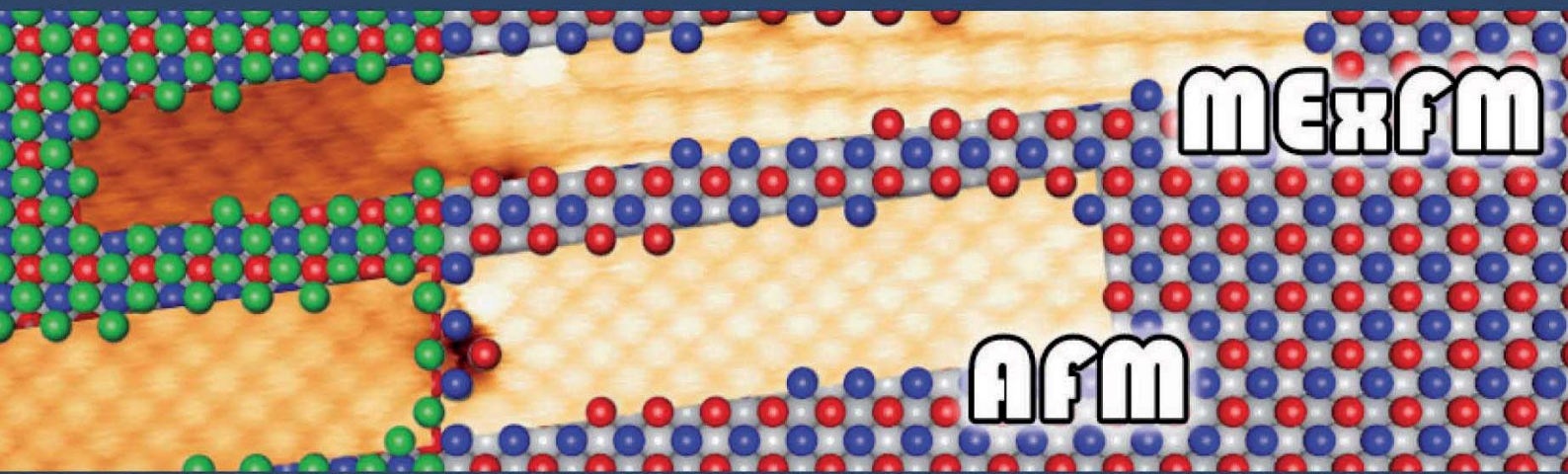


René Schmidt



Magnetic Exchange Force Microscopy and Spectroscopy on Fe/W(001)



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MAGNETIC EXCHANGE FORCE MICROSCOPY AND SPECTROSCOPY ON Fe/W(001)

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ABSTRACT

In this work scanning probe techniques, namely frequency-modulated atomic force microscopy (FM-AFM) in the non-contact regime and related methods like Kelvin probe force microscopy (KPFM), magnetic force microscopy (MFM), and magnetic exchange force microscopy (MExFM), are utilized in ultra high vacuum and at low temperatures to structurally, electronically and magnetically study the monolayer regime of iron on tungsten (001) in real space. Implementing the spectroscopic mode of MExFM, that is, magnetic exchange force spectroscopy (MExFS), the exchange interaction between single iron atoms with antiparallel coupling is experimentally accessed for the first time.

Iron grows pseudomorphically on W(001) whereby the layers are highly strained. Differences in strain between first and second layer iron and hybridization with the substrate lead to differences in electronic properties and magnetism: both layers exhibit a different work function, mapped with KPFM. Interestingly, even on the same layer, different work functions are observed. Moreover, both layers are magnetically different. The second layer is ferromagnetic (FM) with in-plane anisotropy as verified by MFM, while the first layer is antiferromagnetic (AF) with out-of-plane anisotropy. Using MExFM the AF alignment of the monolayer magnetic moments is resolved by detecting the short-ranged magnetic exchange force between tip and sample. The origin of the magnetic contrast formation is discussed and compared to *ab initio* calculations. Later, MExFS, which allows to directly measure the distance dependence of the magnetic exchange interaction between an atomically sharp magnetic tip and the antiferromagnetically ordered Fe monolayer on W(001), is employed. The site specific distance dependence of the total tip-sample interaction is recorded above Fe atoms which exhibit parallel as well as antiparallel atomic magnetic moments. The contribution of the magnetic exchange interaction between both sites can be extracted by subtracting the two curves from each other. All other interactions are identical on both sites. The experimental results are compared to *ab initio* calculations accounting for magnetically different tips composed of either Cr or Fe, or mixtures of both. Depending on symmetry and stability of the experimentally used probe tips, qualitatively different MExFM contrasts and MExFS data with a stronger distance dependence are observed. By analyzing the energy loss per

single cantilever oscillation cycle, simultaneously recorded with topography and frequency shift in the experiments, a bottom-up characterization of the structurally and magnetically unknown probe tip apex is given. Considering the tip apex as magnetically and structurally independent cluster allows to explain the observed tip behavior.

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CHAPTER 1

INTRODUCTION

The semi-empirical Bethe–Slater curve, known since 1930 (figure 2.3), shows that, when the separation between atomic moments in a solid is varied by changing the element and hence the lattice constant, the exchange interaction changes from antiferromagnetic to ferromagnetic or vice versa. To directly access and measure this distance dependence of the exchange interaction strength between two magnetic atoms of the same element is not possible, because the separations between magnetic atoms in a solid of a given material are fixed by the crystal structure. On surfaces the situation changes and surface imaging techniques can be applied to address this theoretical hypothesis.

Scanning probe methods such as spin-polarized scanning tunnelling microscopy (SP-STM) [1–4], spin-flip spectroscopy [5, 6], and the recently developed atomic force microscopy (AFM) [7, 8] based magnetic exchange force microscopy (MExFM) [9, 10], allow one to study magnetic ordering on surfaces with atomic scale precision. SP-STM and MExFM allow for direct characterization of even more complex magnetic structures with atomic-scale resolution. These techniques help to gain a fundamental understanding of spin-related magnetic phenomena within the field of condensed matter research.

In the past, scanning tunneling spectroscopy (STS) has been employed to measure the oscillatory distance dependent nature of the Ruderman-Kittel-Kasuya-Yosida (RKKY)-type magnetic exchange interaction between pairs of individual Co adatoms on Cu(111) by evaluating the Kondo resonance using a non-magnetic tip [11], and on Pt(111) by analyzing magnetization curves using a magnetic tip [12]. In both cases the magnetic coupling was mediated via conduction electrons of the non-magnetic substrate.

While the application of SP-STM and SP-STs, which combine the atomic-resolution capability of STM with spin sensitivity, is limited to probe conducting systems, that is, metallic and semiconducting magnetic nanostructures, MExFM opens up the possibility to extend spin characterization with at least equal precision towards insulators. Proposed by R. WIESENDANGER *et al.* [13] in 1991, the basis of MExFM is to combine the atomic resolution capability of

AFM with the magnetic sensitivity of magnetic force microscopy (MFM) [14], but down to single spin resolution. Applying MExFM, the exchange interaction between a magnetic probe and the single magnetic moments of surfaces is visualized in real-space at length scales that are not accessible by other magnetic sensitive techniques, such as MFM [15] and magnetic resonance force microscopy (MRFM) [16]. Hence, MExFM promises to be a powerful tool to investigate many different types of exchange interactions, such as direct exchange or the prominent RKKY-interaction, either mediated by a substrate, between single molecules, or even single atoms.

The feasibility of MExFM to map spin structures with atomic resolution on insulating surfaces was demonstrated on antiferromagnetic NiO(001) [9, 17]. The key to success, in contrast to previous attempts to perform MExFM [18–22], was the application of an external magnetic field. The field was used to align the magnetic moment of the foremost probe tip apex atoms to enhance the interaction strength between the tip and sample moments. Implementation of the magnetic field paved the way for direct measurement of the magnetic exchange coupling between tip and sample atoms and for the visualization of the rowwise antiferromagnetic contrast between neighbouring rows of Ni atoms.

This work expands upon the first successful application of MExFM towards more systems and more capability. The sample system studied within this work is the first and second atomic layer of iron on tungsten with surface orientation (001). The focus, however, is put on the first atomic iron layer. This layer has been subject to theoretical considerations using density functional theory (DFT) [23], and it has already been studied earlier using SP-STM [24]. It has been found that, due to hybridization with the tungsten substrate, the iron monolayer becomes antiferromagnetic with out-of-plane anisotropy, that is, monolayer Fe atoms arrange in a checkerboard pattern with the moment of every second iron atom pointing either up or down, respectively.

The electronic and magnetic structure of iron is very different to that of the insulating NiO. Namely, the itinerant d -electron spins of the iron ML are delocalized, while, in NiO, the d -electrons are localized at the Ni atoms and couple via superexchange. Therefore, the study of Fe/W(001) with MExFM and the comparison to NiO(001) allows new insights into the contrast mechanism in MExFM. Since no further systems have been investigated successfully with MExFM, and since there is a lack of experiments on insulators which can be compared with SP-STM studies [1, 4, 12, 25–27], it is vital to understand the relevant contrast mechanisms in detail to clarify whether MExFM can be developed into a versatile tool for the analysis and manipulation of atomic scale magnetic structures.

Up to now, MExFM was only utilized in imaging mode. However, its spectroscopic mode, that is, measuring the interaction between probe tip and sample as a function of tip-sample distance, should allow to directly measure the distance dependence of the exchange interaction between single magnetic mo-

ments and a magnetic tip across a vacuum gap. By performing such measurements, as shown here, it is now possible to quantify the magnitude of the exchange interaction for the first time. Hence, this work presents the first successful application of the spectroscopic mode of MExFM, i.e. magnetic exchange force spectroscopy (MExFS), where, in contrast to previous STM-based experiments [11,12], the magnetic exchange interaction is not mediated by a substrate.

After an introduction into the field of atomic magnetism in chapter 2, chapter 3 introduces the basic principles of AFM, where a super-sharp tip probe, mounted at the end of a vibrating cantilever, scans a surface. Within a certain distance between tip and surface, tip-sample interactions lead to a mechanical response of the cantilever vibration. Measuring this response allows for the analysis of the various interaction forces, such as chemical and magnetic exchange force, with a sensitivity of a few pN. A detailed description of the experimental setup and the preparation of Fe/W(001) are found in chapter 4.1. Chapter 5 discusses different properties of the used probes and the sample system, studied with KPFM and MFM.

After characterization of both, probe and sample, the $c(2 \times 2)$ surface magnetic unit cell of the iron monolayer is obtained by MExFM utilizing iron and chromium coated probes, presented in chapter 6. By comparison with theory, the origin of the obtained image contrast of the magnetic moments oriented perpendicular to the surface is revealed. Due to the difference in electronic structure, the corrugation amplitude as obtained on Fe/W(001) is essentially larger than it was observed in the first MExFM experiments performed in 2007 on NiO(001) [17]. Furthermore, chromium coated probes turn out to be much better suited than iron coated probes at small tip-sample separation for stable imaging with atomic and spin resolution. In contrast to the preliminary experiments on NiO(001), first successful MExFM experiments without external magnetic field are performed using chromium coated probes.

Chapter 7 presents the first direct measurement of the magnetic exchange interaction across a vacuum gap by combining magnetic exchange force spectroscopy (MExFS) and three-dimensional force field spectroscopy (3D-FFS). In MExFS, the spin sensitive probe is approached perpendicular to the sample surface and the total interaction potential between tip and sample is measured. Subtracting two curves obtained on oppositely oriented atomic magnetic moments on the surface yields the magnetic exchange interaction between both moments. All non-magnetic interactions are elegantly eliminated using this method, since all surface iron atoms are chemically identical. Comparison with DFT calculations reveals that theory is able to reproduce the measured magnetic exchange energy qualitatively and quantitatively using pyramidal shaped tips. However, some experimental results are not reproducible. They indicate that the used tips are not stable but undergo a strong modification during approach and retraction within single cantilever oscillation cycles. This assumption is supported by a strong variation of the energy dissipated while

keeping the oscillation amplitude of the cantilever constant. A survey on dissipation is presented in chapter 8 and leads to a classification of the used probe tips as either stable or unstable.

Chapter 8 further presents methods for the *in situ* preparation of magnetic sensitive tips. It is shown that, although coated with magnetic material, the tips used in this work do not show spin sensitivity from the beginning. Instead, spontaneously or deliberately induced modifications of the tip apex are needed to eventually perform successful MExFM and MExFS experiments. The findings of the last chapter are of further interest concerning the manipulation of single atoms in MExFM for realizing future atomic spin logic devices [28].

CHAPTER 2

MAGNETISM IN SOLIDS

The background of magnetic phenomena in solids are magnetic moments (spins) of electrons. Spins are able to interact in a cooperative way, which leads to a behavior quite different from what is observed, if magnetic moments are isolated from each other. Spin-coupling via one of the various types of magnetic exchange interaction leads to a surprisingly rich variety of magnetic properties in solids. This chapter shall introduce into the field of magnetism in a rather short and simple way from single magnetic moments to magnetic interactions between ordered moments in a solid. For simplicity, from knowledge base, as one can find it in recent textbooks [29–31], only the parts fundamental to understand this work are discussed. The discussion is focused on the magnetism of the 3d-metals iron and chromium, as they are the matter of interest in this work.

2.1 Atomic Magnetism

The quantum mechanical spin \mathbf{S} and the orbital angular momentum \mathbf{L} of an electron result in a magnetic dipole moment. For the sake of simplicity this atomic magnetic moment will be referred to as ‘spin’ throughout this work¹. In atoms with filled electron shells, the spins are in up/down² pairs and the total magnetic moment of all electrons is zero. Atoms with partially filled shells do have a net magnetic moment, written as a multiple of the *Bohr magneton*

¹Not only electrons have a magnetic moment, but also nuclei can possess a non-zero spin resulting from their angular momentum. However, nuclear magnetic moments are typically a thousand times smaller than electronic moments and are not relevant in the context of this work.

²The spin quantum number s takes the value of $\frac{1}{2}$ for electrons. For the value of the spin angular momentum $m_s\hbar$ this means only two possible values so that $m_s = \pm\frac{1}{2}$. The component of angular momentum along a particular axis is then $\hbar/2$ or $-\hbar/2$, referred to as ‘up’ and ‘down’, respectively.

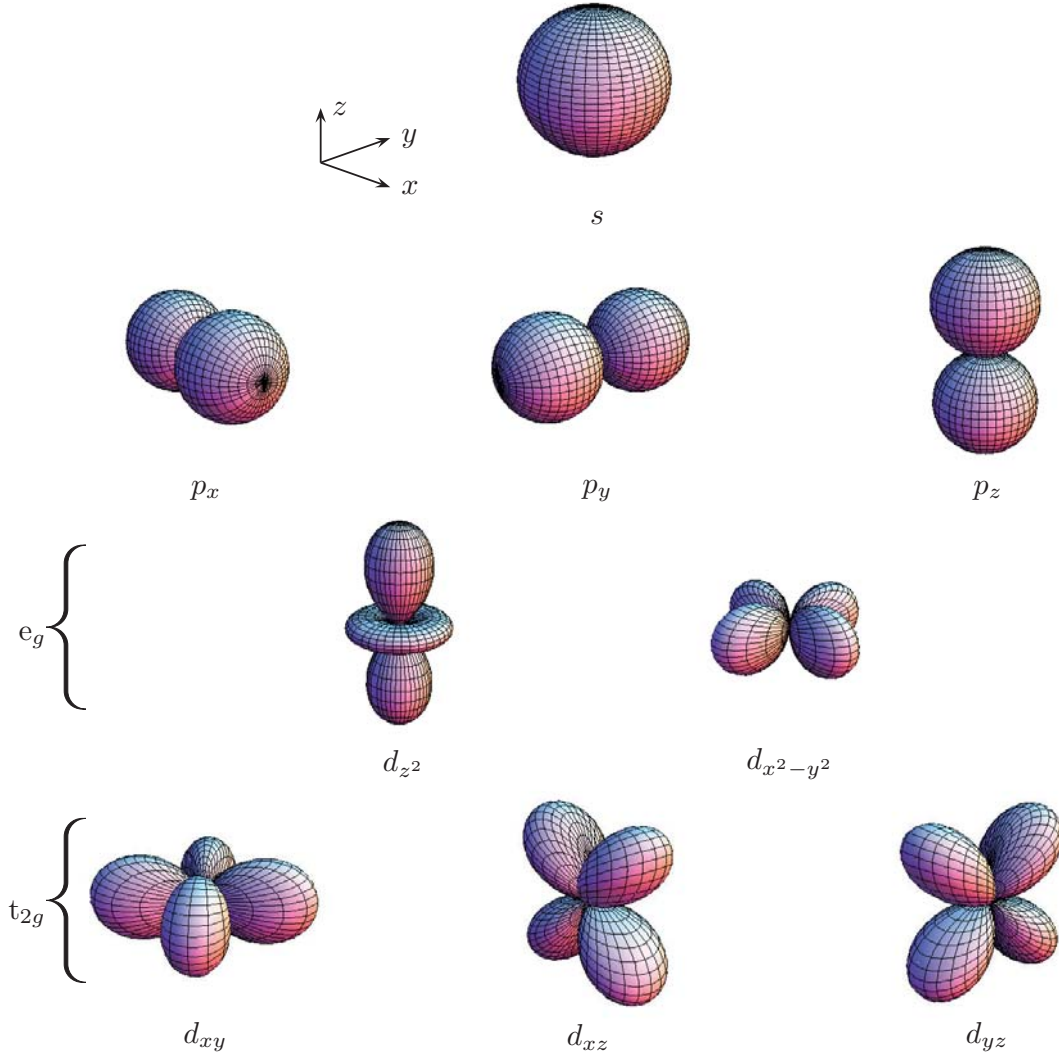


Figure 2.1: Angular electron density distribution of s , p and d orbitals. The d_{z^2} and $d_{x^2-y^2}$ levels are grouped together and called the e_g levels. The d_{xy} , d_{xz} and d_{yz} levels are grouped together and called the t_{2g} levels.

$\mu_B = \frac{e\hbar}{2m}$, which is a convenient unit to describe its magnitude. For bulk iron this value amounts to $2.2\mu_B$ [32,33].

Every solid is formed by atoms, which can either possess zero or a net magnetic moment larger than zero. To be able to characterize the magnetism of a material we have to take into account the cooperation of all magnetic moments carried by the individual atoms forming the solid. These moments and their interaction can depend on the particular environment of each atom, that is, its nature and the position of neighboring atoms, temperature, and external magnetic field. Moreover, the magnetic moments in a solid can be either localized or carried by delocalized conduction (itinerant) electrons that can move nearly free inside the solid.

The atoms of a paramagnet do have a non-zero magnetic moment because of unpaired electrons, but the moments of neighbouring atoms do have a negligible interaction with each other and can be assumed as independent. Without external magnetic field, they can orient themselves randomly in any direction, resulting in a zero net magnetic moment of the paramagnet. On applying a magnetic field, the spins are able to align with the field. This results in a net magnetic moment parallel to the applied field. Hence, paramagnetic materials are attracted to magnetic fields, but the total magnetization will drop to zero in the absence of the applied field.

To be able to consider the interactions between an atom and its immediate surroundings and the magnetic interactions between adjacent atoms in a crystal, it is convenient to review the shapes of the atomic orbitals [29]. Figure 2.1 shows the angular dependences of the electron density of the s , p and d orbitals. While the s orbital is the only one with spherical symmetry, the others have a pronounced angular dependence with zero electron probability density at the nucleus. The d orbitals are divided into two classes, the t_{2g} orbitals, pointing between the x , y and z axes (d_{xy} , d_{xz} and d_{yz} orbitals) and the e_g orbitals which point along these axes (the $d_{z^2-x^2-y^2}$, abbreviated to d_{z^2} , which has lobes pointing along the z axis and the $d_{x^2-y^2}$ with its lobes pointing along the x and y axes).

2.1.1 Exchange Interaction between Atoms

As the magnetic moments have been introduced as magnetic dipoles, the first interaction to be considered between two moments is the magnetic dipole interaction. The magnitude of the interaction of two iron dipoles with $2.2 \mu_B$ each, separated by their nearest neighbour distance in the metallic iron, $r = a/\sqrt{2}$, can be estimated to $\approx (\mu_0 \cdot (2.2\mu_B)^2 / 4\pi r^3) = 30 \mu\text{eV}$ corresponding to 0.35 K. Given that many magnetic materials arrange at much higher temperatures, like iron does up to its Curie temperature of $T_C = 1043 \text{ K}$, this interaction is too weak to account for the ordering. From molecular field theory we can calculate the exchange constant of iron to $J = 11.9 \text{ meV}$ [30], which is a four hundred times larger than the dipolar interaction. The molecular field³ can be estimated to $B_{\text{mf}} = 2100 \text{ T}$. Hence, it is a thousand times bigger than the contribution to a B -field due to the magnetization of iron, $\mu_0 M = 2.2 \text{ T}$. The high Curie temperature and the large internal field of iron can only be explained by exchange effects.

Up to this point all arguments are based on the overlap between orbitals of neighbouring atoms in a solid. Noteworthy, neither direct nor indirect exchange can explain the non-integral value of iron atoms of $2.2 \mu_B$ in the solid

³The molecular field model had been proposed by WEISS in 1907. It assumes that the exchange interaction is nothing more than an internal magnetic field B_{mf} and is related to the exchange interaction characterized by J_{ij} . It can be shown that T_C scales with the strength of the exchange interaction [30].