Combined Scanning Tunneling and Atomic Force Microscopy and Spectroscopy on Molecular Nanostructures

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"However, I would like to point out that many high barriers exist in this world: Barriers between nations, races and creeds. Unfortunately, some barriers are thick and strong. But I hope, with determination, we will find a way to tunnel through these barriers easily and freely, to bring the world together so that everyone can share in the legacy of Alfred Nobel."

Leo Esaki, Nobel Prize Winner 1973^1

¹ [1] The Nobel Prize was divided, one half jointly to Leo Esaki and Ivar Giaever "for their experimental discoveries regarding tunneling phenomena in semiconductors and superconductors, respectively".

Abstract

Several key aspects in the exciting field of surface science on the nanoscale were addressed during this thesis. The common denominator of this work is the microscope used for the experiments; the combined scanning tunneling and atomic force microscope (STM and AFM). These scanning probe methods allow the study of electronic, magnetic and mechanical properties on surfaces down to the level of an individual atom.

In the scope of this thesis and a previous diploma thesis, I designed and built a combined STM/AFM head for an existing low temperature ultra-high vacuum system with a 14 Tesla magnet. The development of such novel instruments in this competitive field of research is a precondition to be capable of addressing the increasingly complex questions and to conquer ambitious experiments. In Chapter 3 I will summarize its design and highlight key features and important technological advancements, especially concerning the quartz tuning fork based force sensor. The versatility and reliability of the instrument was proven by a series of experiments at the atomic level.

The interplay between the individual atoms or molecules under investigation and the supporting substrate can have a significant influence on the properties derived. Therefore, also the investigation and thorough characterization of the versatile surfaces available is an important requirement. With the combined STM and AFM capabilities of the instrument I investigated the mechanical properties of the insulating layer of hexagonal boron nitride on a rhodium crystal (h-BN/Rh(111)). I will present a thorough data analysis that reveals surprisingly low stiffnesses of the strongly corrugated layer with unprecedented resolution. By this study also the experimental performance of the instrument and its potential to detect forces with sub-pico Newton resolution is demonstrated.

Also magnetism at the individual atomic and molecular level is accessible by scanning probe methods with excellent spatial and energy resolution. Spin-flip processes and the Kondo effect that arises due to the interaction between a localized magnetic impurity and the surrounding electrons, are the physical framework and a "fingerprint of magnetism" of the experiments on cobalt atoms I will discuss in Chapter 5. The perturbative approach to describe the spin-spin interaction can be derived from Kondo's original approach and will be introduced. It describes the data with convincing agreement. Already the topographic investigation of the cobalt atoms and cobalt-hydrogen complexes that formed on the h-BN/Rh(111) will reveal the richness of the underlying physics. I will further present the broad variety of spectroscopic signatures obtained during the investigation by scanning tunneling spectroscopy (STS). Here, the huge spread in magnetocrystalline anisotropies derived is worth highlighting. I will conclude with some elucidation and also some puzzling observations.

The ability of the AFM to measure very small forces with high spatial resolution is the key to investigating the fundamental force related to the exchange coupling, which governs magnetism. In Chapter 6 I will present our first experimental findings and a theoretical discussion of the ambitious experiment to measure the force related to the transition of two spins being parallelly aligned in an external magnetic field to the antiparallel alignment, when they are brought into closer proximity.

The first experimental observations related to the Kondo effect date back to the 1930s, while the first theoretical descriptions only emerged in the 1960s. These theories require discussion of the Kondo effect in different regimes, including strong and weak coupling and ferromagnetic as well as antiferromagnetic coupling. Most Kondo studies are discussed in terms of the strong coupling regime. The experiments done on a purely organic radical molecule that was directly deposited on a gold surface led to the intensive discussion of the different regimes and the underlying physics and models, which I will outline. The convincing agreement between the perturbation theory model and the experimental results on this true spin-1/2 system in the antiferromagnetic weak coupling regime will be summarized in the last chapter.

Single-molecule magnets (SMM) are envisioned for a broad range of possible application in information technology, but are at the same time of tremendous scientific interest, as they can be considered the link between quantum mechanical and classical magnetic systems. While previous studies (on Mn_{12}) had shown to be very successful, the STM/STS investigation of the SMM Cr_7Ni on a gold surface and on the *h*-BN layer did not result in conclusive findings. The work is discussed in Appendix A.

I will conclude this thesis with a summary and a selection of suggestions for interesting, as well as challenging further experiments the microscope should be capable of addressing.

Keywords: STM, AFM, combined STM/AFM, *h*-BN, mechanical properties, molecular nanostructures, magnetism, Co atoms, molecular magnetism, low temperatures

Motivation und Zusammenfassung

In der *molekularen Elektronik* werden einzelne Moleküle als Bausteine in elektronischen Schaltungen verwendet. Sie wird mittelfristig die konventionelle Silizium-basierte Elektronik ablösen, wenn die Miniaturisierung der Elektronik weiter voranschreitet [2–4]. Dies zeigt, dass die Grenzen, die G. Moore in seinem Gesetz formuliert hat (Verdopplung der Komplexität integrierter Schaltkreise, bzw. Transistordichten mit minimalen Komponentenkosten alle ca. 18 Monate), ständig in Frage gestellt werden [5, 6]. Auf dem Gebiet der *Spintronik* wird der Spin-Freiheitsgrad des Elektrons (der quantenmechanische Eigendrehimpuls) als zusätzlicher Informationskanal verwendet, was zu einer deutlichen Geschwindigkeitssteigerung und einer erhöhten Energieeffizienz führt [7, 8].

Durch die Untersuchung der elektronischen und magnetischen Eigenschaften einzelner Atome und Moleküle auf Oberflächen können Rückschlüsse auf die Eigenschaften gewonnen werden, die für solche Technologien relevant sind. Dabei ergeben sich grundlegende Einblicke in die faszinierende Welt der Quantenphysik im Nanometerbereich.

Während sich die meisten Ansätze auf diesem Gebiet noch im Bereich der Grundlagenforschung bewegen, gibt es immer Ansatzpunkte um Anwendungen für die Technologie für "Übermorgen" zu erkennen. Einige Beispiele sollen dies verdeutlichen: Die *Esaki-Diode* beispielsweise, die als erstes elektronische Bauteil auf dem quantenmechanischen Tunneln von Elektronen basiert [9, 10], die Beobachtung des *Kondo-Effekts* in einem Ein-Elektron- oder einem Ein-Atom-Transistor [11, 12], oder der Datenspeicher bestehend aus nur 12 Eisen-Atomen für ein Bit [13]. Die Arbeit und die Experimente, die im Rahmen dieser Doktorarbeit durchgeführt wurden, haben dazu beigetragen, diverse Aspekte auf verschiedenen Ebenen dieses umfangreichen Forschungsgebietes der Oberflächenphysik im Nanometerbereich weiterzubringen.

Als gemeinsamer Nenner der Kapitel dieser Arbeit kann das Mikroskop gesehen werden, welches für die Experimente verwendet wurde: Ein kombiniertes Rastertunnel- und Rasterkraftmikroskop (englisch STM für *scanning tunneling microscope* und AFM für *atomic force microscope*). Das STM erlaubt, durch das Abrastern der Oberfläche mit einem scharfen metallischen Draht und der Bestimmung der elektrischen Leitfähigkeit in jedem Punkt ein Bild der elektronischen Struktur der Oberfläche zu erstellen. Durch geschickte Variation der Spannung zwischen Probe und Spitze (Rastertunnelspektroskopie), sind ebenfalls Rückschlüsse auf die magnetischen Eigenschaften möglich. Das AFM erlaubt hingegen durch Messung der Kraftwechselwirkung zwischen Probe und Spitze auch nichtleitende Proben zu untersuchen und mechanische Eigenschaften zu bestimmen. Beide Methoden ermöglichen es, diese Eigenschaften auf atomarer Ebene zu bestimmen. Im Rahmen dieser Doktorarbeit und einer vorangegangenen Diplomarbeit [14] wurde ein kombiniertes STM/AFM entworfen und aufgebaut. Es wurde im Laufe der Doktorarbeit in einen bestehenden experimentellen Aufbau integriert. Dieser erlaubt es, Experimente bei extrem tiefen Temperaturen (1.5 K) und hohen Magnetfeldern (14 Tesla) im Ultrahochvakuum durchzuführen. Die experimentell benötigte Infrastruktur für Probenpräparation und grobe Charakterisierung (Auger- und Massenspektrometer) ist ebenfalls vorhanden.

Die Entwicklung eines solchen Instruments, in diesem wettbewerbsintensiven Bereich der Physik, ist eine entscheidende Voraussetzung für erfolgreiche Forschung. Nur wer aktiv an der Entwicklung neuer experimenteller Methoden mitwirkt, kann die immer komplexeren Fragen beantworten. Das Design des Mikroskops wird in Kapitel 3 zusammengefasst und die wichtigsten Eigenschaften hervorgehoben. Der Fokus liegt auf der Weiterentwicklung des Kraftsensors, der auf einer Quarz-Stimmgabel basiert [14, 15]. Das Mikroskop hat im Laufe der letzten Jahre seine Vielseitigkeit und Zuverlässigkeit in den durchgeführten Experimenten bewiesen.

Das Trägersubstrat, welches bei den vorgestellten Experimenten entweder eine Metalloberfläche wie Gold, oder eine dünne isolierende Schicht auf einem Metallkristall war, kann einen wesentlichen Einfluss auf die Eigenschaften des untersuchten Atoms/Moleküls haben. Daher ist auch die Untersuchung und gründliche Charakterisierung der Oberflächen eine wichtige Voraussetzung. Mit der Kombination der STM- und AFM-Fähigkeiten des Mikroskops wurden die mechanischen Eigenschaften der isolierenden monoatomaren Schicht aus hexagonalem Bornitrid auf einem Rhodium-Kristall (*h*-BN/Rh(111)) untersucht. Die Ergebnise der ausführlichen Datenanalyse werden in Kapitel 4 präsentiert. Dabei wurde eine überraschend niedrige Steifigkeit in der Größenordnung von 1 N/m der stark gewellten Schicht entdeckt, und mit atomarer Auflösung ausgewertet. Mit dieser Studie wurde die experimentelle Leistungsfähigkeit des Mikroskops und die Möglichkeit mit sub-pico-Newton-Auflösung zu messen überzeugend demonstriert.

Auch Magnetismus ist auf atomarer und molekularer Ebene durch STM mit hoher örtlicher und Energie-Auflösung zugänglich, wobei typischerweise der Spin untersucht wird. Bei sogenannten *Spin-Flip-Prozessen* wird dieser gezielt in einen energetisch höher gelegenen Zustand angeregt, wodurch Rückschlüsse auf dessen Eigenschaften möglich sind. Auch der *Kondo-Effekt*, der durch die Wechselwirkung zwischen einer lokalisierten magnetischen Verunreinigung und den umgebenden Elektronen entsteht, erlaubt Rückschlüsse auf die Verunreinigung. Diese "magnetischen Fingerabdrücke" werden in den Experimenten an Kobaltatomen in Kapitel 5 diskutieren. Die Störungstheorie, die in Ansätzen schon von Kondo vor 60 Jahren entwickelt wurde [16], wird vorgestellt und die experimentellen Daten werden mit überzeugender Übereinstimmung mit diesem Modell quantitativ beschrieben. Schon die topografische Untersuchung der Kobaltatome und Kobalt-Wasserstoff-Komplexe, die sich auf der h-BN/Rh(111) Probe gebildet haben, zeigt die vielfältige Physik dieses Probensystems. Die Vielzahl spektroskopischer Signaturen, die mittels Rastertunnelspektroskopie aufgenommen wurden, wird ebenfalls diskutiert. Hier ist die breite Verteilung der magnetischen Anisotropie-Parameter hervorzuheben. Sie ist möglicherweise darauf zurückzuführen, dass die hochgradig anisotrope Oberfläche oder Kohlenmonoxid-Adsorbate die lokale Umgebung der Kobalt-Komplexe derart beeinflusst, dass die magnetische Kopplung lokal stark variiert. Die Kopplung zwischen den Kobalt-Komplexen und der Probe als auch der Spitze werden eingehend untersucht und quantifiziert. Neben ersten gesicherten Erkenntnissen werden auch einige bisher unerklärte Beobachtungen gezeigt.

Die Fähigkeit des AFMs sehr kleine Kräfte mit hoher räumlicher Auflösung zu bestimmen, ist der Schlüssel um die Kraft, die durch die sogenannten Austauschwechselwirkung zwischen zwei Spins hervorgerufen wird, zu messen und darüber einen fundamentalen Parameter des Magnetismus zu charakterisieren.

In Kapitel 6 werden die ersten experimentellen Ergebnisse und eine theoretische Beschreibung des anspruchsvollen Versuchs diskutiert. In einem stark vereinfachten Bild kann das Experiment wie folgt beschrieben werden: Ein (magnetisches) Kobaltatoms sitzt auf der Spitze des AFMs und wird über einem anderen Kobaltatoms auf der Oberfläche platziert. Befinden sich die beiden in ausreichender Entfernung sind ihre Momente (Spins) in einem externen Magnetfeld parallel ausgerichtet. Wenn der Abstand nun verringert wird, wird die antiferromagnetische Austauschwechselwirkung einen der Spins zur Neuausrichtung zwingen, sobald diese Kopplung stärker ist als das äußere Magnetfeld. Dieses "Umflippen" vom parallelen in den antiparallelen Zustand geschieht auf Grund der Quantenmechanik instantan und sollte in den Kraft-Abstands-Kurven zu beobachten sein.

Die ersten experimentellen Beobachtungen im Zusammenhang mit der Kondo-Effekt gehen zurück in die 1930er Jahre, während die ersten theoretischen Beschreibungen erst in den 1960er Jahren entstanden. Diese Theorien klassifizieren den Kondo-Effekt in verschiede Bereiche, die der starken und schwachen und der ferromagnetischen oder antiferromagnetischen Kopplung. Eine universelle Beschreibung ist nicht möglich. Die meisten Experimente an Kondo-Systemen erlauben eine Beschreibung in der Klasse der starken Kopplung. Die Experimente und deren Interpretation an einem rein organischen Molekül auf einer Goldoberfläche führten zu einer intensiven Diskussion der verschiedenen Klassen und der zugrunde liegenden Modelle, die in dieser Arbeit ebenfalls wiedergegeben wird. Die überzeugende Übereinstimmung zwischen dem störungstheoretischen Modell und den experimentellen Ergebnissen ist in Kapitel 7 gezeigt. Erst mit Hilfe von sowohl temperaturals auch magnetfeldabhängigen Messungen konnte gezeigt werden, dass es sich um ein Spin-1/2-System im Bereich der antiferromagnetischen schwachen Kopplung handelt.

Die vorliegende Arbeit schließt in Kapitel 8 mit einer Zusammenfassung und einer Auswahl an Vorschlägen für interessante weitere Experimente, welche das ganze Potential des Mikroskops herausfordern.

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CHAPTER 1

Introduction

1.1. Motivation

The advent of *molecular electronics*, where single molecules function as building blocks in electronic circuits, is inevitable if miniaturization of electronics proceeds [2–4]. This illustrates that the limits "set" by *Moore's law* are constantly challenged [5, 6], or, in the spirit of R. Feynman: "There's plenty of room at the bottom" [17]. In the field of *spintronics*, the spin degree of freedom of the electron is additionally used as information carrier in electronics devices [7, 8]. In the research performed on single-molecule magnets [18, 19], the spin properties of the constituents have to be combined with the molecular properties for a comprehensive understanding.

By studying the electronic and magnetic properties of single atoms and molecules at surfaces, fundamental insights into the fascinating world of quantum physics at the nanoscale are provided. While most of the experiments in this field are still in the realm of fundamental research, there are always ways to envision applications for the technology for the "day after tomorrow": Starting from the *Esaki diode* that can be considered the first electronic device relying on quantum-mechanical electron tunneling [9, 10], over the observation of the Kondo effect in a single electron and single atom transistor [11, 12], to the recently shown data storage consisting out of only 12 Fe atoms for one single bit [13], or the spin-based logic operation in a chain of Fe atoms by Khajetoorians *et al.* [20], to just name a few. The work and the experiments performed during this thesis contributed to several aspects and on different levels of this area of research.

Scanning probe methods like scanning tunneling microscopy (STM) and atomic force microscopy (AFM) are the tools of choice for investigating the fundamental electronic, magnetic and mechanical properties of individual molecules and even atoms with continuously increasing resolution. The new combined STM/AFM head put into full operation during this thesis is, in combination with the powerful system of high magnetic field, low temperatures, single "cold" atom evaporator and high mechanical stability, a unique tool that is capable of pushing the frontiers of science. This was proven during the last years by a series of diverse experiments. In the context of fundamental research, the experiments on single atoms can be considered the supreme discipline, as usually a high degree of clarity and control is ensured. This especially includes the ability to control and manipulate them on the surface [21–24]. In the context of magnetism, the work on single Co atoms can be considered the "drosophila of magnetism", as lots of groundbreaking results were obtained on Co [25, 26]. The experiments performed on Co atoms and Co-H species (Chapter 5) can be considered as an important contribution at the transition between single atoms and small molecules.

The research performed also expands to bigger systems, where an organic radical molecule (Chapter 7) and a single-molecule magnet (Appendix A) were studied. This work showed that the supporting surface has a non-negligible influence on the properties of the adsorbates. Besides electronic interactions, also the mechanical properties of the substrate can be relevant (Chapter 4).

1.2. Structure of the Thesis

The experimental techniques and the underlying theory of the physics involved will be described in Chapter 2. Chapter 3 focuses on the combined STM/AFM whose construction was completed during this work. This chapter overlaps partly with the corresponding chapter in ref. [14], where the designing process and the construction of the STM/AFM head by the same author are discussed in detail. While maintenance and continuous performance upgrades on the experimental setup are an existential and substantial part of the work during this thesis, only the most relevant changes will be discussed.

In Chapters 4 to 7 the scientific contributions are discussed in detail. The order is chosen depending on the author's contribution and the amount of time it occupied – i.e. it is not in chronological order. It starts with AFM experiments dedicated to investigate the mechanical properties of the hexagonal boron nitride (*h*-BN) single layer on rhodium(111) (Chapter 4). It continues with the most recent discoveries on single Co atoms and Co-H systems on the *h*-BN layer with STM and some initial AFM experiments (Chapter 5 and 6, respectively). A summary of the spectroscopic study of an organic radical Kondo system is given in Chapter 7. In Appendix A a short overview of the work done on the single-molecule magnet Cr_7Ni is given, which did not result in conclusive findings. A conclusion of the work performed during this thesis, its impact and suggestions for further experiments (short and long-term) can be found in Chapter 8.

1.3. Location and History of the Experiment

All experiments discussed in this thesis were performed in the group of Prof. Klaus Kern at the Max Planck Institute for Solid State Research in Stuttgart, Germany. Unless otherwise stated, the STM and AFM data was exclusively recorded at the same home-built experimental system discussed in Chapter 3. The first microscope was designed and built from 2001 – 2005 by Messina and Wittich [27, 28] and was since then constantly changed and improved. This is especially true for the microscope head, where four versions are still partly operational in storage. During 2009 a new combined STM/AFM head was designed by the author [14] and put into operation during this thesis in 2011. In 2013 the whole system was moved to a new high precision laboratory, where some significant technical changes were made that will be discussed.

All STM/AFM images are processed either with WSxM [29], MatLab or GWYDDION. For data processing Origin, Excel, Scilab and Matlab were used. Figures were made with the following programs: Power Point, Corel DRAW X6, Corel PHOTO-PAINT X6, Inkscape and Adobe Photoshop CS6. The designing and the technical drawings shown in the thesis were done with Creo Elements from PTC.

Chapter 2

Theory and Techniques

The STM was invented in 1981 by G. Binnig and H. Rohrer [30, 31] and earned them the Nobel prize in physics already five years later in 1986 (jointly with E. Ruska for the invention of the electron microscope). While a full coverage of the technique and the more than 30 years of evolution is not feasible, only the very basic principle of STM will be discussed. The same holds true for other scanning probe methods that emerged already shortly after, like AFM in 1986 [32]. For an introduction Chen's "Introduction to Scanning Tunneling Microscopy" [33] and "Noncontact Atomic Force Microscopy" from Morita *et al.* [34] are recommended.

After looking at the STM in the following section AFM is introduced in Section 2.3 with a special focus on the design where STM and AFM are combined in the tuning fork design (Section 2.4).

2.1. Scanning Tunneling Microscopy

2.1.1. Working Principle

In a simplified picture the working principle and the physics of STM can be summarized as follows: A conducting wire (the tip) is placed with a distance of the order of a few Ångstrom (1 Å = 10^{-10} m) to a conducting sample. When a voltage is applied between tip and sample, a small current (in the range of pico- to nanoamperes) can be detected, which flows due to the quantum mechanical nature of the electrons. This effect is called "tunneling". By scanning the tip over the sample and recording the current, a map can be recorded that is (in a first approximation) an image of the topography of the sample. Figure 2.1 illustrates the working principle.

Two modes of operation are commonly deployed: In *constant height mode* the tip is scanned at a fixed height and an image of the current is recorded. Modern electronics also allow adjustment of the scan plane to align it parallel to the sample surface. This mode requires rather flat surfaces and stable overall performance to preclude crashing of the tip into the surface. In *constant current mode* the current is used as a feedback signal and the tip-sample distance is adjusted to maintain a constant current and is recorded as the signal. For the feedback a proportional-integral controller has to be set up according to



Figure 2.1.: Working principle of an STM: The metallic tip is brought into close proximity of the sample. The tunneling current flowing due to the applied bias is measured and used as a feedback signal to regulate the distance between tip and sample (z-direction) while the tip is scanned in the x- and y-direction to acquire an image.

scan speed, resolution and sample roughness to obtain optimum results.

The quantification of the tunneling process is based on the overlap of the electronic wave functions, which describe the states of the tip and the sample. The probability of tunneling depends on the electron energy (bias) and the height and thickness of the barrier. The barrier height corresponds to the work function that accounts for the energy necessary to remove an electron from the tip and inject it into the sample (or vice versa). The thickness of the barrier is the gap (typically vacuum) between the tip and the surface.

As will be derived in Section 2.1.2, the tip-sample distance dependence of the tunneling current is exponential. This is crucial for STM operation, as the current is extremely sensitive to very small height corrugations (it changes by an order of magnitude for a change in height of only about 1 Å) and because only the last few atoms at the tip apex contribute to the current. This makes the exact geometry of the tip usually not so crucial for imaging.

STM images do not directly reflect the topography of the sample, but rather reveal the spatial distribution of the electronic structure, which is the convolution of the local density of states (LDOS) of tip and sample, as will be discussed in the following section. Analogous to the system used in this work, the following discussion will be limited to the case where the bias voltage is applied to the sample, i.e. for positive bias electrons flow from occupied states of the tip to the empty states of the sample.

2.1.2. Theoretical Description



Figure 2.2.: Schematic of the one-dimensional tunneling barrier, as discussed in the text.

Because the simple one-dimensional model depicted in Figure 2.2 with a square barrier of height V, thickness d and an electron with energy E leads to an exponentially declining tunneling probability, it will be briefly derived in the following. Starting point is the Schrödinger equation:

$$E\psi(x) = \left(-\frac{\hbar^2}{2m_e}\nabla^2 + V(x)\right)\psi(x), \qquad (2.1)$$

with m_e the electron mass and V(x) the potential barrier. This equation is solved by plane waves outside the barrier and by an exponential decay inside the barrier, with the boundary conditions determining the amplitudes. With $\kappa \coloneqq \sqrt{\frac{2m(V-E)}{\hbar^2}}$ the transmission coefficient that describes the probability of an electron to penetrate through the barrier, can be calculated to be:

$$T = \frac{4E(V-E)}{4E(V-E) + V^2 \sinh^2(\kappa d)}$$

$$\approx 16 \frac{E}{V} \left(1 - \frac{E}{V}\right) \cdot e^{-2\kappa d} \quad \text{for } \kappa d \gg 1.$$
(2.2)

This shows the important exponentially declining probability of an electron to penetrate through the barrier as a function of barrier thickness d.

In a more realistic system, such as that depicted in Figure 2.3, (V - E) is replaced by the average work function of sample and tip $\Phi = \frac{1}{2}(\Phi_S + \Phi_T)$ and all possible conductance channels are summed up. Therefore, the local density of states (LDOS) of the sample and the tip ρ_S and ρ_T , respectively, are introduced to describe the states available at a certain energy. A net current is obtained when a bias V is applied. For a positive (negative) voltage electrons flow from the filled states of the tip (sample) to the empty states of the sample (tip).

To quantify the current, one starts from Fermi's golden rule:

$$I(V) \propto \int_{-\infty}^{\infty} \rho_S(E) \rho_T(E - eV) |M(E, V, z)|^2 (f_T(E - eV, T) - f_S(E, T)) \, dE, \qquad (2.3)$$



Figure 2.3.: Simplified energy diagram of the tunneling junction with the density of states of tip and sample depicted in gray.

where f_T and f_S are the Fermi-Dirac distributions of tip and sample, respectively, T is the temperature, and M is the transmission matrix for the tunneling barrier. According to Bardeen's theory for tunneling between metals [35], the matrix element is given by the overlap of their wave functions:

$$M(E,V,z) = \frac{\hbar^2}{2m} \int \left(\psi_S^* \nabla \psi_T - \psi_T \nabla \psi_S^*\right) \, \mathrm{d}A \,, \tag{2.4}$$

with integration over a surface A separating sample and tip. The calculation of this matrix element is in general not feasible, because the wave functions are not exactly known. In 1983 Tersoff and Hamann introduced a model [36, 37] that makes it possible to calculate M with the fundamental assumptions of a single (spherical) *s*-orbital for the tip. The sample wave function is described by plane waves. For the matrix element it follows:

$$M^2 \propto \exp\left(-2z\sqrt{\frac{m}{\hbar^2}(\Phi_S + \Phi_T - 2E + eV)}\right),$$
(2.5)

where the effect of a finite temperature is neglected. With all the approximations made, one gets for T = 0, which corresponds to a step function instead of the Fermi distribution:

$$I(z,V) \propto \rho_T \int_{E_F}^{E_F+eV} \rho_S(E) \exp\left(-2z\sqrt{\frac{m}{\hbar^2}(\Phi_S + \Phi_T - 2E + eV)}\right) dE, \qquad (2.6)$$

which shows the same exponential distance dependence as the simple one dimensional model (Equation (2.2)). If one further assumes the bias voltage to be small compared to Φ and thus the matrix element being independent of E, the only voltage dependence which remains is:

$$I(V) \propto \int_{E_F}^{E_F + eV} \rho_S(E) \, \mathrm{d}E \,.$$
(2.7)

Furthermore, if the bias is assumed to be small, the only proportionality which remains is:

$$I \propto \rho_S(E_F).$$
 (2.8)

This emphasizes that the recorded current in STM can be interpreted – with the mentioned limitations – as an image of the LDOS around E_F of the substrate. The exponential distance dependence of the current remains valid and contributes the topographic information to the recorded image.

2.2. Scanning Tunneling Spectroscopy

While STM is mainly deployed to learn about the topography of a sample, scanning tunneling spectroscopy (STS) is a powerful technique to investigate the electronic properties of the system of interest at the atomic scale. A number of fundamental questions were successfully addressed by this technique. Already before the rise of scanning probe techniques tunneling spectroscopy had shown to be a powerful technique, as nicely summarized in ref. [38], were also spin-flip and Kondo scattering is discussed.

In the following, an introduction to inelastic dI/dV-spectroscopy is given, as a significant part of the results in this thesis was obtained by this technique. The measurement setup deploys a lock-in amplifier and the limitations relevant for the energy resolution are briefly discussed.



Figure 2.4.: Example of an inelastic tunneling process. (a) Tunneling junction with a molecule inside. A vibrational mode is excited if the electron energy eV is larger than E_0 . (b) I(V)-curve showing the additional conductance channel opening for $V > E_0$. In the dI(V)/dV-curve below this is visible as a step (and in the second derivative as a peak).

A constant DOS is desirable (and in the following assumed) for the tip in the bias range of interest. In the experiments the tip termination is usually unknown, therefore reference spectra on the substrate have to be recorded allowing for unambiguous identification of features that are only present on the structure of interest.

Starting from Equation (2.7) and differentiating it with respect to V one finds the proportionality:

$$\frac{\mathrm{d}I}{\mathrm{d}V}(V_0) \propto \rho_S(eV_0)\,.\tag{2.9}$$

By recording I(V)-curves and calculating the derivative one has hence direct access to the LDOS of the sample as a function of bias. In practice a more elegant method deploying lock-in detection is used, which allows for direct measurement of the differential conductance. Therefore a small AC voltage is added to the tunneling bias by the lock-in amplifier:

$$V = V_{Bias} + V_{LI}\sin(2\pi ft), \qquad (2.10)$$

with V_{LI} being the lock-in modulation voltage and f the frequency of the modulation. The detection signal, which is proportional to the LDOS at V_{Bias} averaged over the range of $\pm V_{LI}$, is then recovered from the tunneling current by the lock-in amplifier electronics. The lock-in excitation voltage V_{LI} has to be chosen according to the experimental requirements: For the experiments performed in this work, where usually features with widths of a few meV are investigated at T = 1.5 K, it should be in the range of 0.1 – 1 mV. It can be shown that at 1 mV the obtained resolution is mainly limited by the modulation voltage to 2.5 meV, while at 0.1 mV excitation the temperature broadening of the features is more crucial, allowing an increase in resolution down to 0.3 meV at 1.5 K [39]. The frequency of the excitation voltage has to be chosen below the bandwidth of the current amplifier and above the bandwidth of the scan feedback loop to avoid interference, and is typically in the range of 600 – 800 Hz. System inherent parasitic frequencies should be also avoided to obtain a clear signal.

A broad range of phenomena can be investigated by inelastic electron tunneling spectroscopy (IETS) where the tunneling electrons excite processes in the junction by losing some of their energy. The first application of this method dates back to 1966 where Jaklevic and Lambe used it to investigate molecular vibrations (O-H and C-H bending and stretching modes) in metal-oxide-metal junctions [40]. Only the invention of STM made it possible to address those (and further) properties on the individual molecule level and with unprecedented knowledge of the environment on the supporting substrate. Here, the first measurements of inelastic vibrational spectra on single molecules by STM in the group of W. Ho in 1998 are worth highlighting [41].

Inelastic tunneling occurs if the sample provides two discrete energy states and if the applied bias provides enough energy for the tunneling electron to excite the state by overcoming the energy difference between the two states, i.e. if $eV \ge E_0$. This additional channel results in an increase of the observed tunneling current above the threshold voltage E_0 , as depicted in Figure 2.4. Note that this kink in the I(V)-curve will show up as step and peak in the dI/dV and second derivative (d^2I/dV^2 -signal), respectively. As the excitation does not depend on the direction of the current the observed features are symmetric around zero bias.

Further aspects of IETS, especially spin-flip spectroscopy, where the pioneering work by Heinrich *et al.* [42] on the observation of the excitation of single electron spins has to be mentioned, will be discussed in the context of the experiments in Chapter 5.



2.3. Atomic Force Microscopy

Figure 2.5.: Illustration of the working principle of an AFM: (a) In the most common setup utilising an optical detection mechanism a laser beam is reflected from the cantilever and the bending motion due to the interaction with the sample is measured with a detector array. (b) In the setup implemented in this system an oscillating quartz tuning fork with a tip attached to it is used as a force sensor that is scanned over the surface. Due to forces acting between tip and sample the frequency and amplitude of the oscillating prong change from its unperturbed values. The oscillation amplitude is directly accessible as a small current, which is induced due to the piezoelectric properties of the quartz.

2.3.1. Working Principle

In AFM a sharp tip is attached to a cantilever and scanned over the sample. Due to the forces that act between tip and surface (see Figure 2.6 (a)) the cantilever bends and thereby the interaction force can be indirectly measured. The cantilever deflection can be measured in different ways: While in the first AFM an STM was used [32], also capacitive, piezoelectric, or optical schemes are deployed. The deflection of a laser beam as sketched in Figure 2.5 (a) is the most common implementation. The most important advantage of AFM over STM is its ability to also investigate insulating samples. This makes AFM also popular in the life sciences.

The different characteristics of AFMs are as broad as the range in which they are used. To understand the huge advantages of the chosen sensor setup deployed in this work, it is worth quickly summarizing the most popular modes of operation. In ref. [44] an extensive review on the AFM modes is given by Garcia and Perez.

A first reasonable criterion to distinguish operation modes is based on whether or not a feedback is controlling the scan, and if so, which kind. In constant height mode, where the cantilever is scanned at a fixed height above the surface, no feedback is active and only the deflection is measured. While in normal setups this mode is rarely used, as it requires extremely flat samples to avoid crashing, it has to be deployed in a slightly modified way



Figure 2.6.: (a) Forces acting between a tip and a surface, based on [43]. (b) The force-distance curve based on a Lennard-Jones potential (with parameters as discussed in Chapter 4). The attractive part of the potential is assumed $\propto r^{-6}$ (based on van der Waals interaction, green curve) and the repulsive part $\propto r^{-12}$ (Pauli repulsion, red curve). Note that the forces are plotted and not the potential ($F = -\nabla E$).

in order to correctly quantify the tip-sample interaction, as will be discussed below. On the other hand, several signals like deflection, amplitude, frequency shift, and phase can be used to establish a feedback loop regulating the tip-sample distance. In contrast to STM with its monotonic exponential dependence of the current on the tip-sample distance, no such simple functional dependence between the force and the distance exists. This is due to the interplay of several different types of forces present. Figure 2.6 (a) gives an overview of the forces that might be involved, including typical distances. As the work performed here is carried out in UHV fluid damping and capillary forces can be disregarded. If only van der Waals and repulsive forces due to the Pauli repulsion are considered, a good approximation is given by the force-distance curve shown in Figure 2.6 (b), which is based on a Lennard-Jones potential [45].

Chronologically, the first AFMs operated in contact mode, where the tip, attached to a very soft cantilever, is "scratched" over the surface. This quickly allowed fairly high resolution as reported by Marti *et al.* in 1987 [46]. A serious advancement was the introduction of tapping mode AFM. This is a dynamic operation mode, where the cantilever is externally excited to oscillate, while the amplitude is used as a feedback signal. Amplitudes in the range of 10 - 100 nm and fast scanning speeds make it popular for application in biology. The impact from the tip to the sample in contact mode is highly reduced in tapping mode AFM, as is nicely shown by Zhong *et al.* where the two methods are compared [47].

A further advancement, which is also relevant for this work, is the invention of the true non-contact mode, also a dynamic mode, with amplitudes typically below 10 nm. This mode can be achieved using the oscillation amplitude as feedback ("AM nc-AFM") [48], or the frequency ("FM nc-AFM") as introduced by Albrecht *et al.* in 1991 [49]. The latter requires rather stable oscillation, hence relatively stiff cantilevers are used. This technique provided true atomic resolution to resolve the reactive Si(111) surface and its

7×7 reconstruction [50].

Similar to STM, where the acquired image is a convolution of topography and electronic structure, the interpretation of dynamic mode AFM images is nontrivial. In the following section the method of choice to calculate the forces quantitatively from the AFM signal will be presented.

2.3.2. Calculation of the Force



Figure 2.7.: A simple model illustrating the frequency shift of the free cantilever oscillation (with spring constant k and effective mass m) due to the interaction k_i between the tip and the sample.

The calculation of the interaction forces between tip and sample from the frequency shift is not straightforward. Because the cantilever oscillation is harmonic it can be characterized by a spring constant k ($f \propto \sqrt{k/m}$). If it is exposed to a force gradient, which can be described by a spring constant ($dF/dz = k_i$), the oscillation frequency will change [49]. This interplay is depicted in Figure 2.7. The two springs are considered to be in series resulting in the following frequency of the oscillation:

$$f = \frac{1}{2\pi} \sqrt{\frac{k+k_i}{m}},\tag{2.11}$$

which is only valid if Hooke's law holds, i.e. if $k_i \neq k_i(z)$ (i.e. k_i is constant over the oscillation cycle). For highly nonlinear force-distance laws found at the atomic scale (Figure 2.6 (b) shows an example of a Lennard-Jones type force) this requirement is not met. To circumvent this limitation, the averaged value $\overline{k_i(z)}$ is introduced. If the interaction is small compared to the stiffness of the used cantilever ($\overline{k_i(z)} \ll k$), the frequency shift can be expressed as:

$$\Delta f = f - f_0 \tag{2.12}$$

$$\approx f_0 \frac{k_i(z)}{2k} \,. \tag{2.13}$$

Giessibl calculated $\overline{k_i(z)}$ with first order perturbation theory using the Hamilton-Jacobi

approach [51]:

$$\overline{k_i} = \frac{2}{\pi} \int_{-1}^{1} k_i (z - A \cdot u) \sqrt{1 - u^2} \, \mathrm{d}u \,, \tag{2.14}$$

with A the amplitude of the oscillation, z the distance of closest approach and u the parametrization of the oscillation. To determine the interaction energy and the forces from the measured frequency shift this equation has to be inverted. Sader and Jarvis found analytical solutions [52]:

$$E(z) = \frac{2k}{f_0} \int_{z}^{\infty} \Delta f(u) \left\{ (u-z) + \frac{1}{4} \sqrt{\frac{A(u-z)}{\pi}} + \frac{A^{3/2}}{\sqrt{2(u-z)}} \right\} du$$
(2.15)

$$F(z) = \frac{2k}{f_0} \int_{z}^{\infty} \left\{ \left(1 + \frac{\sqrt{A}}{8\sqrt{\pi(u-z)}} \right) \cdot \Delta f(u) - \frac{A^{3/2}}{\sqrt{2(u-z)}} \cdot \frac{\mathrm{d}\Delta f(u)}{\mathrm{d}u} \right\} \,\mathrm{d}u \,.$$
(2.16)

Those equations enable the calculation of the interaction energy and force at height z from the measured frequency shift Δf by integration over all farther tip-sample distances $(z \text{ to } \infty)$. In experiment this integration has to be replaced by a summation over a discrete set of a limited number of heights. The implementation will be discussed in Chapter 4. An extensive comparison of the deconvolution quality of this method ("Sader-Jarvis") and the "matrix-method" introduced by Giessibl [53] can be found in ref. [54].

2.4. Tuning Fork AFM

2.4.1. Introduction and History

The first use of tuning forks in scanning probe microscopy dates back to work by Günther *et al.* in acoustic near field microscopy at the University of Konstanz [55]. It was used as distance sensor by detecting the decrease in resonance frequency and amplitude caused by hydrodynamic forces in the acoustic near-field region. A lateral and vertical resolution of 3 μ m and 5 nm, respectively, was achieved in the reported experiments.

In 1997 Edwards *et al.* used a quartz tuning fork as cantilever in AFM, being deployed as an actuator and sensor with both prongs oscillating freely [56]. The induced asymmetry by the tip being attached to one of the prongs makes the interpretation of the obtained signals difficult. The problem is overcome if one of the prongs is completely fixed or removed, as will be discussed in Section 2.4.3. This design (qPlus) was invented by Giessibl.

2.4.2. Properties of Tuning Forks

To understand the working principle of the tuning fork sensor it is worthwhile to look at the intrinsic properties of quartz tuning forks, which are used in watches and other time sensitive circuits for frequency stabilization. In Figure 2.8 a cross section of the two prongs is illustrated and discussed in the figure caption. The electrodes of opposing faces on the same prong are electrically connected, while the two prongs are connected in the opposite way, to ensures that only antisymmetric oscillation modes in-plane are allowed. Hence,



Figure 2.8.: Photograph of the quartz tuning fork used in experiments with a schematic zoom-in. The cross section of the tuning fork prongs from A to A' is shown on the right side. If the tuning fork is bent some regions are extended (green) and in others contraction occurs (orange). This deformation creates an electric field in respect to the intrinsic polarization (P) of the quartz leading to small currents detectable at the electrodes. Modified from ref. [57].

only if the second prong is removed, also oscillation out-of-plane are electrically allowed. A quantitative discussion of the induced currents in quartz tuning forks can be found in ref. [58].

Two relevant properties of tuning forks are its "quality factor" (Q-factor) and its stiffness. The Q-factor is defined by the number of oscillatory cycles until the amplitude has decreased to $^{A/e}$. It is thereby a measure for how stable it oscillates, or how little of the stored energy is dissipated per cycle. In FM nc-AFM a high Q-factor is desirable as it allows precise determination of the frequency shift by the PLL and little heat dissipation. The stiffness of the type of quartz tuning forks most commonly used for scanning probe microscopes (E158 supplied by Nanosurf AG) is approximately 1800 N/m (see discussion in Section 3.4). This allows small oscillation amplitudes of ≤ 1 nm. Due to those small amplitudes it is possible to simultaneously measure the tunnel current when a conducting sample is investigated, which will be the topic of the next section.



Figure 2.9.: SEM image of the tuning fork sensor used in this setup. For clarity it is colorized. Orange: tuning fork with the lower prong removed, red: STM/AFM tip, yellow: gold wire connecting the tip for the tunnel current, light blue: connection post for the tunnel current, dark blue: leads connecting the tuning for, dark green: gold connection patches on the sapphire block, light green: all spots of conductive glue. Scale bar: 400 μ m. SEM image: B. Fenk, MPI-FKF, Stuttgart. (b) Schematic of the sensor design: The oscillation of the beam externally driven by the scan piezo. The tip sample interaction due to the force is symbolized by the red spring (k_i) .

2.4.3. Combined STM/AFM Sensor

In 1998 Giessibl introduced a design where one of the prongs of a tuning fork is fixed; the so-called **qPlus** sensor [15, 59, 60], which has evolved significantly since. In Figure 2.9 a schematic explains the basic parts of the sensor and an SEM image is shown of the sensor used in this setup.

Because the combined sensor is also commercially available [61, 62], the number of teams working with microscopes deploying such systems is continually rising and cannot be completely covered. The broad range of topics addressed in the following selection of groups, should be understood as inspiration for viable experimental pathways.

Already before the introduction of the qPlus sensor F. Giessibl was active on the field of AFM. In ref. [63] a broad review about AFM is given that also describes the beginnings of the tuning fork sensor. His group is still leading in the field, especially in sensor design and addressing fundamental questions about the sensor. Examples include the study of higher-order eigenmodes of the sensor [64], the investigation of the friction at the atomic scale [65], the recent determination of the stiffness of a CO molecule by a lateral tuning fork geometry [66], or the revelation of the angular symmetry of chemical bonds [67] by selectively functionalized tips. In the group of G. Meyer and L. Gross much pioneering work was performed to increase spatial resolution of the sensor. This was impressively achieved by CO functionalization of the tip [68]. Similarly, the force related to charge states of gold and silver adatoms was quantified [69]. Also work on the discrimination of bond-order in polycyclic aromatic hydrocarbons was shown [70] and

the charge distribution within a single molecule could be resolved [71]. More recently also high resolution KPFM measurements on single molecules were performed in the group [72]. **M. Ternes** performed in the group of **A. Heinrich** more quantitative experiments with the combined setup. This includes determination of the forces necessary to move atoms on surfaces [23] and a study where the interplay of conductance and force in metallic point contacts was studied, i.e. what happens if a bond is formed between two atoms as they are brought into close contact [73]. **R. Temirov** and **F. Tautz** have performed experiments with H terminated tips [74], which allows limited chemical identification and work on controlled lifting of molecular wires is worth mentioning [75]. In the group of **S. Morita** a broad range of AFM sensors is available. Studies worth highlighting are the atomic manipulation and combined STM/AFM measurements at room temperature [76, 77] and the chemical identification of atoms on surfaces by AFM [78]. In ref. [79] from the group of **M. Crommie** the recent imaging of internal covalent bond configurations during a chemical transformations of a single molecule is presented. In a similar spirit mechanical switching is studied in the group of **P. Moriarty** [80].

The main advantage of this versatile force sensor operating at small amplitude is the possibility to electrically connect the conducting tip and simultaneously record the tunnel current. An in-depth discussion of the sensor used in this work is given in Section 3.4.

2.4.4. Amplitude of the Tuning Fork Oscillation



Figure 2.10.: Relation of the tunneling current, amplitude of the oscillation, and z height. (a) The tip heights for excitations off (gray) and on (red) plotted as a function of time. (b) The current during the oscillation (I_{OSC} , red) and for the constant tip height (I_0 , gray) is depicted. The average value is in both cases the same, while the piezo position differs by Δz .

As shown in Equation (2.16) the amplitude of the tuning fork oscillation is necessary to calculate the forces acting between sample and tip. In this section the measurement



Figure 2.11.: (a) I(z)-spectra (black) with exponential fit (red) to determine the decay constant $\kappa = 0.74 \cdot 10^{10} \text{ m}^{-1}$. (b) The tip height while the oscillation is switched off and on again twice to determine $\Delta z \approx 119 \text{ pm}$ for the calibration.

procedure for calibration of the amplitude is presented in detail. It is based on the simultaneously measured tunneling current. The calibration depends on the operating parameters of the amplifiers and the actual tuning fork sensor and has to redone whenever parameters have changed.

In Figure 2.10 a sketch illustrates the tunneling current depending on whether the tip oscillates (red) or not (gray). I_0 corresponds to the case where the excitation is switched off and where z is therefore constant at a distance z'. When the tip is excited the current varies in time due to the oscillation. To achieve the same average current (due to the limited bandwidth of the I/V-converter the detected current is averaged over the oscillation cycle) the z-piezo moves the tip Δz away from the surface to $z = z' + \Delta z$. If Δz is known, the true amplitude of the oscillation can be deduced, as derived below.

The following scheme is therefore applied: At closed feedback loop the z-change is recorded when the oscillation of the tuning fork, i.e. the modulation of the z-piezo, is manually switched off and on, as shown in Figure 2.11. In this example the average change in z is $\Delta z = 119$ pm.

The average current over one oscillation period is given by [81]:

$$\langle I(z) \rangle = I(z' + \Delta z) J_0(2\kappa A), \qquad (2.17)$$

with $J_0(x)$ the modified Bessel function of first kind and $\kappa = \frac{2\pi}{h}\sqrt{m(\Phi_S + \Phi_T)}$. Because of the exponential distance dependence of the current, it follows:

$$I(z' + \Delta z) = I(z') \cdot e^{-2\kappa\Delta z}.$$
(2.18)

From this, and the condition that the averaged current of the oscillating tip is the same

as $I_0(z')$ because the height is accordingly controlled by the feedback, it follows:

$$I_{0}(z') \stackrel{!}{=} \langle I(z) \rangle$$

= $I(z' + \Delta z) \cdot J_{0}(2\kappa A)$
= $I(z') \cdot e^{-2\kappa\Delta z} \cdot J_{0}(2\kappa A)$ (2.19)

$$\Rightarrow J_0(2\kappa A) = e^{2\kappa\Delta z}.$$
(2.20)

With the values $\kappa_{\text{exp}} = 0.738 \cdot 10^{10} \text{ m}^{-1}$ deduced from the exponential fit of the I(z)curve shown in Figure 2.11 (a) and $\Delta z = 118.7 \pm 1.6$ pm Equation (2.20) is solved numerically to find: $A = 217 \pm 3$ pm. Hence, as in this example the set amplitude of 300 pm was measured to correspond to 217 ± 3 pm the calibration has to be corrected to: $(4.53 \text{ nm/V}) \times (0.217 \text{ nm}) / (0.3 \text{ nm}) = 3.278 \text{ nm/V}.$

2.5. Kelvin Probe Force Microscopy



Figure 2.12.: (a) Energy levels of sample and tip without electrical contact. (b) Change of energy levels upon contact formation. (c) With an external bias the contact potential difference is compensated and hence the force minimized. Adapted from ref. [82]. (For used symbols compare to Figure 2.3.)

Kelvin Probe Force Microscopy (KPFM) was introduced in 1991 by Nonnenmacher *et al.* [83] as a technique to measure the local contact potential differences (CPD) by AFM, as schematically depicted in Figure 2.12. Because it was only sparsely used during this work, this section is kept rather short. An excellent overview of recent developments can be found in the review by Melitz *et al.* [82].

While ultraviolet photoelectron spectroscopy is a well established method to measure the work function (the energy difference between Fermi and vacuum level) of solids, it is an area averaging technique, sensitive to the surface and a depth of several monolayers [84, 85]. On the other hand, KPFM, as a scanning probe technique, achieves intrinsically very high spatial resolution. Due to the different work functions of the tip and the sample

an electric field is created. This results in a corresponding electrostatic force at a fixed height of:

$$F_{ES} \propto V_{CPD}^2, \tag{2.21}$$

with $V_{CPD} = (\Phi_T - \Phi_S)/e$. Hence, the effect of the Coulomb interaction can be detected by the AFM as a contribution to the Δf -signal. The quadratic voltage dependence of the force is preserved in the Δf signal. By adjusting the voltage between tip and sample to V_{CPD} the intrinsic field can be compensated and the effect on Δf eliminated. This simple method, i.e. recording $\Delta f(V)$ -curves and determining the minima pixel by pixel was deployed in this work to obtain KPFM maps.

In a more sophisticated and faster approach the electric field is detected by varying the distance between tip and sample (at a frequency different from the resonance frequency of the cantilever). Due to the change in capacitance a current proportional to the intrinsic field will flow that can be neutralized by an external voltage. By using a calibrated probe, i.e. by measuring against a reference with known work function, also absolute work functions can be obtained by KPFM.
CHAPTER 3

The Experimental Setup

Work on the STM/AFM head deployed throughout this work was already started in 2009 in the scope of a diploma thesis [14]. An in-depth discussion of the designing process can be found there. As the head was up to that point only tested at moderate vacuum and at room temperature some further improvements and changes were necessary. In April 2011 it replaced the STM head in a cryostat, in June it was for the first time cooled to liquid helium temperatures and was fully operational (single atom resolution in imaging and first STS measurements at 1.5 K) in August 2011.

The first part of this chapter will introduce the system and discuss its important parts. The STM/AFM head will be discussed in Section 3.2 and some changes, improvements and technical extensions that were made during this thesis are highlighted in Section 3.3, where also the move to the new high precision lab is summarized (Section 3.3.4). The further developed tuning fork sensor is presented in Section 3.4.

3.1. Experimental Setup of the System

3.1.1. Overview of the System

The system was built from 2001 to 2005 [28] and has since then been continually modified. Figure 3.1 shows the full current setup. It was initially designed as a 14 tesla UHV low temperature STM with ³He Joule-Thomson cryostat. For the last years the Joule-Thomson cooling is based only on ⁴He, resulting in minimum temperatures of 1.2 - 1.6 K, measured close to the sample. An update in the pumping setup (greatly increased pump speeds allowing for higher flow of He gas) should reduce the temperature further and will be operational in the near future.

Working with ³He should, in principle, allow temperatures down to 0.3 K. The lowest temperature reached on this system with ³He (several years ago) was 0.8 K, where additionally the cryostat was cooled down to ~ 2 K by pumping on the He reservoir (which is unavoidably associated with excessive He consumption). Relatively bad thermal anchoring of the sample and tip, low thermal conductivity of the materials used for the STM body and low cooling power due to very low flow of ³He limited the temperature reached in experiments. Despite the additional thermal intake due to the necessary AFM ampli-



Figure 3.1.: CAD view of the experimental setup. A: Vertical manipulator for sample transfer, B: Transfer magnet, C: Gate valve between the two parts of the chamber, D: Mass spectrometer, E: Horizontal manipulator, F: Cooling connection for sample in preparation stage, G: Passive air dampers, H: Molecule evaporator, I: Base frame, J: Cryostat, K: Helium refill connector, L: Second damping stage (blue, with cryostat and whole chamber connected), M: Third damping stage (yellow, with STM tube and STM/AFM head), N: Wobble stick, O: Ion and titan sublimation pumps, P: Turbo pump, Q: Metal evaporator (backside, not visible), R: Load lock (backside, not visible). fier close to the STM/AFM head temperatures of 1.5 - 1.6 K are now routinely reached, and most measurements presented in this work are done at these temperatures. Cooling down time from liquid helium temperature (~ 4.2 K, i.e. without the Joule-Thomson cycle running) to 1.5 K is in the range of 10 minutes.

The base pressure at the sample position is assumed to be $< 5 \cdot 10^{-10}$ mbar, the energy resolution in spectroscopy at 1 K was shown to be below 200 μ V and the vibrational noise in the z-direction was quantified to be < 1 pm [86]. This stability was reached even at the sixth floor with sophisticated active and passive damping stages. In the new laboratory (Section 3.3.4) the mechanical stability increased significantly. The system has a broad range of *in situ* sample preparation possibilities, including sputter gun, heating stage for annealing, evaporators and a variety of gas inlets, and for monitoring the preparation an Auger electron spectrometer and a mass spectrometer.



3.1.2. Magnet

Figure 3.2.: STM image of h-BN/Rh(111) recorded during sweeping of the field. (a) Unprocessed image for the sweep from 0 – 1 T, with ~ 2 mT/s sweep rate. (b) Same image as (a) but after flattening and filtering by a Gaussian to show the maintained scan capabilities. Black arrows mark small tip changes. Lateral distortion is also visible. (Measurement parameters: I = 20 pA, V = -50 mV, scale bar: 4 nm.) (c) Height profile as indicated by the black line in (a).

A superconducting single coil magnet with a core diameter of 7.6 cm is submerged in the liquid helium bath, as can be seen in Figure 3.3. It is specified to an out-of-plane magnetic field of up to 14 Tesla, which was also used in this thesis. A hall sensor (model HSP-T from Cryomagnetics) close to the sample position is used to measure the magnetic field (note that the deviation to the calibration by the current with 9.07 A/T is well below 1%). The new control unit / power supply (Model 4G-200 from Cryomagnetics) is capable of smoothly reversing the field direction (sweeping the field through zero). This feature allows for interesting switching experiments of magnetic systems (discussion in Chapter 5). Due to eddy currents resulting from sweeping the field the STM/AFM head warms up making the compensation of the unavoidable drift a challenging task. Nevertheless, as shown in Figure 3.2, it is possible to maintain the stability to record STM images while sweeping the field with slow rates (~2 mT/s). This was not possible in previous designs



Figure 3.3.: CAD image of a cut through the cryostat where the STM/AFM (C) is visible close to the bottom and surrounded by the magnet. A: Radiation shields, B: Liquid helium reservoir, C: STM/AFM head, D: End of capillary from Joule-Thomson cycle / cooling center, E: Magnet, F: Superinsulation, G: STM tube (housing of the STM/AFM head), H: AFM preamplifier and electrical feedthroughs (UHV to exchange gas volume).

of the STM head and is now achieved mainly through the thorough avoidance of any magnetic materials. Note, however, that the related drift is approximately 0.8 nm / T or 100 pm / min as shown in panel (c). The scan stability decreases towards higher fields (a reasonable resolution could be maintained up to 5 T), with smaller tip changes occurring already at low fields, as depicted by the black arrows in panel (b), which shows an edited version of image (a).

3.1.3. Electronics and Software

During this thesis, the Nanonis electronics from Specs replaced a Createc system. The control software is easily extendable, as it is LabVIEW compatible and a broad range of adaptable modules are supplied with it. The AFM is controlled by a phase-locked loop (PLL) circuit integrated in the Nanonis Oscillation Controller OC4, which is embedded in the system. A Femto amplifier (DLPCA-200), which is a variable gain $(10^3 \text{ to } 10^{11} \text{ V/A}, \text{ switchable through the software})$ low noise current-to-voltage converter amplifies the tunneling current. The AFM amplifiers are discussed below (Section 3.3.2).

3.2. STM/AFM Head



Figure 3.4.: Photograph of the STM/AFM head. A: Guiding cone for sample transfer, B: Rotor sensor, C: Sample temperature sensor, D: Hall sensor, E: Coarse movement springs, F: Electrical connections, G: Plugs (coaxial wires for I, z and Bias).

The design work and construction of the STM/AFM head started prior to this thesis in the scope of a diploma thesis by the same author [14]. Nevertheless, the important features will be summarized and the focus will be on the changes and evolution since.

The design is based on a series of previous STM heads that were designed in previous theses [27, 28], which were inspired by the work from Pan *et al.* [87]. While not having to start designing from scratch is an advantage, it also means that there were limitations and boundary conditions in the design that have to be met and are unfortunately still a constraining factor for stability of the system¹.

In Figure 3.5 the STM/AFM head with its important parts is shown. Key elements are the tuning fork sensor (see Section 3.4) on top of the scan piezo. Important for the experiments with single Co atoms (Chapter 5) is the feature to rotate the sample by 180° ("rotor", see

¹The distance between the STM tube and the magnet bore (see Figure 3.3) is in the order of 1–2 mm. This makes alignment tricky and frequently causes scratching between the STM tube and the inner cryostat, which is usually "changing" the STM/AFM tip. Additionally, all movements inside the cryostat like He boiling after refilling the cryostat as well as during and for several hours after ramping the magnetic field, are transferred to the STM and affect the stability.



Figure 3.5.: CAD image of the STM/AFM head. A: Coarse movement springs, B: Sapphire balls, C: Sapphire plate holding top coarse approach piezos, D: Coarse approach piezo stacks, E: Rotary motor (see Figure 3.6), F: Electrical connections, G: Cable protection plate, H: Scan piezo with tuning fork unit (see Figure 3.16), I: Guiding cone for sample transfer, J: Electrical connections, K: Sample, L: Rotor, M: Rotor sensor.

Figure 3.6) and have a readout of the position (variable capacity "position sensor"). Compared to previous designs more care was taken for high rigidity to reduce internal vibrations, higher overall weight to lower resonance frequencies, and, most importantly, for better thermal conductivity to allow faster cooling down. While pure copper would fulfill those requirements, it is too soft to be machined with the necessary accuracy. Therefore phosphor bronze was chosen for all metal parts, which is an copper alloy (no. C52100) composed of 92 weight-% copper, 8% tin and 0.03-0.35% phosphorus [88]. The thermal conductivity is lower than that of pure copper, but with ~ 0.017 W/(cm K) at 4.2 K [89, 90] it is still more than one order of magnitude better than that of Macor and Shapal, which are materials used in previous designs of the head. To minimize problems due to different thermal expansions coefficients also phosphor bronze screws were used. For the insulating parts of the head alumina (sintered Al_2O_3) and sapphire (crystalline Al_2O_3) were used. While the former is easier machinable the thermal conductivity of only $5 \cdot 10^{-3}$ W/(cm K) at 4.2 K [91] is low and therefore it should be replaced wherever possible by sapphire, as its thermal conductivity (up to 1.1 W/(cm K) at 4.2 K [91]) is significantly higher. For the assembly two types of glue are used: TorrSeal from Varian, which is a two



Figure 3.6.: CAD image of the rotor holding the sample in the STM/AFM head allowing for 180° rotation, as depicted by the black arrow. A: Sample holder, B: Sample, C: Sample holder cap, D: Rotor bayonet, E: Spring holding the sample, F: Sapphire cone for rotary motor piezos, G: Fixed site of the rotary motor holding 3 piezo stacks, H: Spacer for rotor sensor, I: Fixed sensor plate (stator), J: Rotating sensor plate (rotor), K: Temperature sensor, L: Rotor main body, M: Gold foil for field emission (90° turn), N: Rotary motor piezo stack, O: Spring pressed site of rotary motor, P: Rotating axis fixing screw, Q: Spring pressing (O) onto (F), R: Sample holder screws, S: Thermocouple contacts (used for sample annealing).

component UHV compatible glue with a toothpaste-like texture, which makes it easy to apply also in very small amounts. It works reliable at low temperatures, as long as glue patches are kept small to avoid breaking due to mismatched expansion coefficients when being cooled down. EpoTek E4110 from Epoxy Technology is a silver based two component epoxy, which is used for conductive connections. The glue spots should not be too small, to avoid "semiconducting" behavior due to the granular or flake-like texture of the silver particles.²

3.3. Improvements and Changes

While it is not feasible to cover all changes and improvements of the entire system made during this thesis, several important aspects will be discussed in the following.

3.3.1. Sample Transfer

As indicated in Figure 3.1 the vertical sample transfer into the head is based on a linear magnetic manipulator custom built by Ferrovac. This allows for a much faster sample

²One tip connection shown in Figure 3.15 (b) showed this behavior at low voltage and low temperatures.



Figure 3.7.: (a) Schematic of the counterweight system which allows very sensitive sample transfer.(b) Picture of the counterweight system of the sample transfer. A: Magnet, B: Transfer tube, C: Weights.

transfer compared to the previous stepper motor driven bellow design. The additionally installed counter weights (Figure 3.7) balance the weight of the whole transfer rod and magnet and permit for a very smooth and sensitive transfer. This is advantageous, as no optical access exists for controlling alignment. Note that the mechanism depicted in Figure 3.7 (a) allows for an evenly distribution on both levers at the magnet due to the single wire pulley design.

3.3.2. Tuning Fork Amplifier

The preamplifier for the tuning fork signal should be mounted as close as possible to the tuning fork [92], while its unavoidable heat dissipation prohibits placement too close because of the limited cooling power of the Joule-Thomson cycle. Therefore it is mounted outside the UHV, next to the STM tube inside the exchange gas volume, as indicated in Figure 3.3. Several models of operational amplifiers were tested and several versions of amplifiers were built. In Figure 3.8 (b) the current design is shown. It is based on two **OPA657** (1.6 GHz (gain bandwidth product) low-noise FET-input operational amplifiers from Texas Instruments), which are heated by two 100 Ω resistors (Figure 3.8 (c)). The amplification factor is set by the two 100 M Ω resistors (×10⁸). The power consumption of the amplifier $(4 \text{ V} \times 2.5 \text{ mA per channel})$ is used as setpoint for externally controlling the heating power. It is important to note that the calibration of the tuning fork signal (as explained in Section 2.4.4) depends on the operating parameters, like exchange gas pressure, temperature, etc. Therefore it is essential to calibrate the amplitude for the desired experimental parameters. Two small capacitors buffer the supply power towards ground to ensure smooth power supply and reduce the risk of self-oscillation. As depicted in Figure 3.8 (a), the two channels from the tuning fork are amplified individually, which increases the signal-to-noise ratio by a factor of $\sqrt{2}$ [60].

The second amplifier with switchable gain of 10^n , n = 2, 3, 4 is an differential amplifier and located outside the cryostat. It also includes a bandpass filter that allows adjusting the center frequency and amplification band-width.



Figure 3.8.: (a) Schematic of the tuning fork unit with the two amplification stages inside and outside the cryostat. Based on ref. [60]. (b) Photograph of the tuning fork preamplifier. A: Input, B: Supply voltage filter capacitors, C: Output, D: Supply voltage, E, F: Amplifier IC with 100 Ω heating resistors on top, G: 100 MΩ resistors. (c) Side view of the operational amplifier (E) with mounted 100 Ω resistor (F).

3.3.3. Metal Evaporator



Figure 3.9.: (a) The operating scheme of the metal evaporator: Electrons are emitted from a tungsten filament (blue) to heat a metal rod (red) which causes metal atoms ("M") to be evaporated. (b) Mass spectrum for Co (58.9 amu) recorded with increasing filament currents at fixed high voltage of 1 kV over time. The initial spikes are mainly due to degassing of the filament and rod, while the main evaporation starts at 5.5 A, where (in this example) the Faraday cup saturates.



Figure 3.10.: (a) CAD view of metal evaporator. For exact positioning on the linear motion stage several screws allow adjustments (A). The transferable metal rod holder (B) can be exchanged through the load-lock due to its sample holder interface / wobble stick accessibility. (b) CAD cut through the metal evaporator. C: High voltage contact, D: Filament (yellow), E: Metal rod (red), F: Aperture.

The design and construction of a versatile metal evaporator was also part of this thesis. After investigating operation parameters in a separate test chamber (see Figure 3.9 (b)), the first "real" testing was achieved by evaporating single cobalt atoms on Au(111) (Section 5.3). Since then it is routinely used, with the experiments reported in Chapter 5 showing its capabilities.

The working principle is sketched in Figure 3.9 (a): A high current (5 - 6 A) is driven through a thorium doped tungsten filament that emits electrons. They are accelerated towards the metal rod due to the high positive potential (0.5 - 1 kV). Thereby the metal rod is heated and metal atoms are evaporated. An aperture in front of the rod ensures that atoms are emitted mainly towards the sample. The whole unit (Figure 3.10) has to be positioned over the entrance to the STM tube, which allows for direct evaporation of single atoms onto the cold sample surface inside the microscope over a distance of almost 1.5 m. While unavoidably making it slightly more fragile, it was designed to have exchangeable metal sources. They are supplied as small rods in a housing similar to the sample holder, i.e. they are transferable through the load-lock and can be handled with the existing wobble stick. One drawback of the current design is a missing flux monitor, which would allow better control of the emission/coverage, rather than just by the electron heating current. (An ion current monitor or a micro balance is planned to be implemented in the sooner future).

3.3.4. Precision Laboratory

A non-negligible time of this thesis was dedicated to move the instrument to the new laboratory ("Precision Lab") on the same campus in Stuttgart. The move started in February 2013 and by June 2013 the experiments could be continued, with optimizations



Figure 3.11.: (a) STM image of the Au(111) surface as test after the move and reassembly in the new lab. (Measurement parameters: I = 1 nA, V = 1 V; scale bar: 3 nm; data treatment: flattening.) (b) Height profile of the herringbone reconstruction as indicated by the line in (a) revealing a high z-stability.



Figure 3.12.: (a) Photograph of the old lab. (b) Photograph of the new lab.

on the setup and small alterations in the building infrastructure lasting several more months. In the following some improvements of the system performance after the move are presented. Additionally, some built-up maintenance work was carried out.

The superb vibration isolation of the new laboratory and the accompanying stability for the whole setup is undoubtedly the most significant change compared to the 6th floor environment. While also there, on exceptionally lucky days, the impressive microscope performance could be shown (e.g. the data discussed in Chapter 4) it is the greatly enhanced reliability in stability that makes the difference. Due to the vibrational and acoustic isolation the performance is almost completely unaffected by mechanical work around the box. In the old laborator two passive and one active damping stage had to be employed (and perfectly set up) for operation, it is now experienced that the main base of 120 metric tons of concrete that rest on air dampers is sufficient to stabilize the whole system. Nevertheless, two passive damping stages are still held available. An early STM image is shown as an example in Figure 3.11, where the low z-noise level on the Au(111) surface is evident. The long-term stability, especially in combination with experiments performed at magnetic fields, allowed for > 50 hours of measurements on the same atoms and molecules (see Chapter 5, where individual Co atoms were investigated at different magnetic fields).

Other additional advantages of the new building include the increased work space inside the measurement box (Figure 3.12) and the perfectly concerted infrastructure the building offers (several additional workshops, preparation and chemistry labs, cryogenic liquids supply, etc.).

3.4. The Tuning Fork Sensor



Figure 3.13.: Evolution of the tuning fork sensor used in this work. (a) Very early and rudimentary design. (b) More recent version that was used during the first real tests of the new head. The connection plate (that is screwed onto the scan piezo) is still used. The tuning fork (two prongs) has to be glued upright onto the sapphire plate. (c) CAD view of currently used version of the tuning fork unit, where the tuning fork (one prong) is glued laterally against the sapphire support. The 25 μ m Pt tip (red) is directly glued to the connection post (green). (A photograph of the current design is shown in Figure 3.14.)

Because the tuning fork sensor can be regarded as the "heart" of the microscope it will be discussed in depth. Figure 3.13 gives an overview of the evolution. In Section 3.4.3 the properties of the actual sensor and results of a finite element method (FEM) will be presented.

3.4.1. Design of the Tuning Fork Sensor

The most crucial part of the tuning fork unit is the tip. It needs to be light and short to minimize the decrease in resonance frequency of the tuning fork and possible resonances of the tip itself [93], it should be sharp also on a mesoscopic scale to minimize long range forces (electrostatic and van der Waals) and it needs to be electrically connected to allow for detection of the tunnel current. While in the first designs the current was collected at one of the tuning fork electrodes [94], which caused serious crosstalk issues, a separate connection with minimal influence on the oscillation is desirable [95].

The basis of the design remained the same in the last several versions to allow the reuse of



Figure 3.14.: Photographs of the tuning fork unit. (a) Tuning fork unit mounted on the scan piezo inside the STM head. (b) Side view of the tuning fork with tip and all connections attached.



Figure 3.15.: SEM images of an tuning fork sensor design with tip that had to be replaced after the tip connection showed Coulomb blockade effects. (a) The manually cut, short (0.2 mm) tip sits in a spot of non conducting glue. The dirt / glue scrap are clearly visible. (Scale bar: 200 μ m.) (b) The connection of the 12 μ m Au wire to the tip with a small amount of conductive glue is brittle and showed semi conducting behavior. (Scale bar: 60 μ m.) (c) The tip, where glue fragments are spread up to the apex. (Scale bar: 40 μ m) (d) No defined tip apex is evident, which might be due to heavy crashing. (Scale bar: 10 μ m) (The distortion visible in the background is due to charging effects of non conductive parts (glue, tuning fork). SEM images: B. Fenk, MPI-FKF, Stuttgart.) some parts, the reliability of the alignment, and the compatibility to the mounting mechanism to the scan piezo. The unit is mounted with two $M1.2 \times 4$ screws to the ground plate that is glued onto the scan piezo. The whole unit is made out of phosphor bronze and kept at the same potential as the tip. Insulating parts are either sapphire or alumina. The tuning fork signal is collected with two separate cables from two intermediate connection points.

Most experiments presented here were done with the previous design. There a 12 μ m diameter gold wire was used to connect the tip to a separate connection post. This requires additional conductive glue on the tip, which makes it difficult to work with short tips. An example of a comparably short tip (~ 0.2 mm long, 75 μ m diameter Ir) is shown in Figure 3.15, where the problem of too little glue is clearly visible in panel (b). Some dirt / residual glue is also unavoidable when mounting the unit manually.

In an updated design the thin gold wire was sacrificed to circumvent the need for conductive glue on the tip, by bending the lower part of the tip and using it to connect it to the connection post. While this makes it significantly easier to handle compared to the thin gold wire, it perturbs the oscillation and results in a decreased Q-factor. One strategy to overcome the problematic tradeoff between reliability and reduced Q-factor might be the use of custom made Nauganeedle sensors, which are based on the same tuning fork but add a third electrode (after an isolation layer) on to the top flank of the prong for the tunneling signal.

3.4.2. Assembly of the Tuning Fork Sensor

The assembly procedure is depicted in Figure 3.16 and is summarized in the following: One prong of the tuning fork (L) is removed and the tip (E), a 25 μ m diameter Pt wire, is glued with non-conducting glue onto the front end of the prong. After curing the glue, the lower part of the wire is bent 90° and the upper end is cut to a length of 400 – 600 μ m measured from the top of the prong. Gold contacts (N) are evaporated onto the cut sapphire plate (M) before the tuning fork is glued to it. The alignment (no tilt and lateral position) of the tuning fork is crucial in this step. The electrical connections from the tuning fork to the electrodes are made by bonding with a thin gold wire, but adding some additional silver glue has proven to make the connections more robust and reliable. The connection wire (4-5 mm long), which will connect the gold contacts to the connection point (I) on the ground plate (K) are glued to the gold contact. Now the sapphire plate is glued to the holder (H) and the connection post (75 μ m diameter PtIr wire), which collects the tunnel current from the tip is glued to the sapphire plate and the holder. The tip is bent around the post and glued with conducting epoxy. The tip is then cut with a focused ion beam (FIB). Here a V-shaped ion beam in a small angle geometry against the tip allows single sweep cutting of a sharp tip, as shown in Figure 3.17.

In the STM/AFM the whole unit is connected with two modified (self aligning) phosphor bronze M1.2×4 screws (F) to the ground plate (K) and the tuning fork wires are connected to the connection points (I) with silver glue.



Figure 3.16.: CAD view of the tuning fork unit. (a) "Slider" holding the scan piezo that is moved by the coarse approach. A: Connection to the ground plate K, B: Scan piezo, C: Sapphire prism, D: Piezo holder, hold by springs inside C. (b) Full tuning fork unit, connection wires are not shown for clarity. E: Tip (25 μ m Pt wire), F: Screws, G: Connection post, H: Holder, I: Tuning fork signal connection point, J: Isolators, K: Ground plate, L: Tuning fork, M: Sapphire plate, N: Gold contacts.

3.4.3. Properties of the Tuning Fork Sensor

Figure 3.18 shows the frequency spectrum of a new sensor as recorded in the setup at low temperatures. Besides some unwanted mechanical resonances, two peaks at 16.42 and 34.12 kHz can be clearly related to the oscillation of the tuning fork, as they are also excited by the mechanical excitations from the coarse approach steps.

To elucidate the implications of the significantly lighter tip and the tip being directly glued to the connection post on the resonance frequency of the new design a FEM was performed³. The precise dimensions used for the simulations are taken from the unit shown in Figure 3.14 (b), therefore they cannot directly be related to the resonances measured for a different sensor in Figure 3.18. Material properties are taken from the programs library or literature. The prong is divided into roughly 150 000 parts and the tip wire into 34 000 for the analysis. In Figure 3.19 the two lowest found eigenmodes of the unit are shown. Panel (a) shows the out-of-plane mode found at 18.5 kHz and in panel (b) the second mode (in-plane) is depicted, which was found at 32.6 kHz. This is remarkably close to the unperturbed (no tip) eigenfrequency of 32.768 kHz. It can be understood by the fact that while the tip weight decreases the resonance frequency the stiff tip connection

³The MSC.Nastran software, which is integrated in the CAD program Creo Elements was used for the calculation. This software is based on the around 1960 developed Nasa Structural Analysis System (Nastran) and developed by MSC Software.



Figure 3.17.: (a) SEM images of the tip cut by FIB mounted on the tuning fork (Scale bar: 40 μ m). (b), (c) SEM images with different levels of magnification, with a clearly defined tip apex. (Scale bar: 2 μ m (b), 500 nm (c).) (SEM images: B. Fenk, MPI-FKF, Stuttgart.



Figure 3.18.: Resonance curve of new tuning fork unit at low temperatures driven by a sweep of the z-piezo. The mechanical modes of the tuning fork at 16.423 kHz and 34.154 kHz are plotted in red.

increases it. The effect of the tip weight or alternatively the added glue to mount the tip is studied by repeating the calculations for different amounts of glue. In Figure 3.19 (c) the results are shown. A rough estimation of the amount of glue visible in Figure 3.14 (b) suggests a glue weight of approximately 3 μ g.

This results in a reasonable agreement of ± 2 kHz between measurement (16.4 and 34.1 kHz) and simulation (18.5 and 32.6 kHz) allowing a tentative assignment of the two resonances.



Figure 3.19.: (a) First and (b) second eigenmode of the prong as calculated by FEM. Dimensions are the same as in Figure 3.14. The color code represents the displacement. The dark blue areas (end of prong and end of tip wire) are fixed in position. (c) Resonance frequency of the prong depending on amount of glue as calculated by FEM for the same mode and geometry as (b).

A second property of the tuning fork possibly affected by the more constraining tip connection is the stiffness. Extensive testing was performed with a simple setup consisting of a sensitive balance and a sharp tip (indenter) mounted on a micrometer screw, similar to the discussion in ref. [96]. The tip is pressed vertically against the end of the prong and the resulting force is measured by the balance. Subtracting the intrinsic spring constant of the balance the stiffness of the tuning fork can be derived from a linear fit of the force vs. deflection measurement [97]. The measured spread is quite significant ($1800 \pm 400 \text{ N/m}$) due to the difficulty in positioning the indenter at the very end of the prong. The main conclusion regards the effect of the new tip connection, where only minor changes of the stiffness are recorded depending on a prestrained connection.

For the calculation of the force from the Δf -signal (Equation (2.16)) the widely accepted value of 1800 N/m is used and the error is considered in the interpretation. A more thorough study by Berger *et al.* discusses several feasible ways to experimentally determine the stiffness and concludes that a stiffness of 1800 N/m is a reasonable value for the used type of tuning fork [98].

While "normal" operation is based on the in-plane mode of the oscillation, also very interesting experiments are feasible, where the first mode of the sensor is used. In this case lateral forces are directly accessible – examples will be discussed in the outlook (Section 8.2).

CHAPTER 4

The Hexagonal Boron Nitride Monolayer on Rh(111)

The focus of this chapter is on the investigation of the stiffness of the hexagonal boron nitride (h-BN) single layer on rhodium(111), which is presented in Section 4.3 and was recently published in Nano Letters [99]. In the second part of this chapter several more aspects of the extensive data analysis performed during this work are presented, which go beyond the determination of the stiffness. As it is the first frequency shift data recorded to calculate energy and force maps on this microscope, and because there might be some of the existing STMs in the same department being modified to incorporate tuning fork sensors in the future, the chapter will also contain some more basic guidelines of how to record and handle such data, i.e. it is intended to serve as a guideline and reference for future students.

After a short motivation in the following section h-BN will be thoroughly introduced in Section 4.2, where mechanical properties and corresponding experiments are also discussed. Here the simultaneous discussion of graphene is reasonable, as it clearly preponderates the research done on single layer h-BN but is transferable in many aspects. An elastostatic model is applied to the nanoscale system investigated to judge the values reported. A summary and conclusion about this project are given in Section 4.5.

4.1. Motivation

The discovery of graphene by Geim and Novoselov in 2003 [100] triggered tremendous research [101–103]. It soon led to surprising results on the electronic and mechanical properties of this 2D material. One example is the electrical conductivity that reaches values of up to 200 000 cm²/(V·s) [104]. AFM indentation experiments by Lee *et al.* in 2008 found a Young's modulus of Y = 1 TPa and thereby established graphene "as the strongest material ever measured" [105]. The recently awarded 1 billion Euros to the *Graphene Flagship Project* by the European Commission [106], the roughly ten patents related to graphene published on average per day in 2012 [107] or the more than 13 500 papers with graphene in the title published 2013 [108] underline the unabated interest in this material.

Relatively recently, single layer h-BN, also called "white graphene", has appeared on the same stage. The name can be easily understood, as it has similar lattice constants



Figure 4.1.: STM topography that shows the coexistence of *h*-BN and graphene on Rh(111) discovered where partly covered growth of *h*-BN was desired. The carbon for the graphene is expected to come out of the Rh crystal or from residual hydrocarbons in the chamber. They can be distinguished easily by the different periodicity of the superstructure, which is clearly visible in the image and their appearance when scanned at higher voltages, where contrast inversion of the *h*-BN occurs. (Measurement parameters: I = 30 pA, V = 100 mV, scale bar: 15 nm; data treatment: slope subtraction.)

and promises, due to its insulating behavior, versatile applicability for graphene based heterostructures [109–112]. The combination of those two materials was underlined by the findings of Dean *et al.* who showed in 2010 that the mobility in graphene can be improved almost one order of magnitude in devices on h-BN over SiO₂-supported devices. But h-BN's spectrum of physics and possible application is much broader and should not be reduced to an ingredient in graphene based electronics. In Section 4.2 h-BN will be discussed in depth. The following three topics highlight the broad range: Its application as a nanotemplate when grown on transition metals as was first shown by Dil *et al.* [113]. The application of its allotropes, like hydrogen storage in multiwalled h-BN nanotubes at room temperature investigated in ref. [114]. And even water purification with porous BN was reported [115, 116].

4.2. Hexagonal Boron Nitride

4.2.1. Overview

Due to the electronic configuration of boron ([He] $2s^2 2p^1$) and nitrogen ([He] $2s^2 2p^3$) a 1:1 combination of the two is isoelectronic to a corresponding carbon system ([He] $2s^2 2p^2$). Hence, also several polymorphs of BN exist, which have similarities to their carbon counterparts. The hexagonal form of BN corresponds to graphite, cubic BN (*c*-BN or β -BN) with a sphalerite crystal structure to diamond and the wurtzite structure of BN (w-BN)is similar to lonsdaleite ("hexagonal diamond"). h-BN and c-BN are of huge technological importance, while even though w-BN has shown extreme hardness that rivals or even exceeds that of diamond [117] its scarcity (similar to lonsdaleite) prohibits application. The sp² hybridization in h-BN creates strong covalent bonds between the atoms in the layer, while the layer as a whole is only loosely bound by van der Waals forces to adjacent layers. This makes it interesting as non-conducting lubricant and even as an additive to cosmetic products [118, 119]. Its Mohs hardness is similar to graphite, in the range of 1-2, whereas for c-BN the hardness is slightly below 10, but its thermal and chemical stability is superior to diamond. This makes it the material of choice as an abrasive [120]. While the first X-ray studies of BN date back to 1952 [121] research nowadays is mainly focused on single or few layers of h-BN, hence in the following only those will be discussed. In ref. [122] Golberg et al. give a good overview of BN nanotubes and nanosheets, whereas Song et al. discuss in ref. [123] especially the growth and mechanical properties of large $(\approx 1 \ \mu m \text{ diameter})$ membranes with two and more layer sheets. Further research done on the mechanical properties of single layer h-BN will be discussed later (Section 4.2.4).

4.2.2. h-BN on Transition Metals

In this thesis *h*-BN on Rh(111) was investigated. Nevertheless, it is worth mentioning other examples of transition metals besides Rh(111) [125, 126] that have been shown to serve as substrate for *h*-BN. This is based on their ability to decompose borazine at high temperatures and thereby supplies B and N onto the metallic substrate, leading to a self-limiting growth of *h*-BN. The following list includes references to the first discovery, first STM investigation and/or important theoretical work: Ni(111) [127–129], Ni(110) [130], Ru(0001) [131, 132], Ir(111) [133], Pd(111) [128], Pd(110) [134], Ag(111) [135], Pt(111) [128, 131] and Cu(111) [136, 137]. Also 1-D structures of *h*-BN have been observed on Cr(110) [138], Fe(110) [139], and Mo(110) [140] that can be grown by using similar procedures. On this microscope setup many years of expertise exists for *h*-BN on Rh(111) [19, 141, 142], while also *h*-BN on Ni(111) is investigated within the group [143].

On a Rh(111) crystal the lattice mismatch between the substrate (269 pm) and the *h*-BN (250 pm [144]) results in a growth in which the *h*-BN monolayer forms a Moiré-like superstructure with 3.2 nm periodicity, corresponding to 13 B-N units on top of 12 Rh atoms $[145]^1$. Surface areas in which the N atoms of the *h*-BN are aligned with the Rh atoms of the substrate are strongly bound and are called "valley sites", while areas in which the N atoms are aligned with hollow sites buckle away from the metal substrate ("rim sites"). This is schematically shown in Figure 4.2, where also the two different rim sites (with (B,N) at positions (*hcp*, *fcc*) and (*top*, *hcp*), respectively) become evident.

Besides the interest in *h*-BN as an insulating layer (with an energy gap of ≈ 5 eV [147]) for heterostructures, *h*-BN has also been shown to be an excellent nanotemplate [113] due to

¹While the first work on h-BN on Rh(111) falsely suggested a double layer model based on STM topography images [125] and introduced the term "nanomesh" (which is still widely used, but misleading) the single layer model is nowadays uncontroversial [146].



Figure 4.2.: Frequency shift image and schematic drawing of h-BN on Rh(111). The three models show how the h-BN is aligned in respect to the Rh(111) surface, which is due to the lattice mismatch and causes the corrugation. The differences between the red (hcp, fcc) and blue (top, hcp) areas is discussed in Section 4.4.2.

the corrugation where atoms, molecules and clusters can be easily trapped. In addition, it electronically decouples those adsorbates from the underlying substrate [126, 132], which allows investigation of their intrinsic properties without or with reduced coupling to the substrate. For STM measurements it is important to note that it only slightly modifies the tunneling barrier – in typical voltage ranges (< 2 V) the rim region appears transparent in respect to the underlying surface, while the Rh states are slightly suppressed in the valley region due to the stronger bond between the N and the Rh atoms. For bias voltages above 2 V a "contrast inversion" can be observed, where the valley regions appear elevated in respect to the rim. Outside the BN energy gap the apparent height increases [86]. In Figure 4.3 STM topography examples of *h*-BN as a nanotemplate are shown that were investigated with this setup during this and previous theses.

The geometrical dimensions of the h-BN/Rh(111) system found by theory were of fundamental importance to put the derived forces into perspective (Figure 4.4 shows some



Figure 4.3.: Application of h-BN on Rh(111) as nanotemplate. Examples investigated with this microscope (a) Co atoms (-50 mV, 20 pA, scale bar: 10 nm, see also Chapter 5) (b) Cr₇Ni with several impurities or fragments (-20 mV, 20 pA, scale bar: 3 nm, see also Appendix A), (c) Mn₁₂ (0.1V, 50 pA, scale bar: 5 nm) (d) Pb cluster (1 V, 0.1 nA, scale bar: 30 nm, adapted from [124]).



Figure 4.4.: Examples from theoretical investigations of h-BN that were consulted during the interpretation of the discussed experiments. (a) Early force field approach by Laskowski et al. [145] that triggered the interpretation of a single layer model. (b) Height color map of B and N and (c) B-N bond length distribution as calculated by Diaz et al. in a recent large simulation cell DFT calculation study [148].

examples). A continuous reference during the AFM measurements was the work of Schwarz and Blaha in Vienna [145, 149, 150]. Also the recent study of Diaz *et al.* has shown to be helpful, where the density functional theory calculations were expanded to more than 1000 atoms to gain a more reliable characterization of the geometrical and electronic structure [148]. Ref. [151] can serve as a good starting point to get an overview of the theory oneand two-dimensional honeycomb structures of h-BN. Mechanisms of breaking and deformation due to stress are discussed using first-principles plane-wave methods. In ref. [152] an *ab initio* study reveals the more fundamental mechanical properties of h-BN. They found that a non-linear elastic deformation is followed by a softening of strain for further increased stress.

4.2.3. Preparation of h-BN on Rh(111)



Figure 4.5.: (a) Chemical formula of borazine with dimensions, adapted from [153]. (b) Photograph of the borazine liquid in a custom made container used for the discussed experiments. The inset shows the milky (slightly degraded) borazine, which is still suitable for sample preparation.

First, the Rh(111) crystal is prepared by repeated cycles of sputtering with Ar⁺ ions (typically 20 minutes at 1.5 kV) and annealing up to 1100 K for 3–5 minutes. For the last few cycles the ion energy and the temperature of annealing are reduced to 1.3 kV and approximately 1080 K, respectively. No significant difference for annealing in oxygen atmosphere was observed. For "debugging" purposes the clean metal sample can be checked in the STM, otherwise the *h*-BN can also be directly grown by chemical vapor deposition [127] during the last annealing cycle: Borazine² ((HBNH)₃) is dosed through a leak valve for two minutes at a pressure of $1.2 \cdot 10^{-6}$ mbar (≈ 110 Langmuir³) while the sample is kept at a temperature of approximately 1080 K. The Rh serves as a catalyst to decompose the borazine. The temperature is slowly decreased afterward to allow uniform formation of the layer before the sample is *in situ* transferred into the cold microscope. In ref. [156] Dong *et al.* image the formation of *h*-BN on Rh(111) with STM up to temperatures of 1200 K and show by their image sequences how the structure grows and how defects are

²The first samples were made with borazine that was produced in house, while now it is bought from ChemicalPoint [154] and produced by Katchem [155].

 $^{^31}$ Langmuir $\widehat{=} 1.33 \cdot 10^{-6} \ \mathrm{mbar} \cdot \mathrm{s}$

introduced.

By dosing less borazine, also half covered samples can be prepared [86]. This requires clean Rh crystals and good UHV conditions due to the high reactivity of the Rh. In Figure 4.1 an example is shown where next to *h*-BN also small patches of graphene are clearly distinguishable, which originate from carbon contamination from inside the crystal or were formed due to residual hydrocarbons in the chamber. A huge advantage of unexposed metal areas is a significant improvement of tip preparation possibilities, as this is indisputably cumbersome on insulating surfaces. For the controlled pick-up of atoms or molecules this might be also advantageous.

An alternative approach to obtain h-BN is based on B-Trichloroborazine ((ClBNH)₃) [157, 158], while also the "scotch tape" cleavage technique [159] first reported for graphene [160] and a surface segregation method [161] can be used to obtain few layer h-BN.

4.2.4. Mechanical Properties

While the discussion about graphene nanoribbons or carbon nanotubes in the scope of the space elevator idea [162, 163] might seem rather like science fiction, the mechanical properties of graphene are truly impressive. Therefore, the focus of the following discussion is on the methods to study mechanical properties of 2-dimensional systems. While most experiments focus on graphene the techniques are usually also transferable to h-BN.

The most common method to study mechanical properties of thin layers (that are in terms of mechanics usually called *membranes*) is by indentation experiments, where an indenter (with a hemispherical tip) is used to push into the membrane and record deformation vs. force curves [164]. This method is refined for micro- and even nanoscale systems, where AFM tips are used to apply the force. An example is the indentation experiment that revealed a record-breaking Young's modulus of Y = 1.0 TPa for graphene [105], while Song *et al.* investigated mechanical properties of ~1 μ m diameter membranes with two and more layer sheets of *h*-BN [123]. It is important to note that in those experiments the force and deformation are always determined independently, which allows direct access to the corresponding mechanical properties. In the experiments discussed below, those two values cannot be obtained separately, as the "true" topography is unknown and the force distance relation on the atomic scale is nonlinear. Nevertheless, it is remarkable how the advances of scanning probe methods enable detection of mechanical deformations at the nm-scale.

An interesting field of current research deals with the limitations of "classical" mechanical models. E.g. in ref. [165] and [166] mechanical deformations of graphene at the margins of continuum mechanics are discussed.

While graphene and h-BN can be considered as purely two-dimensional for most cases, Meyer *et al.* found that out-of-plane deformations of suspended graphene sheets reach up to 1 nm [167] and Bao *et al.* could generate one- and two-dimensional periodic ripples in graphene by spontaneously and thermally generated strain [168]. This should further motivate the discussion about the investigation of the stiffness in the corrugated h-BN on Rh(111), which will follow in the next section.



4.3. Determining the Stiffness of h-BN

Figure 4.6.: The schematic concept of measurements probing the deformation of the h-BN/Rh(111). (a) Schematic side view of the studied system. The h-BN depicted by the black balls is in equilibrium position, i.e. the tip being far away (no interaction). Dark gray and light gray symbolizes the situation where the interaction between tip and h-BN is attractive and starting to be repulsive, respectively. The z-scale is based upon data extracted from DFT calculation from ref. [148]. (b)-(d) Model drawings of the effective stiffnesses probed in the three discussed cases of vertical attractive (b), vertical repulsive (c) and lateral attractive forces (d).

In the following the experiments allowing the determination of the stiffness of h-BN on Rh(111) are discussed. In Figure 4.6 the concept of the experiment is schematically outlined: Combined atomic force and scanning tunneling microscopy is used to measure the response of the monolayer to probing forces.

The high intrinsic corrugation of the system precludes a simple 2D treatment; probing the stiffness by only applying forces perpendicular to the layer, like in indentation experiments on planar sheets, neglects the effects that occur due to the corrugation. Only by investigation in all spatial dimensions can a full picture be obtained. Therefore, 3D force maps will be recorded and atomic resolution images of the layer will be used to determine the lateral and vertical stiffness of this prototypical system with unprecedented spatial resolution.

4.3.1. Setup, Data Acquisition and Data Treatment

All data was recorded at 4.2 - 5.0 K or at 1.5 K and under UHV conditions (~ 10^{-10} mbar). The cantilever stiffness is $k_0 \approx 1800$ N/m, the resonance frequency is $f_0 = 18.441$ kHz and the Q-factor in the range of 50 000. As discussed in detail in Section 2.4.3, the small cantilever oscillation amplitude of ~ 130 pm enables detection of the frequency shift Δf of the AFM cantilever and additionally the electrical conductance G = I/V between tip and



Figure 4.7.: The *h*-BN layer. (a) The interaction energy landscape between tip and the *h*-BN layer at z = 0.55 nm shows the strong corrugation of 3.2 nm periodicity. The lateral scale bar corresponds to 3 nm. (b) Frequency shift and (c) conductance of a small region at the rim site allowing assignment of B (blue) and N (red) atoms. The lateral scale bars correspond to 0.3 nm.

sample. This technique has two advantages: First, it allows use of the exponential dependence of G on the tip height z to determine the absolute distance between tip apex and substrate (see Section 4.3.1 and Figure 4.10) and second, the small oscillation amplitude ensures the detection of minute lateral deformations of the corrugation without averaging over large z ranges. The current signal can also be used to exclude some tip effects, like a dangling tip apex.

The following procedure was carried out before recording the data: By scanning a larger area of the sample the overall tilt between sample and scan plane is identified and compensated deploying the tilt correction feature of the control electronics. After waiting until the drift is marginal, constant-height 2D images of tunneling current, frequency shift, oscillation amplitude, and excitation voltage are recorded. A self-written LabVIEW script automatically increases the tip-sample distance after each scan by a set value. This distance change was increased during acquisition for the last images where the change in signals becomes smaller or no lateral resolution is obtained anymore and only the average value is of significance. For the same reason the pixel density was reduced and the application of a Gaussian smooth is legitimate and appropriate to eliminate the predominance of the noise that occurs due to the integration.

Two sets of 3D Δf and G data will be evaluated in the following. The "large-scale" set consists of 48 2D maps of 8 × 8 nm² and a z-range of 1.3 nm. The bias voltage was -0.9 V which corresponds to the minimum of the contact potential difference, i.e. the electrostatic forces are approximately compensated at this voltage. The "high resolution" set, consisting of 15 images with three times higher pixel density, was recorded over the dimensions of



Figure 4.8.: Artistic representation of selected frequency shift images from a set of constant height measurements. The atomic-scale resolution of the lower image is clearly visible, while in the higher images only the superstructure is resolved. To obtain the energy land-scape – which is the basis for all further deduced properties – Δf has to be integrated for every pixel as described in the text.



Figure 4.9.: Histograms of the amplitudes for the two investigated data sets for all pixels in the images of closest approach with a Gaussian fit (red) to determine the width of the distribution. (a) Larger scale data set with $\sigma \approx 1.4$ pm. (b) High resolution data set with a shorter tip-sample distance and slightly broader distribution ($\sigma \approx 1.8$ pm).

 $4 \times 4 \times 0.73$ nm³ at 0.2 V⁴. Some slides of the high resolution data set are shown in Figure 4.8. During measurement the excitation and amplitude signals should be monitored and checked for signs of dissipation and stability, respectively. For the two sets the standard deviation of the amplitude signal for all pixels of the image of closest approach is calculated to quantify the stability. The deviations are below 1.5% and 1% of the set value for the high resolution and large-scale set, respectively (see Figure 4.9 for the distribution).

A qualitative discussion of the reliability of the performed analysis will accompany the evaluation. For systematic errors the following sources are taken into account by a conservative total estimation of 10% uncertainty: The piezo and amplitude calibration, the stiffness of the tuning fork, loss of accuracy due to limited resolution (and interpolation), and limited amount of slides, i.e. integration distance.

Drift Correction and z-Scale Calibration



Figure 4.10.: Drift calibration and determination of the z-scale. The averaged tunneling current at the rim region from the image set and a subsequently recorded I(z)- spectra are used to compute and subsequently compensate for the vertical drift over time. The blue crosses denote the raw data plotted against its original z values, while the green diamonds show the data in a drift compensated z-axis. The kink in the raw data at $z \approx 0.2$ nm is due to an interruption of the measurements for a few hours. The exponential fit (red) of the current is extrapolated (magenta) until it reaches point contact ($G = G_0$, corresponding to 15.5 μ A at 200 mV) which is assigned z = 0. Note that for the exponential fit values between 0 and 0.2 nm of the spectra are neglected, because the I/V converter approaches its nonlinear regime.

During the measurement time of up to 15 hours lateral and vertical drift cannot be avoided

⁴It was checked that the two sets do not differ significantly except with respect to the tip-dependent long-range forces and the resolution. Hence the effect of the uncompensated electrostatic forces is not relevant for the determination of the stiffness in the following.

completely. First, the lateral drift should be compensated manually before processing the data. It can be noted that the manual compensation, where the images are adjusted in terms of integer pixel rows/columns (i.e. no interpolation) gave comparable results to employing automated (correlation) methods. For the vertical calibration, reference spectra (frequency shift and tunneling current) are recorded at the end of the data acquisition. By comparison of these spectra with the tunnel current extracted from the images of the set in the same region the vertical drift can be compensated by adjusting the height of the images (see Figure 4.10)⁵. To increase the signal-to-noise ratio, the values from the images are averaged over small discs of 0.2 nm diameter. The same procedure can be applied to the frequency shift data resulting in the same drift corrections.

While absolute heights are difficult to quantify in STM a good estimation is nevertheless desirable to assess topographic deformations and potentially even the "contact" between tip and sample. To define a scale that is appropriate to the experiment, the exponentially increasing current is extrapolated at the rim site until it reaches point contact, i.e. where G(z) is equal to G_0 (the quantum of conductance) [73]. For the example shown in Figure 4.10 the interpolation (orange line) shifts the uncalibrated z-scale by $z_{UC} = -423$ pm. Due to the oscillation of the tip and the much lower bandwidth of the current detection (which leads to an averaged current over the oscillation amplitude) this scale has to be compensated by $\Delta z = \ln(J_0(2\gamma A))/(2\gamma) = 68 \text{ pm with } \gamma = 10 \text{ nm}^{-1}$ the decay constant of the current and J_0 the Bessel function of first kind, as discussed in Section 2.4.4 [81]. This allows the height in terms of tip-sample distance of closest approach to be obtained, resulting in an overall offset of $\delta z = z_{UC} + \Delta z = -355$ pm, which is assigned z = 0. It is worth pointing out that this definition can only be a rough estimation, as the linear behavior of the conductance can only be expected in the tunneling regime and the distance dependence can change quite significantly [169]. The tip height of closest approach in the large-scale set is 0.55 nm.

From STM topographies at the corresponding bias voltages with only partial coverage of h-BN it is known that the apparent height of the rim is comparable to the Rh, i.e. is essentially transparent. The valleys are slightly more insulating, hence appearing as depressions below the Rh reference [86]. The true topographic height difference is impossible to quantify by STM, but is expected from theory to be in the range of 100 pm. (A z-scale calibration in the valley is with this assumption in good agreement and results in a shift of 85 pm compared to the rim). This means that, by taking the rim as z = 0 reference, the height of the h-BN layer itself is neglected. However, because recent DFT calculations performed by Diaz *et al.* [148] suggest that the vertical distance between N atoms and the top Rh layer is in the range of 225 to 335 pm, it is still below the height of closest approach of z = 355 pm reached in the experiments.

4.3.2. Calculating the Interaction Energy and Force Landscape

The now drift compensated frequency shift images can to be integrated to obtain the interaction energy and the force landscapes for the system of probing tip and the h-BN

⁵As there was a disruption in measurements during the high resolution image set, the drift compensation is done for the two periods separately.



Figure 4.11.: Example of a simultaneously recorded (a) current and (b) frequency shift curve and (c) the corresponding integrated interaction force. Note the logarithmic scale of the current and that the z-range used for integration extends to 7.7 nm, where the force is assumed to be zero. (d), (e) Zoom-in of (a) and (b) with the values of the current and Δf , respectively, from an image set is overlaid (green points), which show perfect agreement. (f) Comparison of the forces calculated from (b) and (e) which show a similar trend but differ significantly in magnitude and also in slope. This problem arises due to the shorter integration range of the image set.

layer [170]. This is accomplished by a discretized Sader-Jarvis method [52] (see Section 2.3.2):

$$E(i) = E(i) + \frac{k}{f_0} \cdot (f(n) + f(n+1)) \cdot \left(c + \frac{\sqrt{A}}{4} \cdot \sqrt{\frac{c}{\pi}} + \frac{A^{3/2}}{\sqrt{2c}}\right) \cdot (z(n) - z(n+1)) ,$$

$$F(i) = F(i) + \frac{k}{f_0} \cdot \left[\left(1 + \frac{\sqrt{(a)}}{(8 \cdot \sqrt{\pi \cdot c})}\right) \cdot (f(n) + f(n+1)) \cdot (z(n) - z(n+1)) \dots - 2 \cdot \frac{A^{3/2}}{\sqrt{2c}} \cdot (f(n) - f(n+1)) \right]$$
(4.1)

with c = (z(n) + z(n+1))/2 - z(i) for sake of clarity. *i* runs from the furthest away height to the data point of closest approach $(i = N \dots 1)$ and *n* sums over all images up to the current height $(n = 1 \dots (i-1))$. An example calculated by the above equations of a frequency shift curve and the corresponding interaction force is shown in Figure 4.11. For a full set this procedure has to be applied to all pixels of the image. To obtain the lateral forces, the gradient of the interaction energy landscape is calculated [171].

An inherent limitation of the Sader-Jarvis method [52] to determine forces is the fact that the data point furthest away is set to F = 0. Therefore the height range over which data is recorded should be large enough so that there is negligible interaction between tip and sample, i.e. that f approaches f_0 . The right panels in Figure 4.11 illustrate the problem by comparing the data from an image set (green points) to a spectroscopy curve recorded over a much larger tip-sample distance (0.6 versus 7.1 nm). Increasing the step size between the images and reducing the pixel density is a feasible approach to increase the measurement speed, while attaching a single spectroscopy curve (recorded over several nm) to every pixel to account for long range behavior has shown to be impracticable. Focusing on the short-range forces helps to avoid this problem to a certain degree, as the long-range interactions are relatively independent of the specific environment, i.e. whether measured on a rim site or in a valley.



4.3.3. Lateral Forces

Figure 4.12.: Lateral forces of the *h*-BN. (a) Interaction energy landscape above the atomically resolved center of the rim recorded at a tip-sample distance z = 355 pm with an overlaid atom model. The arrows represent the lateral forces F_{\parallel} . Note that the forces are attractive, i.e. the tip is pulled towards the atoms, and vice versa. The scale bar corresponds to a distance of 0.1 nm and the reference arrow to a force of 30 pN. (b) Image of the total lateral forces at the length scale of the corrugation. The forces are zero in the center of the valley and on the top of the rim and reach the maximum in the intermediate region. (z = 550 pm. Scale bar: 1 nm.) (c) High resolution image of an area corresponding roughly to the one marked in (b) from the same data set as (a). The image was recorded with a sharper tip at a smaller tip-sample distance, so atomic resolution could be achieved. Here the force minima are at the center of the BN hexagon and on top of the atoms. (z = 355 pm. Scale bar: 0.5 nm. Vertical color code: same as (b) but 0 - 44 pN.)

At close tip-sample distances (z < 0.5 nm), where Pauli repulsion becomes significant, clear atomic contrast at the rim sites of the *h*-BN layer in the Δf and *G* maps is visible



Figure 4.13.: Determination of the positions of the BN hexagons. (a) The Δf image with increased pixel size (×10) and after a Gaussian smooth, scale bar: 1 nm. (b) Image after application of a high pass filter with the red areas determined by an edge detection routine. (c) The centers of the red areas are calculated and marked by black crosses. The number of next neighbors is determined by counting the spots within a set distance. Some initial correction and removal of outliers has been applied.



Figure 4.14.: (a)-(d) Frequency shift images with plot of the positions of the BN hexagons for all four evaluated images with sufficient signal to allow the discussed semi-automated determination of positions. The color coding represents the average nearest neighbor distance. (All images: 4 by 4 nm².)



Figure 4.15.: (a), (b) Histograms of l and of F_{\parallel} at the four evaluated heights. The Gaussian fits are guides to the eye. The numbers in the panels are the averages. A change of l_{avg} by 11 pm and $F_{\parallel avg}$ by 7 pN is observed for a decrease of the tip height by 67 pm.



Figure 4.16.: The relative shift of l_{avg} derived from the statistical analysis (black) and by FFT (red) decreases linearly with $F_{\parallel avg}$. A linear fit (green line) enables the determination of the lateral stiffness of $k = 0.66 \pm 0.17$ N/m.

(Figure 4.7 (b), (c)). A maximum of G and $-\Delta f$ is found at the position of the atoms, becoming weaker at the inter-atomic center of the BN hexagons. The interaction energy difference between the atom sites and the centers of the hexagons reaches $\Delta E = 15\pm 5$ meV at closest approach of z = 355 pm. This modulation of the total energy leads to lateral

forces F_{\parallel} between the tip and the atoms of the *h*-BN (Figure 4.12 (a)). Independent of the vertical force component F_{\perp} the lateral force acting on the tip are always found to be attractive towards the atoms. In return, this causes a small decrease of the average distance between B and N atoms in the hexagon directly below the tip apex. This shift is determined by a statistical evaluation of the distance *l* between the BN hexagons in the rim region (Figure 4.12 (b), (c)) and by a Fourier transformation of the Δf images, which is presented separately in Section 4.3.3.

For determination of the hexagon centers in the atomically resolved frequency shift images were scaled up by a factor of ten and interpolated by a Gaussian smooth to attain higher sub-pixel accuracy. The images were then high-pass filtered to remove the corrugation. The positions of the rings were determined by a threshold routine. Artifacts and outliers were manually removed before next neighbor distances were calculated and averaged for each ring. Those steps are presented in Figure 4.13, while Figure 4.14 shows the four images of closest approach with the determined positions and distances in the color code. From those four images histograms of the determined distances are shown in Figure 4.15 (a). In panel (b) the histogram of the absolute values of the lateral forces in the region where atomic resolution was achieved is shown.

The distances and forces are averaged and a decrease of l by 4%, giving an increase in F_{\parallel} from 13 to 20 pN, is observed. This change corresponds to a change in tip height of 67 pm. By relating the change of l to the average F_{\parallel} (Figure 4.16) in a first order approximation (Hooke's law), i.e. by reducing the complex geometry of the entire rim region to a single spring (as introduced in Figure 4.6 (d)) an effective lateral stiffness of

$$k_{\parallel} = \frac{\mathrm{d}F_{\parallel}}{\mathrm{d}l} = 0.66 \pm 0.16 \text{ N/m}$$
(4.2)

is derived. The main contribution of the uncertainty results from the distribution of derived distances (Figure 4.15 (a)).

While mechanical layer properties are usually expressed in terms of 2D Young's moduli, it should be noted that transferring concepts of classical mechanics is cumbersome or even impossible for such complicated and highly anisotropic system as the corrugated h-BN on Rh(111). Therefore the model of a single spring for the entire rim region is a drastic simplification. In Section 4.3.6 a more advanced elastostatic model will be discussed.

As the lateral compression in the sheet is caused by the presence of the tip it has to be compensated for by stretching in other regions of the layer where F_{\parallel} exerted by the tip is significantly weaker. This allows the conclusion that the derived stiffness is indeed a property of the entire rim region, and not only the quantification of the stiffness of the single BN unit below the tip.

Density functional theory calculations found differences of B-N bond lengths within the superstructure of up to 4 pm due to the lattice mismatch when grown on Rh(111) [148]. The experimentally observed decrease of l at the applied forces is of the same magnitude, even though the deformation, which is probed, originates from two effects: First, deformations within the layer, i.e. direct changes of the bond lengths below the tip apex and, second, movements of the whole rim region due to the forces applied by the tip. These two effects cannot be disentangled. Nevertheless, it is worth highlighting that only the achieved atomic resolution together with the spatial resolved lateral forces make a quan-

tification of the overall movement possible.

The lateral flexibility can be imagined to play a significant role in the frequently observed off-center adsorption of molecules on the h-BN [19, 113, 172]. The low stiffness of the entire rim region will promote topographic adaptation by the h-BN layer for larger molecules, while the flexibility within the layer might play a role on the level of individual bonds.

FFT of High Resolution Images



Figure 4.17.: The lateral distance change between the BN units determined by a method relying on FFT. (a) The FFT of the frequency shift images clearly shows the expected hexagonal symmetry. For better visibility the low frequency part is cut out. (b) Interpolated zoom-in used to determine the position of the maxima by fitting 2D-Gaussians. (c) The change in position of the feature in the FFT is transferred into real space and plotted against the lateral force to derive the stiffness. For comparison the values of the direct Δf image analysis are also included.

In order to circumvent the inherent difficulty of determining the exact center positions of the BN hexagons for the lateral distance change presented above, a second method was employed. It relies on a Fourier transformation of the frequency shift images and is presented in Figure 4.17. The hexagonal structure of the atomically resolved layer is clearly reproduced. The two marked maxima are investigated by fitting a 2D-Gaussian for the first four tip-sample separations measured. Figure 4.17 (b) shows an example. The change in position is then converted into real space distance changes and put into relation to the acting lateral forces. From Figure 4.17 (c) it is evident that both methods lead to comparable results. Therefore the overall stiffness was calculated based on the average of the two methods.


4.3.4. Repulsive Vertical Forces

Figure 4.18.: Deformation due to repulsive vertical forces. (a) 3D representations of constant total force landscapes $(3.4 \times 3.4 \text{ nm}^2)$ at -450 pN, -575 pN and -640 pN (top to bottom). The color code ranges from 460 to 520, 370 to 450 and 355 to 410 pm for the three images, respectively. An indentation of the layer when high forces are applied is clearly visible in the rim region. (b) The intersections (black, red, green) of the light blue plane with the force landscapes shown in (a) underline the vertical compression, which can be estimated to be ≈ 25 pm of the rim site by decreasing F \perp from -575 to -640 pN. Note that the height scale corresponds to the -640 pN curve and that the -575 and -450 pN curves are offset by -30 and -100 pm, respectively.



Figure 4.19.: (a) The short-range forces at the rim site are fitted by a Morse type force up to z = 0.42 nm (gray dotted line), after which a significant change of slope is visible that is attributed to the pushing of the layer. (b) The difference between the fit and the data in (a) is used to deduce a vertical stiffness of $k_{\perp} = 1.5$ N/m.

Besides the lateral layer deformation the presence of the tip also impacts the shape of



Figure 4.20.: (a) The short-range forces are fitted by a Lennard-Jones type force up to z = 0.42 nm, after which the discrepancy of the fit and the data is attributed to the pushing of the layer. (b) By a linear fit a vertical stiffness of $k_{\perp} \approx 1.0$ N/m is deduced from the data shown in (a).



Figure 4.21.: (a) A Morse type force is fitted to the data up to different cut-off-points (z = 0.40, 0.42, 0.47 nm, pink, black and green curve, respectively). A fit to the full range results in worse agreement (orange line). (b) The difference between the fit and the data in (c) is used to deduce vertical stiffnesses of $k_{\perp} = 1.5, 1.5$ and 2.1 N/m, respectively.

the corrugation normal to the surface. Constant force landscapes interpolated from the vertical force component F_{\perp} clearly show an indentation of the rim region in an area of about six hexagonal units of up to 25 pm at short tip-sample distances (Figure 4.18). This apparent indentation cannot be solely attributed to the topographic response of the layer to the acting force, as it also includes long-range electrostatic and van der Waals forces. To get a quantitative measure of the deformation, focus is put on the distance dependence of the short-range forces. They are obtained by using the valley region as a reference for long-range forces and subtracting them from the total forces at the rim regions. Note that in the following only single F(z)-curves are discussed, which are obtained by averaging over several pixels in the region of interest from each slice of the set. (The spectroscopy curves used for the drift compensation in Section 4.3.1 can also be used, leading to the same results.)

The fit of a Morse type force [173]:

$$F = -F_0 \cdot \left(e^{-a(z-z_0)} - e^{-2a(z-z_0)} \right)$$
(4.3)

to the attractive part of the short-range forces results in $F_0 = 370$ pN, a = 12 nm⁻¹, and $z_0 = 0.37$ nm. This fit is interpolated and the discrepancy of it and the data below z = 0.42 nm⁶ is attributed to topographic deformation of the layer. By relating the topographic changes to the acting vertical force an effective stiffness of $k_{\perp} = 1.5 \pm 0.6$ N/m is derived.

So far the fitting of the repulsive vertical forces is discussed in terms of a Morse type force. Now an evaluation based on fitting a Lennard-Jones type force

$$F_{\perp} \propto \left(\frac{s^{12}}{z^{13}}\right) - \left(\frac{s^6}{z^7}\right) \tag{4.4}$$

is presented, as shown in Figure 4.20 (a). In Figure 4.20 (b) the discrepancy of the fit and the data below z = 0.42 nm is attributed to the softness of the layer and a stiffness of $k_{\perp} \approx 1.0$ N/m can be derived, which fits well into the range of values obtained.

While so far the cut between the fit and the interpolation was set to z = 0.42 (corresponding to the fourth height recorded in the data set) in Figure 4.21 (a) the effect of choosing different ranges for the Morse type force fit are shown. While the fit to the full range clearly shows the highest discrepancy for larger heights, the effect of choosing different cut-off points (e.g. the cyan curve for a cut-off at z = 0.40 nm) has on a small effect on the stiffness (4.21 (b)). Even the relatively bad fit starting at z = 0.47 nm (green curve) results in a comparable stiffness (within the error range) of 2.1 N/m.

Comparison to Indentation Measurements

To put the effective stiffness into perspective as far as larger scale measurements that usually aim at the Young's modulus are concerned, it is worth while to compare the data presented here to the measurements of ref. [123]. They derive the 2D elastic modulus $(Y^{2D} = 200 - 500 \text{ GPa} \cdot \text{nm})$ from indentation of 1 μ m diameter free few-layer *h*-BN membranes with a diamond tip. In their Figure 4c two indentation measurements are shown that allow the estimation of the indentation to be approximately 20-30 nm for an applied force of 50 nN. This would correspond to an effective stiffness of approximately 2 N/m. Hence, the stiffness that is derived here for the rim regions of *h*-BN on Rh(111) is of similar magnitude as for a much larger, free membrane.

In another recent publication aiming at the quantification of the stiffness of a graphene superstructure Koch *et al.* investigated graphene on Ru(0001) that forms ~ 0.1 nm high "nanodomes" with ~ 3 nm periodicity [174]. Due to the observed indentation they tentatively estimate a stiffness of $k_{exp} = 0.65$ N/m by attributing the slope of the repulsive short-range forces solely to the deformation, i.e. by neglecting the intrinsic change of force. In the above discussed model this problem is avoided by the comparison against

⁶Note that the position of the cut is arbitrary but can be justified by the fact that only the force range where repulsive forces become relevant is of interest. The small number of data points prohibits an analytical treatment as it is done in Section 4.3.5 for the attractive vertical forces.

the Morse type force. From extensive DFT calculations where the deformation is achieved by fixing one single atom at a reduced distance to the surface and relaxing the structure, they derive a comparably high stiffness of $k_{DFT} = 43.6$ N/m. Also this definition of the force is different from the approach discussed here, as they relate the deformation to the force acting on that single atom due to the restoring forces of the dome, while here the distance change is attributed to the short-range forces applied by the tip.

4.3.5. Attractive Vertical Forces



Figure 4.22.: Deformation due to attractive vertical forces. (a) The short-range forces in the attractive regime show an over-exponential increase below approximately -20 pN (gray dotted line) at the rim site, which is attributed to pulling the *h*-BN away from the surface by Δz (red bar). The exponential fit (with a decay constant of 4.2 nm⁻¹) and the interpolation below -20 pN is shown in green and blue, respectively. (b) The slope of a linear fit (red line) of the displacement against the forces is used to deduce a vertical stiffness of $k_{\perp} = 0.36 \pm 0.05$ N/m.

At larger tip-sample distances one can imagine that the attractive vertical forces lift the rim sites away from the supporting Rh(111) substrate. To observe this pulling the short-range forces are investigated at distances where the Pauli repulsion can be neglected (z > 0.55 nm) but where forces are still strong enough to have an influence on the *h*-BN. An exponential decrease of F_{\perp} can be observed and quantified when decreasing *z* as long as F_{\perp} is above approximately -20 pN. At shorter tip-sample distances the measured force decreases faster than the exponential fit (Figure 4.22). The height difference between the measured force and interpolated exponential value (blue line) can be attributed to the lifting of the sheet. Relating this lifting to F_{\perp} results in a vertical stiffness of $k_{\perp} = 0.36 \pm 0.05 \text{ N/m}.$

While this evaluation requires an arbitrary cut between the exponential fit and the inter-



Figure 4.23.: (a) Same data as in Figure 4.22 (a) but with a fit based on the Lambert W function (red). (b) The stiffness is evaluated at each point by deploying the solution with the Lambert W function. A Gaussian smooth of 2 by 2 pixels is applied for clarity. The scale bar corresponds to 1.5 nm.

polation, also an analytical relation can be used:

$$F_{\perp}(z) = F_0 \cdot \exp\left(-\kappa \left(z + \frac{F_{\perp}(z)}{k_{\perp}}\right)\right), \qquad (4.5)$$

with κ being the decay constant. This takes the pulling of the tip on the BN sheet at all distances into account by replacing z with $z + F_{\perp}(z)/k_{\perp}$. This equation can be solved to yield

$$F_{\perp}(z) = \left(\frac{\kappa}{k_{\perp}}\right) \cdot W_0\left(\frac{F_0\kappa}{k_{\perp}} \cdot e^{-\kappa z}\right),\tag{4.6}$$

with W_0 the real-valued branch of the Lambert W function (which is defined as the inverse relation of the function $z = f(W) = W \exp(W)$). An average of $k_{\perp} = 0.4 \pm 0.1$ N/m is derived when evaluating the rim region (Figure 4.23 (a)). This value is in close agreement to the value derived by the method of quantifying the over-exponential part below -20 pN. In panel (b) of Figure 4.23 the fit based on the lambert W function is performed for the entire image. Here again, as the valuey serves as a reference for the long-range forces, it is not accessible by this method.

As only the short-range forces are considered, the comparison against the exponential distance dependence in the investigated distance is legitimate [73, 169, 175] and consistent with the Morse type force in the repulsive regime. As discussed already in Section 4.3.2, the exact determination of the long-range behavior is not feasible, and therefore the fitting routines presented are forced through the last data point at $F_{\perp} = 0$.

4.3.6. Application of an Elastostatic Model

Comparing the experimentally derived values from the previous three sections to a classical elastostatic model of a thin shell with a single point load results in an effective stiffness of $k_{CM} \approx 1.9 \text{ N/m}$ [176]. The difficulty to apply a macroscopic model to this nanomechanical system needs to be emphasised. Nevertheless, even though the crude simplification of this classical model, which uses mechanical constants from unstrained *h*-BN, is prone to fail when applied to single layers [165], the obtained stiffness is of similar magnitude. The estimation of the stiffness with a thin shell model with a point force is based on Chapter 3 of ref. [176]. From a very general consideration of stress-strain and deformation relations for arbitrarily formed bodies some more special cases are discussed. After limitation to rotationally symmetric bodies the problem can be reduced to Bessel functions which are then solved for the very special case of small deformation by a force pressing on the apex of a thin shell. For the depth of the indentation the following formula is obtained:

$$\Delta z = F \cdot \frac{\sqrt{3(1-\mu^2)R^2 + \frac{d^2}{4}}}{2\mu \cdot Y \cdot d^2}, \qquad (4.7)$$

with F the applied force, Y the Young's modulus, μ the Poisson's ratio, d the thickness of the layer and R the radius of the shell. As already pointed out, the choice of values for deployment in such a model is non-trivial and can only be considered a rough estimate. The following values have been chosen: A Poisson's ratio of 0.22 [152] and a Young's modulus of E = 270 GPa [177] is a reasonable approximation. The layer thickness of 0.33 nm corresponds to the layer spacing in bulk *h*-BN [121] and the "radius" of the rim is derived to be roughly 1.85 nm from geometrical considerations. A stiffness of ~ 1.9 N/m is derived. While the model is based on the in-plane Young's modulus, considering the use of the much softer bending modulus of ~ 30 GPa [178] is also worthwhile and leads to a considerably softer value of 0.2 N/m.

Even if this exceeds the scope of research possible on h-BN on Rh(111) it is worth mentioning that the relation of stress and strain also in macro scale objects can result in remarkable effects for other mechanical properties. Structures are discussed that, due to uncompensated stress, result in zero-stiffness configurations, i.e. they can be deformed without any additional external load [179–181].

4.4. Further Discoveries on h-BN

4.4.1. Atomically Resolved Images

While the data evaluated previously already showed clear atomic-scale features even higher resolution images were obtained. Figure 4.24 (a) shows an example with a tentative assignment of B and N based on ref. [145]. A clear assignment is in this case not possible, as the simultaneously recorded current signal does not reveal clear maxima that can usually be employed for discrimination between the atoms and the centers of the BN hexagons. Contrary to the data presented above, here it is assumed that the slope of the $\Delta f(z)$ dependence has already changed from positive to negative. In Figure 4.24 (b) this is



Figure 4.24.: (a) High resolution image that allows for an assignment of B and N atoms. (Measurement parameters: A = 150 pm, $f_0 = 18.454$ kHz, -20 mV, scale bar: 0.1 nm; data treatment: slope subtraction and Gaussian smooth.) (b) A typical $\Delta f(z)$ -curve. The region in which the image in (a) was recorded is marked in red, while most data was recorded in the green region.

depicted by the red part of a typical $\Delta f(z)$ -curve, while the previously presented data was recorded in the green region.

Another approach for identification of the atoms could be based on the method introduced by Sugimoto *et al.* in 2007 where the maximum attractive total force was used to distinguish between Pb, Sn and Si atoms on a Si(111) substrate [78].

4.4.2. Difference of Rim Sites

As shown in Figure 4.2 there are two different configurations of rim regions. One, where the B atoms sit on top the Rh atoms of the first layer and the N atoms sit in the *hcp* site, called (top, hcp) and the other, where B sits in the *hcp* and N in the *fcc* site, called (hcp, fcc). While theory suggests slight differences in topography between those sites [148, 150] they could not be distinguished in the raw Δf or I data.

Nevertheless, as shown in Figure 4.25, the lateral and vertical forces show a slight difference between the two types of rim regions. While this behavior could in principle also be investigated in respect to the stiffnesses influenced by the different binding geometries, the main problem to unambiguously quantify this difference is due to a possible tip asymmetry. A wedge shaped tip that is aligned with the superstructure will cause an asymmetry in the force landscape. A small but unavoidable scan plane tilt can also cause asymmetries in the integration and has shown to be cumbersome and impractical to compensate, especially if the spacing of the individual slices is small as the correction can produce misleading artifacts. To exclude tip effects, measurements on different domains with different alignments, but with the same tip, are necessary.



Figure 4.25.: The lateral and vertical forces evaluated at the rim regions show slight differences for the (top, hcp) (blue circle) and (hcp, fcc) sites (red circle). (a) Δf image, where the differences could not be resolved. (Scale bar: 1.5 nm). (b) For the different rim regions the lateral forces are averaged over small discs. (c) The difference is shown for all heights. Note that the effect corresponds to approximately 6% of the total lateral forces in those areas. (d) Color coded waterfall plot of histograms of the vertical force regions evaluated (same regions as shown in (a) and (b)). The scale bar (color code) corresponds to the difference of counts (pixel) being above/below the zero per bin for the two different sites. A clear trend of higher (negative) forces for the (hcp, fcc) sites (red) is visible. (e) Plot of the average force differences for all heights showing a small trend towards higher forces on the (hcp, fcc) sites. Note that the effect corresponds to less than 1% of the total vertical forces in that area.

4.4.3. Alternative Definition of Stiffness

In the scope of the work to define the stiffness of the *h*-BN, a broad range of other methods for quantification was investigated. One example worth mentioning is the definition of a "total force stiffness", where long range forces were not subtracted. Exemplary forcedistance curves for the two investigated data sets are shown in Figure 4.26 (a) and (d) from an averaged area of the rim region. The part far away from the surface, where no lifting is expected, can be nicely fitted by an exponential (red curves, only partly shown in the plot). In the closer proximity the forces decrease faster than the exponential dependence would suggest. The discrepancy is defined as the lifting Δz and a stiffness is derived by $k_{TF} = \Delta z/F_{total}$. (The problem of the cut-off position is the same as discussed in Sections 4.3.5 and 4.3.4.) This method allows for a direct comparison of the rim and the



Figure 4.26.: A different method to derive a vertical attractive stiffness from the long range forces, based on the discrepancy between data and an exponential fit. (a) For the high resolution data set the lifting happens in the intermediate region, while at close tip-sample distance the onset of repulsive forces is visible. Up to a cut-off point (gray line) the force is fitted by an exponential (red) and afterward interpolated in green. (b) The fit is done for every pixel and the average of k for the four quantified images is shown. The difference of rim and valley region is clearly visible. A Gaussian smooth was applied for clarity. (c) Histogram of (b) showing clear distinct peaks with maxima at 16.3 N/m at the rim and 22.6 N/m in the valley region. (d), (e), (f) The same evaluation for the large-scale data set, where only the lifting region of the forces was investigated. The derived values are slightly shifted to 15.2 N/m and 21.3 N/m for rim and valley region, respectively.

valley region. For the images presented in Figures 4.26 (b) and (e) the derived stiffnesses are averaged over several heights and smoothed for clarity. The two regions are clearly distinct and the stronger binding of the valley region to the Rh(111) substrate is distinct, which is also clear from the histograms shown in panels (c) and (f).

The inherent limitation of this method originates from the fact that the biggest contribution of the long-range forces present is expected to result from the interaction between the bulk of the substrate and not just the h-BN below the tip apex. A clear disentanglement of the forces acting only on the h-BN from the forces resulting from the interaction with the Rh surface is not feasible. Additionally the different heights of the valley and rim regions cannot be adequately accounted for, i.e. the force acting on the h-BN in the valley is smaller than at the rim.

The evaluation discussed in this section can serve as an example that the interpretation of the forces derived by AFM is complicated and an elaborate analysis is necessary to allow the best possible interpretation. The straightforward but nevertheless oversimplified definition of the short-range forces by taking the valley region as a reference is an accepted method [68, 182] and has been shown to be the most reliable for the discussion of the stiffness.

4.5. Summary and Conclusion

In summary, the experiments discussed above served two important aspects: First, in this experimental challenge the newly designed STM/AFM head showed its potential and versatility.

Second, it was shown how forces in all spatial dimensions in combination with atomically resolved images can be used to determine the lateral and vertical stiffness of a quasi-2D strained epitaxial system. While clear evidence is presented for lateral and vertical deformation due to the forces exerted from the tip on to the *h*-BN layer, the quantification of the stiffnesses is difficult, has a relatively large uncertainty and depends to a certain degree on the reference forces chosen for quantification. For the loosely bound rim region of the *h*-BN/Rh(111), very soft lateral and vertical stiffnesses were found in the range of 0.4 - 1.5 N/m.

To reconsider the presented findings in the scope of the full system of h-BN on Rh(111), several aspects are worth highlighting, which underline the significance of the performed research: Contrary to what the in-plane elastic moduli (which are orders of magnitude higher) found for mesoscopic h-BN sheets suggest, the high local lateral flexibility allows adaptation of the h-BN to quasi-commensurate growth in the valley regions. Regardless of the high residual strain, the layer grows free of dislocations and buckles in the rim regions into the observed soft superstructure. Comparison to indentation experiments reveals that the elasticity observed at the rim region is comparable to the one of free membranes [123] despite the much smaller size of only about 1 nm in the superstructure and the close proximity to the underlying Rh substrate. Recent calculations of higher order elastic constants corroborate the softening of the h-BN when it is highly strained [152], which might be key to the surprising result.

CHAPTER 5

Cobalt on h-BN/Rh(111)

The challenging goal to measure the force related to flipping the spin of a single atom was the driving motivation to study Co atoms on a thin insulating layer. Such an experiment requires the full potential of the microscope, including the combined STM/AFM capabilities, high magnetic fields, low temperatures and high stability. The first promising results of this ongoing research of force measurements in magnetic fields will be discussed in Chapter 6.

5.1. Overview and Motivation

In this chapter, the topographic and the spectroscopic investigation of Co on h-BN/Rh(111) will be discussed (Section 5.4 and 5.5, respectively). The surprisingly broad variety of spectroscopic features will be subdivided into the findings related to a Kondo resonance and to a spin-1 system. Both are assumed to be Co-H systems. The underlying models of spin-flip and Kondo physics are discussed. A (preliminary) classification and interpretation of the data is given in Section 5.6.

Studying Co in the form of single atoms or small clusters has some tradition in the department. Gambardella *et al.* showed in 2003 unprecedentedly high anisotropies of 9 meV for single Co atoms and nanoparticles on Pt(111) by XMCD [183]¹. Wahl *et al.* investigated the distance dependence of the Kondo resonance between two Co atoms directly on a Cu(111) surface [185] and Bork *et al.* proceeded to study the same dimer with one atom at the tip and the other on a Au(111) surface in the scope of quantum critical behavior [186]. Previous studies on this microscope setup focused on larger Co islands grown by buffer layer assisted growth on h-BN/Rh(111), where the decoupling was investigated by means of studying Coulomb blockade effects [141]. The work presented here can be understood as a combination and continuation of the mentioned work, as it combines single atoms and deposition on to the highly anisotropic, insulating template of h-BN/Rh(111). This actual study was accompanied by a series of experimental publications in the group of

 $^{^{1}\}mathrm{In}$ a recent publication a record-high value of 58 meV was obtained for a single Co atom bound to the O site of a MgO(100) surface by Rau *et al.* [184]

H. Brune [172, 187, 188], which were both anticipation of results and a source of valuable information related to the studied systems.

One experimental challenge worth mentioning is that, to date, it has not proven possible on this instrument to address the same individual atoms/molecules at different fields, i.e. to find the same region again after changing the magnetic field. This was achieved during this thesis for the first time due to the new STM/AFM head and the high stability in the new laboratory. In the most successful series, measurements at six different fields (0, 2.5, 5, 7.5, 10 and 14 T) were achieved for several species in a time frame of more than 50 hours. This data is fundamental to elucidate the broad range of spectral features observed.

5.2. Theoretical Foundation

Studying magnetism at the nanoscale is of enormous interest in fundamental research as well as for future applications. In the following, spin-flips and the Kondo effect will be discussed, which are both phenomena related to the spin degree of freedom of the electron, and hence to a fundamental magnetic property. Also the principles of *magnetic anisotropy* will be introduced.

5.2.1. Spin-Flip Spectroscopy



Figure 5.1.: Energy states of a spin 1 system in magnetic field. (a) In an magnetic field the energy of the states splits by the Zeeman energy. (|1,1⟩: red |1,0⟩: blue and |1,-1⟩: green.)
(b) Due to uniaxial magnetocrystalline anisotropy the |1,0⟩ state is now higher in energy at zero field, while |1,1⟩ and |1,-1⟩ remain degenerate. (c) With both, uniaxial and transverse anisotropy also the degeneracy of the |1,1⟩ and |1,-1⟩ states is lifted and additional mixing of the states occurs, as discussed in the text.

Spin-flip spectroscopy is an STM based method introduced by Heinrich *et al.* in 2004 [42], where the excitation of single electron spins can be observed. It is an inelastic spectroscopy method (see Section 2.2), i.e. if the tunneling electrons have sufficient energy they can change ("flip") the spin's z-component m_z of the system of interest. This flip is accompanied by the change of the tunneling electron's spin direction, as angular momentum has

to be preserved. If multiple excitation processes are neglected, the states available for a spin change can only be $\Delta m_z = 0, \pm 1$ away from the initial state.

To observe a spin-flip (in form of a step in the dI/dV-signal) the corresponding states have to be non-degenerate. This can be due to an applied magnetic field B (as presented by Heinrich *et al.*), where the energy of the states will differ by the Zeeman energy $E_Z = g\mu_B B$, where g is the gyromagnetic ratio of the electron and μ_B is the Bohr magneton (corresponding to the fundamental magnetic dipole moment of the electron).

Another possibility to lift the degeneracy between states (without using an external magnetic field) is based on the influence of the surrounding of the system of interest (e.g. the asymmetry of the system introduced by the surface [189] or due to spin-orbit coupling to nearby adsorbates [190]), which is called the magnetocrystalline anisotropy. Due to this effect a certain alignment of the spin is energetically favored, which is described by the following Hamiltonian (which also includes the Zeeman term for completeness) [191]:

$$\mathcal{H} = -g\mu_B \vec{B} \cdot \vec{S} + DS_z^2 + E(S_x^2 - S_y^2), \qquad (5.1)$$

where by convention the z-axis of the system is chosen so that $|D| \ge |3E|$, with D describing the uniaxial and E the transverse anisotropy. Note that anisotropy is only relevant for systems with S > 1/2. The most simple case of a spin-1 system is depicted in Figure 5.1. While in the case without anisotropy at zero magnetic field the states $|S, m_z\rangle = |1, 1\rangle$, $|1, 0\rangle$ and $|1, -1\rangle$ are degenerate, the degeneracy for the $|1, 0\rangle$ state is lifted if an uniaxial anisotropy is present. If also a transverse anisotropy influences the spin (depicted in panel (c)) also the degeneracy of the $|1, 1\rangle$ and $|1, -1\rangle$ is lifted and the two states are mixed, as will be derived in the following. This discussion is presented in detail, as it is also relevant for the calculation of the force associated to the spin-flip presented in Chapter 6.

For the three different m_z values (1, 0, -1) three orthogonal states are defined as follows:

$$|1, 1\rangle = \begin{bmatrix} 1 & 0 & 0 \end{bmatrix}^{T} |1, 0\rangle = \begin{bmatrix} 0 & 1 & 0 \end{bmatrix}^{T} |1, -1\rangle = \begin{bmatrix} 0 & 0 & 1 \end{bmatrix}^{T} .$$
 (5.2)

To transform Equation (5.1) into a form that is easier to handle, creation and annihilation operators are introduced that will help to define S_x^2 and S_y^2 :

$$S_x = \frac{1}{2} \left(S^+ + S^- \right)$$
 and $S_y = \frac{i}{2} \left(S^+ - S^- \right)$, (5.3)

with

$$S^{\pm}|S,m_z\rangle = \sqrt{S(S+1) - m(m\pm 1)} |S,(m_z\pm 1)\rangle.$$
(5.4)

(\hbar and $g\mu_B$ are set to 1 for simplicity.) Using this equation and the defined states (Equations (5.2) - (5.2)) the matrix representation of S^+ and S^- is:

$$S^{+} = \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad S^{-} = \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix}.$$
(5.5)

With Equations (5.3), S_x^2 and S_y^2 can easily be derived:

$$S_x^2 = \begin{pmatrix} 1/2 & 0 & 1/2 \\ 0 & 1 & 0 \\ 1/2 & 0 & 1/2 \end{pmatrix} \quad \text{and} \quad S_y^2 = \begin{pmatrix} 1/2 & 0 & -1/2 \\ 0 & 1 & 0 \\ -1/2 & 0 & 1/2 \end{pmatrix}.$$
(5.6)

The S_z operator does not change the state:

$$S_z|S,m_z\rangle = m_z|S,m_z\rangle \tag{5.7}$$

and hence

$$S_{z} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{and} \quad S_{z}^{2} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$
(5.8)

With the assumption that the external magnetic field is aligned with the uniaxial direction of the anisotropy, i.e. $\vec{B} = (0, 0, B)$, the full Hamiltonian is:

$$\mathcal{H} = \begin{pmatrix} B & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -B \end{pmatrix} + D \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + E \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \\
= \begin{pmatrix} D + B & 0 & E \\ 0 & 0 & 0 \\ E & 0 & D - B \end{pmatrix}.$$
(5.9)

For Equation (5.9) the characteristic polynomial of the matrix has to be solved to obtain the eigenvalues. One trivial value (which remains unchanged in magnetic field) is the $|1,0\rangle$ state. For the other two, the following eigenvalues are found:

$$\lambda_{2,3} = D \pm \sqrt{B^2 + E^2} \,. \tag{5.10}$$

For B = 0 one can easily see that the remaining two states are now also non-degenerate and differ by 2E, as shown in Figure 5.1 (c). To find the eigenstates Ψ_i , the following equation has to be solved for i = 2, 3:

$$\mathcal{H}\Psi_i = \lambda_i \Psi_i \,. \tag{5.11}$$

Together with the normalization, the two remaining states are:

$$\Psi_{2} = \begin{pmatrix} a_{2} \\ 0 \\ a_{2} \left(\frac{\sqrt{B^{2} + E^{2}} - B}{E} \right) \end{pmatrix} \qquad \Psi_{3} = \begin{pmatrix} a_{3} \\ 0 \\ a_{3} \left(\frac{-\sqrt{B^{2} + E^{2}} - B}{E} \right) \end{pmatrix}$$
(5.12)

with

$$a_{2,3} = \sqrt{\frac{1}{1 + \left(\frac{-\sqrt{B^2 + E^2} - B}{E}\right)^2}}.$$
(5.13)

For B = 0 the mixing of the $|1, -1\rangle$ and $|1, 1\rangle$ simplifies to:

$$\Psi_2 = \begin{pmatrix} 1/\sqrt{2} \\ 0 \\ 1/\sqrt{2} \end{pmatrix} \qquad \Psi_3 = \begin{pmatrix} 1/\sqrt{2} \\ 0 \\ -1/\sqrt{2} \end{pmatrix}.$$
(5.14)

Due to this mixing of states, excitations from the ground state (Ψ_3 , cyan curve in Figure 5.1 (c)) to Ψ_2 (orange curve) and Ψ_1 (blue curve) are quantum-mechanically allowed. For B = 0 this results in steps of equal height at energies of $eV = \pm 2E$ and $= \pm (D + E)$. With increasing magnetic field the energies required for the flip will increase (and hence the positions of the steps will move to higher bias) and the mixing of states will become increasingly asymmetric, which influences the transition probabilities. This will be visible in the spectra (for the spin-1 case) as a decrease of step-height of the first steps.

5.2.2. Introduction of the Kondo Effect

The unexpected increase of resistance observed when decreasing the temperature to values around and below liquid helium temperatures are considered the first reported observation of the Kondo effect [192, 193]. As was much later revealed, this effect can be explained by the presence of magnetic impurities and the coupling of conduction electrons to them. This coupling decreases with increasing temperature, as the thermal energy counteracts the coupling.

The first explanation of this effect dates back to 1964, where Kondo described the scattering of conduction electrons by a magnetic impurity using perturbation theory [16]. His theory will be the basis for understanding and describing the spectra observed on the Co species as well as on the molecules discussed in Chapter 7.

In 1998 the first STM/STS studies showed the Kondo effect for Ce adatoms on Ag(111) [194] and Co atoms on a Au(111) surface [25, 195]. Madhavan *et al.* also discuss the quantum interference resulting from the interaction between the d-orbital of the impurity (Co atom) and the conduction electrons, which manifests itself in a so-called Fano line shape [196]. In STS experiments, the signature of the Kondo effect can be revealed by studying the energy around the Fermi level. In a simplified picture derived from the Anderson model [197], this can be understood by the fact that the scattering of the spin, which is described by a spin-flip process, requires an intermediate step involving a virtual state above the Fermi energy. Due to energy and spin conservation, the electrons involved have to originate from the Fermi level, which gives rise to the resonance at this position. For a detailed and descriptive discussion, see also refs. [39, 198]. It might be worth highlighting that a key difference between spin-flip and the Kondo effect is that for the former tunneling electrons are needed to provide energy, while the latter is a process occurring independent of the tunneling electrons.

5.2.3. Classification of Kondo Regimes and Models

The relevant mechanism in the Kondo effect, i.e. the interaction between the localized spin of the impurity and an itinerant spin bath of conduction electrons, can be accounted



Figure 5.2.: (a) The classification of the Kondo effect into three regimes. Depending on the sign of the coupling, either ferromagnetic (fm) or antiferromagnetic (afm) coupling between the spins of the electrons (small black arrows) and the magnetic impurity (big arrow) is favored. For the afm coupling and temperatures below the system dependent Kondo temperature T_K (green line) a singlet with total spin S = 0 is formed, which is then considered to be a Kondo system in the strong coupling regime. For fm coupling and at temperatures $T > T_K$, the system is in the weak coupling regime and can be treated by perturbation theory. (b) Toy model for the contributions accounted for when modeling the tunneling process between tip and impurity on the surface. Spin-spin scattering (blue) causes the spin of the impurity to flip, while the Coulomb scattering (orange) does not influence the spin. Also spin-spin interactions of the substrate electrons with the impurity spin are allowed (pink), while the coupling between impurity and tip is expected to be low and is neglected. If additionally the tunneling electron (from tip to impurity) interacts with an electron from the sample also third order terms become relevant (red dotted arrows).

for by a spin-spin exchange coupling:

$$\mathcal{H}_{ex} = -\frac{1}{2} \sum_{i,j \neq i} J_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j , \qquad (5.15)$$

with J < 0 for an antiferromagnetic (afm) coupling (J > 0 for a ferromagnetic (fm) coupling). Already in his work from 1964 it is evident (Equation (22) in ref. [16]) that the conductivity diverges for $T \rightarrow 0$ K, due to the $\log(T)$ -dependence. In other words, Kondo's perturbation approach is only valid for temperatures higher than the so-called Kondo temperature, a ratio of interaction strength to temperature. The region around and below this value was inaccessible by his description, which became known as the *Kondo problem* and later the strong coupling regime. Hence, as depicted in Figure 5.2 (a) one distinguishes three regimes for the Kondo effect: The strong, the afm weak and the fm weak coupling regime.

While the results of this chapter and Chapter 7 fall into the weak coupling regime, the strong coupling Kondo is also discussed. First, because most systems (like Co atoms on metal surfaces) are investigated in this regime and second, because it was intensively discussed for the data presented in Chapter 7. The weak(er) coupling in this experiment,

can be understood (in a very simplified picture) by the presence of the decoupling layer (h-BN), which reduces the coupling to the metal substrate.

The Kondo temperature T_K is a key parameter for classification of the Kondo effect. It can be defined by the width of the resonance (broadened by measurement temperature T) in the strong coupling regime, as is discussed by Nagaoka *et al.* in terms of a Lorentzian resonance in ref. [199] for Ti atoms on Ag(100) and convincingly verified by Otte *et al.* for Co atoms in the vicinity of Fe atoms on Cu₂N/Cu(111) [200]:

FWHM =
$$2\sqrt{(\pi k_B T)^2 + (k_B T_K)^2}$$
, (5.16)

with k_B being the Boltzmann constant. If the similar (but more accurate) Frota function f(V) is used [201], which was first introduced by Frota and Oliveira for photoemission experiments [202]:

$$f(V) \propto \Re\left(\sqrt{\frac{i\Gamma_F}{i\Gamma_F + V}}\right)$$
 (5.17)

$$\propto \sqrt{\frac{1}{2} \left(\frac{\Gamma_F}{\sqrt{\Gamma_F^2 + V^2}} + 1 \right)},\tag{5.18}$$

with V being the energy and Γ_F a parameter for the width, the corresponding Kondo temperature can be derived to be [203]:

$$T_K = \frac{\Gamma_F}{1.455k_B}.$$
(5.19)

For the derivation by Kondo (i.e. the weak coupling limit) the limit below which the perturbation does not converge, can be expressed by:

$$T_K \propto e^{\frac{1}{J\rho_0}},\tag{5.20}$$

which is only a reasonable definition for the afm (J < 0) regime.

5.2.4. 3rd-Order Perturbation Theory

In the following, the perturbative approach used to describe and fit the recorded spectra is summarized. The derivation presented follows unpublished work of M. Ternes [204]. The model is based on work of Anderson and Appelbaum [205–207].

As mentioned in Section 2.1.2 the key to quantifying the tunneling process is the derivation of the transmission matrix \mathcal{M}_{fi} . If the matrix is known, the following formula can be used to directly calculate the corresponding spectrum (dI/dV) that is also experimentally accessible by STS. In the final form it will be used as model for fitting relevant parameters to the experimentally obtained spectra.

$$\frac{\mathrm{d}I}{\mathrm{d}V}(V)^{T\to S} = \frac{2\pi e^2}{\hbar} T_0^2 \sum_{i,f} p_i |\mathcal{M}_{fi}^{T\to S}|^2 \Theta(eV - (E_f - E_i)), \qquad (5.21)$$

T and S denote tip and sample, respectively and i and f the initial and final states, respectively. p_i is the state occupation of the spin system (governed by a Boltzmann distribution of effective temperature T_{Eff}) and T_0^2 stands for the barrier transmission, which includes all relevant parameters that scale the tunneling current, especially the distance dependence. $\Theta(x) = (1 + (x - 1) \exp(x))/\exp(x)^2$ is the temperature broadened step function. Note that if spin polarization is present, the current in both directions $(I^{T \to S} \text{ and } I^{S \to T})$ has to be considered separately and the net current has to be considered in the end.

For the case where only spin-spin scattering (blue arrow in Figure 5.2 (b)), Coulomb scattering proportional to U (orange) and spin-spin scattering between the impurity and the substrate (pink) are allowed, the following Hamiltonian has to be considered to describe the interaction:

$$\mathcal{H}_{1} = T_{0} \sum_{k',k} \left[a_{sk'}^{\dagger} a_{tk} \left(\frac{1}{2} \boldsymbol{\sigma} \cdot \mathbf{S} + U \right) + a_{tk'}^{\dagger} a_{sk} \left(\frac{1}{2} \boldsymbol{\sigma} \cdot \mathbf{S} + U \right) + J a_{sk'} a_{tk}^{\dagger} \left(\boldsymbol{\sigma} \cdot \mathbf{S} \right) \right],$$
(5.22)

where the second quantization with creation and annihilation operators is used to describe the electrons in tip and sample. **S** denotes the total spin system, while σ describes the tunneling electron. For the tunneling matrix in Equation (5.21) one has to solve the following equations:

$$\mathcal{M}_1 = \langle \Psi_f | \frac{1}{2} \sigma \cdot \mathbf{S} + U | \Psi_i \rangle = M_{fi} + U \delta_{fi} , \qquad (5.23)$$

with $\Psi_{i,f}$ denoting the complete description of initial and final state of the system. In the next step, the square of the matrix has to be calculated:

$$|\mathcal{M}_1|^2 = |M_{fi}|^2 + |U|^2 \delta_{fi} + 2\Re(U \cdot M_{fi}) \delta_{fi}, \qquad (5.24)$$

where δ_{fi} is the delta function ensuring energy conservation. The term $|M_{fi}|$ accounts solely for spin-exchange processes between the tunneling electron and impurity spin, while the second term does not change the spin. The third term is an interference term, which can be shown to be strongly dependent on the spin of the impurity and significantly influences the conductance at zero bias.

If also higher order terms, as represented by the red arrows in Figure 5.2, are considered, the additional effects due to an intermediate state (m) have to be considered. This is performed in the second order Born approximation, while only sample electrons are considered for this additional effects as the coupling of the tip to the impurity is assumed to be significantly smaller:

$$\mathcal{M}_2 = J\rho_s \oint_m \left(\frac{M_{fm} M_{mi}}{E_i - E_m} + \frac{M_{fm} M_{mi}}{E_m - E_f} \right), \tag{5.25}$$

with the summation and integration over all possible (including virtual) intermediate spin states of the impurity and substrate electron states, respectively. In the fitting this integration is limited to a small bandwidth around the Fermi energy of typically $\omega_0 = 20$ mV. For

the total conductance this term has to be added to \mathcal{M}_1 and plugged in to Equation (5.21):

$$|\mathcal{M}_{1} + \mathcal{M}_{2}|^{2} = |\mathcal{M}_{1}|^{2} + J\rho_{S}\sum_{m} \left[\left(M_{if}M_{fm}M_{mi} + cc \right)F(E_{im}) + \left(M_{if}M_{fm}M_{mi} + cc \right)F(E_{mf}) \right] + J\rho_{S}U\sum_{m} \left[\left(I_{if}M_{fm}M_{mi} + cc \right)F(E_{im}) + \left(I_{if}M_{fm}M_{mi} + cc \right)F(E_{mf}) \right]$$

$$(5.26)$$

with cc denoting the complex conjugate of the corresponding aforementioned product and

$$F(E,T) = -\int_{-\infty}^{\infty} dE'' \int_{-\omega_0}^{\omega_0} dE' \frac{f(E',T)}{E'-E''} f'(E''-E,T), \qquad (5.27)$$

with $f(x) = (1 + \exp(x/(k_B T)))^{-1}$ being the Fermi-Dirac distribution. The integration of this equation causes the (temperature broadened) logarithmic singularity, which was already identified by Kondo [16]. The integration and the task of determining the individual spin scattering matrices are not discussed any further. For larger systems this has to be done numerically.

If the effects of Coulomb scattering are neglected and only zero magnetic field is considered for a single spin-1/2 system, the conductance can be expressed as a single logarithmic peak whose shape is only governed by the temperature T_{Eff} :

$$\frac{\mathrm{d}I}{\mathrm{d}V}(E) = -(J\rho_0) \int_{-\omega_0}^{\omega_0} \frac{f(E',T)}{E-E'} \,\mathrm{d}E' * \frac{\partial f(E,T)}{\partial E} + C\,,\tag{5.28}$$

with C being a constant background and "*" denoting a convolution. This formula will be sufficient to also describe the spectra observed on the molecule discussed in Chapter 7.

5.3. Sample Preparation



Figure 5.3.: 3D representation of an STM image of the first successful deposition of Co atoms on the cold Au(111) surface. (Measurement parameters: I = 20 pA, V = -100 mV; height: 0.3 nm, lateral dimensions: 25×12 nm².)

For testing purposes the first Co evaporation was performed on to a Au(111) surface (Figure 5.3), where the spectral signature is known [25]. For the preparation of the Au(111) the following procedure is followed: The crystal is prepared by typically 3-5 cycles of

sputtering with Ar^+ ions for 20 minutes at 1.0 kV and subsequent annealing up to 870 K for 3–5 minutes. The last cycle is performed with slightly reduced ion energy (0.8 kV) and temperature (~ 860 K). The temperature is slowly decreased before the sample is *in situ* transferred into the cold microscope. The sample preparation for the *h*-BN/Rh(111) is the same as discussed in Section 4.2.3.

The clean surface is checked for quality before the sample is turned by 180° to allow evaporation of the Co atoms. For the deposition of Co atoms the evaporator (Section 3.3.3) is brought into position and the filament and Co rod are degased and preheated for several cycles for cleaning purposes. The actual evaporation (melting temperature of Co: 1768 K [208]) is done at filament currents of 5 - 6 A and acceleration voltages of typically around 500 V. The current to the Co rod is monitored (in a range between 15 - 40 mA) and used as rather rough reference. Evaporation times were 30 - 120 seconds. As this wide spread of values already suggest, adjustment and a reasonable calibration of evaporation power and duration was difficult. The parameters showed to be highly dependent on the actual filament. The quality of the deposition itself was also influenced significantly by the cleanliness of the Co rod and was improved by thorough degassing and preheating of the rod, as also discussed in ref. [187].

During the whole process the sample temperature rises from approximately 10 K (no radiation plugs installed) to a maximum of 15 - 20 K during Co evaporation², which is low enough to sufficiently reduce the mobility of the atoms and prevent clustering.

As proof of principle the adsorbed Co was spectroscopically investigated on the gold surface, where clear signs of a Kondo feature were observed [25, 195]. The results of the Co on the h-BN/Rh(111) are discussed in the following.

5.4. Topographic Imaging of Co on h-BN/Rh(111)

The deposition of Co on Au(111) results in clearly addressable single atoms as shown in Figure 5.3. On the h-BN/Rh(111) surface this has proven to be significantly different and several forms of adsorbed Co species are obtained. The most surprising topographic form is shown in Figure 5.4. Natterer *et al.*, who intensively investigated this form for Mn, Fe, and Co introduced the term "ring state" [172]. They attribute this appearance to the local detachment of the h-BN from the Rh(111) surface. They reported reversible switching of the ring state into a single, spherically symmetric protrusion ("dot state") with a height of ~ 4 Å [209]. In the experiments discussed here, the ring states are very rarely observed, as can be seen in Figure 5.5 where in a large-scale overview only three ring states are visible. (The images presented in Figure 5.4 are an exception.) While the disappearance of the ring states was occasionally observed, the controlled and reversible switching reported could not be reproduced.

While not quantified, it was clearly observed on the more than 15 investigated samples that the abundance of the ring states decreased over time (or were not even observed in the first place) and whenever the sample was heated to above ~30 K. This behavior is tentatively attributed to the formation of Co-H complexes. This assumption is based on

²The range is mainly due to the cooling power supplied during rotation. If operated at high exchange gas pressure the cooling is superior, but the risk of arcing increases at the high voltages necessary for the rotary piezos.



Figure 5.4.: (a) Large scale STM image showing a majority of Co atoms as ring states. (Measurement parameters: (a) I = 20 pA, V = 50 mV; scale bar: 20 nm; (b) I = 20 pA, V = 50 mV; scale bar: 4 nm; (c) I = 200 pA, V = 1 V; scale bar: 1 nm.)

the following: First, a rather high H concentration is present in the system, which is also identified in STM images typically as instability and two-level noise. Second, the heating of the sample and microscope will temporarily increase the mobility of H, which makes the formation of complexes more likely. Third, the abundance of what is expected to be the "pure" Co decreases with time. This is related to the observation that the apparent height of most species investigated is less than the expected 4 Å [209]. This is a known effect also for molecules on metal substrates upon H uptake [210]. The investigation of the apparent heights will be discussed in the following Section 5.4.1.

The most conclusive experiment concerning the proposed mechanism of the ring states would be the investigation by AFM. If the h-BN is detached over the proposed range, atomic resolution (as presented in Chapter 4 for the rim region of the h-BN) would eliminate all doubts. Unfortunately, this could not be achieved up to now, due to the short lifetime and low abundance of ring states and due to additional experimental difficulties.

5.4.1. Apparent Height Investigation

As already evident from Figure 5.5 different heights of the other adsorbates besides the ring states are obtained. An investigation of the adsorbates of the image shown in Figure 5.6 (a) results in a tentative assignment of two height bins in panel (b). The first bin is centered at around 1.4 Å and the second at ~ 3 Å. A possible third bin could be around 4 Å, which is presumably the pure Co. The large spread of heights remains one of the greatest puzzles. While different tip geometries can be a source of different apparent heights for the same individual adsorbate, this can be excluded for the statistical evaluation of a single image (without a changing tip). A preliminary assignment for the observed three bins could be related to the amount of H adsorbed, i.e. single atoms for the 3 Å species and molecular or two individual H atoms for the smallest.

Another effect that will influence the apparent height is the corrugation of the h-BN, which



Figure 5.5.: (a) Large scale STM image showing a uniform distribution of Co species on the surface. No clustering or step edge agglomeration is observed. The three ring states are marked by green circles. (b) Smaller scale STM image, showing the different types of Co species. (c) Magnification of the area marked in (b). Three different species (white circles) are observed in this image with significantly different heights, as will be discussed in Section 5.4.1. (Measurement parameters: (a) I = 20 pA, V = 100 mV; scale bar: 50 nm; (b) I = 20 pA, V = -100 mV; scale bar: 8 nm; (c) same as (b); scale bar: 2 nm.)

makes the determination of the height also prone to systematic errors, as the reference height can only be guessed from the corrugation. While cluster formation could be the explanation of the few bigger species (above 4 Å), this can be excluded as comparable spreads were also observed in images with lower Co coverage.

Besides the H also other impurities from inside the crystal, Ar and CO are present that might slightly influence the quantification of heights. This effect is expected to be small, as the bare h-BN/Rh(111) was always checked prior to evaporation of Co. One notable exception is CO, as will be discussed in the following section.

5.4.2. Abundance of CO

The topographic appearance of CO in STM images is relatively unique, as it appears as round depressions on metal surfaces [23, 66]. In Figure 5.7 (a) a small patch of h-BN free Rh surface is shown with several Co atoms and one depression that is identified as



Figure 5.6.: Evaluation of heights. (a) STM topography showing a typical distribution of Co species. The four visible ring states are marked by green circles but are not further considered. (Measurement parameters: I = 20 pA, V = -150 mV; scale bar: 12 nm.) (b) Histogram of the heights where two bins can be tentatively assigned.



Figure 5.7.: Identification of CO. (1) Co species (protrusions) and a possible CO visible as a clear depression on a small patch of bare Rh(111), marked by a red circle. (Measurement parameters: I = 10 pA, V = -100 mV; scale bar: 1 nm.) (b) STM topography recorded with standard parameters, where CO is difficult to identify in the *h*-BN superstructure. (Measurement parameters: I = 50 pA, V = -1 V; scale bar: 2 nm.) (c) The same area as (b) scanned at different parameters, where the *h*-BN becomes transparent and the CO clearly visible. (Measurement parameters: I = 100 pA, V = -100 pA, V = -100 pA, V = -2.2 V; scale bar: 2 nm.)

CO. For areas with *h*-BN the detection of CO is much more tip dependent, as for slightly blunter tips is difficult to identify, as shown in Figure 5.7 (b). An elegant way is presented in panel (c) where the same region is scanned at a bias of 2.2 V, where the *h*-BN layer is transparent [86]. The CO molecules are clearly visible and it becomes apparent that a rather high concentration is present on the surface. They adsorb preferentially inside the valley region of the superstructure and on the corners of the rim region. A selection of STM images recorded with special tip apexes with (some with CO termination) is shown



Figure 5.8.: (a)-(c) STM images revealing the abundance of CO on the surface. Note the different appearance and contrast depending on the tip. Possible Co species are marked by green circles. (Measurement parameters: (a) I = 20 pA, V = -20 mV; scale bar: 2 nm. (b) I = 10 pA, V = -100 mV; scale bar: 3 nm. (c) I = 20 pA, V = -100 mV; scale bar: 2 nm.)

in Figure 5.8.

Besides H, CO is known to be the most prominent residual gas in UHV systems, as it diffuses out of grain boundaries in stainless steel and is generated by ion gauges and mass spectrometers [211, 212]. A second likely source of CO desorption is during extensive heating of the Co rod (and unavoidable heating of the surrounding metal parts).

Unfortunately, the rather large appearance of the Co adsorbates makes the investigation of the influence of the CO in the direct neighborhood of the Co species cumbersome. Especially the likely effect on the spectroscopic signatures, which will be discussed in the following section, is likely to be affected by their presence. Controlled manipulation of the CO has proven to be difficult in the vicinity of Co.

5.5. Spectroscopy in Magnetic Fields

In the following the experimental results of the extensive spectroscopic investigation of the Co species on h-BN/Rh(111) are presented. The discussion will be divided into the Kondo resonance of what is expected to be the spin-1/2 system and the spectra obtained for the spin-1 species. Both chapters are subdivided into the investigation at zero magnetic field and into the field dependent measurements. A qualitative discussion can be found in Section 5.6.

The STS data was typically recorded in the range of the following parameters: An excitation voltage of 0.1 - 0.5 mV (with most data at 0.2 mV) was used at f = 799 Hz. The bias range was typically from -15 to +15 mV or -20 to +20 mV. The setpoint was in the range of 300 - 500 pA at the sweep voltage minimum. The integration time per data point was $\tau = 30$ ms, with 300 - 400 data points averaged over two sweeps (in forward and backward direction).



Figure 5.9.: A Kondo feature observed on a Co species measured for different setpoints of up to 700 nS (7 nA at 10 mV), before it jumped away at 900 nS. The red lines are fits after the perturbation model and the green lines are Frota fits (discussion and parameters in the text). Spectra are offset for clarity by 0.5.

5.5.1. Kondo Resonance

Figure 5.9 shows a typical Kondo resonance that is observed as a single peak at the Fermi level at zero field. While the species showing Kondo resonances are more frequently observed on freshly prepared samples, they do not vanish as fast as the pure Co species and the ring states. Compared to the spin-1 species it was experienced that they are more prone to jump away at higher currents (~ 500 nS), with the example presented in Figure 5.9 being an exception.

The slight broadening of the resonance as presented in Figure 5.9 at high setpoints is quantified by an increases of the effective temperature from $T_{\text{Eff}} \approx 0.9$ K for the 40 and 100 nS spectra to 1.4 K of the 700 nS spectrum when fitted with a temperature broadened logarithmic function (see Section 5.2.4). Note that this is smaller than the experimental temperature, an effect that was also observed in the work presented in ref. [213] (Chapter 7). If fitted by a Frota function (green curves in Figure 5.9) a width is deduced to be $\Gamma_F = 0.58$ mV for the lower setpoints and $\Gamma_F = 0.50$ mV for the 700 nS measurement. This can be understood, as the close proximity of the tip (in the case of very high conductivity) will cause an additional coupling $J'\rho'_0$ between the Co species on the sample and the tip. This coupling is not included in the model, but can be neglected, when measured at smaller currents.

5.5.2. Kondo Resonance: Measurements in Field

The investigation of the Kondo feature in magnetic field shows the expected splitting presented in Figure 5.10. It is consistent with the model discussed in Section 5.2.2 and can be well understood as a spin-1/2 system. *g*-factors of 1.7 - 2.0 are derived for the fits shown in Figure 5.10 (b).

In Figure 5.11 two very different examples concerning the coupling $J\rho_0$ are shown. While the first shows a rather typical value of -0.04, the fit result of -2.05 for the second species



Figure 5.10.: (a) dI/dV-spectra at different magnetic fields (0, 5, 10, 14 T) on the same individual Co species. A clear splitting of the peak is observed for increasing magnetic fields. (b) The fits to the spectra in (a) show a convincing agreement. (Parameters: $T_{\rm Eff}$ fixed at 2 K, g = 1.7 (at 5 T) and 2.0 (at 10 and 14 T)).



Figure 5.11.: (a), (b) Two Co species, which have very similar topographic appearance, but show distinctively different Kondo resonances in magnetic field, as shown in (c) and (d), respectively. The positions of the spectra are marked by the "×". (Measurement parameters: (a), (b) I = 20 pA, V = 20 mV; scale bar: 1 nm, same height scale. B = 5 T. g = 2 fixed for fitting.)

is unrealistic $(|J\rho_0| = 1$ is perfect coupling) and points towards a strong coupling Kondo and the limitations of the model.

5.5.3. Discussion of the Kondo Resonance

While the observation of the Kondo effect is not too surprising for Co atoms on h-BN/Rh(111), it is worth recalling that it is only observed on species where H is involved. This is comparable to the discoveries of Natterer *et al.* for Ti and hydrogenated Ti atoms on the h-BN/Rh(111) [187]. Besides the difficulty of unambiguously identifying the adsorbate, it can be claimed that the observed spectroscopic signature can be well assigned to a spin-1/2 system. The theoretical description and the splitting in magnetic field are consistent. Clear differences in coupling to the substrate were observed. Unfortunately, the apparent height does not differ consistently from the range observed for the spin-1 species, which will be discussed in the following.



5.5.4. Spin-1 System

Figure 5.12.: (a)-(f) Different examples of spectra recorded on Co species showing the surprising spread of positions for the two steps. Corresponding fits are plotted in red. The parameters are discussed in the text.

The most abundant feature observed on the Co species consists of a double step feature that is symmetric around the Fermi energy. The first step is obtained in the range of 0.9 - 1.9 mV and the second between 2.6 - 7.2 mV. At zero field the heights of the steps are approximately equal. This appearance is consistent with the spin-1 spin-flip model discussed in Section 5.2.1, where also the relation between step positions and anisotropy parameters D and E is derived. Some examples of such spectra are shown in Figure 5.12. In panel (a)–(c) examples are shown that represent the wide spread observed in D values, while (d)–(f) show examples where D is in the range of -4 to -5 mV but E changes by up to 70 %. All fitting parameters for this selection are summarized in Table 5.1.

Parameter	(a)	(b)	(c)	(d)	(e)	(f)
D	-6.27	-4.03	-2.29	-4.59	-4.58	-4.92
E	0.90	0.66	0.64	0.56	0.75	0.96
$J ho_0$	-0.13	-0.18	-0.11	-0.11	-0.15	-0.09

Table 5.1.: Results of the fitting of the spectra shown in Figure 5.12.

5.5.5. Statistical Evaluation of the Spin-1 System



Figure 5.13.: The height distribution of the investigated Co species that show typical spin-1-like behavior shows a broad peak around 130 pm.

In the scope of this work more than 30 individual species showing double step features at energies below 10 mV were investigated at zero magnetic field.

The average height distribution of all Co species obtained on the surface was discussed in Section 5.4.1. In Figure 5.13 the height distribution of the spin-1 species investigated is shown. The approximate center of this distribution is at z = 0.12 nm, which corresponds (despite the spread) to the first peak of the distribution obtained for the full range of adsorbates shown in Figure 5.6, which is at $z \approx 0.13$ nm. Note that besides different tips (which can give significantly different heights also for the same individual molecule) also the definition of the height on top of the *h*-BN is error-prone and could lead to a systematic error correlated to the position on the *h*-BN.

Besides the cumbersome definition of the height, also the anisotropy and the coupling can be expected to be influenced by the high corrugation (topographic and electronic) of the h-BN/Rh(111). Therefore, the landscape of the h-BN is subdivided, as shown in Figure 5.14 (a). In Figure 5.14 (b) all pairs of D and E values obtained for the investigated Co species are plotted in the color corresponding to the position (as marked in panel (a)). Neither a general clustering pointing towards a correlation of D and E nor a correlation between the position and those values is visible.

Averaging over the species in each subgroup suggests, on initial inspection, a small correlation, which is presented in Figure 5.14 (c). Closer analysis reveals that the standard deviation in combination with the too small statistical basis (the number of species per



Figure 5.14.: (a) Definition of the different positions on the *h*-BN corrugation used for categorization. Due to its hexagonal symmetry only one out of the six equal regions are marked for clarity. (R: rim corner, C: center valley, B: rim bridge, VC: valley corner, VB: valley bridge, IC: intermediate region corner, IB: intermediate region bridge. Scale bar: ~ 1 nm.) (b) The huge spread of *D* and *E* values obtained for the ~ 30 investigated Co species. No clustering for the position (color coded, see (a)) and no correlation between *D* and *E* is apparent. (c) Investigation of heights of the Co species, of *D*, of *E* and of $J\rho_0$ in the bins depending on position. Small differences for the different positions are visible and a correlation between *D* and *E* could be deduced from the averages. Diligent judging of the errors and the small statistics prohibits further evaluation. (The numbers next to the position acronym represents the number of species in the corresponding group.)

group are shown in parentheses on the x-axis of the figure) prohibits conclusions based on this categorization.

For the whole data set investigated, the range of coupling parameter $J\rho_0$ obtained expands over more than one order of magnitude from -0.02 – -0.32. Again the small statistical basis prohibits a conclusion concerning the correlation to the position of the corrugation (Figure 5.14 (c)).

Reconsidering the discussion in Section 5.4.2, a remaining influence could be the abundant CO molecules on the surface. Unfortunately the exact position determination of the CO

close to (or even appearing underneath) the Co species is not feasible with the available contrast for most images.



Figure 5.15.: The double step feature observed on a Co species for different setpoints of up to 900 nS (9 nA at 10 mV). The red lines are fits using the perturbation model. Spectra are normalized and offset for clarity by 0.5.



Figure 5.16.: (a) Dependence of D on the conductance setpoint, or, as approximated by the logarithmic representation, the dependence on the proximity of the tip. (b) Same plot for E. (Note that the data for 200 nS is not shown in Figure 5.15.)

In Figure 5.15 the effect of increasing setpoint conductivity (tip proximity) is investigated. It is clearly visible that the position of the outer step, which is related to D, changes, while the inner step (related to E) changes less strongly. An almost linear decrease of |D| and increase of E with decreasing distance (logarithm of conductance) is shown in Figure 5.16 (a) and (b), respectively. Hence, if the coupling between tip and adsorbate increases upon approaching the tip |D| decrease and E increases slightly.

In Figure 5.17 the inverse effect is investigated by studying the correlation between the coupling $(J\rho_0)$ of the adsorbates to the substrate and the derived anisotropies. The trend emphasized by the linear fit (red line) reveals larger |D| and smaller E for increasing cou-



Figure 5.17.: Correlation between the coupling $J\rho_0$ of the adsorbates to the surface and D and E, top and bottom panel, respectively. A trend is visible, with the red line being a linear fit. (From the full set of 30 spectra some outliers (possible clusters, deviating fits) were removed.)

pling to the surface. While there are undoubtedly outliers visible, the trend is statistically significant.

Surprisingly, this behavior is in contrast to the recent findings by Oberg *et al.* who saw the opposite correlation between $J\rho_0$ and D for Co atoms on a Cu₂N island [214].

5.5.6. Spin-1 System: Measurements in Field

The evolution of the spectra in magnetic field was studied for ~ 15 species (being a subgroup of the ~ 30 species studied at zero magnetic field) at 2 – 6 different fields of up to 14 T. In Figure 5.18 the spectra recorded on an individual Co species for fields between 0 and 14 T are shown. The model discussed in Section 5.2.4 nicely reproduces the data. The position of the steps moves outwards with increasing magnetic field (panel (c)), as explained in Section 5.2.1, which proves that the features observed are indeed of magnetic origin and allow determination of the g-factor. The ratio of heights between the first and the second step decreases with increasing field, which is also consistent with the spin-flip model.

Parameter	0 T	$2.5 \mathrm{T}$	$5 \mathrm{T}$	$7.5 \mathrm{T}$	$10 \mathrm{T}$	$14 \mathrm{T}$
D	-4.28	-4.71	-4.62	-4.90	-4.86	-4.87
E	0.69	0.64	0.74	0.77	0.85	0.98
$J ho_0$	-0.20	-0.27	-0.19	-0.25	-0.32	-0.27

Table 5.2.: Results of the fitting of the spectra shown in Figure 5.18.



Figure 5.18.: Spectra showing the double step feature in magnetic fields of 0 - 14 T for the same individual Co species with fits in red. (Parameters: $T_{\text{Eff}} = 2$ K and g = 2 fixed.) Spectra are offset for clarity by 0.5. The fitting parameters are presented in Table 5.2. (b) STM image of the investigated Co species, with the approximate position of the spectra recorded marked by the "×". (Measurement parameters: I = 20 pA, V = -100 mV; scale bar: 1 nm.) (c) The position of the steps derived from fitting Gaussian peaks to the derivative of the spectra (not shown). The average of the positive and negative bias position is plotted. Note that the energy scale is adapted to the discussion as in Figure 5.1. The green arrows mark the transitions also highlighted in (a) for the inner and outer step at 0 T and 10 T, respectively. The fit reveals a g-factor of ~ 1.9.

In Table 5.2 the resulting parameters from the fits shown in Figure 5.18 (a) are presented. g was fixed at 2.0 and D and E were used as free parameters for all individual spectra, resulting in an average of $D = -4.7 \pm 0.4$ mV and $E = 0.8 \pm 0.2$ mV, i.e. with both showing a non-negligible spread (which might be attributed to minor tip apex changes). The derived coupling $J\rho_0 = -0.25 \pm 0.07$. If the step positions (panel (c)) are used and fitted by Equation (5.10), the following parameters are obtained: $D = -4.5 \pm 0.1$ mV, $E = 0.65 \pm 0.1$ mV and $g = 1.9 \pm 0.2$, which results in a good agreement, strongly supporting the spin-1 assumption.



Figure 5.19.: Three consecutive bias sweeps on the same adsorbate. From a clear spin-1 signature (a) it changes instantaneously (b) to a single dip (c). Recorded at 2.5 T.



Figure 5.20.: (a), (b) STM images of the same Co species at 10 and 2.5 T, respectively. The position of the species marked by the circle has clearly changed between the two images. The symmetry of the *h*-BN is depicted by white lines. (Measurement parameters: I = 20 pA, V = -100 mV; scale bar: 2 nm.) (c) Spectra recorded on the adsorbate at different magnetic fields. The red spectra (at 2.5 and 5 T) were recorded on the shifted adsorbate, as shown in (b). Spectra are offset by 0.2 for clarity. (d) Height profile of the adsorbate as measured at different fields. A height difference of ~ 30 pm can be estimated between the two positions/configurations. (e) The energies of the spin-flips (step positions in (c)) separately drawn for the two cases (red and black data points), revealing the significant change in D and E from 2.0 to 3.8 mV and from 0.7 to 0.5 mV, respectively, as indicated by the interpolation.

5.6. Further Observations and Discussion

To gain further insight into possible mechanisms responsible for the huge range of anisotropies and to understand the difference of the two spectroscopically investigated species (Kondo and spin-1 system), some switching events should also be brought into consideration. While no definite conclusions are possible, two examples are presented in this section that might give a glimpse into the physics observed. In Figures 5.19 a typical double step feature changed to a single step. This change is accompanied by a jump in current of 20 pA, which could be a manifestation of a removed or added H atom. The images obtained for this adsorbate do not allow any further conclusions.

Figure 5.20 shows images (a), (b) and spectra (c) of a Co species, where during the investigation at different fields it moved by approximately 0.5 nm and a small change in height (~ 30 pm, panel (d)) occurred. Evaluation of the energies for the spin-flips (panel (e)) produces a quite surprising "misalignment" for the data at 2.5 and 5 T (red spectra in (c)) compared to the other data points, which were chronologically taken before the species moved. Estimating the anisotropies from the 2.5 and 5 T data sets results in $D \approx 3.8$ mV and $E \approx 0.5$ mV, while the fit of the zero field (and 10 and 14 T) data reveals D = 2.0 mV and E = 0.7 mV.

This observed range for one single Co species is quite representative for the whole range of anisotropy values observed on all other species (Figure 5.14), and allows the tentative conclusion that the very local surrounding or delicate binding differences to the h-BN on a sub-corrugation scale are the key to understanding the spread in values.

5.7. Summary and Conclusion

From a technical perspective, the discussed experiments have shown the versatility and stability of the experimental setup. The rotation of the cold sample and the evaporation of single atoms over a distance of almost 1.5 m have proven to work reliably. The evaporator sample exchange allows for recharging of metal rods through the load lock without breaking the main vacuum. The stability of the system in the new laboratory and the captiously designed microscope head, concerning the avoidance of any magnetic materials allowed – for the first time – the addressing of the same individual atoms/molecules at different magnetic fields. Series of measurements at up to six different fields between 0 and 14 T were achieved in a time frame of more than 50 hours.

The rich physics observed for the Co species on the h-BN/Rh(111) manifests itself in several aspects: First, by the topographic appearance, which was discussed in terms of height distribution of the spherical-appearing objects and the observance of the ring states. The planned investigation of the ring states by AFM should allow the unambiguous identification of the origin of this peculiar appearance, which was assigned to the unpinning of the *h*-BN layer from the Rh substrate [172].

Second, by the observed type of spectral feature: While some of the adsorbates (surprisingly including what is assigned as bare Co) did not show any spectral signatures at small bias, the identification of the composition and difference of the species showing a clear Kondo resonance and a double step spin-flip signature (assigned as spin-1/2 and spin-1 system, respectively) remains an open question. Here ongoing DFT-based calculations, which are in progress (performed by O. Brovko in Jülich), might elucidate some aspects. Third, by the huge spread in anisotropies obtained influencing the spectral signature of the spin-1 species. Here the effect of the abundant CO could be of influence. Careful optimization of the sample preparation and Co evaporation procedures might be a solution to reduce CO contamination and possibly even allow for controlled (subsequent) dosing of CO onto the sample to study its influence.

Fourth, by the correlation between coupling and D and E for both, the coupling to the surface (where stronger coupling leads to higher |D| and smaller E) and to setpoint dependent higher coupling to the tip, where the opposite effect is observed.

Fifth, by vibrational spectra observed at higher bias voltages (in ranges investigated up to 200 mV), which were not discussed here. In some cases also the presence of H could be concluded from vibrational features.

In summary, up to five different Co species can be assigned on the h-BN/Rh(111) (three different heights, the ring state and the two spectroscopically different species with spin-1/2 and spin-1, but same apparent height). The influence of H is immanent, as also confirmed by ref. [187]. The role of CO is less obvious, but calculations by Zhang *et al.* suggest that spontaneous magnetization upon CO adsorption is possible for vacancy-defected h-BN [215]. This magnetization would influence the anisotropy. While the quality of the h-BN in the experiments was predominantly very high, such that a high abundance of vacancies can be excluded, the high corrugation and flexibility of the h-BN/Rh(111) itself (see Chapter 4 and ref. [172]) or the influence of impurities in or on the Rh substrate might also affect the h-BN properties. A comparative study on the flat h-BN on Cu(111) [137] could give further insights, as there influences from the corrugation can be excluded.
CHAPTER 6

Measuring the Force of the Exchange Coupling

The planned AFM experiments discussed in this chapter were the reason to start studying Co atoms on h-BN/Rh(111). The surprising variety of spectroscopic signatures obtained shifted the focus for several months and led to the results presented in Chapter 5. Due to technical limitations with the used tuning fork sensor (very low *Q*-factor, especially at higher magnetic fields), the presented results can only be considered a first glimpse.

The chapter is structured as follows: After a short overview the theoretical foundations and implications for the conceived experiments are discussed in Section 6.2. In Section 6.3 the first experimental observations are presented and discussed.

6.1. Overview and Motivation



Figure 6.1.: dI/dV-spectrum of a spin-1 Co species showing a clear asymmetry at a magnetic field of 5 T that can be attributed to a spin polarization of the tip of ~ 60%. Comparison of the relative heights (H_1 and H_2) of the second steps can also serve as estimate for the spin polarization.

In a simplified picture the conceived experiment can be described as follows: A single magnetic Co atom (or, alternatively, a molecule) is attached to the tip and placed on top

of another magnetic atom on the surface. If the two are far apart, their moments will align in an external magnetic field due to the Zeeman energy. If they brought into closer contact, an antiferromagnetic coupling will force one of the spins to realign, if the coupling is stronger than the external field. This flipping should be observable in the force-distance curves accessible by the combined STM/AFM.

The results of the STS study in Chapter 5 are a requirement to understand the adsorbates and their corresponding spectral signatures. The process of picking up Co atoms on the tip, i.e. obtaining a spin polarized tip, was also studied as prerequisite. In Figure 6.1 a clearly spin polarized spectrum of a spin-1 Co species is shown. The asymmetry of the second steps (different heights) is the indication of spin polarization, as can be understood in the scope of the spin-1 spin-flip model discussed in Section 5.2.1. While the first steps remain almost symmetric (gray lines), as only the m_z -component is changed, the amplitude of the second steps (green and blue lines) is influenced by the mixing of states (due to the S^+ and S^- operators) and the spin-dependent DOS of the tip, which is asymmetric for a polarized tip. This asymmetry results in an unequal probability for electrons to tunnel from the tip to the sample and vice versa. The relative ratio of the two steps can serve as an estimate for the magnitude of spin-polarization, while the actual magnitude of 60 % was derived from the fit. Spin polarized tips could be reproducibly obtained by increasing the tunneling current to ~ 500 pA (at typical bias voltages of -100 mV) and applying several short 1–2 V pulses. The success rate differed in the range of 10 – 30%.

Pioneering work on exchange coupling was done by Schmidt *et al.* on the distance dependence of the exchange interaction. It was studied by AFM for a Fe monolayer on W(001) with magnetically sensitive tips and compared to extensive calculations [216]. In ref. [217] they study the same system by comparing $\Delta f(z)$ -curves from Fe atoms with opposite spins. In refs. [218, 219] the experiment is discussed with respect to possible tip conformations and relaxations. In [220] the controlled manipulation of the magnetization is shown using the distance dependence of the magnetic exchange interaction. In the *ab initio* study ref. [221] by Tao *et al.* the switching of single spins of 3d magnetic adatoms on Cu(001) by the exchange coupling is investigated.

Because the experimental requirements are quite high for the discussed experiment, as will become evident in the following, measuring the actual force related to the spin flip remains a huge challenge. Ref. [222] by Wieser *et al.* provides an in-depth discussion of the theoretical background.

6.2. Theoretical Prediction

If a system of two coupled spins is investigated, the previously discussed single spin Hamiltonian (Equation (5.1)) has to be extended to incorporate the spin-spin interaction terms. For the discussed experiments the *Dzyaloshinskii-Moriya*, or antisymmetric exchange interaction ($\mathcal{H}_{DM} \propto \mathbf{S}_{i} \times \mathbf{S}_{j}$) is not relevant, and the sole focus will be on the Heisenberg



Figure 6.2.: (a) Energy states of two spin-1 systems in a magnetic field of 10 T with anisotropy (D = -4 mV and E = 0.7 mV). The lowest state is plotted in red. The transition discussed is marked by the red arrow. (b) The force-distance curve related to the lowest state for the same parameters as in (a) at different magnetic fields of 5 T (blue), 10 T (red) and 14 T (green) shows a small bump at the transition. Note that only the contribution of the two spins is considered and that other force components need to be added. (c) The effective frequency shift is calculated as it would be observed in experiment by averaging over the oscillation cycle. Plotted are the expected spectra at 5 T for amplitudes of 50 and 10 pm in light and dark blue, respectively, with the effect of the transition being almost invisible. (d) Same as (c) for a magnetic field of 14 T showing a much stronger signal in the spectrum when measured with amplitudes of 50 and 10 pm plotted in light and dark green, respectively.

exchange interaction:

$$\mathcal{H}_{ex} = -\frac{1}{2} \sum_{i,j \neq i} J_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j , \qquad (6.1)$$

with $J_{i,j} < 0$ for antiferromagnetic coupling. For two coupled spins the term simplifies to:

$$\mathcal{H}_{ex} = -J \mathbf{S}_1 \cdot \mathbf{S}_2 \,. \tag{6.2}$$

The coupling parameter J is usually assumed to be exponentially distance dependent as it based on the overlap of the wave functions of tip and sample spin system. For the calculation, the following simple relation is used:

$$J = J_0 e^{-2\kappa z} \,, \tag{6.3}$$

with $J_0 = -12 \text{ mV} [223]$ and $\kappa = 0.74 \cdot 10^{10} \text{ m}^{-1}$ (from Figure 2.11 in Section 2.4.4, i.e. the same as for tunneling, as it is approximated by the same overlap integral).

In the following the force distance curve expected for two spin-1 Co species is discussed and the results done with MatLab are shown¹. For the calculation parameters derived from Chapter 5 of D = -4.0 mV and E = 0.7 mV are used. In Figure 6.2 (a) all nine possible states of the system are plotted as a function of distance. In a simplified picture where mixing of states is neglected, they can be derived by the simple combination of possible states of both separate systems ($m_{z,1,2} = -1$, 0, 1). (See discussion about the mixing of states in Section 5.2.1.) In the calculation the mixing is accounted for.

Figure 6.2 (b) shows the force and panels (c) and (d) the effective frequency shift for different parameters as it would be detected by the AFM associated with the lowest energy state. Note that only the spin contribution is considered and other interaction components are not included. From those fits it is evident that very small amplitudes (ideally in the range of 10 pm) and high magnetic fields of ideally 10 - 14 T are necessary to obtain a reasonable signal intensity. For the experiments only the frequency shift is accessible, and a discretized integration needs to be performed to obtain the related vertical force distance curve, as was discussed in Section 4.3.2.

6.3. Experimental Observations

6.3.1. Force-Distance Curves

The low Q-factor of the AFM sensor did not permit sensitive enough measurements at the required small amplitudes in high magnetic fields. Therefore the presented "results" can only be considered a collection of related observations, but not the intended experiment.

The following procedure for data acquisition has proven to work reliably and to give reproducible results.

- 1. With the AFM disabled the Co adsorbate is imaged by STM.
- 2. The Co adsorbate is spectroscopically investigated to confirm the spin polarization of the tip (in magnetic field).
- 3. The tunneling setpoint is decreased (relatively large tip-sample distance, typically I = 20 pA at V = -100 mV).
- 4. The amplitude of the oscillation is slowly (manually) increased with the AFM feedback controller disabled to allow the z-controller adjusting the height of the tip and to avoid interference between the two feedback controllers.

¹The code used is adapted from work by J. van Veen [97]



Figure 6.3.: (a) Example of $\Delta f(z)$ and simultaneously recorded current measured on a Co adsorbate shown in (b) and (c) before and after the measurement, respectively (positions marked by "×"). The adsorbate jumped away at the point that is marked by the green arrow. Note the non-exponential current increase in (a), which is expected to be related to contact formation between a non conductive sub-apex of the tip, giving rise to the nicely visible onset of repulsive forces. (Measurement parameters: (a) $A = 145 \text{ pm}, f_0 = 34.128 \text{ kHz}; V = -15 \text{ mV}.$ (b), (c) I = 20 pA, V = -80 mV; scale bar: 2 nm.)

- 5. If the desired amplitude (currently A = 0.1 0.3 nm, goal: A = 10 pm) is approximately reached, the AFM feedback is enabled.
- 6. The setpoint is increased (typically I = 500 pA at V = -10 mV, i.e. to a smaller tip sample distance).
- 7. The z-controller is disabled and the tip is retracted by a small distance (typically $\Delta z^R = 0.5 1.2$ nm).
- 8. Now the actual z-sweep is performed by approaching the sample by $\Delta z^F = \Delta z^R$. Forward and backward sweeps are recorded to distinguish between intrinsic and non-reversible effects. The amplitude and excitation signal are monitored to identify dissipative effects. (Note that the calculation of the force requires a constant oscillation amplitude.) The bias can be decreased (~ 1 mV, or to zero) to allow simultaneous recording of the current or the dI/dV-signal (for zero bias) at the typical current amplifier settings. If higher voltages are required (e.g. for the compensation of the contact potential difference) the gain of the amplifier needs to be changed. The current signal can also be helpful in identifying non-reversible effects like jumping away adsorbates or tip changes.
- 9. The sweep should be repeated with incrementally increased Δz^F , i.e. by carefully approaching the sample more and more closely. By this iterative approach it can be ensured that possible observations are reproduced (by the backward scan) before possible non-reversible effects on the tip-sample system prohibit further investigation.

10. A control image should be recorded subsequently to confirm the integrity of the adsorbate and the tip.

In the majority of spectra recorded in the scope of the discussed experiment the adsorbate jumped away during recording without signs that could be attributed to the spin-flip. In Figure 6.3 a representative example is shown. Spikes in the current (marked by the green arrow) serve as a reliable indication of the "manipulation". One reason for this observation might be related to the strong electrostatic forces. From KPFM measurements (not shown) it is known that the contact potential difference is in the order of -0.8 - -0.9 V for typical tips and the *h*-BN, while the data was usually recorded at voltages of zero bias or 1 - 10 mV to allow simultaneous recording of the current.



Figure 6.4.: Example of a $\Delta f(z)$ spectra with an unstable tip. (a) STM image of the Co species investigated. (b) Forward (black) and backward (red) $\Delta f(z)$ -spectra recorded on the position marked in (a) by the "×". The lower panel shows the simultaneously recorded excitation signal. (Measurement parameters: A = 0.7 nm, $f_0 = 34.128$ kHz.) (c) STM image taken after several spectra were recorded on the same spot until the tipsample distance got too close and the area was destroyed. (Measurement parameters: I = 10 pA, V = -100 mV; scale bar: 2 nm.)

In Figure 6.4 (a) a $\Delta f(z)$ -curve is shown that was recorded at zero magnetic field above a Co adsorbate (panel (b)). Besides a highly irregular slope, also a strong discrepancy between forward and backward scans is visible. The jumps that are accompanied by a series of peaks in the excitation (i.e. dissipation) can be attributed to significant tip apex changes and the formation of true contact to the surface. The assumption is corroborated by the STM image recorded subsequently, which shows the area of the contact formation (crash site). Note, however, that the similar (but hysteretic) features on the forward and backward scan are a signature of the tip, which did not change upon contact formation. This discussion should serve as example for tips that are not suited for the experiment, and that a similar test (on the bare *h*-BN/Rh(111), see also Chapter 4) should always be performed as reference for the tip properties.

6.3.2. Current Anomaly



Figure 6.5.: (a) A Kondo resonance of a Co species investigated at 7 T, which did not show a splitting. The red dashed line marks the voltage at which the z-spectroscopy was performed. (b) The current signal during the z-spectroscopy shows a distinct peak at z = -350 pm. This decrease in conductivity could be tentatively assigned to a splitting of the resonance. (c) The simultaneously recorded Δf -signal might show a small change in slope below z = -350 pm. (Measurement parameters: A = 220 pm, $f_0 = 34.128$ kHz, V = -1 mV.)

Besides the discussed possibility to access the transition of the spin by the force sensed with the AFM, a second effect was observed that might be related to the same physical mechanisms in the tunneling current. Preliminary results are presented in Figure 6.5. The effect shown was observed on several Co species, but with different intensity. Here, for a spin polarized tip a tip-induced splitting of the Kondo resonance might be an explanation for the small increase in current during approach of the adsorbate by the oscillating tip. The small change in slope in the frequency shift signal (panel (c)) can also be assigned to the same position at $z \approx 350$ pm.

6.4. Summary and Conclusion

From a technical perspective, the experiments seem feasible, while the unfortunately low Q-factor (in the range of 2000 at zero magnetic field compared to up to 50000 for previous sensors) prohibited detection of the transition from the parallel to the anti-parallel alignment with increasing proximity. A new sensor will soon be implemented to overcome this limitation. The reduction of the Q-factor in magnetic fields (by up to 80% at 10 T) remains a challenge, yet to be addressed.

The first experimental data presented about the $\Delta f(z)$ -curve investigations on the Co species with spin polarized tips can be regarded as important preliminary work for the actually intended experiments. Besides the likelihood of most Co species to jump away upon investigation (see discussion in Section 5.5 and Figures 5.9 and 5.15 as counter examples), the high dependance on the tip (a very general issue of obtaining atomic resolution in AFM) and parasitic tip effects remains a challenge, which is also discussed in ref. [217] by Schmidt and coworkers. An alternative approach to study the exchange coupling would rely on the feature of the magnetic power supply to slowly reverse the external magnetic field. This is experimentally also very challenging, as it requires dealing with drift inherent to changing the magnetic field.

CHAPTER 7

A Kondo System in the Weak Coupling Regime

In this Chapter the publication ref. [213] will be summarized, which was published in 2013 in Nature Communication by the following authors: Y-h. Zhang, S. Kahle, T. Herden, C. Stroh, M. Mayor, U. Schlickum, M. Ternes, P. Wahl and K. Kern. A more detailed discussion is given in the PhD theses by S. Kahle and Y-h. Zhang [39, 224]. Therefore, only a short summary of the findings published will be given. Additionally, some unpublished work will be presented in Section 7.7. The necessary theoretical background, especially around the Kondo effect was already discussed in Chapter 5.

7.1. Overview and Motivation

Experiments performed at a different STM in the same department showed clear signatures of the Kondo effect on the investigated purely organic 2'-nitronilnitroxide-5'-methyl-[1,1';4',1"]terphenyl-4,4"-dicarbonitrile (called "NiNiox" molecule, for clarity) on Au(111). In Figure 7.1 (c) an example of a differential conductance spectra recorded at $T \approx 9$ K is shown, which can be described in the framework of the strong coupling regime of the Kondo effect. The corresponding Kondo temperature can be calculated to be $T_K \approx 20$ K, i.e. $T_K > T$.

Only the diligent and further investigation of the exact temperature and magnetic field dependence of the Kondo resonance led to the conclusion that the experiments on the NiNiox molecule have to be described in the weak coupling regime. While the intensive discussion about the underlying Kondo physics, models, fitting parameters, etc. was sometimes cumbersome in the scope of the interpretation of the results, the beautiful description by the parameter-free perturbation model was a satisfactory confirmation of the work. By this, it constitutes a Kondo study with unprecedented quantitative agreement between theory and experiment in the framework of the weak coupling regime for a single spin-1/2 system investigated by STM.

7.2. The NiNiox Molecule

The structure and an STM image of the NiNiox molecule as it appears on the Au(111) surface are shown in Figure 7.1 (b) and (a), respectively. The radical molecules that were

first described by Osiecki and Ullman in 1968 [225] are supplied in form of a crystal powder and were synthesized¹ by C. Stroh, at Karlsruhe Institute of Technology.

The NiNiox molecule is purely organic $(C_{28}H_{25}O_2N_4)$ with the excess electron of the radical side group being spatially delocalized over the O-N-C-N-O part, as depicted in Figure 7.1 (b). Surprisingly the molecule retains this electronic structure also on the metal surface, as the backbone protects it against charge transfer. This makes the NiNiox molecule on the Au(111) surface an easy to handle, true spin-1/2 system. As most theoretical work focuses on this most simple spin system, it can serve as a benchmark system between theory and experiment.



Figure 7.1.: (a) STM image of the NiNiox molecule on Au(111). (Measurement parameters: I =30 pA, V = -100 mV; scale bar: 1 nm. A Gaussian smooth was applied for clarity.) (b) The chemical structure of the molecule with the backbone at the lower part consisting of three benzene rings and the nitronyl-nitroxide radical side group carrying the electron marked by the cyan and yellow clouds, for opposing spin orientations. Color code: N: blue, O: red, C: gray, H: pink. (Simulation by D. Le, University of Central Florida.) (c) Spectrum recorded at zero magnetic field and 9 K at the position marked by the "x" in (a). The red curve shows a Frota fit nicely reproducing the line shape, which would suggest a Kondo temperature of ~ 20 K in the strong coupling regime.

7.3. Sample Preparation

The preparation of the Au(111) surface is done as discussed in Section 5.3. The NiNiox crystal powder consists of equal amounts of the molecule and dichloromethane stabilizing the molecule during synthesis. The dichloromethane is also evaporated to the surface and appears as smaller adsorbates in the STM images (directly attached to the molecules and separately). Its presence does not influence the investigated properties. The molecule is sublimated using a quartz crucible at $T \approx 480$ K for 0.5 - 20 minutes with sample temperatures of 150 - 180 K, as the deposition on samples at room temperature leads to nucleation at the step edges of the Au(111) surface.

¹Synthesis: The molecule (2'-nitronilnitroxide-5'-methyl-[1,1';4',1"]terphenyl-4,4"-dicarbonitrile) was synthesized using a Suzuki-type cross-coupling reaction with the spin-labeled diiodo-precursor and 4-cyanophenyl-boronic acid in the presence of Pd(PPh₃)₄ as catalyst and Na₂CO₃ as base.



Figure 7.2.: (a) STM image of NiNiox molecules deposited on the Au(111) surface. Two dichloromethane molecules are marked by white arrows. Nucleation at the elbow sites of the herringbone reconstruction of the Au(111) is clearly visible. (b) Higher resolution STM image of the molecule marked in (a). (Measurement parameters: (a) I = 30 pA, V = 20 mV; scale bar: 5 nm, (b) I = 30 pA, V = 200 mV; scale bar: 1 nm.)

7.4. Experimental Approach

The experiments were performed on the STM described in this thesis and a second homebuilt STM operating in UHV with a base temperature of 6.7 K and with magnetic fields up to 5 T. The first measurements were performed on the latter system and the parts of the temperature evolution was studied there. Additionally, other experiments with higher coverages and the observation of chain formation with the same molecule in combination with Co, Ni, Fe atoms took place on that STM [224].

While no magnetic field measurements for different fields could be obtained on the same individual molecule (as was achieved for the Co-H study presented in Chapter 5), the spread of the spectra is significantly smaller. The magnetic field measurements up to 14 T shown below were performed between 1.5 - 1.8 K.

7.5. Temperature Dependence of the Spectra

Motivated by the strong resonance at the Fermi energy shown in Figure 7.1 (c), temperature dependent measurements were performed at temperatures between T = 1.5 - 15.7 K, which are presented in Figure 7.3 (a). As suggested by the simulated distribution of the radical electron (Figure 7.1 (b)) the spectral feature is only observed at the radical part of the molecule and not at the elongated part, which can be identified as the backbone of the molecule.

The data is fitted by the perturbation model discussed in Section 5.2.4, which shows excellent agreement (red curves). The temperature parameter $T_{\rm Eff}$ in the model is kept as the only free parameter (besides an offset and scaling) for fitting and is plotted in Figure 7.3 (b) against the experimentally measured temperatures for comparison, which



Figure 7.3.: Temperature dependence of the Kondo resonance. (a) dI/dV-spectra taken on the radical side group of the NiNiox molecule at T = 1.5 - 15.7 K with fitted spectra using perturbation theory in red. Spectra are offset for clarity. (b) The effective temperature from fitting plotted against the experimental temperature, with the red line being $T_{\rm Eff} = T$. Error bars result from the variation of different molecules. (c) Half-width at half-maximum resulting from fitting a Frota function to the spectra in (a). The red lines show the expected temperature dependence of the width for a Kondo resonance in the strong coupling regime for different Kondo temperatures.

shows a high degree of consistency. If the data is fitted in the framework of the strong coupling regime by a Frota function (see Equation 5.16) the width evolution is not consistent, as shown in Figure 7.3 (c).

7.6. Magnetic Field Dependence of the Spectra

The splitting of the Kondo resonance was investigated in out-of-plane magnetic fields up to 14 T. In Figure 7.4 typical dI/dV-spectra are presented. The splitting of the Kondo resonance is accompanied by the signature of a spin-flip (symmetric steps at the same energy as the split Kondo resonance peaks), which becomes more prominent (due to the stronger Zeeman splitting) at higher magnetic fields. In the perturbation model both effects are accounted for and hence the convincing agreement between the data and the fit (red) in Figure 7.4 is not too surprising. However, a second convincing argument that the



Figure 7.4.: Magnetic field dependence of the Kondo resonance. dI/dV-spectra taken on the radical side group of the NiNiox molecule at magnetic fields between 0 – 14 T at temperatures of 1.5 – 1.8 K. Fitted spectra in red are based on the perturbation theory model. Spectra are offset for clarity.

Kondo resonance of the NiNiox molecule has to be discussed in the weak coupling regime. The splitting of the Kondo peak already at 2 T cannot be consistently explained in the strong coupling limit, if a Kondo temperature of $T_K \approx 25$ K is assumed from the width of the resonance. As Costi derives in ref. [226], the relation between the critical field for splitting and the Kondo temperature is given by $B_C = 0.5 T_K$, with T_K in units of $K \cdot [k_B/(g\mu_B)]$, which would prohibit the observed splitting below fields of $B_C \approx 9$ T. Or, if the discussion is reversed, the observed splitting at 2 T would correspond to a maximum Kondo temperature of 5.4 K, which would then be inconsistent to the width of the Kondo resonance.

From the fits of the data for several molecules the energies of the peak positions and the spin-flip excitations scale linearly with the magnetic field, which can be fitted to obtain a g-factor of 1.98 ± 0.04 . The coupling $J\rho_0$ derived from the fits is in the order of -0.04 ± 0.02 . The negative sign of the obtained $J\rho_0$ as well as the appearance of a peak instead of a dip at the Fermi level clearly show that the observed feature is an afm Kondo effect. The g-factor slightly below the value of a free electron supports this assignment [227].



7.7. KPFM Measurements

Figure 7.5.: (a) STM image with positions of the contact potential difference measurements indicted. (Measurement parameters: I = 20 pA, V = 800 mV; scale bar: 1 nm.) (b) Contact potential differences on positions indicted in (a).

During the experiments on the NiNiox molecule the combined STM/AFM replaced the previous STM. This opened up the possibility to investigate the molecule also by AFM. As discussed in Section 2.5, KPFM allows spatial resolution of the contact potential difference, i.e. to image the distribution of the charge. For the NiNiox molecule this should allow investigation of the excess electron at the radical part of the molecule.

In Figure 7.5 an example of a KPFM measurement is presented. The clear negative contact potential difference at the position of the molecule clearly indicates the negative charge of the molecule. This general trend was observed on several molecules, while drift in the setup at that time prohibited the investigation by means of maps with significantly higher resolution.

7.8. Summary

The investigated NiNiox radical molecule has proven to be a "textbook example" for a true spin-1/2 system in the weak coupling regime. The description by the perturbation theory model shows perfect agreement, while the combination of temperature and magnetic field dependent data reveals inconsistencies if described in the strong coupling regime. The small coupling of $J\rho_0 \approx -0.04$ and the g-factor close to g = 2.0 for a free electron, corroborates the assumption that the radical side group is almost unaffected by adsorption on to the metal surface.

Another aspect of the corresponding physics, and especially the high level of agreement reached with the theoretical description is worth remembering: As the Kondo effect originates from many-body correlations, it is rather striking how well perturbation theory in this universal model describes the data of this organic molecule with a mass of 449 amu.

CHAPTER 8

Summary and Outlook

8.1. Summary

In the first part of this thesis I discussed the most important aspects of the setup and the microscope head, with a focus on the combined STM/AFM sensor and its evolution. It was put into full operation during this thesis and has proved in several experiments its capabilities for a broad range of experiments in combination with the powerful system of high magnetic field, low temperatures, single "cold" atom evaporator and high mechanical stability.

In the second part of my thesis, I presented a thorough study that aimed to investigate the mechanical properties of the h-BN/Rh(111) system that is widely used as an insulating template. Very low stiffnesses in the range of 1 N/m were derived for the highly corrugated surface in lateral and vertical direction. This study was only possible due to the high stability of the system and the capability of the sensor to detect very minute forces in the sub-pN regime. I hope that this study also proves to be helpful for further studies related to experiments where the quantitative knowledge of acting forces is relevant.

The studies of single Co atoms and Co-H systems on the h-BN/Rh(111) are divided into two chapters. The first one addressed the surprisingly rich physics manifested by five different species obtained by combining imaging and spectroscopy. I discussed possible mechanisms that might influence the spectral variety, especially concerning the huge spread derived for the magnetocrystalline anisotropies of D = -1.9 - -6.3 mV and E = 0.4 - 1.0 mV. The apparent height of the adsorbates (showing the same spectral signature) varied between 20 - 220 pm. The underlying models of spin-flip and Kondo physics were discussed. For a more complete picture we hope that ongoing density functional theory calculation will provide us with more insights into the coupling of the Co with the H and the influence of the (corrugated) h-BN. From a technical point of view, the metal atom evaporator I designed proved to work reliable. In the scope of this work I was able to collect data for a time span of more than 50 hours on the same individual adsorbates at several different magnetic fields up to 14 T. This extensive data set has proven to be extremely helpful for interpretation of the data. The second chapter on Co adatoms dealt with the preliminary experiments that were originally intended: The determination of the force needed to switch a single spin from being aligned in magnetic field to being antiferromagnetically coupled to a second spin if they are approached towards each other. Here some preparative work on obtaining spin polarized tips, i.e. picking up Co species with the tip is worth mentioning. From the recording of force-distance curves with the unfortunately low AFM performance at that time, which hindered the detection of the transition, I showed a typical example were the atom was forced to jump away upon approach by the oscillating tip. A refined method of the experimental approach is presented and I highlight the importance of tip characterization. The theoretically expected signature of the transition is discussed.

The study of a Kondo system consisting of an organic radical based on a nitronyl-nitroxide moiety was summarized. It was discussed in terms of the weak coupling limit of the Kondo effect and represents a rare spin-1/2 system that retains its spin properties also after deposition on to Au(111). Detailed temperature and magnetic field dependence were studied. The high degree of agreement to the theoretical model and the easy handling of the molecule makes it a possible "drosophila of spin-1/2 Kondo physics" in the weak coupling limit.

Single-molecule magnets are considered to play an important role in future molecular electronics. Unfortunately the experiments performed on the Cr_7Ni were unconclusive on Au(111) and h-BN/Rh(111), and could not prove that the magnetic properties are retained, as was previously observed for the Mn_{12} single molecule magnet for deposition on h-BN/Rh(111). We performed experiments with two Cr_7Ni derivatives.

8.2. Outlook

While a large fraction of work during my thesis was related to construction, maintenance and the relocation of the instrument to the new lab, the current status of the system in the new laboratory offers unprecedented opportunities for future experiments. In addition to the following discussion of feasible experiments, a broad selection of work done with combined STM/AFM in other groups was discussed in Section 2.4.3. I will subdivide the outlook into three parts. The first summarizes the next steps in the framework of the experiments already started during my thesis. In Section 8.2.2 some vague ideas are presented that rely on technical features of the microscope, while the last section features some fundamentally different ideas for long-term experimental orientation.

8.2.1. Follow-up Experiments

In my opinion the most exciting experiment well within reach is the detection of the force related to the flipping of the spin of the Co atom due to exchange coupling as discussed in Chapter 6. This experiment is very comprehensible in the simple picture of two magnets being brought into close proximity where they interact and realign. In a more profound view, it addresses very fundamental physics of quantum mechanics at the single atom, or even single spin level. In this experiment, the full potential of the microscope setup is challenged in answering this fundamental question. As became evident in the discussion in Chapter 6, the current limitation is the force sensor. Previous sensors showed Q-factors of 50 000, and allowed stable oscillation amplitudes also below 100 pm, while the current one did not allow small enough amplitudes due to the low Q-factor. In other groups, Q-factors of up to 200 000 [67] and amplitudes down to 20 pm [68] were shown to be achievable.

The puzzling results obtained in the STS study on the Co and Co-H species (Chapter 5) could be further elucidated in several ways. First, the ongoing DFT calculation seem to converge and a first tentative interpretation allows identification of the Co-H species as spin-1 system and the Co with two H as the candidate for spin-1/2. This would confirm that H is the key to understand the two different spectral features observed. No conclusive answers for the anisotropies for the spin-1 system were obtained so far. The effect of the CO is not within the scope of the current DFT work. The second way would be to systematically eliminate the very abundant CO and to decrease the H concentration in the chamber. This would allow the study of the effects in a more controlled manner by dosing the two gases in a controlled fashion. A third option would be to change the substrate and use h-BN on Cu(111) instead, which would eliminate the possible effect of the corrugation and the highly anisotropic electronic interaction landscape. In a fourth approach, manipulation of the adsorbates on the surface by the STM/AFM might also reveal further insights. However, I want to stress that such experiments can get "messy". as tip preparation on the insulating h-BN layer without in situ tip exchange possibility can be a cumbersome endeavor.

The topographic investigation of the ring states that are attributed to single Co atoms unpinning the h-BN layer from the rhodium substrate by the AFM with atomic resolution should be a straightforward experiment. Especially in the combination with the potential to obtain interaction forces, the reported switching would be interesting to quantify [172]. By studying this striking effect in more detail, This might give insights into the general coupling between the Co species and the h-BN and that we could derive valuable information with regard to the spectroscopic study.

Another feasible experiment I suggest trying, also aims at the intrinsic *h*-BN properties on the Rh(111) surface: Contrast inversion of the superstructure was observed depending on the bias voltage in STM topographies due to the alternating dominance of rim and valley regions in the LDOS [86]. In a more recent work, a very similar contrast inversion was triggered by large amplitude AFM measurements (A = 10 nm) by Koch *et al.* [228]. Combining these two effect with our superior force resolution might reveal further insights into the electronic and mechanical properties, as was investigated in the scope of Chapter 4 and more excitingly the interplay, i.e. how the LDOS is modified by mechanical deformations on this scale.

8.2.2. Experiments from a Technical Point of View

The possibility of our sensor design to also detect the first out-of-plane vibrational mode of the tuning fork (Section 3.4.3), i.e. to observe oscillations parallel to the sample surface, allows for a new class of experiments, where the lateral force is directly accessible [66, 229, 230]. While usually designs where the tuning fork is mounted perpendicular to the surface (pendulum geometry) are deployed, our setup would allow switching between vibrational modes, in principle, instantaneously. In this context also the use of the higher harmonics of the AFM sensor might be worth considering [231].

As discussed in the scope of Chapter 4 for the highly corrugated h-BN/Rh(111), it is impossible to disentangle the true topography from the LDOS signal obtained in STM imaging (typically close to the Fermi energy). In AFM on the other hand, all electrons contribute to the interaction and thereby a higher resolution is reached [68]. Imaging at constant height is very limited for corrugated surfaces, while constant frequency shift measurements are prone to give non-conclusive results due to the effect of long range forces. By following a predefined, but adaptable contour with the tip along the expected topographic profile of the corrugation, the observation of uniform atomic resolution with the AFM should allow one to judge the quality of the tested contour. The influence of the electronic landscape (and hence the influence of the underlying Rh substrate) could be simultaneously investigated.

The feature of the magnet power supply to reverse the magnetic field direction without discontinuity through zero field, opens the possibility to investigate hysteretic features, which is especially interesting in the field of the single-molecule magnets [232].

8.2.3. Future Orientation

A long-standing idea is to "decode" proteins and peptides by spatially resolving their building blocks, the amino acids. Here, controlled lifting experiments and spatially resolved STS could serve as complementary channels for an otherwise cumbersome identification. The lifting could be done in the spirit of work presented by Fournier *et al.*, who used an STM/AFM to lift a single molecular wire off the surface and monitored the wire conformation as well as the changing contact configuration due to breaking of individual bonds [75]. Alternatively, this could be achieved as shown by Langewisch et al., who showed the controlled displacement of organic molecules with a special emphasis on the lateral and vertical force profiles and energy dissipation [233]. In similar approaches with STM, conformational properties from pulling long single-molecule wires away from the surface and recording the modulation of the current could be obtained [234, 235]. In previous studies by AFM, Patil et al. reached lateral resolution of only about 10 nm, but identified compositional changes along the protein fragments, due to the high force sensitivity of 0.2 pN resulting from deployment of the second harmonic of their AFM [236]. From an experimental point of view, this project can benefit from the experience of the close collaboration with the electrospray ionization group of S. Rauschenbach in the same department

[237], which has proven to be very fruitful in previous experiments [19].

The first molecular theory of friction was developed in 1929 by Tomlinson [238], while the topic of noncontact friction was addressed considerably later, e.g. in the study of Stipe *et al.* for a Au(111) surface and a soft vertical Si cantilever. They deployed an optical readout to derive temperature dependent friction coefficients [239]. Similar experiments on superconducting surfaces were pioneered by Dayo *et al.* in 1998, where the friction of solid nitrogen on superconducting films of lead was studied by a quartz crystal microbalance technique [240]. Their discovery of the sharp transition of the friction coefficient below the transition temperature triggered a series of theoretical studies, especially by Persson *et al.* [241–243].

Kisiel *et al.* studied a Nb film with a soft cantilever that oscillates parallel to the surface (pendulum geometry), where they observed a rather smooth transition in the distance and voltage dependence of the friction during the transition into the superconducting phase [244]. They attribute this to the disappearance of the electronic contribution of friction in the superconducting state, while the phononic contributions are still present but slowly decrease with decreasing temperature. Our experience with superconducting clusters of Sn and Pb, which have already been studied on the system by means of STM/STS [124, 142], allows us to produce significantly clearer defined sample systems. Their studies were done on Nb films with roughness of the order of 1 nm and with 5 nm oscillation amplitude, which results in a rather broad averaging that could be improved in our setup. The possible experiments in this field are diverse: It ranges from studying the friction of single atoms on superconducting samples to the friction on size dependent superconducting clusters. It could also be imagined to be expanded towards recently pioneered "spin friction" experiments [245] and could benefit from deploying both modes of the force sensor.

As this selection of ideas demonstrates, I think that there is still "plenty of room at the bottom" where the introduced STM/AFM with the versatile experimental setup can be utilized to gain a deeper understanding of quantum mechanics at the nanoscale.

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APPENDIX A

The Single-Molecule Magnet Cr7Ni

The project on the single-molecule magnet (SMM) Cr_7Ni was a collaboration with Alberto Ghirri (CNR-Institute of NanoSciences, Modena, Italy) and was planned as a follow-up of the Manganese-12-Acetate (Mn₁₂) study [19, 247]. As contrary to the Mn₁₂ project no conclusive results were obtained, this section will be kept rather short. Most aspects of the data recorded on the Cr_7Ni -bu species will not be discussed here and can be found in ref. [39].

A.1. Overview and Motivation



Figure A.1.: (a) Molecular structure of a Cr_7Ni single-molecule magnet. Color code: Cr: green, Ni: purple, C: black, H: white, O: red, F: yellow [248]. (b) The eight spins are antiferromagnetically coupled as depicted to a total spin S = 1/2. (c) Energy scheme of Cr_7Ni with the position of the level crossing indicated by the red arrow. Note that the ground-state energy is set to 0 for all fields. Adapted from ref. [249].

SMMs are considered interesting for two main reasons: First, in academic research, as their magnetic properties are at the interface between quantum mechanical and classical



Figure A.2.: (a)-(d) Series of STM images of lateral manipulation (triggered by 30 ms -1 V pulses) of Cr_7Ni -bu, which shows the rather high mobility of this species. (Measurement parameters: I = 30 pA, V = -100 mV.)

systems [18, 250–252] and second, because their properties inspire application in information storage, spintronics, and quantum computation [253, 254].

 Cr_7Ni , which was first synthesized and investigated by Larsen *et al.* in 2003 [255], belongs to the SMM family of antiferromagnetic rings, with Cr_8 being the parent ring [256–258]. The core of eight metal atoms is bridged together by carboxylate and fluoride groups, as depicted by Figure A.1. Due to the antiferromagnetic coupling that can be described by a Heisenberg Hamiltonian:

$$\mathcal{H}_{ex} = -\frac{1}{2} \sum_{i,j \neq i} J_{i,j} \vec{S}_i \cdot \vec{S}_j , \qquad (A.1)$$

with $J_{i,j} < 0$ the seven $\operatorname{Cr}^{3+}(s = 3/2)$ and one $\operatorname{Ni}^{2+}(s = 1)$ sum to a total spin of the ring of S = 1/2.

Most studies of Cr_7Ni are based on surface averaging techniques (XPS, XMCD, inelastic neutron scattering, heat capacity measurements) and only more recently investigation of individual species by STM and AFM was started [259]. Here also the experience of Ghirri *et al.* has to be highlighted [246, 260].

Similar to the Mn₁₂ study, it was planned to use the STM to directly detect the preserved magnetism by investigating inelastic spin-flip processes. Additionally, a second topic was intended to be investigated: Due to a level crossing of the $|S, m_z\rangle = |1/2, -1/2\rangle$ and $|3/2, -3/2\rangle$ states at approximately 11.4 T a spectral signature should be observable, as the continuous spin transitions ("S mixing") between $m_z = -1/2$ and $m_z = -3/2$ result in a non-zero average spin (contrary to the normal Kondo effect, where $m_z = 1/2$ and $m_z = -1/2$ average to 0). This "avoided crossing" is indicated in the energy scheme in Figure A.1 (c) [249, 261].

In the discussed experiments $\operatorname{Cr}_7\operatorname{Ni}-bu^1$ and $\operatorname{Cr}_7\operatorname{Ni}-SH^2$ were used, which are both derivatives of $\operatorname{Cr}_7\operatorname{Ni}$. While the first species has a diisobutylamine placed in the ring center as linker to bind to the surface, the second species was chosen because the sulfur ligand had been shown to bind more strongly to the Au(111) [259]. This was also experimentally discovered, as the $\operatorname{Cr}_7\operatorname{Ni}-bu$ species were more easily moved by the tip, as shown in Figure A.2. As mentioned above, the focus will be on the $\operatorname{Cr}_7\operatorname{Ni}-SH$ and some findings not covered already in ref. [39].

All spectra are recorded with the following parameters: Excitation voltage of 0.5 - 1 mV at f = 799 Hz. The setpoint was in the range of 300 - 500 pA at the sweep voltage minimum. The integration time per data point was $\tau = 30$ ms, with 200 - 250 data points averaged over 6 - 10 sweeps (in forward and backward direction). In the figures the maximum of the dI/dV-signal is scaled to 1. Measurement parameters are given in the figure captions. The images on *h*-BN are all filtered by a Gaussian smooth for higher clarity.



A.2. Sample Preparation

Figure A.3.: (a) $\operatorname{Cr}_7\operatorname{Ni}$ -SH deposited at room temperature on a Au(111) crystal. The molecules clearly diffuse to the steps. Only very few molecules remain on the terraces and are reasonably addressable by STS. (Measurement parameters: I = 25 pA, V = -2 V, scale bar: 15 nm; data treatment: flattening.) (b) Several $\operatorname{Cr}_7\operatorname{Ni}$ -bu adsorbed at the elbow sites of the Au(111) surface reconstruction. (Measurement parameters: I = 30 pA, V = -200 mV, scale bar: 5 nm.) (c) Height profile of two molecules as indicated by the line in (b) confirming the apparent height of ~ 0.2 nm as reported in ref. [246].

The Au(111) surface is prepared as discussed in Section 5.3, and the h-BN/Rh(111) as shown in Section 4.2.3. A big advantage of Cr₇Ni over Mn₁₂, which needs to be deposited by electrospray ionization, is the possibility to evaporate the molecules (supplied in form of a greenish crystal powder) directly from a crucible in a normal molecule evaporator (4x OMBE Source from Dodecon Nanotechnology). Evaporation times varied between

 $^{{}^{1}{[(}CH_{3})_{2}CHCH_{2}]_{2} - NH_{2}}{Cr_{7}NiF_{8}[O_{2}CC(CH_{3})_{3}]_{16}}$

 $^{^{2}{(}CH_{3})[CH_{2}]_{3}-NH_{2}[CH_{2}]_{2}-SH}{Cr_{7}NiF_{8}[O_{2}C(CH_{3})_{3}C]_{16}}$

1 and 10 minutes and temperatures between 200 - 220°C. The substrate was usually at 90 - 150 K, i.e. cooled by liquid nitrogen whilst, if necessary, counter heated for 150 K. Some samples were also prepared by evaporation on a 300 K warm sample, as shown in the example in Figure A.3 (a). The sample is then directly transferred into the cold microscope. To minimize warming up during transfer the vertical manipulator can be cooled by lowering it into the the cryostat.



A.3. Cr7Ni on Au(111)

Figure A.4.: (a) Larger scale STM topography of several $Cr_7Ni - SH$ adsorbed on the Au(111) surface. (Measurement parameters: I = 20 pA, V = -100 mV; scale bar: 5 nm; data treatment: plane subtraction.) (b) Height profile of two molecules as indicated by the black line in (a) showing an apparent height of ~ 0.1 nm. (c) STM topography of isolated $Cr_7Ni - SH$. (Measurement parameters: I = 20 pA, V = -25 mV; scale bar: 0.5 nm.) (d) Spectrum taken on $Cr_7Ni - SH$. The blue curve shows the recorded spectrum at the marked position of (c).

While the X-ray studies of Corradini *et al.* [262] suggested that the oxidation state of Cr_7Ni and the local symmetry of the Cr and Ni sites are not affected by deposition on to a gold surface, which is an indication that the magnetic properties are retained, this could not be proven for individual molecules by STM/STS in the work discussed here (see Figure A.4 for representative spectra.). On the other hand this is not too surprising, as also for the Mn_{12} the magnetism of the molecule was quenched upon deposition directly on the metal surface.

The deposition on Au(111) is nevertheless worthwhile, as deposition rate, topographic appearance (to a certain degree) and mobility can be studied while allowing for convenient tip preparation. Contrary to Cr_7Ni -bu, where adsorption at the elbow sites of the herringbone reconstruction is observed (Figure A.3 (b)), the Cr_7Ni -SH molecules do not show a preferential adsorption site when deposited on a cold surface, as shown in Figure A.4. The high mobility of Cr_7Ni -bu was also underlined in preliminary lateral manipulation experiments, as presented in Figure A.2. From the height profile shown in Figure A.4 (b) it can also be tentatively concluded that the binding to the surface is significantly enhanced, as the apparent height is decreased to only 100 - 110 pm.



A.4. Cr7Ni on h-BN/Rh(111)

Figure A.5.: (a). Typical STM image recorded at zero magnetic field with one $Cr_7Ni - SH$ visible in the center. (Measurement parameters: I = 20 pA, V = -25 mV.) (b) Larger scale STM image recorded at 10 T with some $Cr_7Ni - SH$ species visible on the *h*-BN. Also some clusters and other dirt or fragments are visible. (c) Zoom-in from (b). (Measurement parameters (b), (c): I = 20 pA, V = -20 mV.) (d), (e) Spectra taken taken at 0 field and 10 T, respectively. The blue curves show the recorded spectra at the marked position of (a) and (c), respectively.

In order to reduce the coupling to the metal substrate and thereby lower the accompanying risk of quenching of the magnetic properties, the molecules were also deposited on h-BN/Rh(111). While imaging of Cr₇Ni-bu was cumbersome, if not impossible, due to the relatively high mobility (that results in jumps and streaks in the STM images) and the generally poor instrument performance during that time (in the old building), it motivated the investigation of Cr₇Ni-SH. Some examples of STM images and typical spectra recorded on those molecules are shown in Figure A.5. Roughly 80 individual Cr₇Ni-SHwere probed on h-BN with and without magnetic field during the study.

A.5. Summary and Conclusion

It can be concluded that imaging of both species on the Au(111) surface was achieved with unprecedented quality, but no spectral features indicating any magnetic properties could be observed. Due to the stronger binding of the Cr_7Ni -SH compared to the rather mobile Cr_7Ni -bu species imaging on h-BN was slightly more feasible. Unfortunately, also on those species no convincing signs of spin-flip excitations were observed. This leads to the conclusion that either the magnetic properties are not maintained upon adsorption or that the corresponding fingerprint is too small to be detected by the instrument. Another possibility is the degradation of molecules after several evaporation / heating cycles [248]. The mentioned poor system performance during those experiments also needs to be mentioned again, as especially the measurements in field were problematic.

It is worth highlighting that research on Cr_7Ni is still ongoing in other groups, especially in the group of R. Winpenny in Manchester, UK, where in a recent NMR study the coupling of two Cr_7Ni molecular rings via a Cu^{2+} ion was investigated [263].

Appendix \mathbf{B}

Abbreviations

afm	Antiferromagnetic
AFM	Atomic force microscope / microscopy
DFT	Density functional theory
DOS	Density of states
FEM	Finite element method
FFT	Fast Fourier transform
fm	Ferromagnetic
LDOS	Local density of states
SMM	Single-molecule magnet
STM	Scanning tunneling microscope / microscopy
STS	Scanning tunneling spectroscopy
UHV	Ultra-high vacuum
XMCD	X-ray magnetic circular dicroism
XPS	X-ray photoelectron spectroscopy

${}_{\rm APPENDIX} C$

Publications

At Yale University, New Haven, CT, USA

- Holger Schneider, J. Mathias Weber, Evgeniy M. Myshakin, Kenneth D. Jordan, Joseph Bopp, **Tobias Herden** and Mark A. Johnson. *Theoretical and infrared* spectroscopic investigation of the O₂⁻·benzene and O₄⁻·benzene complexes. The Journal of chemical physics, (2007) [264].
- Joseph C. Bopp, Anastassia N. Alexandrova, Ben M. Elliott, Tobias Herden, Mark A. Johnson. Vibrational predissociation spectra of the, n = 3-10, 12 clusters: Evenodd alternation in the core ion. International Journal of Mass Spectrometry, (2009) [265].

At the Max Planck Institute, Stuttgart, Germany

- Yong-hui Zhang, Steffen Kahle, **Tobias Herden**, Christophe Stroh, Marcel Mayor, Uta Schlickum, Markus Ternes, Peter Wahl, and Klaus Kern. *Temperature and magnetic field dependence of a Kondo system in the weak coupling regime*. Nature Communications, (2013) [213].
- Tobias Herden, Markus Ternes, and Klaus Kern. Lateral and vertical stiffness of the epitaxial h-BN monolayer on Rh(111). Nanoletters, (2014) [99].
- Sören Krotzky, Jan Honolka, Tobias Herden, and Klaus Kern at MPI for Solid State Research, Stuttgart; Violetta Sessi and Nicholas Brookes at ESRF, Grenoble; Matthias Menzel, Kirsten von Bergmann and Roland Wiesendanger at University of Hamburg. XMCD and XMLD on Mn/W(110) spin-spirals. In preparation.
- Tobias Herden, Peter Jacobson, Matthias Muenks, Oleg Brovko, Markus Ternes, and Klaus Kern. The interplay of coupling and magnetic anisotropies of Co-H species studied on h-BN/Rh(111). In preparation.

APPENDIX D

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