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Magnetism of a single atom

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Chapter 2

Probing Atomic Spin States

2.1 Spin Excitation Spectroscopy

Magnetism is carried by the spin of electrons. Therefore, it is electrons that might help us in the task at hand: to access the world of atomic scale magnetism and translate its properties into signals that we can understand. In the work described here, we study individual spin states by means of Inelastic Electron Tunneling Spectroscopy (IETS). This technique focuses on systems that have well-defined energy levels and are situated at a tunnel barrier. At low voltages V electrons flow through such a system elastically. But once eV (with e the elementary charge) exceeds the energy required to make an excitation to a higher level, electrons have the additional option of performing this excitation by tunneling inelastically. From this threshold voltage onward, there will be an extra contribution to the current for every voltage increment dV . This results in a step in dI/dV as a function of V , the height of which depends on the excitation probability and the relaxation time of the system.

Previously, IETS was used in an STM geometry to identify vibrational modes of a single C_2H_2 (acetylene) molecule adsorbed onto a Cu(100) surface [16]. In this case the gap between tip and molecule forms the tunnel barrier. The electrons that tunnel inelastically lose their energy by exciting the stretching mode of the C-H bonds. The resulting dI/dV -step has an intrinsic width of only ~ 8 meV which is very low compared to its energy (around 360 meV) and can therefore be considered well-defined.

If IETS is to be employed to study excitations of a single localized spin state rather than vibrational modes, we will refer to the technique as *Spin Excitation Spectroscopy* (SES). Spin excitations, however, occur at much lower energies. This is largely determined by the magnitude of the externally applied magnetic field in which the experiment is conducted. Since that is experimentally limited to a few Tesla, we can expect most SES features to be found below 10 meV. Furthermore, since the spin state is itself an electron state, its coupling to the electrons in the bulk is likely to be much stronger than that of a molecular

vibration mode. The resulting additional lifetime broadening combined with the low excitation energies makes observation of spin excitations unlikely to occur in magnetic atoms that are placed directly onto a metal surface.

For this reason, SES has so far only been performed successfully on atoms that lie on top of a thin insulating layer that separates them from the bulk. Such a layer has to meet several requirements, the most obvious of which is that it should be thin enough to still enable electron tunneling. But exactly how limited the choice is can best be estimated by considering the lifetime of the excited state, which strongly depends on the coupling strength and hence the layer thickness. On the one hand, in order to clearly resolve multiple excited levels their widths should not be much more than ~ 0.1 meV, corresponding to a relaxation rate $\omega_r \lesssim 100$ GHz. But on the other hand, the excitation events have to occur often enough for it to produce an observable effect. So in order to discern the signal on top of a 100 pA background, the inelastic current should be no less than a few pA, or $\omega_r \gtrsim 100$ MHz. Some materials that are known to meet these requirements are Al₂O₃ on NiAl(110) [18] and Cu₂N on Cu(100) [19]. In a similar fashion, NaCl was found to sufficiently decouple molecular orbitals (rather than spin states) of pentacene from both Cu(111) and Cu(100) substrates [28].

2.2 Object of Study

2.2.1 Sample Preparation

The experiments discussed in this thesis, all carried out in the experimental setup described in section 1.4, were performed on Cu₂N/Cu(100). To produce this we started with a clean Cu(100) crystal surface that had been prepared with repeated Ar sputter (1 keV, 2×10^{-6} mbar) and anneal ($\sim 600^\circ\text{C}$) cycles, in a base vacuum of 1×10^{-9} mbar. Next, the sample was sputtered for two minutes at 1 keV in 5×10^{-6} mbar N₂ gas, followed by one minute annealing at $\sim 400^\circ\text{C}$. This results in approx. 5 nm wide Cu₂N islands that are one atomic layer thick and roughly square shaped (fig. 2.1a). Since the conductance of the islands is lower than that of the surrounding bare copper, they appear as 0.14 nm deep depressions (fig. 2.1c). The preference for the square geometry is believed to be the result of a mismatch of the Cu₂N lattice with the underlying Cu(100) [29]. Saturated nitrogen coverage of the copper surface causes the islands to arrange themselves in an array like fashion.

After this we transferred the sample into the STM scanner and left it to cool down to liquid helium temperature before evaporating the magnetic atoms. We evaporated three different metals that all exhibit *d*-shell magnetism: Mn, Fe and Co. What evaporation parameters should be used depends strongly on the geometry and temperature distribution of the vacuum chamber and can only be found by trial and error. We tuned the values such that they resulted in an almost equal dose of the three elements with a combined coverage of two to three atoms per island [30].

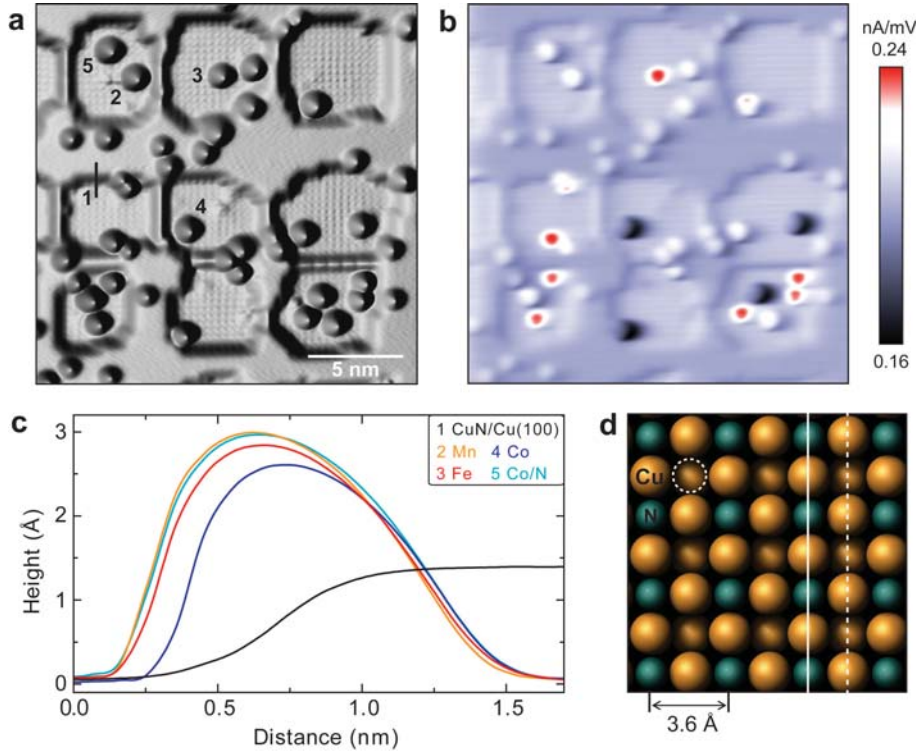


Figure 2.1: (a) STM image (20×20 nm, 1 mV/0.2 nA, 0.5 K) of Mn, Fe and Co atoms on $\text{Cu}_2\text{N}/\text{Cu}(100)$. (b) dI/dV -map taken simultaneously with (a) at $250 \mu\text{V}$ AC-modulation. Fe atoms appear as red and Co as black. Mn atoms and atoms on N sites are white. (c) Height profiles taken from (a), each in vertical direction (upward). (d) Crystal structure of the Cu_2N surface (top view). At the positions of the vacancies (dashed circle) Cu atoms in the second layer can be seen. The solid and dashed lines indicate a N-row and a vacancy-row respectively.

2.2.2 Tip Preparation

The STM tip we used was made out of a pure iridium rod (0.25 mm \varnothing) that was cut to have a somewhat sharp ending. While under vacuum, the tip was taken into field-emission range of a clean Cu sample (1 nA at -300 V tip voltage) and cleaned at $10 \mu\text{A}$ (corresponding to approx. -600 V) until the current became stable (~ 5 minutes, depending on tip cleanliness).

During operation of the STM the tip was further conditioned by indenting (‘poking’) it into the surface. In order to do so we positioned the tip over a region of bare copper in between the Cu_2N islands (at 10 mV/1 nA, i.e. ~ 3 Å tip height), opened the feedback loop and increased the voltage to 2 V. Then we lowered the tip by 10 Å where it stayed for a second after which we reduced the voltage to 1 mV and restored its original height. This procedure could be

repeated until a suitable tip for scanning or atom manipulation (section 2.3.3) was obtained. Hereafter we will refer to the ‘tip’ only as the microscopic object – meaning the last few atoms, presumably Cu – that remains after such poking.

2.3 Experimental Techniques

2.3.1 Measurement Procedure

Unless specified otherwise, all dI/dV -spectra shown in this thesis were taken in single-shot ^3He mode (section 1.4), corresponding to 475 mK indicated on a CERNOXTM thermometer that was mounted directly onto the scanner close to the sample. With the feedback loop closed, the tip was positioned roughly over the center of the atom of interest after which an automated ‘atom-lock’ procedure placed it exactly over the local maximum in the topography. The feedback parameters (typically 10 mV/1 nA, unless stated differently) serve as the quiescent settings for the measurement. Next, the feedback loop was opened and the voltage set to its start-of-sweep value where it stayed for at least one second before commencing the measurement sweep.

We recorded the dI/dV as a function of V by lock-in detection, using an SR830 lock-in amplifier at 200 mV sensitivity, 30 ms integration time. For this purpose a small AC-signal (~ 700 Hz, $50 \mu\text{V}_{\text{rms}}$ unless specified otherwise) was added to the bias voltage. Data was taken with a 16 bit analog-to-digital converter (ADC) for 1024 points in the voltage domain. One sweep (forward and backward) took approx. 2 minutes. After this the tip was relocked onto the atom (with closed feedback at quiescent settings) and the entire process repeated at least once for averaging.

Depending on the sweep rate, the forward and backward scans were slightly offset in voltage with respect to each other. This error was corrected for by shifting them back onto each other after which the forward scan was averaged with its backward counterpart to cancel out potential drift of the tip. During each set of measurements an off-atom spectrum was taken with the same tip on bare Cu or Cu_2N (as discussed above except for the atom-locking) and checked for non-linearities.

2.3.2 Chemical Identification

When working with different kinds of adsorbents simultaneously, one needs a way to tell them apart. As discussed above, vibrational spectroscopy has been used to identify isotope composition within otherwise identical molecules [6, 16, 31]. More recently, chemical identification of Si, Sn and Pb atoms on Si(111) was achieved non-electronically by means of Atomic Force Microscopy (AFM) [32]. In this section we will discuss the identification abilities that SES provides.

Fig. 2.1d shows the crystal structure of Cu_2N on top of Cu(100): a square lattice with a 3.6 \AA wide unit cell containing two Cu atoms and one N atom [29]. The square pattern of this atomic structure is also clearly visible on the islands

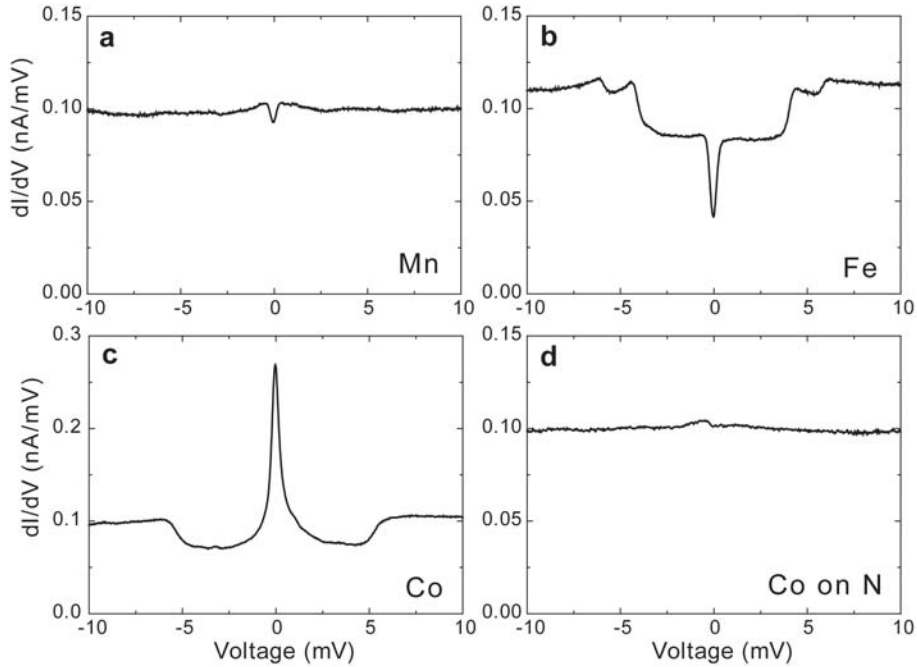


Figure 2.2: Conductance spectra ($50 \mu\text{V}$ modulation, $10 \text{ mV}/1 \text{ nA}$ quiescent, 0.5 K , $B = 0 \text{ T}$) taken on individual Mn (a), Fe (b) and Co (c) atoms located on Cu sites and a Co atom on a N site (d). Note that panel (c) has a different vertical scale.

in the topograph. The empty sites that are bordered by four Cu atoms will be referred to as ‘vacancies’. As a consequence of this arrangement there are rows of N-separated Cu atoms (N-rows) as well as rows of vacancy-separated Cu atoms (v-rows). The thinnest border between two islands (as seen for instance between the center island and its left neighbor in the image) is actually a row of ‘missing’ N atoms. These can be used to exactly locate the N-rows within the island and with that we can in principle pinpoint every lattice site. In section 2.3.3 we will discuss a more practical way to distinguish the N-rows from the v-rows.

Magnetic atoms on Cu_2N can be found either sitting on top of Cu atoms or on top of N atoms. At first sight they all appear to be identical (fig. 2.1a). This is where SES comes in: figures 2.2a–c show spin excitation spectra taken on each of the three species when located on a Cu site. The curves are remarkably different. Evaporating one element at a time enabled us to tell which is which: Mn has a small but distinct dip at zero bias, Fe features three steps on either side and Co can be recognized by a sharp peak around zero and a single step on either side. Spectra taken on other atoms of the same kind are identical except for only slight variations of less than 5% in the positions of the steps. Although the physics behind the exact shapes of these curves will not be discussed until chapters 3 and 4, it is evident that SES provides a way to accurately determine

the chemical identity of these atoms. At least, as long as the atoms are located on the Cu sites: the spectrum in fig. 2.2d was taken on a magnetic atom that sat on a N atom. Here, it shows no features whatsoever (except for a slight bump near the center which was only incidental). This particular atom later turned out to be Co (see section 2.3.3), but the other two elements appear similarly featureless when located on N¹.

Another way to visualize the strength of SES concerning chemical identification is by making a dI/dV -map. When doing this it is tempting to choose the bias voltage V_0 such that there is a high contrast between the atoms in $dI/dV|_{V=V_0}$. But we should not forget that during scanning the feedback loop is closed. The tip height is adjusted to maintain a constant current, or: each dI/dV -curve is scaled to keep its integral until $V = V_0$ constant. Therefore we should be looking for a bias voltage that gives maximum contrast in $(dI/dV)/I|_{V=V_0}$. The map shown in fig. 2.1b, taken at 1 mV, has enough contrast to instantly identify the three different atoms while lying on Cu sites.

The long integration time required to record such a map makes this method not too useful for quick reference. Possibly the fastest way distinguish the atoms is therefore by looking directly at the topography. The profiles of fig. 2.1c (constant current at 1 mV, 0.2 nA) indicate the heights of the three species located on Cu sites: 2.6 Å for Fe, 2.8 Å for Co and 3.0 Å for Mn. But we have to be careful here: as each of them has a different $I(V)$ characteristic because of spin excitations, their relative apparent heights will depend strongly on the bias voltage. It is therefore not surprising that a Co atom on N (atom 5 in fig. 2.1a), being spectroscopically similar, is not distinguishable from Mn on Cu by its ‘height’.

2.3.3 Vertical Atom Manipulation

The technique of controllably repositioning individual atoms with an STM tip can be divided into two categories. Most well-known is the original lateral atom manipulation [2], which is based on the notion that in general it takes less force to move an atom across a surface than it takes to pull the atom off the surface. Here the attractive force of the tip is tuned by adjusting its height and voltage, such that when the tip moves laterally the adatom either slides along smoothly [3, 33] or follows the tip’s path by hopping to stable lattice sites closest to it [34]. This manipulation mode, that stands at the basis of many experiments that involve increasingly complex atomically engineered structures [5, 6, 35], is limited to surfaces that have only little corrugation and therefore not suitable for Cu₂N.

The second category, vertical atom manipulation, uses the ability of an adatom to switch its position from surface to tip and vice versa as first seen for Xe on Ni(110) [36]. This process, occurring during voltage pulses that temporarily increase the current, results from vibrational heating caused by inelastic

¹For Mn on N most of the time the spectrum shows a weak but reproducible signal which we will ignore.

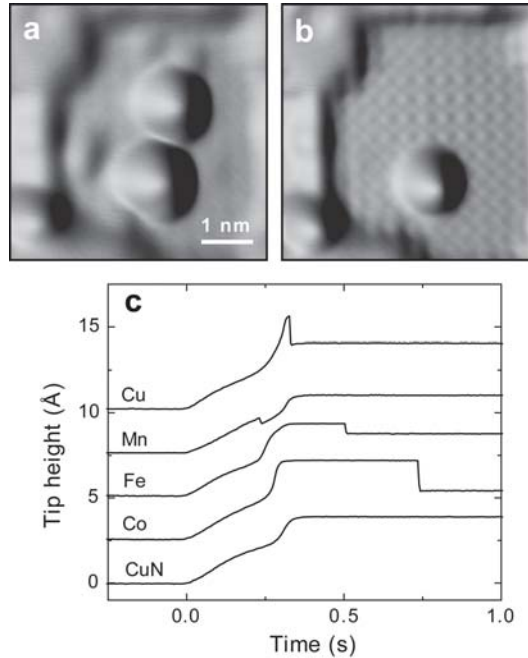


Figure 2.3: Topographs (10 mV/1 nA) taken before (a) and after (b) picking up a Co atom. The lower atom in both images is Mn. (c) Recording of the tip height during hopping. From $t = 0$ the tip voltage is ramped to 1.5 V in about 0.3 s over atoms that are located on N sites. The lower curve shows the same procedure when no adatom is present.

electron tunneling [37]. The direction of atom-transfer is found to be the same as that in which the electrons tunnel, such that by switching the polarity of the voltage pulse one can choose between picking up and dropping off an atom.

Pick Up and Drop Off

On Cu_2N we use the vertical manipulation method as follows. After scanning an image we position the tip over the atom we want to pick up with the feedback loop closed at 10 mV/1 nA. Next the loop is opened and the voltage set to a small value like 1 mV. Now we lower the tip by 2.0 Å and wait for one second, after which we set the tip voltage to +2.0 V for the atom transfer and wait another 200 ms. Finally we reset the tip height to its original value, followed by resetting the voltage. Putting down atoms goes exactly as picking up, the only changes being the stroke length (2.2 Å) and the transfer voltage (−0.5 V).

It should be noted that the success rate of this procedure depends strongly on the microscopic geometry of the tip. However, repeated tip pokes as discussed in section 2.2.2 have reproducibly generated tips that could reliably pick up and drop off one specific atom tens of times in a row. In these cases the ‘loaded’ tip,

having only one apex-atom, could be clearly distinguished from the ‘unloaded’ tip. A good example is shown in figs. 2.3a and b: the topograph produced by the loaded tip is sharp enough to reveal the atomic structure of the Cu_2N , whereas the unloaded tip creates ghost-images of nearby objects as a result of multiple-tip effects.

Although magnetic atoms can be encountered both on Cu and N sites, during a drop-off procedure they always land on a N site. As a result the potential drop-off sites are 3.6 Å apart. This turns out to be sufficient to select the exact landing site before putting down an atom with practically 100% accuracy, provided that the tip is in a good condition for manipulation.

Hopping Atoms

Surprisingly, the N sites are not the lowest energy positions for the adatoms. When being treated with a 1.5 V pulse (from a tip that is at ~ 3 Å distance, corresponding to 10 MΩ contact resistance), the Mn, Fe and Co atoms always hop to one of the four neighboring Cu sites, from where they cannot be removed other than via a pick-up. Whether this change of preferred configuration is caused by a voltage-induced reconstruction of the lattice we do not know. Also, we have not been able to control the direction of hopping. Nonetheless, this property can be very useful in determining an adatom’s exact position: by recording its hopping direction we can tell whether it ended up on a N-row (and v-column) or on a v-row (N-column), lifting the need to ‘count from the edges’ as discussed in section 2.3.2.

Sometimes an adatom hops diagonally instead, towards a vacancy site. This behavior is atom-specifically reproducible (i.e. once an atom has been observed to hop diagonally it will do this repeatedly and exclusively, while other atoms never make diagonal hops) and must therefore be an intrinsic property of the atom. As this happens more often with atoms that fall off the tip after poking (section 2.2.2), we believe that it is specific to Cu adatoms. Additional indications for this hypothesis are that the diagonal-hopping atoms appear smaller in topography than the magnetic adatoms and that they show no spectroscopic feature whatsoever, regardless whether located on a vacancy or a N site.

The hopping behavior provides another way to identify a certain adatom. As shown in fig. 2.3c each atom hops at a slightly different voltage, giving rise to characteristic tip-height traces. Intriguing is the delay involved in Fe and especially Co, which can stay on a N site for several seconds after the tip voltage has reached 1.5 V before hopping.

To summarize, spin excitation spectroscopy has developed into a very precise and powerful tool for studying individual magnetic atoms, and Cu_2N seems to be an ideal surface on which to place those atoms. The stage is set for some beautiful experiments that will be presented in the following three chapters.