Surface Science 630 (2014) 331–336

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Dynamic magnetic excitations in 3d and 4f atoms and clusters

Timofey Balashov [a,*], Toshio Miyamachi [a,b], Tobias Schuh [a], Tobias Märkl [a],
Christopher Bresch [a], Wulf Wulfhekel [a]

[a] *Physikalisches Institut, Karlsruhe Institute of Technology, Wolfgang-Gaede-Str. 1, 76131 Karlsruhe, Germany*
[b] *Institute of Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwashi, Chiba 277-8581, Japan*

ARTICLE INFO

Available online 1 August 2014

Keywords:
Inelastic excitations
Magnetic atoms
Rare-earth atoms
Inelastic tunneling spectroscopy
Magnetic anisotropy

ABSTRACT

Spins in magnetic nanostructures can be excited by an electric current. In the inelastic scattering events, the spin of a tunneling electron provided by a scanning tunneling microscope may be flipped and angular momentum is transferred to the magnetic system. We used this technique to determine magnetic anisotropies and exchange couplings in 3d transition and 4f rare earth metal atoms and clusters on surfaces. Further, we discuss that the magnetic anisotropy, i.e. the zero field splitting, in rare earth atoms requires a fully relativistic description, in which not only the spin of the atoms but also their orbital angular momentum is taken into account. When describing the magnetic anisotropy with the Hamiltonian including all Stevens operators and combining it with spin flip scattering by conduction and tunneling electrons, we find that long spin lifetimes are theoretically expected for specific total angular momenta and crystal field symmetries and show experimental evidence that such a situation is realized in Ho on Pt(111).

1. Introduction

The magnetic states of a free atom with the total angular momentum $\vec{J} = \vec{L} + \vec{S}$ form a degenerate multiplet of $2J+1$ states in vanishing magnetic field $\vec{B}$ due to the continuous rotation symmetry of the Coulomb potential of the core. When preparing the atom in a specific magnetic state, this state is not stable against the slightest interaction of $\vec{J}$ with other systems, e.g. even a measurement of the magnetic state of the atom induces transitions between the magnetic states without the need of energy.

To store magnetic information, the magnetic moment of the atom or cluster can be stabilized by placing it onto a substrate where the electrostatic interaction with the neighboring atoms in combination with the spin–orbit coupling gives rise to magnetic anisotropy splitting the formerly degenerate magnetic states. In the case of an easy axis anisotropy, two degenerate ground states are formed, separated by an energy barrier preventing thermally activated reversal by the interaction with conduction electrons and phonons of the substrate. A decade ago, Gambardella et al. showed that single Co atoms and clusters adsorbed on Pt(111) display a giant magnetic anisotropy of nearly 10 meV with an easy axis normal to the surface plane [1]. Classically, this barrier should prevent thermal reversal at cryogenic temperatures opening up a hysteresis loop of individual atoms, which was experimentally not observed. These measurements were, however, carried out on assemblies of atoms and clusters and the experimental data were interpreted in terms of classical magnetic moments, i.e. magnetization tunneling and other quantum effects were neglected.

With the advent of inelastic spin–flip spectroscopy using scanning tunneling microscopy (STM) it became possible to determine from spin–flip events the magnetic anisotropy of single adatoms [2]. This technique revealed that a classical description of the magnetic moments and their anisotropy on the level of single atoms or clusters is not sufficient to explain the observed signals [3–5]. Instead, a description based on crystal field theory is necessary. Moreover, a fully relativistic description taking into account both the spin and angular moment of the atom and its polarization cloud is needed [6–8].

2. Transition metal atoms and hybridization

In transition metal atoms, the spin–orbit interaction is rather weak but the crystal fields can readily interact with the outer 3d electron orbitals. This has two consequences: First, the orbital momentum L of the adsorbed atom is at least partially quenched so that often only the spin S of the atom is considered in a quantum description of the anisotropy. We note that this is only a rough approximation, as a fraction of the orbital moment might still survive [1] such that the total angular momentum J may differ from S [6]. Second, the anisotropy might be approximated by its lowest order terms (quadratic terms), i.e. out-of-plane and twofold in-plane constants. With these approximations

---

* Corresponding author.
E-mail address: timofey.balashov@kit.edu (T. Balashov).

http://dx.doi.org/10.1016/j.susc.2014.07.025

(skipping terms of fourth order), the effective crystal field Hamiltonian is often written as [3]

$$H = DS_z^2 + E\left(S_x^2 - S_y^2\right) = DS_z^2 + E/2\left(S_+^2 + S_-^2\right), \tag{1}$$

where S_z, S_x, S_y, S_+ and S_- are the z, x, y, raising and lowering operators within the $2S+1$ magnetic states of the atom and D is the uniaxial out-of-plane anisotropy constant. For $E = 0$, $D < 0$ represents an easy axis normal to the plane and $D > 0$ a hard axis normal to the plane. E is a two fold transverse anisotropy. For $D = 0$, E induces an energetic minimum (easy axis) along the x-axis/y-axis for E negative/positive. While E does not vanish in twofold symmetric adsorption sites such as on CuN layers on Co [3], it vanishes in threefold adsorption sites due to symmetry [4,6]. A nice graphical representation of these and higher order crystal field operators can be found elsewhere [9].

In the following, we focus on transition metal atoms adsorbed onto fcc (111) surfaces, i.e. on fcc and hcp threefold symmetric adsorption sites where $E = 0$. Furthermore, we consider only adatoms and clusters with an easy axis of magnetization perpendicular to the sample surface, i.e. $D < 0$. In this case, the simplified Hamiltonian $H = DS_z^2$ results in two ground states with opposite orientations of the magnetic moments perpendicular to the plane separated by the other states in shape of a down-turned parabola. Note that this parabola is linked to the classical uniaxial anisotropy energy $E = -K\cos^2\theta$ by the correspondence principle via $K = -DS^2$, with θ being the angle between the surface normal and the magnetization. The magnetic atom or cluster may be excited from these ground states to one of the first excited states by an inelastic scattering event with the tunneling electrons of the STM. The interaction between the tunneling electron and the localized spin can be described with the following operator

$$V = \vec{S}\cdot\vec{\sigma} = S_z\sigma_z + \frac{1}{2}\left(S_+\sigma_- + S_-\sigma_+\right), \tag{2}$$

where $\vec{\sigma}$ is the spin of the scattering electron [3,10]. Thus, a spin–flip scattering event changes S_z by $\pm 1\hbar$. For a tunneling electron to perform the excitation, it needs at least the energy of the first excited state. Thus, below this energy, inelastic scattering is forbidden and only at a threshold voltage of $eV_{sf} = D((S-1)^2 - S^2)$ an inelastic tunneling channel opens up, which manifests as an antisymmetric peak-dip pair at the sample bias of $\pm V_{sf}$ in the second derivative of the tunneling current I with respect to the sample bias V (d^2I/dV^2). Thus, once V_{sf} is known, the classical uniaxial anisotropy can be determined as $K = eV_{sf}S^2/(2S-1)$ using the correspondence principle [4].

All experimental data has been recorded using two home-built low-temperature STMs. Inelastic tunneling spectra on Fe, Co, Gd and Ho were recorded with a 4 K STM. Spin-polarized STM data on Ho were recorded with a Joule–Thomson cooled STM [11] between 4.2 K and 700 mK. Inelastic tunneling spectra were recorded with an analogue lock-in amplifier at a modulation frequency of ≈16 kHz. A 1:100 voltage divider on the bias voltage was used to reduce electronic noise for all spectra except for Fe. The substrates were cleaned by repeated Ar-ion sputtering and annealing cycles. Prior to deposition of magnetic atoms at cryogenic temperatures, the sample surfaces were checked for cleanliness by STM.

Fig. 1a shows typical inelastic tunneling spectra of single Fe and Co atoms on Pt(111) recorded at 4.3 K using a lock-in detection with an RMS modulation voltage of 3 mV. Peak-dip pairs at 10.25 ± 0.15 and 5.83 ± 0.08 meV were extracted from the spectra. Under the assumption of a pure spin momentum in these atoms ($S = 1$ for Co and $S = 3/2$ for Fe), these values correspond to classical magnetic anisotropy energies of 10.25 and 6.35 meV/atom, respectively [4]. When also taking the orbital angular momenta into account (going from S to J in the Hamiltonian with $J = 2$ for Co), the anisotropy of Co atoms rises to 13.6 meV/atom [6]. For Co atoms, this is in good agreement with X-ray magnetic circular dichroism (XMCD) data [1].

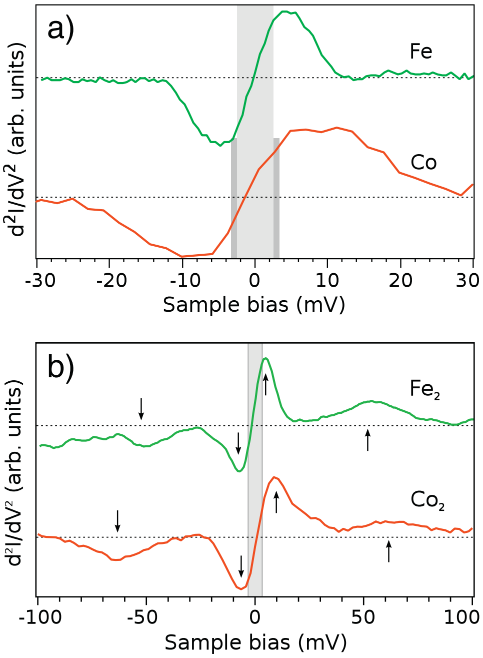

Fig. 1. Spin excitations of adsorbed 3d atoms and clusters on Pt(111): Inelastic tunneling spectra of single Fe and Co atoms (a), as well as Fe and Co dimers (b), respectively. Arrows in (b) indicate the two lowest excitations explained in the text. The lower bound experimental energy resolution is indicated by the light gray area, the upper bound by dark gray area. Measuring conditions were $T = 4.2$ K and 3 mV modulation. The tunneling resistances for stabilizing the tip are a) 1.8 MΩ for Fe and 1 MΩ for Co and b) 1.2 MΩ for Fe_2 and 6.8 MΩ for Co_2.

Recently, inelastic excitations of Fe atoms on Pt(111) were remeasured by Khajetoorians et al. [7] at 300 mK and 40 μV modulation voltage, greatly improving the energy resolution of the spectra. For atoms in fcc positions, an easy axis normal to the plane was found but with an excitation energy of 0.72 meV, i.e. almost an order of magnitude smaller than previously measured at lower energy resolution. These seemingly conflicting results show a dramatic effect of the instrumental resolution on the interpretation of the inelastic spectra. In the general case, the effect of temperature and/or bias modulation amplitude can be modeled as a convolution of the theoretical spectrum at vanishing temperature and modulation with a Gaussian of width $W = \sqrt{(5.4k_BT)^2 + (1.72eU_{mod})^2}$ [12], when neglecting other sources of electronic noise of the instrument. Numerical examples are shown in Fig. 2a. In case the peak-dip distance ($2E_0$) is larger than the width W, the peak positions appear essentially unshifted. When, however, $2E_0$ becomes comparable to W, the peaks appear at positions increasingly shifted from the excitation energy and never appear below ≈ $0.42W$. Alongside that, the peak intensities are reduced making the peaks harder to detect experimentally. In the case of our study at 4.2 K and 3 meV modulation, the broadening is of the order of 5 meV, such that for excitation energies below 2.5 meV a shifted peak can be expected. This threshold is indicated as light gray bars in all inelastic tunneling spectra. As this estimate only takes into account thermal and modulation broadening and neglects other electronic noise sources, we also give a more conservative limit for the energy resolution as dark gray bars. These bars were taken from the full widths at half maximum of observed inelastic excitations at high energy (Gd and Ho data). Thus, these include besides potential electronic noise also broadening due to the lifetime of the states and as such give the upper resolution limit. Note that due to the absence of a voltage divider, this limit is not indicated for the Fe spectra and can potentially be even larger.

In our previous work on Fe, we determined the excitation energy not from the observed peak positions but from fitting a Gaussian peak-dip