

Atomic Scale Characterization of Organic Thin Film Growth on the Two-Fold Al-Pd-Mn Quasicrystal

Liam Joyce

200977053

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Declaration

I hereby declare that the thesis given before you has been produced solely by myself and has been submitted exclusively for completion of my Bachelor of Science in Physics and has not been submitted for any other award. The inclusion of exterior sources of information relevant to this thesis have been acknowledged and provided with the bibliography.

I would like to thank Dr.Hem Raj Sharma for allowing me to study and produce the following work and also to Samuel Coates for aiding me with my understanding of the field of Surface Science.

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Abstract

Scanning Tunnelling Microscopy (STM) and Low Energy Electron Diffraction (LEED) have been used to image the clean and C60 dosed surface of the icosahedral two-fold surface of the $Al_{70}Pd_{21}Mn_9$ quasicrystal under UHV chamber conditions. Inspection of both the clean and dosed surface returned regions of periodic and quasiperiodic phase behaviour. The sequence of terrace step edge heights during investigation of the clean surface demonstrated tau-scaling with step height values which were found to be consistent with previously published works [O.Gröning et al] [1]. Tau-scaling was observed on the C60 doped surface and matching of the square Fibonacci tiling template with the quasiperiodic C60 arrangement was also identified. Examination of the periodically arranged C60 phase described an average row separation value of $1.205 \pm 0.078nm$ which again was found to be consistent with previous investigations into row separations [D.Reid et al.] [2].

1. Introduction

With quasicrystals being publicly discovered in 1984 [3], the field of surface physics began to investigate and interpret the structural unconventionality of quasicrystalline materials with respect to their crystalline counterpart and the possible uses of quasicrystalline based, epitaxial grown thin films. When considering aspects such as surface interface formation during crystal growth and further growth kinetics, it was necessary to investigate these new quasicrystalline structures so as to gain a better understanding of their formation and fundamental properties and therefore help establish how the physics behind crystalline materials translates to quasicrystals.

Quasicrystals are often referred to as complex metallic alloys (or complex intermetallics), which are intermetallic materials which inherently possess disorder in their structure and also possess extremely large unit cells, however recent discoveries show that quasicrystalline behaviour is also demonstrated in soft matter supramolecular chemistry [4] [5]. Similar to conventional crystalline materials, quasicrystals possess perfect long-range order however differ in the fact that they are aperiodic constructs that lack translational periodicity and their unit cell is infinitely large due to the lack of periodicity. The forbidden rotational geometries of quasicrystals do not conform to the crystallographic restriction theorem [6] [7] [8]. This was initially witnessed by Professor Dan Shechtman who observed a forbidden ten-fold symmetrical diffraction pattern during his discovery of quasicrystals when observing a rapidly cooled Al-Mn alloy. Even though it has been argued that the need for "forbidden" rotational symmetries is not required when defining the nature of quasicrystals, it is extremely useful when considering the application of Penrose tiling's to quasicrystalline atomic structure [9].

The field of quasicrystal research has been investigated for just over thirty years and elucidation of their properties is slowly being understood. With the majority of investigated complex metallic alloy quasicrystals tending to contain aluminium as a component, quasicrystals have been found to possess high hardness properties when compared to other aluminium alloys, however ductile behaviour has also been observed in certain quasicrystals [10] [11]. Moreover, quasicrystals have been found to possess low friction coefficients when compared to crystalline aluminium alloys and steel composites and therefore transposition of this quasicrystal property onto an epitaxy, grown on these quasicrystals may be industrially beneficial in non-laboratory environments [12] [13].

During the research on the icosahedral two-fold surface of the $Al_{70}Pd_{21}Mn_9$ quasicrystal, it was initially fundamental to gain an understanding of the underlying mathematics which are used to define the nature of the Penrose tilings and to incorporate the use of Fibonacci Tau τ scaling when identifying quasicrystals. As we are investigating an icosahedral quasicrystal, which possesses a twofold, threefold and fivefold rotation axes [14] [12], it is crucial to state that an icosahedral quasicrystal incorporates the use of a two dimensional mathematical Penrose tiling construct as a structural template and by applying this template to a three-dimensional case scenario will return the icosahedral quasicrystal's two-dimensional surface structure when considering the five-fold quasicrystal surface [15]. Similar to quasicrystals, Penrose tiling's are an example of a long ranged, non-periodic tiling system and therefore are extremely similar when considering that quasicrystals are also aperiodic, long range constructs hence the use of Penrose tiling's in this experiment as an analogy is self-explanatory [16]. The long range order of Penrose tiling's arises from using inflation & deflation rules, which allows the tiling system to possess a self-similar property and therefore when determined to infinity, allows alignment of the tile edges and therefore conforming to the crystallographic restriction theorem. The use of these concatenation matching rules arises from the use of the Fibonacci sequence and manipulation of the sequence so as to obtain the irrational "Golden Ratio" $\Phi = \tau = \frac{1+\sqrt{5}}{2} = 1.618$. The Golden Ratio is usually determined as Φ , however throughout this paper, " Φ scaling" has been referred to as τ scaling. This τ scaling obeys the following set of spacing rules, where S denotes a separation measurement and L denotes a separation measurement which has been tau-scaled;

$$S \to L$$
$$L \to LS$$

When considering that our investigation is focused on the $Al_{70}Pd_{21}Mn_9$ quasicrystal two-dimensional surface, from the use of the superposition of two perpendicular Fibonacci grids, where the inter-line spacing's obey the distance Fibonacci τ scaling, it is possible to construct the "square Fibonacci tiling" which is extremely useful when visualising the surface structure of the quasicrystal surface. [9]



Figure 1: The Square Fibonacci Tiling [9].

When considering the relation between quasicrystals and the inflation/deflation rules of the Fibonacci sequence, it is evident that the Fibonacci, τ scaled separation sequence itself is a one-dimensional quasicrystal [17]. Furthermore, decorating the vertices of a Penrose tiling with relevant atomic clusters actually characterises the underlying quasicrystals chemical composition and structure hence the use of these two separate mathematical principles are fundamental in the field of quasicrystal research. This paper demonstrates identification of quasiperiodic behaviour and periodic behaviour of the $Al_{70}Pd_{21}Mn_9$ clean-surface quasicrystal and also the identification of the self-organisation of the Carbon-60 (C60) dopant molecules on the quasicrystal surface, using the surface structure as a structural template [11].



Figure 2: Carbon 60 (Buckminsterfullerene) molecule.

C60 has been used as a dopant due to our advanced understanding of the molecule and also due to its ability to maintain its structural shape upon adsorption onto the quasicrystal surface, providing the capability of gaining structural information when atomically imaged using LEED & STM techniques [18], which will be used throughout this experiment. It has also been discovered that C60 adsorption lowers the frictional force acting on the quasicrystal surface and in turn improves the quasicrystals frictional properties when C60 adsorption occurs hence providing a possible use of an epitaxial grown C60 thin film in low friction environments [19]. From the use of the Omicron STM imaging software & hardware, the diameter of the Carbon-60 molecule is measured to be $\approx 1.0nm$, which is consistent with the calculated Van der Waals diameter [11].



Figure 3: Molecular Configuration of the $Al_{70}Pd_{21}Mn_9$ quasicrystal. [Al = Blue, Pd = Grey & Mn = Red].

Even though it has been discussed that the Fibonacci square tiling provides a structural template for adsorption of C60 molecules, it is necessary to identify molecular adsorption sites of the quasicrystal sample. Agreed

observations state that the nucleation site network depends on the abundances of the constituents defining the quasicrystal sample. It is hypothesised that the distribution of the least abundant element, in this case Manganese (9%), tends to define the nucleation site network [11]. From inspection of Figure 2, it appears that the almost circular formation of the manganese atoms possibly relates to the C60 adsorption sites. However, for this to be confirmed, mathematical measurements of the apparent adsorption site spacing's and the clean surface would be required so as to identify geometries and tau-scaling.

This report investigates the twofold nature of the $Al_{70}Pd_{21}Mn_9$ quasicrystal. Throughout this paper we report the investigation of the clean icosahedral, two-fold $Al_{70}Pd_{21}Mn_9$ quasicrystal surface from the use of STM and LEED imaging techniques, succeeded by the investigation of the C60 doped surface. Section 2 details experimental procedure followed. Section 3 discusses the results of the clean quasicrystal surface and the doped quasicrystal surface. Section 4 contains a discussion of the given results and a comparison with previously published results and a brief commentary of the theoretical two-perpendicularly superimposed square Fibonacci tiling [9]. Section 5 terminates this report with a conclusion.

2. Methodology

Due to the nature of the following experiment, it is fundamental that the following procedure be carried out in Ultra High Vacuum (UHV) conditions. As we are observing the quasicrystalline structure of $Al_{70}Pd_{21}Mn_9$ at atomic levels using STM & LEED imaging, it is paramount that the structure be free of any impurities such as oxides and carbides. Oxygen adsorption leads to oxidation of Aluminium within $Al_{70}Pd_{21}Mn_9$ which in-turn destroys the quasiperiodicity of the structure [18] [20]. Once the STM imaging occurs, any impurities situated on the surface will contaminate the material and will also disrupt the image taking due to interference between the STM probe and any detected molecules, hence will affect the end data. Therefore, from this, it is clear that this experiment requires the removal of any contaminants, which is achieved by using UHV conditions.



Figure 4: Diagram of UHV system, demonstrating all pump components used in unison to obtain UHV conditions.

The UHV conditions are obtained within a stainless steel chamber which is connected to a series of roughening and UHV pumps to obtain precisely high vacuum conditions. The elements contained in stainless steel work together to produce anti-corrosive properties. The stainless steel chamber contains elements such as chromium which reacts with ambient gases, causing the chromium to rust onto the stainless steel chamber, producing a stable thin film. However, this thin layer of rusting chromium acts as a barrier between the environment and the iron within the steel composite. This stable film prevents introduction of unnecessary contaminants & impurities by preventing the iron from reacting with oxygen to produce iron oxide, hence causing rusting within the stainless steel [21]. To obtain UHV conditions from atmospheric pressure, it is required for the chamber to be baked whilst undergoing the vacuuming process. The chamber is baked to 395*K* for two days, whilst the system of pumps are operational as baking the chamber for this amount of time accelerates the vacuuming process due to surface desorption of water molecules and any residual ambient gases and hydrocarbons from the internal surface of the chamber resulting in an improved vacuum quality [22]. A thermocouple measures the temperature of the UHV chamber whilst the temperature of the sample is measured using a pyrometer. Knowing the emissivity of the quasicrystal sample, the pyrometer measures the infrared spectrum produced during baking/annealing and from the use of kinetic gas theory is able to deduce the temperature of the sample [23].

The main pump system used to obtain UHV conditions is the rotary (roughening) pump which is used for atmospheric pressure environments. This rotary pump is powered by an electric motor which causes an off-centre, spring tensioned vane, compressed against the chamber walls, to constantly rotate (analogous to a revolving door). The outlet of the turbo-molecular UHV pump is connected to the rotary pump's inlet, with the rotary pump's outlet expelling gas molecules to the atmosphere. At one stage of the spring vanes rotation, the volume within the chamber expands, causing a partial suction, causing air to flow through the inlet and into the rotary chamber. The spring vane continues to rotate, resulting in the gas molecules to be trapped and pushed around the chamber and expelled through the outlet. The gas molecules are compressed due to the rotation of the spring vane, which allows them to force open a valve between the rotary chamber and outlet, allowing the gas molecules to be expelled. Airtight seals and low vapour-pressure oil is used where necessary in the rotary chamber, so as to aid with lubrication of the spring tensioned vane against the chamber walls and also to reduce backstreaming of ambient gases [24]. The rotary pump is used continuously throughout the whole process, resulting in the pressure decreasing from atmospheric pressure 1013 mbar to a pressure of 1×10^{-3} mbar. The rotary pump is a key component in this process as it expels the bulk contaminants which is unachieved by the UHV pumps however can be considered as a systematic downfall for the atomic imaging process due to the vibrations generated by the electric motor. These vibrations affect the atomically sharp STM probe therefore it is necessary to attempt to reduce these vibrations generated by the electric motor as much as possible. The flat surface in which the UHV chamber lies on is raised off of the floor by dampening material, which reduces the magnitude of vibrations experienced by the atomically sharp STM probe, allowing suitable STM images to be produced. Usually before any STM imaging occurs, two valves are shut off. One situated between the roughening pump and the turbomolecular pump, and one between the UHV chamber and the turbomolecular pump. This prevents any backstreaming of contaminants and also allows the ability to shut off both the rotary roughening pump and the turbomolecular pump. By shutting off these two pump systems after UHV conditions are obtained removes significant vibrations caused by the pumps. This reduces systematic error when considering the STM imaging, as the STM probe is no longer affected by these vibrations.

Starting with the UHV pumps, there are two fundamental UHV pump systems which have two completely different methods of contaminant removal. One of these pump systems is a turbo-molecular pump which is a cylindrical chamber composed of a series of rotor/stator pairs which have opposite blade inclinations to each other. The inlet of this pump is connected to the vacuum system and the outlet connected to the roughening pump which expels the bulk load of the contaminants. When operational, the rotary blades operate between 24,000 - 60,000rpm [24]. Gas molecules and contaminants enter the pump via the inlet and into the turbomolecular chamber. The high rotation speeds of the rotor/stator pairs allow the gas molecules to gain momentum and travel from the compressed chamber in the rotor to the transfer holes in the stator, and hence the contaminants filter down through the pump and are expelled through the outlet valve and into the roughening pump.



Figure 5: Sectional view of a Turbomolecular pump, indicating inlet & outlet positions with respect to rotor/stator inclinations.

The second UHV pump works on a different principle compared to all other pump systems. Unlike the macroscopic bulk flow removal of microscopic gas molecules & contaminants, the ion pump system removes contaminants by manipulation of the electrical properties of the gas molecules at lower pressures. An anode plate and a cathode plate lie parallel to one another and induce gas molecules into becoming ions. This is caused by the two plates, which create a several keV potential electric discharge. This discharge causes electrons within the gas molecules to dislocate from the atom, causing the gas molecule to becoming positively charged. The residual cation is then accelerated towards the negative cathode plate due to the molecule becoming positively charged due to the loss of the negatively charged electron. An external magnetic field is introduced, causing the motion of the ions to transfer from a linear path between the anode and cathode, to a helical path. This increases the probability of collisions of ions with gas molecules between the two plates by increasing the mean free path travelled for the cation. Therefore, by increasing the cation's mean free path, the amount of ions produced due to the collisions between the ions and other gas molecules also increases, which in turn, induces more gas molecules to become positively charged ions. The anode/cathode plates are made from chemically-active Titanium, which allows the chemisorption of the ions attracted to the plates and hence removal of contaminants from the system. This chemisorption property is useful when considering the complexity of the removal of residual hydrogen molecules, as due to its low mass, hydrogen does not sputter the cathode significantly enough when compared to other ambient gases [24]. Therefore the removal of residual hydrogen molecules is usually left to neutral adsorption [25], however titanium hydride formation on the cathode plates at certain temperatures can lead to significant cathode plate deformation which decreases the speed of hydrogen gas removal. Therefore it is

considered useful if a sublimation pump or a getter pump is introduced within the system also, however is not fundamentally required.

The turbo-molecular pump, the Ion pump and the rotary roughening pump all work in unison to achieve the required ultra-high vacuum conditions needed for this experiment and result in a drastic pressure change within the chamber, decreasing the pressure from 1013 mbar (atmospheric pressure) to a pressure of $\sim 1.33 \times 10^{-10}$ mbar.

The resultant ambient gas pressure within the chamber is measured using an ionization gauge. A cathode filament is heated, resulting in the liberation of electrons from the filament surface which are then accelerated due to a potential difference between the cathode filament and an opposite facing anode. These accelerating electrons collide with residual gas molecules between the anode and cathode, resulting in the ionization of the gas molecules, similar to the operation of the ion pump. These ionized gas molecules are detected by a negatively charged Collector plate which attracts the positively charged ions and measures the ion current of the residual gas. This detected ion current is then amplified and displayed for the user's purposes. However, ionization gauges possess a lower pressure limit at which any detected ion current will be equal to the background current in the system therefore are considered useful until pressure's decline to 1×10^{-12} mbar. As our system is roughly maintained at ~1.33 × 10⁻¹⁰ mbar, ionization gauges are still useful and therefore necessary for the vacuum system. [24]

The unavoidable residual gas is measured and analysed using a quadrupole mass spectrometer (QMS). Again, similar to the operation of the ion-pump and the ion-gauge, current flows through a filament wire, causing it to heat up and liberate electrons from the material surface which are accelerated to a positively charged plate. These electrons ionise material passing through the passage which go onto travel through to the detector via a region containing four rods which are all parallel to each other. These opposing rod pairs are connected electrically and produce an electric field which is made up of the superposition of the direct current passing through the rods and the radio frequency. The QMS also possesses a mass filter which allows only certain ions which match specific mass/electric-charge ratios to be detected by the QMS due to the trajectory conditions set up by the electric field [26]. Disallowed ions cannot be detected due to their trajectory influenced by the electric field, causing them to collide with the four parallel rods, and are then filtered out. The ions which match the mass/charge ratios are able to enter stable oscillations and be detected and hence create a spectrum of elements/compounds which are detected within the chamber. [24]

The sample used in this procedure $(Al_{70}Pd_{21}Mn_9)$ was grown at Forschungszentrum Jülich GmbH [2]. The sample was initially cut perpendicularly to its high symmetry two-fold axis and then the quasicrystal sample was then treated with 6, 2, 1 & $0.25\mu m$ diamond paste. The 6, 2 & $1\mu m$ diamond paste is required to remove any bulk contaminants from the surface material, whilst the $0.25\mu m$ diamond paste is required so as to remove any damage caused by the previous diamond paste treatment whilst also removing any residual contaminants. The $Al_{70}Pd_{21}Mn_9$ sample is then placed into a beaker of methanol which is then placed into a bath of water.

The $Al_{70}Pd_{21}Mn_9$ sample is then ultrasonically treated within an ultrasonic bath to remove any residual diamond paste and contaminants from the quasicrystal sample. Ultrasonic waves are produced by a piezoelectric transducer which operates at an ultrasonic frequency due to the mechanical stress applied to the transducer, which also operates at ultrasonic frequencies. This generates compressive waves in the water medium, oscillating at ultrasonic frequencies which then clean the quasicrystal sample in the methanol solution. The methanol solvent is necessary as it enhances the effect of the ultrasonic cleaning technique by contaminant removal. After this process has been completed, the quasicrystal sample is removed from the methanol solution and is inserted into the atmospherically pressurised load lock of the UHV chamber.

Before the UHV chamber is depressurised, the $Al_{70}Pd_{21}Mn_9$ sample must be introduced into the load lock. Once the load lock is pumped down, the sample can be introduced into the main chamber. The $Al_{70}Pd_{21}Mn_9$ sample is initially cleaned as mentioned previously and is attached to a sample plate by tantalum wires which is then secured within the chamber by the manipulator. The tantalum wires are necessary due to possessing high melting/boiling points which are considered useful when concerning the annealing process. The manipulator allows various translational and rotational movement within the chamber and is used so as to position the $Al_{70}Pd_{21}Mn_9$ sample directly opposite the Argon gun for sputtering.

Argon is introduced into the UHV chamber by a pressurized container. Argon cations are produced via an electron gun, which are then fired at the sample surface hence creating a low pressure Argon plasma environment. The manipulator holding the $Al_{70}Pd_{21}Mn_9$ sample target is grounded, as it is necessary for constant Argon cation bombardment so as to clean the surface, however, due to constant cation bombardment, a build-up of positive charge collates on the $Al_{70}Pd_{21}Mn_9$ surface hence creating an electrostatic repulsion between the $Al_{70}Pd_{21}Mn_9$ sample and the Argon plasma environment. Therefore by grounding the manipulator, this electrostatic repulsion is removed and the sputtering process can continue. By constantly sputtering the quasicrystal sample with Argon cations, any contaminants situated on the surface are removed forcefully by the cations. However, constant Argon bombardment results in the quasicrystal surface structure to become damaged (analogous to meteors producing craters on the surface of the moon) and cause roughening of the surface (as well as destroying quasicrystalline ordering). The Argon environment was monitored using the quadrupole mass spectrometer.

However to obtain suitable STM & LEED data, it is necessary that the surface structure is relatively uniform and well defined. Therefore, to obtain a well-defined quasicrystal surface structure after having initially bombarded the material, it is necessary to undergo the annealing process after sputtering.

The $Al_{70}Pd_{21}Mn_9$ sample is heated between 850K - 950K for two hours so as to allow the quasicrystal surface to undergo reconstruction. This increase in temperature provides atoms within the quasicrystal with more kinetic energy and increases the rate of diffusion within the surface material. This allows redefinition of the damaged atomic structure of the quasicrystal as by increasing the rate of diffusion, the atoms within the structure redistribute throughout the material due to their atomic bonds being broken due to the increase in kinetic energy. By increasing the rate of diffusion, the probability of removal of surface defects such as dislocations within the surface is also increased. This is due to the atoms within the quasicrystal wanting to return the material to an energetically favourable equilibrium state. The quasicrystal must undergo several cycles of sputtering and annealing so as to ensure almost complete removal of contaminants from the sample surface and to ensure the quasicrystal has returned a suitable surface structure so as to allow Carbon-60 doping. Throughout this experiment, it was necessary to undergo 6-7 cycles of sputtering and annealing, with thirty minutes of sputtering occurring, followed by two hours of annealing before proceeding with any form of imaging. The quasicrystal sample is left to cool for thirty minutes after the annealing process so as to proceed with more cold sputtering. Before any initial dosing occurs, it is necessary to image the atomically clean surface of the $Al_{70}Pd_{21}Mn_9$ quasicrystal from the use of STM & LEED imaging.

Scanning Tunnelling Microscopy (STM) and Low Energy Electron Diffraction (LEED) techniques are used to image the two-fold, two-dimensional $Al_{70}Pd_{21}Mn_9$ surface as these two methods of imaging provide atom localisation information and, in turn, provide suitably detailed information on the atomic structure of the quasicrystal's surface. However, these two techniques differ when considering the principle behind their respective imaging techniques.

Low Energy Electron Diffraction operates under the principle of Bragg diffraction. A heated filament releases free electrons which are then accelerated towards the quasicrystal sample due to a potential difference being set up between the heated filament and the drift tube in which the liberated electrons travel through. This results in the electrons to increase their kinetic energy. However it is required that these electrons possess a relatively small energy as bombardment of the quasicrystal surface with high energy electrons will increase the inelastic mean free path of the electrons, hence allowing them to penetrate further into the quasicrystal surface. This would return information concerning more of the bulk molecular structure of the material, rather than characterising the immediate surface structure of the material. Therefore the potential difference between the heated filament and the drift tube is kept constant at a specific voltage so as to produce monoenergetic electrons and restrict the total energy of the liberated electrons, typically within the range of 20 - 50 eV. This allows the LEED imaging technique to specifically be surface sensitive by maintaining a relatively small inelastic mean free path.

The accelerated electrons collide with the stationary quasicrystal sample and are back-scattered towards a fluorescent collector screen, possessing preferred directionality set up by the Bragg diffraction conditions.



Figure 6: Diagram of LEED imaging operation, demonstrating an example of a LEED image. [27]

Elastically diffracted electrons are collected at the Collector screen which is set at a highly biased, positive potential difference whilst the inelastically scattered electrons are removed by the suppressor voltage maintained by the filter grids situated between the sample and the Collector screen.

The elastically diffracted electrons are accelerated due to the positive bias potential difference, providing them with enough kinetic-energy to cause fluorescence within the collector-screen and in turn, creates a pattern of detected, diffracted back-scattered electrons. Atomically clean surface's will return a highly symmetric diffraction pattern therefore the quasicrystal material requires multiple cycles of sputtering and annealing to attempt to obtain a clean surface so as to return a highly-symmetric diffraction pattern. If the surface is not sufficiently cleaned, the diffraction pattern will be distorted and will not provide suitable information. The LEED imaging technique was

used as an imaging precursor to suggest how clean the surface was by returning suitable diffraction patterns before undergoing STM imaging which is highly sensitive to impurities on the material surface. By investigating the symmetry of the LEED pattern, we were able to deduce whether another cycle of sputtering and annealing was required before undergoing STM. Using LEED as an imaging precursor was useful and more time efficient as analysing LEED images is considered more difficult when in comparison to using the WSxM software to analyse the STM images produced. Therefore inclusion of LEED images was not required.

Scanning Tunnelling Microscopy generates a topographical image of the quasicrystal surface due to the principle of quantum mechanical tunnelling. Piezoelectric drives power an atomically sharp, metallic probe, allowing movement along the three principle axes, so as to produce topographical scans of the material surface. The metallic probe is directed towards the conducting quasicrystal surface and a tip-surface separation of less than 1nm is held. A bias voltage is applied to the quasicrystal sample, allowing electrons to quantum-mechanically tunnel from the quasicrystal surface to the atomic probe, through the vacuum barrier, providing us with the ability to measure the tunnelling current and using the proportionality relation between the local density of state at the Fermi level. Using this relation and from the use of feedback circuitry, it is possible to locate specific tunnelling currents with respect to the three principle axes positioning and hence providing a topographical scan of the quasicrystal. STM imaging differs from LEED imaging due to LEED imaging working off the principle of reciprocal space whereas STM operates in real space. The piezoelectric drives are constructed out of piezoelectric transducers which are made up of a barium-titanate-oxide composite. This piezoelectric composite possesses a relatively extreme voltage sensitivity, approximately to the order of $10^{-10} mV^{-1}$. Therefore, to obtain accurate tip-sample separation, the piezoelectric transducers can operate on a low potential difference, so as the piezoelectric material can change in length in proportionality with respect to the induced potential difference [28]. If the atomic probe comes into contact with any adsorbates or contaminants, lateral or vertical manipulation of the adsorbates positioning may occur [29]. This causes extreme image distortion of the returned data therefore from the use of the Nanonis STM imaging software, an option is available in which a significantly strong discharge passes through the atomic probe and causes the now-attached adsorbate to repel from the atomic probe, so as to prevent image distortion and allow the imaging process to continue.

Once the quasicrystal sample has been thoroughly cleaned via multiple sputtering and annealing cycles and briefly imaged using LEED & STM techniques, it is now possible for the $Al_{70}Pd_{21}Mn_9$ to be doped with Carbon-60 molecules. This is done by adjusting the position of the quasicrystal sample by modifying the sample plate position from the use of the manipulator. This allows the quasicrystal sample's position to conform from where it was initially bombarded by Argon cations from the Argon gun, to a position lying directly parallel to a C60 source. C60 is deposited by thermal deposition onto the quasicrystal surface, with a background UHV pressure of ~1.33 × 10^{-10} mbar whilst the quasicrystal sample is held at 600*K*. From the use of the Fibonacci square-tiling and the Van der Waals diameter of the Carbon-60 molecule [30] [11], it was calculated that a coverage of ≈ 0.7 mL be applied to provide a suitable characterisation of the C60 adsorption onto the quasicrystal surface. This coverage is suitable as it conforms to an ideal coverage of C60 molecules which will reside only on the vertices of the square Fibonacci tiling template used throughout this experiment and therefore simplifying the mathematics used to identify quasicrystalline phase behaviour on the surface. It also reduces the probability of C60 clustering to occur which is necessary for suitable analysis to occur. As C60 molecules will adsorb onto the surface, using the 2-D Fibonacci square tiling as a structural template, by choosing this suitable coverage, there will be minimal localisation competition between C60 molecules. Therefore during visual analysis to identify quasicrystalline regions, it will be much simpler to identify these regions as there will be a lack of clustering of C60 molecules, all competing for the same vertex. Once the $Al_{70}Pd_{21}Mn_9$ sample has been successfully dosed with C60 molecules, it is now viable to undergo LEED & STM characterisation.

The quasicrystal used $(Al_{70}Pd_{21}Mn_9)$ was imaged and characterised using STM & LEED imaging techniques. These imaging techniques require specialist computer software to aid with the actual data collection and also with the analysis of the characterisation of the investigated quasicrystalline material by providing localisation information of both the quasicrystal sample and the Carbon-60 dopant. The provision of this localisation data is paramount for any analysis to occur as it allows us to characterise the C60 adsorption sites which provides us with a better understanding of the quasicrystal's topography, the resultant epitaxial grown thin film and finally the resultant properties of the quasicrystal itself.

The Nanonis software is specifically designed for the use of STM imaging. Its primary function provides the ability to study the surface topography of the investigated material and return information which allows characterisation of surface structure such as the epitaxy on crystals/quasicrystals, surface defects (i.e. step heights, faucets, terraces etc.) and also can help infer electro-chemical properties of the material, from analysis of the epitaxy information. The Nanonis software works in unison with the STM imaging apparatus and acts as the control mechanism for the STM imaging probe, employing two possible modes of operation. The STM probe can maintain a constant height mode, which allows the tip to be scanned along the xy plane of the two-dimensional surface and maintain its position with respect to the z axis. This method of operation measures the tunnelling current between the probe and the surface and plots a graph of tunnelling current against a function of the probe's positioning with respect to the surface's xy plane and in turn produces a topographic image of the surface material. The second mode of operation employs a constant tunnelling current which results in the probe-sample separation being fixed throughout operation. This technique allows the probe to oscillate in the z-axis whilst imaging the xy plane of the surface and therefore this mode of operation is best suited for rough surfaces as it has the ability to adjust the probe's height when considering peaks and troughs within the material's surface so as to maintain the tunnelling current. The constant height mode of operation would be considered as a downfall when considering this scenario, as the probe could collide with any protrusions from the material surface and hence would affect the data by distortion of any information collected by the probe. Therefore, throughout the experiment, the constant tunnelling current mode of operation was applied.

The information collected by the Nanonis software is then analysed using the WSxM imaging software. This software converts data collected from the initial Nanonis scan into image files which are then accessed using WSxM and analysed using the WSxM mainframe which allows operations such as Fast-Fourier Transforms (FFT's), distance characterisation of specific aspects of the material surface such as terrace separation, step heights and dopant separation and finally can convert the two-dimensional image into a three-dimensional projection which is useful when considering characterisation of any peaks/troughs within the surface material. This software is a key aspect in the characterisation of the two-fold icosahedral $Al_{70}Pd_{21}Mn_9$ surface as it is fundamental when considering mathematically modelling the quasicrystal structure and by superimposing Fibonacci Tau-scaling separations between dopant molecules.

3. Results and Analysis

3.1 Clean Al₇₀Pd₂₁Mn₉ Quasiperiodic two-fold surface.

Figure 7: Left: Single 57.8nm x 57.8nm WSxM image of the Clean Al₇₀Pd₂₁Mn₉ Quasiperiodic two-fold surface. Right: 20nm, zoomed in figure of Left image with adjusted contrast.

Investigation of the clean $Al_{70}Pd_{21}Mn_9$ quasiperiodic surface required the use of a mathematical model of the quasicrystal structure to allow comparison of step height data collated using WSxM. Using the data analysis software IGOR, combined with a provided mathematically modelled $Al_{70}Pd_{21}Mn_9$ quasicrystal allowed mathematically modelled values of step heights to be provided by measuring the separation between two dense planes of the model (Table 1). Comparison with WSxM Line Analysis measured values for the step height with this mathematical model and with previously published data demonstrates the reliability of the measurements taken.

Figure 8: IGOR analysis of step heights displaying density of planes

Adjustment of the measurement axes (y axes) provided theoretical step height values which occur in Table 1. Using WSxM and analysing multiple step heights for Figure 7 returned step height values.

Figure 9: Line analysis of step heights of Figure 7.

Experimentally measured data (Table 2 & 3) approximately matched the theoretical step height values found from IGOR analysis. A step height consistency check with data published by O.Groning et al. and D.Reid et al demonstrated that the WSxM measured values were conclusive with previous findings. As demonstrated in the tables, it was found that the step height sequence occurred from multiplying the previous step height by a factor of τ each time. Due to their being only several steps in this image, it was only possible to deduce steps correlating to τS , $\tau^2 S$ and $\tau^3 S$. Upon magnification of figure 7 and from inspection alone, it is apparent that all step edge interfaces commonly display ~90° kink angles, which is supported due to the fact that the quasicrystal possesses two high symmetry axes as it is twofold in nature. This has also been witnessed in previous findings [2, 1].

3.2 Dosed Al₇₀Pd₂₁Mn₉ Quasiperiodic two-fold surface

Figure 10 is a WSxM STM image provided from the use of the Nanonis software, describing a $30.0nm \times 30.0nm$ photo of the adsorption of Carbon-60 molecules onto the quasiperiodic $Al_{70}Pd_{21}Mn_9$ surface with the axes corrected to fit the XY axes respectively. All adjustments made on the image were accounted for during analysis.

Figure 10: Single 36.0nm x 36.0nm WSxM image of the adsorption of Carbon-60 molecules onto the $Al_{70}Pd_{21}Mn_9$ Quasiperiodic two-fold surface.

This structure consists of aperiodic rows and columns with small regions of molecular clustering and possible surface defects. From the use of this image, it was necessary to identify areas of quasiperiodicity from the use of Fibonacci Tau (τ) scaling. Using WSxM's line profiling analysis, it was possible to deduce the distance's between C60 molecules. It was then required to find a row of molecules, both along the horizontal and vertical axes, which followed Tau scaling relations whilst attempting to identify a row with reduced amounts of molecular clustering about an adsorption site.

Figure 11: Primary Horizontal Line demonstrating Tau scaling and molecule designation

Figure 12: Secondary Horizontal Line demonstrating Tau scaling (Box highlighting region of suspected adsorption site [Dark spot]).

The primary horizontal line (Figure 11) was chosen as it seemed to possess the least amount of atomic clustering and surface defects along its axis and therefore will most likely demonstrate more accurate tau-scaling amongst the molecular separations. Separation between each designated molecule was measured by placing the distance marker's central to each C60 molecule and the multiplicative factor was calculated so as to identify regions of tau-scaling, hence aiding the identification of S or L separations. Note that the multiplicative factor was calculated by dividing the largest successive distance with the smallest successive distance value for each molecule, therefore aiming to only return values approximately equal to unity or tau. To avoid confusion, the calculations are shown in the third column of each table.

The primary horizontal line has been shown to follow the Fibonacci substitution rules and obeys the sequence (Table 4). Taking an average of the multiplicative factor's which take $S \rightarrow L$ or $L \rightarrow S$ and excluding $L \rightarrow L$ will provide an average of the Tau-scaling multiplicative constant. [PHL = Primary Horizontal Line].

$$\tau_{PHL} = 1.519 \pm 0.030$$

The second horizontal line (Figure 12) was chosen again for similar reasons given for the primary horizontal line however the procedure followed for the secondary horizontal line differed slightly. Due to regions close to the highlighted line containing regions of clustered C60 molecules, it may be clear that many C60 molecules were competing for adsorption sites whilst leaving other adsorption sites (dark spots) empty. This prevented accurate measurements of tau to be taken when considering the approach used for figure 11 due to the atomic clustering affecting the separation values. Therefore the separations including the letter G in Figure 12 were given to be the

separation between each molecule and the central of the highlighted box in Figure 12, enclosing a dark region proposed to be an adsorption site. This highlighted region encloses a suspected manganese atom in the sublayer which are typical C60 adsorption sites due to the distribution of the least abundant element in the quasicrystal tending to define the adsorption site network [18] [11].

From Table 5, it appears that the molecules obey the Fibonacci substitution sequence using this technique and by following the same procedure to obtain an average of the tau-scaling constant, a value was calculated; [SHL = Secondary Horizontal Line].

$$\tau_{SHL} = 1.500 \pm 0.052$$

Identification of a suitable vertical line was not promising due to regions of C60 over-saturation, causing clustering and also due to surface defects across the image sample. Only one vertical line was suitable enough for investigation, with two different line analyses followed.

Figure 13: Primary Vertical Line Analysis

As before, a line profile was made for each separation and collated into a table. For reference sake, inspection of figure 13 demonstrates that the top marker lies on molecule A whilst the bottom marker lies on molecule J. Similar to the previous procedure, it was required to identify whether the molecules obeyed the Fibonacci tau-scaling with respect to their positioning by placing the markers central to each molecule. It was found for this arrangement that the molecules as shown above were not following accurate Tau-scaling separations (Table 6). Making an average

of the Tau multiplicative factors, it was found that the calculated tau value was consistent with the expected value, and the average provided a value of: [PVL = Primary Vertical Line]

$$\tau_{PVL} = 2.030 \pm 0.781$$

Due to the slow scan drift of the STM probe when considering the vertical scan, all values calculated during vertical line analysis have been increased by a scale of 8.83%. This was calculated from the use of WSxM and Inkscape by scaling the difference between a known distance in the x axis and then superimposing onto the vertical axes and adjusting so as to obtain the known distance in the y axis. The percentage difference is supplied by Inkscape and is applied to the value above;

$$\tau_{PVL}(scaled) = 1.865 \pm 0.718$$

However, following a similar procedure used to analyse Figure 12, by considering possible adsorption sites and ignoring C60 atoms who appear to be overly-competing for an adsorption site, analysis of this data seemed to demonstrate Fibonacci Tau-scaling (Table 7).

Figure 14: Primary Vertical Line, demonstrating positioning of possible adsorption sites

Figure 14 highlights a section of the line where a proposed adsorption site lies with respect to the boxed position in the figure. The data provided from this analysis returned a value for the Tau-scaling as;

$$\tau_{PVL} = 1.626 \pm 0.065$$

Again, by taking into consideration this value has been increased by a factor of 8.83%, the tau-scaling value is;

$$\tau_{PVL}(scaled) = 1.494 \pm 0.060$$

Therefore from the investigation of possible adsorption sites, a more accurate value for tau was provided. Consequently this investigated domain appears to be of a quasiperiodic nature, displaying no periodic phase behaviour, however does contain molecule clustering and surface defects.

From the use of InkScape software, the original image was rescaled so that the image axes were uniform at 30.0*nm* x 30.0*nm* and the image was rotated so that the alignment of the C60 molecules followed the XY axes. Note that all WSxM scaling was initially completed using the original image (Figure 10) and the following analysis is to demonstrate the incorporation of the Fibonacci square tiling and the different tile types.

From further inspection of Figure 10, it was necessary to identify how the adsorption of the C60 molecules onto the quasiperiodic surface followed the Fibonacci square tiling (Figure 1). It was necessary to create and superimpose onto Figure 10, the theoretical structural template for quasicrystals, therefore demonstrating the different tile types which arise from the superposition of two perpendicular one-dimensional Fibonacci SL separation sequences.

From the use of Figure 10, it was necessary to identify how the adsorption of the C60 molecules onto the quasiperiodic surface followed the Fibonacci square tiling (Figure 1).

Figure 15: Single 30.0nm x 30.0nm WSxM image.

Figure 16: Left: Figure 15 with superimposed Fibonacci square tiling. Right: Superimposed Fibonacci square tiling with different tile types highlighted

From the adjustment and use of the superposition of the square tiling onto Figure 15, it was possible to demonstrate the relation between the tiling template and the C60 adsorption sites and hence conclusively state that the C60 adsorbs onto the quasicrystal surface, using the square tiling as a template. The procedure used to analyse the Fibonacci Tau-scaling by including possible adsorption sites incorporated the use of Figure 16 by identifying the vertices' positioning and hence possible adsorption sites.

3.3 Dosed Al₇₀Pd₂₁Mn₉ Periodic two-fold surface

Figure 17 displays an 30.0*nm* x 30.0*nm* WSxM image of the periodic arrangement of the adsorption of C60 molecules taken directly after a uniform amount of sputtering and annealing cycles, similarly used for the identified quasiperiodic C60-adsorption arrangement.

Figure 17: Single 30.0nm x 30.0nm WSxM image of the periodic arrangement of the adsorbed C60 molecules on the $Al_{70}Pd_{21}Mn_9$ two-fold surface

Figure 17 displays clear C60 clustering, adopting a honey-comb type formation and displaying clear rows of C60 molecules with periodically separated positions. Multiple regions were investigated over the large image scan of the quasiperiodic surface, returning both regions of periodic phase behaviour and non-periodic phase behaviour. Using WSxM line analysis to measure row separation, two apparent periodic clusters were investigated and their multiple row separation measurements were made.

Figure 18: Line Analysis of Periodically Arranged C60 molecules (Body 1)

Figure 19: Line analysis of periodically arranged C60 molecules (Body 2)

Analysis of Table 8 & 9 returned an average row separation value of;

Average Row Separation = $1.205 \pm 0.08nm$

This averaged value came from two different periodically arranged C60 bodies and the calculated row separation was found to be conclusive with D.Reid et al, however, D.Reid et al didn't incorporate the use of C60 as a dopant but rather used copper deposition to deduce the row separation [2]. No domain boundaries between periodic and quasiperiodic nature were immediately identified however this could be due to the grain boundary causing a physical disturbance of the STM probe which would cause the resultant image to become indistinguishable hence is not recorded in this paper. Multiple measurements of step heights were taken using both line analysis and histogram analysis techniques, using three images displaying periodic behaviour. An average was taken for each method used and an error provided from the standard deviation of the measured values. The data is shown in Table 10;

Line Analysis = 0.213 ± 0.035 nm Histogram Analysis = 0.222 ± 0.038 nm

These values were found to be consistent with previously measured values of the step heights of the $Al_{70}Pd_{21}Mn_9$ two-fold surface, supporting both D.Reid et al & O.Groning et Al. [2] [1].

4. Discussion

The results presented in this paper concerning the clean $Al_{70}Pd_{21}Mn_9$ two-fold quasiperiodic surface and the C60 doped surface are shown to be conclusive with D.Reid et al & O.Groning et al. Adsorption of C60 molecules

appeared to use the Fibonacci square tiling as a structural template which again is supported by Lifshitz [2] [9], with bright protrusions seeming to adopt vertex positions as theorised.

Concerning the investigation of the clean quasiperiodic surface, from the provision of mathematically modelled step heights using IGOR and from the use of previously published data, demonstrated that the WSxM measured step height values were consistent with previous findings and also that the step height sequence was found to support D.Reid/O.Groning et al.'s findings [2] [1]. However, an image with more steps would have been favourably analysed as identification of higher τ scaling values would have provided more accuracy with the statement that the step height sequence are τ multiples of the previous step. On the other hand, figure 7 was suitable to deduce from inspection that the kink angles between step edges was approximately 90°, which is supported by the fact that this quasicrystal sample is twofold, therefore possesses only two high symmetry axes. To argue this point however, an image with more steps would have more regions of kink angles to inspect also.

Examination of the doped quasiperiodic behaviour returned four values for the tau-scaling factor, which is necessary to demonstrate and conclude whether or not C60 adsorption adopts the use of Fibonacci tau-scaling onto the quasiperiodic surface. Three of the four values were consistent with the known value of τ (or Φ), with the inconsistent value arising from the analysis of Figure 12. Therefore, concerning the technique adopted for this analysis, it may be deemed necessary when investigating regions of atomic C60 clustering to take into consideration possible manganese adsorption sites & the use of the square Fibonacci tiling template when undergoing line analysis to determine tau-scaling. This is due to there either being a lack of C60 molecules or an over-abundance of C60 molecules which affects both the quantity and quality of analysed data sample's therefore the previous statement should be considered or reduction of the fractional amount of the C60 monolayer applied to the quasicrystal should also be contemplated. By reducing the amount of C60 dopant onto the quasiperiodic surface could possibly allow more tau-scaling data samples to be taken, as as mentioned previous, it was difficult to conclude which C60 molecule alignment to choose as the majority of the C60 molecules succumbed to clustering, leaving only two horizontal line data samples to be analysed whilst leaving only one vertical line data sample also. Therefore it may be argued that the data set obtained is not adequate enough to produce a conclusive analysis.

Inspection of the doped periodic behaviour on the $Al_{70}Pd_{21}Mn_9$ quasicrystal returned nothing unexpected. Honey-comb-shaped clustering was witnessed and multiple measurements of row separations of two different clusters of C60 molecules returned an average row separation which was conclusive with D.Reid et al [2]. The step heights of the periodic surface was measured using two different techniques and provided an average value for each technique which was consistent with previously published data as denoted in Table 10. It would have been more suitable if there were more images to include in the data set however, briefly over-looking the majority of the images collated concluded that C60 clustering began to cause over-laying of molecules which prevented making accurate measurements of the step height. Hence again supporting the decrease in the amount of C60 applied to the surface sample. Inclusion of the square Fibonacci tiling template was necessary in the understanding of C60 adsorption onto a quasicrystal and exclusion of this template would have stalled the process of this experiment majorly.

5. Conclusion

The clean and C60 dosed icosahedral two-fold surface of the $Al_{70}Pd_{21}Mn_9$ quasicrystal have been investigated from the use of LEED and STM imaging techniques within UHV conditions. This paper demonstrates the processes followed to prepare the quasicrystal sample with respect to cleaning and UHV conditions and also to obtain the required data and is shown to be consistent with previously published data [2] [1]. Both periodic and quasiperiodic phase behaviours were witnessed with respect to C60 adsorption, demonstrating both tau-scaling and periodicity of row separations respectively. Approximate kink angles which are compatible for those expected of a twofold quasicrystal were witnessed and consideration of sublayer manganese adsorption sites seemed to obey with previously discussed findings and obtained data. Therefore it can be considered that the formation of the C60 adlayer succumbed to tau-scaling, tending to adopt manganese molecules as adsorption sites in the absence of C60 clustering.

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7. Appendix

PHYS379 Project (BSc) Proposal

Atomic scale characterization of thin film growth on surfaces of quasicrystals and related periodic crystals

In this experiment, it is required that we characterize thin film growth at atomic scales on quasicrystals of varied periodicities from the use of Low Energy Electron Diffraction (LEED) and Scanning Tunnelling Microscopy (STM) methods in ultra-high vacuum (UHV) conditions. With the ability to use these LEED and STM techniques, it is possible to probe the crystal's structure and relay the information through suitable computer software, providing an image of the crystal's periodic/quasiperiodic structure, along with identifying the thin film growth. A quasicrystal sample has been provided, which possesses sections of a quasiperiodic phase nature and sections of a periodic phase nature. This experiment has been designated between my peer (Robyn Griffiths) and myself, allowing two sub-experiments to be carried out, in which the sample deposition onto the quasicrystal surface is different.

For my experiment, it is required to use Buckminsterfullerene (C_{60}) as the dopant onto the sample surface whilst my peer will be using Zinc Phthalocyanine (ZnPC). It will then be required to use LEED and STM techniques to model the surface structure once the sample is initially prepared and cleaned thoroughly within the UHV chamber. This will occur for various layers of dopant, as well as repeating the experiment for a monolayer of dopant whilst changing the substrate temperature to see what affect this has on the quasicrystal.

The aim of this project is to produce a suitable STM/LEED image of the doped quasicrystal structure and be able to analyse the structure itself with respect to periodicity, dopant and from the use of Bragg diffraction rules and laws. It may be necessary to state that we will be following Fibonacci tiling models for quasicrystals as a precursor, so as to identify quasiperiodicity within the crystal. In doing this, we will be familiarising ourselves with fundamental computer software for this experiment.

Dates	Session 1	Session 2
Week 1 30/01-05/02	Meet with Dr. Hem Raj and Sam	Necessary papers and reading
	Coates to carry out Risk	material provided to gain
	Assessment and tour of the lab	knowledge of surface structure
		physics
Week 2 06/02-12/02	Generic timeline produced and	Project proposal completed
	edited for the upcoming weeks.	
	Project proposal underway	
Week 3 13/02-19/02	Begin to dismantle UHV unit	Continue Sample preparation if
	and prepare sample for cleaning	needed. If not, dose sample with
		layers of C60 and proceed taking
		STM/LEED images
Week 4 20/02-26/02	Analyse any data produced from	Continue with photo/data
	previous week's image	analysis
Week 5 27/02-05/03	Clean and prepare sample again	Dose sample with a monolayer
	within UHV chamber	of C60 whilst changing the
		temperature of the substrate and
		take data
Week 6 06/03-12/03	Analyse any data produced from	Continue with photo/data
	previous week's image	analysis
Week 7 13/03-19/03	Prepare for Oral Presentation	Prepare for Oral Presentation
Week 8 10/04-16/04	Practice Oral Presentation with	Carry out oral presentation
	peer, Hem Raj and Sam	

Timeline

Week9 17/04-23/04	Continue last minute data	Continue last minute data
	analysis	analysis
Week10 24/04-30/04	Collate all pieces of work and	Continue project report & data
	begin to piece together project	analysis
	report	
Week11 01/05-07/05	Continue project report & data	Continue project report & data
	analysis	analysis
Week12 08/05-14/05	Finish lab report right up and	Hand in diary and two hard
	project report write up	copies of final report

Data for Clean Al₇₀Pd₂₁Mn₉ Quasiperiodic Behaviour

Z(Ang)	IGOR DATA (Ang)	IGOR DATA (nm)	Scaling
20.3 → 22.7	2.400	0.240	S
20.3 → 26.3	6.300	0.630	
$22.7 \rightarrow 26.3$	3.870	0.387	τS
22.7 → 29.3	6.270	0.627	
26.3 → 30.4	3.870	0.387	
26.3 → 33.0	6.270	0.627	$\tau^2 S$
33.0 → 43.0	10.200	1.020	$\tau^3 S$

 Table 1: IGOR data with separation values matching between two dense planes (highlighted cells are densest planes).

Line Analyis	Trial 1 (nm)	Trial 2 (nm)	Trial 3 (nm)	Avg (nm)	STDEV	Scaling
S1	0.392	0.367	0.392	0.384	0.014	τS
S2	0.391	0.377	0.396	0.388	0.010	τS
S3	0.659	0.658	0.680	0.666	0.012	$\tau^2 S$
S4	0.370	0.369	0.374	0.371	0.003	τS
S5	1.011	1.088	1.079	1.059	0.042	$\tau^3 S$

Table 2: WSxM Data for analysis of Figure 9.

Scaling	Avg(nm)	STDEV
τS	0.381	0.009
$\tau^2 S$	0.666	0.012
$\tau^3 S$	1.059	0.042

Table 3: Averaged values for analysis of Figure 9

Data for Doped Al₇₀Pd₂₁Mn₉ Quasiperiodic Behaviour

Atom Designation	Distance (nm)		Multiplicative Factor	S or L
A1B1	2.035	B1C1/B1A1	1.025	L
B1C1	2.085	B1C1/C1D1	1.556	L
C1D1	1.34	D1E1/C1D1	1.482	S
D1E1	1.986	E1F1/D1E1	1.025	L
E1F1	2.035	E1F1/F1G1	1.519	L
F1G1	1.34	G1H1/F1G1	1.519	S
G1H1	2.035		-	L

Table 4: Data for Primary Horizontal Line (Figure 11)

Atom Designation	Distance (nm)		Multiplicative Factor	S or L
A2B2	1.980	A2B2/B2C2	1.523	L
B2C2	1.300	C2D2/B2C2	1.475	S
C2D2	1.918	D2E2/C2D2	1.097	L
D2E2	2.104	D2E2/E2F2	1.546	L
E2F2	1.361	F2G2/E2F2	1.409	S
F2G2	1.918	G2H2/F2G2	1.065	L
G2H2	2.042	G2H2/H2I2	1.500	L
H2I2	1.361	12J2/H2I2	1.546	S
1212	2.104		_	L

Table 5: Data for Secondary Horizontal Line (Figure 12)

Atom Designation	Distance (nm)		Multiplicative Factor	S or L
A3B3	2.592	A3B3/B3C3	1.572	L
B3C3	1.649	C3D3/B3C3	1.190	S
C3D3	1.963	D3E3/C3D3	1.480	S
D3E3	2.906	D3E3/E3F3	1.028	L
E3F3	2.827	E3F3/F3G3	1.059	L
F3G3	2.67	F3G3/G3H3	2.834	L
G3H3	0.942	H3I3/G3H3	2.918	S
H3I3	2.749	H3I3/I3JS	1.346	L
I3J3	2.042		_	L

Table 6:	Data for	Primary	Vertical	Line	(Figure	13)
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Atom Designation	Distance (nm)		Multiplicative Factor	S or L
A4B4	1.647	B4C4/A4B4	1.667	S
B4C4	2.746	B4C4/C4D4	1.522	L
C4D4	1.804	D4E4/C4D4	1.565	S
D4E4	2.824	D4E4/E4F4	1.028	L
E4F4	2.746	E4F4/F4G4	1.667	
F4G4	1.647	G4H4/F4G4	1.667	S
G4H4	2.746	G 4H4/H4I4	1.667	L
H4I4	1.647		-	5

Table 7: Data for (Corrected) Primary Vertical Line (Figure 14)

Data for Doped Al₇₀Pd₂₁Mn₉ Periodic Behaviour

Body 1	Row Separation (nm)
Trial 1	1.292
Trial 2	1.25
Trial 3	1.084
Trial 4	1.25
Trial 5	1.209
Trial 6	1.209
Trial 7	1.292
Trial 8	1.084
Trial 9	1.125

Table 8: Data for Row Separation of Periodic C60 adsorption (Body 1)

Body 2	Row Separation (nm)
Trial 1	1.289
Trial 2	1.164
Trial 3	1.331
Trial 4	1.206
Trial 5	1.248
Trial 6	1.123
Trial 7	1.248
Trial 8	1.123
Trial 9	1.164

Table 9: Data for Row Separation of Periodic C60 adsorption (Body 2)

	Line Analysis		Histogram Analysis
Image	Step Heights (Ang)	(nm)	Step Heights (nm)
(00)4	2.281	0.2281	0.2294
(00)5	2.373	0.2373	0.2547
(0)12	1.731	0.1731	0.1804

Table 10: Data for Step Heights of Periodic C60 adsorption

Consistency Check with D.Reid/O.Groning et.al Data for Step Heights

	(nm)	D.Reid Data	(nm)
τS	0.019	<	0.301
$\tau^2 S$	0.034	<	0.302
$\tau^3 S$		Unavailable	
	(nm)	O.Groning Data	(nm)
τS	(nm) 0.009	O.Groning Data <	(nm) 0.027
τ S τ²S	(nm) 0.009 0.036	O.Groning Data < <	(nm) 0.027 0.037

Hence data is consistent with WSxM measured values.

Consistency Check with D.Reid et al Data for Periodic Row Separations

 $(1.205 - 1.070)nm < 3\sqrt{(0.078)^2 + (0.05)^2}$ 0.135nm < 0.278nmHence data is conclusive with D.Reid et al.

Consistency Check with D.Reid et al & O.Groning et al. Data for Periodic Step Height Separation. Line Analysis Method

 $0.230 - 0.213 < 3\sqrt{(0.035)^2 + (0.05)^2}$ 0.017nm < 0.183nm (D.Reid)

 $0.240 - 0.213 < 3\sqrt{(0.038)^2}$ 0.027nm < 0.104nm (O.Groning)

 $\frac{Histogram Analysis}{0.230 - 0.222 < 3\sqrt{(0.038)^2 + (0.05)^2}}$ 0.009nm < 0.188nm (D.Reid)

 $0.240 - 0.222 < 3\sqrt{(0.038)^2}$ 0.019nm < 0.113nm (O.Groning)

Hence both analysis methods are consistent with published data.