperature is 394 K [130]). In this case, the value of 2W for the parameter range of the present measurements is always greater than 1, suggesting a strong contribution of multiphonon scattering. For the particular spectra presented in Figure 5.1 (see figure caption for experimental parameters), the value of 2W is calculated to be approximately 3.5 (note that the surface Debye



Figure 5.1: Representative TOF spectra from the 10-fold surface of d-Al_{71.8}Ni_{14.8}Co_{13.4} recorded at $\theta_i = 46.5^{\circ}$ (a) and 42.7° (b) for the [00110] azimuth and the sample temperature of around 200 °C. (c) and (d): the intensity versus phonon energy transfer. (Solid gray curve: total fit, solid curve: phonon peak, dotted curve: elastic peak, dashed curve: background.)

temperature is roughly equal to the bulk Debye temperature times $1/\sqrt{2}$ [149]).

The inelastic intensities resulting from multiphonon scattering normally appear underneath the single phonon peaks as background [114]. On the other hand, the contribution from the bulk phonons is also expected in the measured TOF spectra because there exists a continuum of surface projected bulk bands very close to the Rayleigh modes for a given wavevector, which may also appear as a broad background in TOF spectra. The observed background intensity in the measured TOF spectra could be the contribution from the both multiple surface phonon and the continuum of bulk phonons.

TOF Spectra at Different Sample Temperatures

TOF spectra were recorded at different sample temperatures ranging from room temperature to 550 °C to investigate the temperature dependence of the different contributions of the TOF spectra. A set of spectra for selected temperatures (beam energy 22 meV and $\theta_i = 43^\circ$) is given in Figure 5.2. The phonon peaks do not shift with temperature. This reveals that the sound velocity does not change appreciably with temperature at least up to 550 °C.

The different components of the TOF spectrum behave differently with temperature. As expected the intensity of the diffuse elastic peak decays exponentially (Figure 5.3, left) with a decay constant of $\alpha \sim 0.006$ K⁻¹. The decay is identical to that for the specular peak (see comparison in figure). The surface Debye temperature is estimated about 335 K from the decay constant considering only aluminum atoms on the topmost surface layer. The bulk Debye temperature of 394 K yields a surface Debye temperature of around 280 K, which is smaller than the value calculated from the experimental attenuation by almost 20 %. It should be mentioned that the presented sample temperatures were extrapolated from a reference temperature at



Figure 5.2: TOF spectra at selected sample temperatures. Sample temperatures are shown above the spectra. The spectra are recorded along the $[001\overline{1}0]$ azimuth at $\theta_i = 43^\circ$ with 22 meV beam energy.



Figure 5.3: Left: the intensity as a function of sample temperature for the diffuse elastic peak (open circles) and for the specular peak (solid squares). The specular intensity has been multiplied by a factor of 1/200. The solid curve represents a fit with an exponential decay. Right: the phonon intensity as a function of temperature.

which the sample starts to glow and were not measured exactly. This may be one of the reasons for the larger error.

The intensity of the phonon peaks increases first, reaches a maximum at around 150-200 $^{\circ}$ C, and starts to fall off (Figure 5.3, right). For temperature higher than 550 $^{\circ}$ C, the phonon peaks completely merge into the background.

5.2 Dispersion Relation

A set of TOF spectra along the two inequivalent high symmetry directions (see Figure 5.5 for the introduction of the high symmetry directions) for different angles of incidence θ_i recorded at 22 meV beam energy and sample temperature of 200°C are shown in Figure 5.4. The positions of single phonon peaks are marked by vertical lines.

An additional peak in the topmost spectrum of Figure 5.4, left (indicated by an arrow) is not due to single phonon scattering. The angle at which the TOF spectrum is measured is very close to a diffraction peak at 52.6° ($\Delta k_{\parallel} = 1.02 \text{ Å}^{-1}$). The diffraction peak contains a broad, low intensity tail derived from the velocity distribution of incident beam which causes the appearance of the additional elastic peak, a so-called decepton (refer to Section 2.1 for a description of decepton).



Figure 5.4: A series of TOF spectra along the [10000] (left) and $[001\overline{1}0]$ (right) azimuth with 22 meV beam energy for different angles of incidence and sample temperature of around 200 °C. Angles are given above the spectra. The positions of single phonon peaks are marked by vertical lines. The peak indicated by an arrow is a decepton.

Figure 5.5 presents the He diffraction pattern of the surface perpendicular to the 10-fold axis. The position and intensity of the spots along the two high symmetry directions are determined from the measured line scans at 22 meV beam energy (see line scans in Figure 3.8). The whole 2D pattern is obtained by symmetrization.

Along the [10000] azimuth, the peaks at 1.02 Å⁻¹ (C) and 1.65 Å⁻¹ (E) are strongest, while the strongest peaks along [001 $\overline{1}$ 0] are at 1.2 Å⁻¹ (G) and 1.94 Å⁻¹ (I). The main QBZ boundaries are thus expected at the midpoint of AC, CE, AG, and GI (marked by crosses) and the QBZ centers at the positions of the strongest peaks.



Figure 5.5: He diffraction of the 10-fold *d*-Al-Ni-Co surface represented by solid circles. The radius of circles is proportional to the intensity (note the specular intensity is not scaled). The high symmetry points of the QBZs are denoted by letters A, B, C,... and the points marked by crosses are the QBZ boundaries.

The resulting dispersion relations from the sets of measured TOF spectra at different beam energies from 10-33 meV are shown in Figure 5.6. Due to the lack of periodicity, the reduced BZ scheme to express the dispersion relation is not meaningful in quasicrystals. The dispersion curve folded in the first quadrant of (ω, k) space is illustrated in Figure 5.7. The QBZ centers and boundaries are marked by the letters given in Figure 5.5.

In the long wavelength limit, the low energy vibrations in solids are sound waves with a linear dispersion relation $\omega_{l,t} = v_{l,t}k$, where v_l and v_t are the velocities corresponding to the longitudinal and transverse sound waves. Thus, the slope of the linear dispersion yields the sound velocity. The slope of the solid lines shown in Figures 5.6 and 5.7 is determined from the velocity v_R of the Rayleigh mode estimated from the bulk velocities of *d*-Al-Ni-Co by using a relation $v_R/v_t = (0.87 + 1.12\sigma)/(1 + \sigma)$ with $\sigma = (1 - 2v_t^2/v_l^2)/2(1 - v_t^2/v_l^2)$, which is obtained by an approximation for an isotropic elastic medium [150]. Since *d*-Al-Ni-Co is found to be elastically isotropic [151], the relation can be employed in our system. Neutron scattering from the *d*-Al-Ni-Co yields $v_l = 7000 \pm 150$ m/s and $v_t = 4100 \pm 150$ m/s. Using these values, v_R is estimated 3750 $\pm 5\%$ m/s. This isotropic sound velocity is used for the solid lines giving the bulk derived linear dispersion along the [10000] and [00110] directions in Figures 5.6 and 5.7.

As seen, clearly the measured dispersion curves hold a linear relation following the bulk



Figure 5.6: The phonon dispersion relation along [10000] (upper) and [001 $\overline{1}$ 0] azimuth (lower). Different symbols represent the data obtained for different beam energy. The solid lines represent the linear dispersion expected from the bulk ($v_R = 3750 \text{ m/s}$).

expected dispersion curves originating from the QBZ centers up to a certain wavevector. For both high symmetry directions, the linearity holds up to around 0.30 Å⁻¹ (energy 7.5 meV). This observation is quite similar to bulk phonon dispersion which also shows a linear relation up to this wavevector [72]. Strong phonon peaks are observed in the dispersion curves close to the Bragg peaks. Although no phonons are detected near the QBZ boundaries, the acoustic mode follows the expected dispersion leveling off towards these points.

The opening of a gap were intensively searched for by varying all possible experimental parameters. However, no indication of gaps were found. Phonon peaks are very broad for higher energy such that it is very hard to separate them from the background. Finding the gaps is almost impossible as the dispersion curves do not clearly extend up to the QBZ boundaries.


Figure 5.7: The dispersion curves folded in the first quadrant of (ω, k) space along [10000] (upper) and [001 $\overline{10}$] azimuth (lower). Symbols are as Figure 5.6.

5.3 Phonon Peak Width

As discussed in the beginning of this chapter, the investigations of the bulk phonons reveal that the phonon peak width is limited by instrumental resolution up to a certain wavevector and increases rapidly with larger wavevector. To determine whether the surface phonons show a similar behavior, experimental TOF spectra are analyzed in detail, which is presented in this section. For the analysis, the peaks attributed to phonon creation are chosen. As the energy resolution strongly depends on energy transfer, an optimum energy resolution can be achieved in the creation peaks (see Section 2.1.4 for details). The dispersion relation for the selected peaks is shown in Figure 5.8, top (beam energy 22 meV, direction $[001\overline{10}]$, $\theta_i = 38^\circ - 43.7^\circ$). Below $\theta_i = 38^\circ (\Delta K > 0.30 \text{ Å}^{-1})$ the phonon peaks of this branch are very weak such that it is impossible to determine their width reliably.

The peak height as a function of momentum transfer is shown in Figure 5.8, middle. The height is determined by a fit of the TOF spectra as described in the previous section. Since the TOF spectra to which the peaks under discussion belong were recorded under different sample



Figure 5.8: Top: The dispersion relation with scan curves (thick solid line) for selected peaks. Middle: Phonon peak height as a function of phonon wavevector. Bottom: the full-width at half-maxima for selected peaks.

conditions, the peak heights are rescaled based on the intensity of the diffuse elastic peak. The plot of peak height versus wavevector shows a monotonic decrease in agreement with expected behavior discussed in Section 2.1.2. The strong decrease in peak height results in a less accurate peak width determination at larger wavevectors. The data can be fitted within a reasonable statistical error for a fairly wide range of the peak width. Exemplary for the selected TOF spectra, those with phonon peaks at $\Delta K = 0.12$ Å⁻¹ and 0.29 Å⁻¹ (TOF spectra at $\theta_i = 42^{\circ}$ and 38°, respectively) are shown in Figure 5.9. At lower wavevector, the phonon peaks have sufficiently high intensity to determine the width with a relatively small error. In contrast, for larger wavevector the intensity of the peaks is very weak compared to the Gaussian background and the peak shape cannot be determined exactly. For the particular spectrum at $\theta_i = 38^{\circ}$, the full-width at half-maxima (FWHM) can be varied from 1.7 meV to 3.4 meV while maintaining a reasonable agreement of fit and data. The FWHM of the entire data set is given in Figure 5.8, bottom, which demonstrates that average value of the widths increases with increasing



Figure 5.9: Demonstration of data fitting to determine peak widths. The upper and lower are the measured TOF spectra at $\theta_i = 42^\circ$ and 38° with the results of fit (see previous section for the description of fitting procedure). The normalized deviation of fitted curve from the measured data is shown at the bottom of each spectrum. The left and right show the fitting for the lower and upper limit of the width. The upper spectrum is fitted keeping the width of second phonon peak at -4.9 meV the same for the left and right.

wavevector. However, the accuracy of the peak width becomes poor with increasing wavevector.

In addition to the intrinsic broadening, the peak width depends on instrumental broadening as well as on the angle of intersection of the scan curve with the dispersion curve (kinematical focusing, Section 2.1.2). The instrumental broadening is very similar for all peaks under discussion. To consider the effect of kinematical focusing, the scan curves for $\theta_i = 38^{\circ}$ and 43.7° are plotted in Figure 5.8, top (refer to Equation 2.37 for the functional dependence of the scan curve on experimental parameters). The angle of intersection does not change appreciably for the TOF spectra under consideration revealing that this contribution is similar for all data. Hence, the external factors influencing the peak width do not significantly contribute to the k-dependence of the broadening and the k-dependence of experimental widths shown in Figure 5.8, bottom reflects changes in intrinsic width.

The bulk phonons (transverse modes) of d-Al-Ni-Co show instrumental resolution limited peaks up to a wavevector of around 0.30 Å⁻¹ and peak width rapidly increase for larger wavevector [72]. Since the phonon peaks are not separable from the background intensity in the measured TOF spectra for $\Delta K > 0.29$ Å⁻¹, a discussion about the peak widths in the wavevector range where the bulk phonons show peak broadening is not possible.

To conclude this section, with all possible experimental parameters and the available capability of the He scattering machine as well as the optimum structural quality of the surface, it is not possible to determine whether the phonon peaks exhibit a strong increase of intrinsic width beyond a specific momentum.

Summary

The surface is found to possess a well defined Rayleigh mode. The dispersion follows a linear k-dependence up to a wavevector of 0.30 Å⁻¹ giving a sound velocity of about 3750 m/s which is isotropic and in good agreement with bulk measurements. Quasi-Brillouin zone centers are identified at the positions of the strong Bragg peaks. The extrapolation of the obtained dispersion relation indicates that the curve becomes dispersionless at the QBZ boundaries. With available instrumental capabilities, the peak broadening as observed in the bulk phonons could neither be confirmed nor be ruled out.

Chapter 6

The 5-fold *i*-Al-Pd-Mn Surface

In this chapter, a brief introduction to icosahedral quasicrystals including the indexing scheme of their diffraction patterns is presented first. The introduction is followed by the experimental details and characterization of the clean surface of i-Al_{71.5}Pd₂₁Mn_{8.5} by He diffraction. Finally, surface phonons measured from the same surface are presented and discussed.

Icosahedral Quasicrystals

Icosahedral quasicrystals are 3D quasicrystals possessing six 5-fold, ten 3-fold, and fifteen 2-fold rotational axes. A macroscopic view of an icosahedral quasicrystal displaying planes of different symmetries is shown in Figure 6.1. Like 1D and 2D quasicrystals, 3D quasicrystals can be described in terms of higher dimension periodic structures. Icosahedral quasicrystals can be obtained by an appropriate 3D cut of a 6D periodic lattice [5].

Among the many examples of icosahedral quasicrystals, Al-Pd-Mn is the most widely investigated because the structure of this phase has a very high degree of perfection and large grain samples have been available. From a point of view of surface researcher, *i*-Al-Pd-Mn, as other icosahedral quasicrystals, provides an opportunity to study a variety of high symmetry surfaces including the unique 5-fold surface.

Indexing of the Diffraction Pattern

The reciprocal basis vectors of an icosahedral quasicrystal are shown in Figure 6.2. The six basis vectors point towards the corners of an icosahedra, and are defined by $\mathbf{a}_1 = a(0, 0, 1)$





and $\mathbf{a}_j = a(\sin\theta\cos\frac{2\pi j}{5}, \sin\theta\sin\frac{2\pi j}{5}, \cos\theta)$ for $j = 2, \ldots, 6$, where θ is the angle between two adjacent 5-fold axes $(\tan\theta = 2)$ and 1/a is the lattice constant in 6D space [5]. These six basis vectors can be considered as the physical space projections of a 6D reciprocal basis given by

$$\mathbf{d}_{1}^{*} = a \begin{pmatrix} 0\\0\\1\\0\\0\\1 \end{pmatrix}, \qquad \mathbf{d}_{j}^{*} = a \begin{pmatrix} \sin\theta\cos\frac{2\pi j}{5}\\\sin\theta\sin\frac{2\pi j}{5}\\\cos\theta\\-\sin\theta\cos\frac{4\pi j}{5}\\-\sin\theta\sin\frac{4\pi j}{5}\\-\cos\theta \end{pmatrix}, j = 2, \dots, 6.$$
(6.1)

The diffraction vectors can be expressed by $\mathbf{H}^{\parallel} = \sum_{j=1}^{6} h_j \mathbf{a}_j$ with h_j integers. Each diffraction spot is characterized by six Miller indices $(h_1 h_2 h_3 h_4 h_5 h_6)$. The diffraction spots pointed to by \mathbf{a}_j (j = 1, ..., 6) are thus represented by (100000), (010000), (001000), (000100), (000010), and (000001), respectively, and the directions along the six 5-fold axes are [100000], [010000], [001000], [000100], [000010], and [000001].



Figure 6.2: Illustration of the reciprocal basis vectors of an icosahedral quasicrystal. The six basis vectors \mathbf{a}_j ($j = 1, \ldots, 6$) are pointing from the center towards the corners of an icosahedra. The directions along the \mathbf{a}_j ($j = 1, \ldots, 6$) can be labeled by [100000], [010000], [001000], [000100], [000010], and [000001], respectively.

6.1 Characterization of the Clean Surface

A single grain Al_{71.5}Pd₂₁Mn_{8.5} quasicrystal was grown by the Czochralski method [152] and annealed for three months at 820 °C. The sample was cut and mechanically polished perpendicular to the 5-fold axis prior to the surface treatments inside the UHV chamber. The single crystal surface was prepared by Ne⁺ ion bombardment (1-4 keV, for 30-60 minutes) and annealing at 600 °C for 30-60 minutes. Experiments were performed in the UHV chamber (base pressure 2×10^{-10} mbar) discussed in Chapter 2.

A typical LEED pattern of the 5-fold i-Al_{71.5}Pd₂₁Mn_{8.5}(100000) surface is shown in Figure 6.3. The high symmetry directions of the surface can be represented by $[001\overline{1}\overline{1}1]$ and $[000\overline{1}10]$. Helium diffraction along these high symmetry directions recorded at 22 meV beam energy are shown in Figure 6.4.

The ratio of specular intensity and higher order diffraction peaks in the observed spectra is on the order of ten suggesting a higher corrugation. Compared to the 10-fold and 2-fold surfaces of d-Al-Ni-Co, the surface has a moderate corrugation while the 10-fold surface has a much lower corrugation and the 2-fold surfaces have significantly higher corrugation. The result is consistent with the bulk terminated surfaces as the 10-fold surface consists of atoms lying in a single plane [66], while the possible termination of the 5-fold surface of i-Al-Pd-Mn [7] and 2-fold surfaces of d-Al-Ni-Co [66] are buckled surface layers [7].



Figure 6.4: He diffraction along the $[001\overline{1}\overline{1}1]$ (left) and $[000\overline{1}10]$ (right) directions at 22 meV beam energy.

The unique symmetry of the surface can be realized from the intensity distribution of diffraction peaks. As expected from the 5-fold LEED diffraction pattern, the intensity of peaks along $[001\overline{1}\overline{1}1]$ at wavevector k is different than that of their counterparts at -k (compare the intensity of peaks at \pm 0.99 Å⁻¹, marked by 3 and $\overline{3}$ or at \pm 1.6 Å⁻¹, marked by 4 and $\overline{4}$). The 5-fold symmetry is better illustrated in 2D diffraction pattern (Figure 6.5). The diffraction pattern is formed by using the position and intensity of peaks from the line scans shown in Figure 6.4. As the line scans along the two directions were measured from the surfaces under different conditions, the specular intensity of two directions is different. The displayed intensity in the 2D pattern is after normalization with respect to the background intensities.



Figure 6.5: He diffraction of the 5-fold i-Al_{71.5}Pd₂₁Mn_{8.5}(100000) surface represented by solid circles. The radius of circles is proportional to the intensity (note the specular intensity is not scaled). The \mathbf{b}_j (j = 2, ..., 6) are the surface projected bulk reciprocal basis vectors (left). The high symmetry points of the QBZs are denoted by letters A, B, ... and the points marked by crosses are the QBZ boundaries (right).

The position of selected diffraction peaks are listed in Table 6.1 demonstrating the τ -scaling relation. The diffraction vectors can be obtained by a linear combination of the surface projected bulk reciprocal basis vectors. The bulk basis \mathbf{a}_j (j = 1, ..., 6) can be decomposed into the components parallel and perpendicular to the surface as $\mathbf{a}_j = (\mathbf{b}_j, b_{jz})$. The surface projected components are shown by solid arrows in Figure 6.5, left, and defined by $\mathbf{b}_1 = (0, 0)$ and \mathbf{b}_j $(j = 2, ..., 6) = a(\sin\theta\cos\frac{2\pi j}{5}, \sin\theta\sin\frac{2\pi j}{5}) = b(\cos\frac{2\pi j}{5}, \sin\frac{2\pi j}{5})$ with $b = a\sin\theta = 0.99$ Å⁻¹.

6.2 Surface Phonons

Series of TOF spectra for different angles of incidence along the $[001\overline{1}\overline{1}1]$ and $[000\overline{1}10]$ directions recorded at a beam energy of 15 meV are shown in Figure 6.6, recorded at a sample temperature of around 200 °C.

As in the 10-fold surface of d-Al-Ni-Co, the TOF spectra consist of a central elastic peak, single phonon peaks, and background intensity. The single phonon peaks are sharp with the

Peaks	1	2	3	4	5	6
$\Delta k_{ }$ /Å ⁻¹	0.38	0.60	0.99	1.60	1.98	2.23
$\Delta k_{\parallel}/{ m b}$	τ^{-2}	τ^{-1}	1	au	2	2τ -1
Peaks	7	8	9	10	11	12
$\begin{tabular}{ c c c c } \hline Peaks \\ \hline \Delta k_{ } \ / {\rm \AA}^{-1} \end{tabular}$	7 2.60	8 3.19	9 3.6	10 1.15	11 1.88	12 3.06

Table 6.1: A list of diffraction vectors of the 5-fold i-Al_{71.5}Pd₂₁Mn_{8.5}(100000) surface for selected peaks. The peak number follows Figure 6.4 or 6.5.



Figure 6.6: A series of TOF spectra along $[001\overline{1}\overline{1}1]$ (left) and $[000\overline{1}10]$ (right) with a beam energy of 15 meV for different angles of incidence. Angles are given above spectra. Single phonon peaks are marked by vertical lines. The peak indicated by an arrow is a decepton.



Figure 6.7: The phonon dispersion relation along the $[001\overline{1}\overline{1}1]$ (upper) and $[000\overline{1}10]$ (lower) azimuth. Different symbols represent the data obtained for different beam energy. The solid lines represent linear dispersion expected from the bulk ($v_R = 3250 \text{ m/s}$).

linewidth limited by the instrumental resolution for smaller wavevetors, while they are very broad for larger wavevectors, such that it is very hard to identify their position. The TOF spectrum at $\theta_i = 41^{\circ}$ along $[001\overline{1}\overline{1}1]$ is found to possess a decepton resulting from the diffraction peak at 40.4° ($\Delta k_{\parallel} = -0.60$ Å⁻¹).

The dispersion relation derived from the TOF spectra are shown in Figure 6.7. The solid lines represent the linear dispersion, the slope of which is estimated from the Rayleigh mode velocity v_R expected from the bulk. The bulk velocities $v_l = 6300 \pm 300$ m/s and $v_t = 3500 \pm$ 100 m/s [71] yields $v_R = 3250 \pm 5\%$ m/s, which is slightly smaller than that of the *d*-Al-Ni-Co surface. All observed data in the dispersion relation fall on the linear regime. One can clearly see that the dispersion follows the linear relation expected from the bulk and that it is isotropic in this linear regime. The linearity holds up to a larger wavevector than in the 10-fold *d*-Al-Ni-Co surface. The bulk phonon dispersion (for transverse modes) of *i*-Al-Pd-Mn also holds a linear relation up to a larger wavevector than the dispersion of the *d*-Al-Ni-Co.

Summary

The 5-fold *i*-Al-Pd-Mn surface, similarly as the high symmetry surfaces of the *d*-Al-Ni-Co, shows a long range, bulk derived quasiperiodic order in the topmost surface layer. Helium diffraction reveals a moderate corrugation compared to the high symmetry surfaces of the *d*-Al-Ni-Co agreeing with the bulk terminated surfaces.

The surface possesses a well-defined Rayleigh mode. An isotropic sound velocity of about 3250 m/s is observed. The observed velocity agrees with the experimental bulk phonon data.

Summary and Conclusion

Quasicrystals are a new class of material with long range order without periodicity, which often show conventionally forbidden rotational symmetries. Apart from the fascinating structure as well as the bulk-related physical properties, quasicrystals exhibit many interesting surface properties. Although many aspects of bulk structure of quasicrystals are well understood, many open questions regarding their surface structure remain.

The presented work focuses on surface studies of quasicrystals to get information about the fundamental features of the surfaces in this new class of material. The investigation is motivated by the following questions: Does the surface maintain a long range order? How is the surface structure related to the bulk? Are the surface features observed in periodic crystals plausible for quasicrystal surfaces? To investigate these, two different quasicrystals were chosen. Specifically, decagonal (d) $Al_{71.8}Ni_{14.8}Co_{13.4}$ and icosahedral (i) $Al_{71.5}Pd_{21}Mn_{8.5}$ were studied to determine their structure, morphology, and surface phonon dispersions.

These two quasicrystals are the most common systems used for surface studies due to the availability of large single grain samples. The decagonal quasicrystal belongs to the class of 2D quasicrystals with quasicrystalline planes stacked periodically along one direction, thus providing the possibility to study crystalline and quasicrystalline order in a single alloy. In contrast to 2D quasicrystals, the icosahedral quasicrystal has quasicrystalline order in all three dimensions. Moreover, the two systems provide an opportunity to study various types of high symmetry surfaces including the unusual 10-fold (in d-Al-Ni-Co) and 5-fold (in i-Al-Pd-Mn) surfaces.

The present works mainly focus on the surfaces of the *d*-Al-Ni-Co. All existing low index surfaces, namely the 10-fold (00001), the 2-fold (10000), and the 2-fold (001 $\overline{10}$) were studied. The [10000] and [001 $\overline{10}$] directions represent the two inequivalent sets of 2-fold axes appearing alternatingly at 18° in the plane perpendicular to the [00001] (10-fold) axis. Both 2-fold (10000)

and $(001\overline{1}0)$ surfaces thus have a common high symmetry direction along the 10-fold axis. The investigation of all high symmetry surfaces provides an opportunity to learn about the relative stability of different surfaces.

Different experimental techniques capable of providing information both in real and reciprocal space were used. To relate the structure of the topmost layer with that of the surface region (up to several topmost layers), highly surface sensitive elastic He atom scattering (HAS) and high resolution spot profile analyzing low energy electron diffraction (SPA-LEED) were employed. In addition to providing information of average structure and limited morphological insights of the topmost layer, HAS is appropriate to characterize the surface quality due to its extremely high sensitivity to all types of defects such as vacancies, adatoms, and steps. To determine other features which cannot be achieved by diffraction techniques such as details on step morphology, local defects, and tiling, the 10-fold surface was imaged by low temperature (6 K) scanning tunneling microscopy (LT-STM) in real space at near atomic resolution. Surface phonons were investigated by inelastic He atom scattering, which is a unique technique to study low energy phonons (the Rayleigh mode).

Surfaces prepared by sputtering and annealing are found to possess a high structural quality suitable for He diffraction. However, the surface termination is found to be dependent on preparation conditions (particularly the 10-fold *d*-Al-Ni-Co surface). The surface prepared at lower annealing temperature shows less intense peaks in He diffraction and its STM images reveal two types of surface terminations (fine and coarse structure) in a single terrace, very rough steps, and narrow terraces. All of these demonstrate that the surface does not reach to its equilibrium at low annealing temperatures. Annealing to higher temperature always yields a more ordered structure.

The topmost layer of all surfaces maintains the rotational symmetry of their respective bulk. Observed diffraction spots are very sharp with widths limited by the instrumental resolution giving evidence of perfect long range order in the topmost surface layer. The correlation length is as good as that normally observed in periodic crystal surfaces, where a long range order is established due to the lattice periodicity.

The diffraction patterns are consistent with those of bulk terminated surfaces. In addition to the peak positions matching the projections of the respective bulk reciprocal lattice structure, He diffraction shows a surface corrugation expected for the bulk terminated surfaces. Other bulk features like the periodicity and the superstructure are also apparent in the diffraction of the *d*-Al-Ni-Co surfaces. Aside from these known bulk features, the 2-fold surfaces exhibit a new periodicity of 16 Å. Both HAS and SPA-LEED show equally weak peaks corresponding to the 16 Å periodicity, demonstrating that it is a bulk feature.

As expected in the bulk derived structure, the diffraction vectors are related by the golden mean ($\tau = 1.618...$, an irrational number related to the pentagonal and decagonal symmetry). The diffraction spots are densely distributed in the reciprocal space. The dense spots can be derived by an irrational projection of higher dimension reciprocal lattice structure into the physical space. Furthermore, the diffraction pattern exhibits a hierarchy of spots (particularly the 2-fold *d*-Al-Ni-Co(10000) surface), which can be explained on the basis of a Fibonacci lattice, a well-known prototype of 1D quasiperiodic structures.

As normally seen in periodic crystal surfaces, step-terrace formation is observed in the 10-fold d-Al-Ni-Co surface. STM images of the surface show atomically flat terraces with a corrugation of a few tenths of an Angstrom. The terraces are separated by steps of monoatomic height. The terraces exhibit different types of 5-fold symmetric features correlated by a long range quasicrystalline order. In spite of a careful surface preparation and the application of a high performance microscope, atomic resolution of the surface could not be achieved. The best resolution obtained was ~ 3 Å. Even with this resolution, the STM image can be overlaid by a rhombic tiling. The vertices of the tiling are located at the centers of 20 Å diameter clusters. Determining the tiling is far from trivial. With an intensive search, only one image is found to demonstrate the tiling on a large area of a terrace.

In additional to the above described structure and step terrace morphology of the surface, a surface energy related phenomena observed in periodic crystals, the faceting, was also observed in quasicrystals. The faceting is caused by the tendency of a crystal to lower its surface free energy. The 2-fold $(001\overline{1}0)$ surface was found to develop facets of (10000)-equivalent orientation due to a lower surface energy of the (10000)- compared to the original $(001\overline{1}0)$ -surface.

With the successful preparation of surfaces with high structural quality, it became possible to measure surface phonons on the 10-fold surface of the d-Al-Ni-Co and the 5-fold surface of the i-Al-Pd-Mn. Both surfaces show a well defined Rayleigh mode with isotropic sound velocities agreeing with the respective bulk phonons measurements data. As expected for an acoustic phonon branch, the dispersion relation holds a linear k-dependent up to a certain wavevector and starts to bend down with increasing k-value. From the observed dispersion relation, the quasi-Brillouin zone (QBZ) centers are identified at the strong Bragg peaks and QBZ boundaries at half way between the two consecutive strong Bragg peaks.

To conclude, despite their very complex atomic structure and lacking periodicity, quasicrystals yield high quality surfaces under suitable preparation that exhibit a very rich variety of structural and morphological properties. The quality of surfaces is comparative to that of periodic crystal surfaces. A long range correlation is maintained even on the topmost surface layer. Phenomenon observed in periodic crystals surfaces such as step-terrace formation, faceting, bulk termination, and surface phonons are also found in quasicrystals surfaces. However, other surface features like reconstruction have yet to be observed. Structure and dynamics of the surface very closely reflect the underlying bulk properties. Finally, a better understanding of the clean surfaces has opened a way to investigate a possible relationship of the unique structure to the outstanding surface properties.

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List of Figures

Chapter 1: Quasicrystals

1.1	Rhombic Penrose pattern	13
1.2	Fibonacci sequence generated by the section method	16
1.3	Illustration of phason-disorder and approximants	18
1.4	Macroscopic view of a decagonal quasicrystal	23
1.5	Phase diagram of Al-Ni-Co alloy	25
1.6	Physical and perpendicular space components of the 5D reciprocal basis vectors .	26
1.7	Indexing scheme of decagonal quasicrystals	26
1.8	Normal and superstructure basis vectors	28
1.9	Penrose patterns generated by the section method	29
1.10	Atomic structure of <i>d</i> -Al-Ni-Co	30
1.11	Fourier amplitude versus $\ \mathbf{H}^{\perp}\ $	32

Chapter 2: Experimental Methods

2.1	Different nature of He atom and electron scattering from the crystal surfaces	36
2.2	Interaction of neutral atoms with a solid surface	37
2.3	Scattering geometry	38
2.4	Ewald construction	39
2.5	Scan curves and phonon dispersion	44
2.6	Schematic diagram of surface phonon measurement with TOF analysis	46
2.7	Schematic of the experimental chamber for He diffraction	48
2.8	Schematic of the vacuum system	49
2.9	Schematic of the SPA-LEED instrument	54

Chapter 3: The 10-fold *d*-Al-Ni-Co Surface

3.1	SPA-LEED image at 65 eV	60
3.2	SPA-LEED image at 75 eV	61
3.3	Comparison between calculated and experimental diffraction pattern \ldots .	64
3.4	SPA-LEED images in magnified scale	64
3.5	Superstructure spots around a strong diffraction spots $\ldots \ldots \ldots \ldots \ldots \ldots$	65
3.6	Indexing with respect to the superstructure basis	66
3.7	Line scans by electron diffraction	67
3.8	He diffraction along the high symmetry directions	69
3.9	Comparison between HAS and SPA-LEED	70
3.10	Comparison of He diffraction from differently prepared surface	71
3.11	He specular intensity as a function of momentum transfer $\ldots \ldots \ldots \ldots \ldots$	72
3.12	STM image demonstrating a high step density	74
3.13	STM image showing two different surface terminations within a single terrace $\ . \ .$	74
3.14	STM image of two adjacent terraces	75
3.15	Gray scale image of the Fourier transform of a STM image $\ldots \ldots \ldots \ldots$	75
3.16	High resolution STM image with a tiling overlaid	76
3.17	Atomic structure of the topmost layer of the bulk terminated surface	77
3.18	Observed individual tiles and rhombic tiling	77
3.19	Comparison between observed and theoretical cluster	78

Chapter 4: The 2-fold *d*-Al-Ni-Co(10000) Surface

4.1	Bulk decagonal basis vectors	82
4.2	SPA-LEED images at different electron energies	83
4.3	Line scans along the quasicrystalline direction	84
4.4	Projection of the in-plane bulk decagonal basis vectors onto the 2-fold axes \ldots	85
4.5	Gray scale plot of LEED intensity $I(k_{\parallel},k_{\perp})$	86
4.6	He diffraction along the quasicrystalline direction	88
4.7	Comparison between the HAS and SPA-LEED along the quasicrystalline direction	90
4.8	He diffraction along the periodic direction	91
4.9	Comparison between HAS and SPA-LEED along the periodic direction	92

Chapter 4: The 2-fold *d*-Al-Ni-Co $(001\overline{1}0)$ Surface

4.10	He diffraction along the quasicrystalline direction	93
4.11	Angular distribution of He diffraction at different beam energies \ldots \ldots \ldots	94
4.12	He diffraction around the facet specular $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$	95
4.13	Comparison of He diffraction from the facet and the (10000) surface \ldots	96
4.14	Comparison of He specular variation from the facet and the (10000) surface \ldots	97

Chapter 5: Surface Phonons of the 10-fold *d*-Al-Ni-Co

5.1	Analysis of TOF spectra	103
5.2	TOF spectra at different sample temperatures	104
5.3	Intensity of phonon and diffuse elastic peak as a function of sample temperature	105
5.4	Series of TOF spectra	106
5.5	High symmetry points of the quasi-Brillouin zone	107
5.6	Experimental surface phonon dispersion	108
5.7	Dispersion folded in the first quadrant	109
5.8	Phonon peak height and intensity as a function of wavevector	110
5.9	Data analysis to determine peak widths	111

Chapter 6: The 5-fold *i*-Al-Pd-Mn Surface

6.1	Macroscopic view of an icosahedral quasicrystal	4
6.2	Reciprocal basis vectors of icosahedral quasicrystals	5
6.3	LEED image	6
6.4	He diffraction along the high symmetry directions	6
6.5	High symmetry points of the quasi-Brillouin zone	7
6.6	Series of TOF spectra 11	8
6.7	Experimental surface phonon dispersion	9

List of Tables

Chapter 1: Quasicrystals

1.1	Different phases of Al-Ni-Co with their periodicities and tilings	24	
Cha	apter 2: Experimental Methods		
2.1	Important experimental parameters	51	
Cha	apter 3: The 10-fold <i>d</i> -Al-Ni-Co Surface		
3.1	Diffraction vectors and Miller indices	62	
3.2	Miller indices with respect to the superstructure basis	67	
Cha	apter 4: The 2-fold <i>d</i> -Al-Ni-Co Surfaces		
4.1	Diffraction vectors of the (10000) surface	89	
Chapter 6: The 5-fold <i>i</i> -Al-Pd-Mn Surface			
6.1	Diffraction vectors	118	

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