Probing magnetic properties of atoms with STM

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The magnetic properties of individual atoms adsorbed on metal and insulating substrates can differ dramatically. While an atom on an insulating substrate can maintain some basic properties such as a free spin, such a free spin is strongly screened by a metal’s conduction electrons when the atom is placed directly on the metal. This screening gives rise to the Kondo effect. Scanning Tunneling Microscopy was used to probe the magnetic properties of atoms adsorbed on metals and thin insulating substrates. We find spin-flip spectroscopy for Mn adsorbed on thin aluminum oxide with no sign of Kondo effect. On the other hand Co atoms on Cu substrates show a clear Kondo resonance around the Fermi energy with no sign of spin-flip spectroscopy. Mn atoms very close to the edge of an aluminum oxide patch can recover the Kondo effect albeit with very small Kondo temperatures because of their relative proximity to the conduction electrons of the underlying metal. [DOI: 10.1380/ejssnt.2006.384]

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I. INTRODUCTION

The Kondo effect is a many-body effect which has been studied in physics and chemistry for many decades. Originally the Kondo effect was observed as a minimum in the resistivity for dilute alloys of magnetic atoms in non-magnetic metals [1]. Later the Kondo effect was seen in tunnel junctions where it can give rise to a sharp increase in the conductivity of the tunnel junction around the Fermi energy [1]. The width of the resonance is characterized by the Kondo temperature, a universal parameter in this many-body effect.

The Scanning Tunneling Microscope (STM) is a versatile tool for the study of the magnetic properties of atoms on surfaces [2]. Especially the development of STM operating at low temperatures has enabled the field of local spectroscopy on individual atoms. With this technique, the Kondo effect was first seen for transition metal and rare earth atoms adsorbed on noble metal surfaces [3, 4].

Inelastic Electron Tunneling Spectroscopy (IETS) was introduced to the world of STM by Ho and coworkers when they studied vibrational excitations of simple molecules adsorbed on noble metal surfaces [5]. In IETS electrons can give off energy to a local excitation which in turn gives rise to a step in the conductivity dI/dV. IETS was recently used by Heinrich et al. to measure the splitting of a magnetic electronic state in externally applied magnetic fields, a direct measurement of the Zeeman energy for a single atom on a surface [6].

This paper is organized as follows. After briefly introducing the experimental setup, we will discuss vibrational spectroscopy of a simple molecule as an introduction to inelastic STM spectroscopy. We will then focus on magnetic spectroscopy with STM, first the Kondo effect on a metal, second the spin-flip spectroscopy on an insulator and finally the Kondo spectroscopy on a thin insulator.

II. EXPERIMENTAL

We used a home-built, ultra-high vacuum STM that reaches a base temperature of 0.6 K by means of a novel single-shot pumped 3He refrigerator. The STM is vibrationally isolated and at the same time thermally coupled to the 3He liquid by suspending the STM chamber directly above the liquid. We liquefied the 3He using the Joule-Thomson effect, obviating the need for a pumped 4He reservoir. Magnetic fields up to \( B = 7 \) T were applied in the plane of the sample. NiAl(110) and Cu(111) samples were prepared in vacuum by repeated sputter/anneal cycles. NiAl samples were then exposed to \( \sim 10 \) Langmuir of O\(_2\) at \( \sim 500 \) K and further annealed at 1200 K. This resulted in the growth of patches of aluminum oxide two layers thick (0.5 nm) interspersed with regions of bare NiAl [7]. Samples were then transferred into the STM and Mn or Co atoms were subsequently evaporated onto the cold surface. Alternatively, CO molecules were dosed on the clean and cold Cu sample by pressurizing the room-temperature vacuum chamber to a typical pressure of \( p = 10^{-6} \) Torr. The differential conductance, \( dI/dV \), was measured using lock-in detection of the tunnel current \( I \) by adding a modulation voltage at 800 Hz to the sample bias voltage \( V \).

III. RESULTS AND DISCUSSION

We will start our experimental results with a brief description of IETS which is best done in the familiar framework of vibrational modes.

A. Vibrational spectroscopy for CO molecules

IETS is characterized by a step in conductance with the higher conductance at larger voltage corresponding to the addition of a channel of conductance when the junction voltage is larger than the energy of the localized mode. Figure 1 shows a \( dI/dV \) spectrum measured with the tip located directly over a CO molecule adsorbed on the on-top site of the Cu(111) surface [8]. The telltale sign for a
vibrational excitation in IETS is the shift of the step in conductivity with the mass (isotope effect, see references) of the molecule [5, 8].

Two vibrational modes are clearly seen: the frustrated translation at $V = 4$ meV ($\mathrm{C}$ and $\mathrm{O}$ moving in plane and in the same direction) and the frustrated rotation at $V = 35$ meV ($\mathrm{C}$ and $\mathrm{O}$ moving in plane and in opposite directions). A third mode at $V = 41$ meV is not seen [9]. The width of the IETS steps is not limited by the temperature ($T = 6$ K) but rather by an intrinsic broadening mechanism, most likely a finite lifetime of the excitation [10].

B. Kondo spectroscopy on metal substrate

A magnetic atom on a metal substrate displays a very rich spectroscopic behavior due to the emergence of the Kondo effect [1]. The conduction electrons partially screen the magnetic moment of the localized atom giving rise to a sharp resonance at the Fermi energy.

Figure 2 shows a topograph of 4 identical Co atoms placed on a Cu(111) substrate. The $dI/dV$ spectrum is measured on top of one of the Co atoms. A slightly asymmetric dip not quite centered at the Fermi energy (zero voltage) is measured [3, 4]. All of these features of the spectrum can be described with a Fano lineshape indicating the interference between different tunneling channels [3, 4, 11]. This spectrum is identical over all 4 atoms indicating that these atoms are not interacting with each other. Even though the temperature is lowered by a factor of 10, the Kondo spectrum is almost unchanged which is primarily due to the fact that both measurement temperatures are significantly lower than the Kondo temperature of $T_K \sim 50$ K [11]. Similarly, a magnetic field of $B = 7$ T has no effect on the spectrum of the Kondo system.

C. Spin-flip spectroscopy on thin insulators

In order to observe the intrinsic magnetic properties of a transitional metal atom on a surface it is necessary to remove that atom from the conduction electrons of the metal sample. This can be achieved by growing a thin insulating film on the metal. This film has to balance two effects: it has to be thick enough to decouple the magnetic atom from the conduction electrons but it has to be thin enough to allow stable operation of the STM.

Aluminum oxide can be grown with relative ease on NiAl(110), see experimental section. A topograph of the partially oxidized NiAl surface, (Fig. 3) shows that the bare metal and the AlO$_x$ oxide regions are atomically flat. However a significant amount of electronic contrast can be seen both on the metal and on the insulator. On NiAl the electronic contrast is caused by standing waves in surface...
state electrons [12]. On the oxide it is caused by the rather large (1.06 nm by 1.79 nm) and complex unit cell of the crystalline oxide [13]. Single Mn atoms are seen as protrusions with an apparent height of 0.13 nm on the bare metal surface and 0.16 nm on the oxide. The density of Mn atoms on the oxide is significantly smaller than on the metal, presumably due to a lower sticking probability and motion along the oxide surface during adsorption.

Open loop spectroscopy was then performed on a Mn atom on oxide (similar to the bump in the right half of the image in Fig. 3) and the results are shown in the lower panel of Fig. 3 for magnetic fields ranging from $B = 0$ to 7 T (only the positive voltage half of the spectrum is shown). A lower conductance is observed at low voltages in magnetic fields with a step up in conductance at about 0.8 meV for the largest field. At zero magnetic field a flat spectrum is observed. The broadening of the step can be attributed to the finite temperature of the sample and the finite AC modulation used in the measurement [6].

From a fit of the measured $dI/dV$ spectra to the well-known theory of the IETS lineshape the center of the step in conductance and hence the energy of the local mode can be determined. In the case of this magnetic spectroscopy one can directly measure the $g$-value in the Zeeman interaction $g_B H$ ($H$ is the external magnetic field, $B$ the Bohr magneton, a fundamental constant). The $g$-value for Mn on AlO$_x$ was found to be $g = 1.88 \pm 0.02$ which is near the value for the free Mn atom of $g = 2.00$ [6].

D. Kondo spectroscopy on thin insulators

It is very instructive to study the emergence of the Kondo effect for Mn atoms on the thin insulator. In the middle of the insulator, no Kondo effect is observed: at zero magnetic field, the $dI/dV$ spectrum is simply flat as can be seen in Fig. 3. However as the Mn atom is moved closer to the edge a tighter coupling of the magnetic moment on the Mn to the metal’s conduction electrons can occur through partially conductive channels at the edge of the insulating island or to close proximity to the metal. In Ref. 6 we measured a Kondo temperature of $T_K \sim 3$ K for an isolated Mn near the edge of the AlO$_x$.

Figure 4 shows an example of Mn near the edge of AlO$_x$, however in this case it is likely that the structure consists of more than 1 Mn atom as it appears higher and wider in the topograph.

As in the case of the isolated Mn atom near the metal [6] the Kondo resonance shows up as a peak in conductance rather than an asymmetric Fano lineshape. The most naive interpretation of the Fano resonance in the Kondo tunneling assumes two channels of conductance: one through the local state and one directly into the continuum. The case of a peak in conductance is then one extreme of this interference behavior, namely exclusively tunneling into the localized state, the Kondo resonance.

The peak height of the Kondo resonance is strongly temperature dependent; it decreases rapidly with increasing temperature. This is a characteristic behavior of Kondo systems [1]. Figure 4 shows in the lower panel how the peak height of the resonance scales as a function of the temperature. The peak height follows a logarithmic behavior until the peak height rolls off to a lower height at lower temperature. Another study is needed to analyze this role-off in more detail.

IV. CONCLUSIONS

In conclusion, we presented low-temperature STM spectroscopy results for a simple molecule on a metal surface and for transition metal atoms on a thin insulator and a metal. The magnetic spectroscopy of Mn on insulator allows a direct measurement of the Zeeman energy for a single Mn atom. With increasing coupling of the Mn or Co magnetic moment to the conduction electrons of the underlying metal the Kondo resonance gathers strength. On the edge of the insulator the Kondo temperatures are small but above the measurement temperature, in the range of a few Kelvin. In contrast, for a transition metal atom directly on a noble metal surface, the Kondo temperature is typically around $T_K = 100$ K.

Acknowledgments

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