

Modification of Magnetic Stability of Co Single Atoms on Pt(111) by Dimer Formation*

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Novel magnetic properties of very small nanostructures have attracted broad interests in the fields of nanoscience and nanotechnology. The magnetic stability of such nanostructures relies on the magnetic anisotropy and magnetization dynamics. These properties were investigated for single Co atoms on Pt(111) using low-temperature scanning tunneling microscopy. The atomic manipulation capabilities of scanning tunneling microscopy allow to extend the study to Co dimers. Information on the magnetic anisotropy and lifetime of magnetically excited states of single atoms and dimers was achieved simultaneously with inelastic tunneling spectroscopy. Manufactured dimers consist of adatoms in nearest-neighbor fcc-hcp sites. For adatoms this close, a strong direct exchange interaction of $14 \text{ meV}/\hbar^2$ was found, much larger than the weak long-range indirect Ruderman-Kittel-Kasuya-Yoshida interaction. [DOI: 10.1380/ejsnt.2011.237]

Keywords: Scanning tunneling microscopy; Scanning tunneling spectroscopies; Adatoms; Clusters

I. INTRODUCTION

The development of nanostructure fabrication techniques has enabled one to control the size of nanostructures on the atomic scale. To utilize such small nanostructures as bits in information storage, the bits have to be magnetically stable. The magnetic stability is governed by the magnetic anisotropy energy (MAE), which keeps their magnetization in one direction against thermal fluctuations. Recent X-ray magnetic circular dichroism (XMCD) study has revealed a giant MAE of 9.3 meV for Co single atoms on Pt(111) [1], raising hope for realizing magnetic bits in future information storage with extremely high density. This technique, however, cannot extract information about the magnetization dynamics, which also plays a crucial role for the magnetic stability of the bits. We present results on the magnetic anisotropy as well as the magnetization dynamics of single atoms and dimers by inelastic tunneling spectroscopy (ITS) using a low-temperature scanning tunneling microscope (STM). The high lateral resolution of STM allows to precisely determine these properties for single atoms. Beside single atoms, small clusters can be artificially created by virtue of the atomic manipulation capabilities of STM [2]. In this study, we show that the lifetime of the collinear excited state in dimers is significantly longer than that of single atoms. Additionally, the inter-atomic exchange was estimated from the non-collinear excitation.

II. EXPERIMENTAL

All the measurements were performed with a home-built low-temperature STM in ultrahigh vacuum ($p < 3 \times 10^{-11} \text{ mbar}$) at 4.3 K . The Pt(111) surface was cleaned by several cycles of Ar^+ sputtering and annealing. A high surface quality was confirmed by STM, which showed no contamination. A small amount of high-purity Co (99.999%) was then deposited onto this surface at 4.3 K by electron beam evaporation.

III. RESULTS AND DISCUSSION

Figure 1(a) shows STM image of Pt(111) surface after Co deposition. Owing to the low temperature deposition, the diffusion of Co atoms is restricted, resulting in isolated atoms. The atoms are then manipulated by the STM (Fig. 1(b)) to create a dimer (Fig. 1(c)). The difference between the single atoms and the dimer can be clearly seen in the STM height profiles, where the height of the atoms ($\sim 160 \text{ pm}$: Fig. 1(d) and 1(e)) is significantly smaller than that of the dimer ($\sim 200 \text{ pm}$: Fig. 1(f)).

The MAEs of small clusters were so far experimentally evaluated using two models. Firstly, the effective spin model is used for inelastic tunneling spectroscopy (ITS) [3]. In this model, only an effective spin S is treated but an orbital momentum L is not considered to evaluate the MAE. In X-ray magnetic circular dichroism (XMCD), often a description of the MAE is used where it is linked to only L (strictly ΔL : difference of L between easy and hard axes) [4]. These two models are not consistent. To come to a consistent description, we here use a recently proposed relativistic model considering the total angular momentum $J = L + S$ [5]. The MAEs

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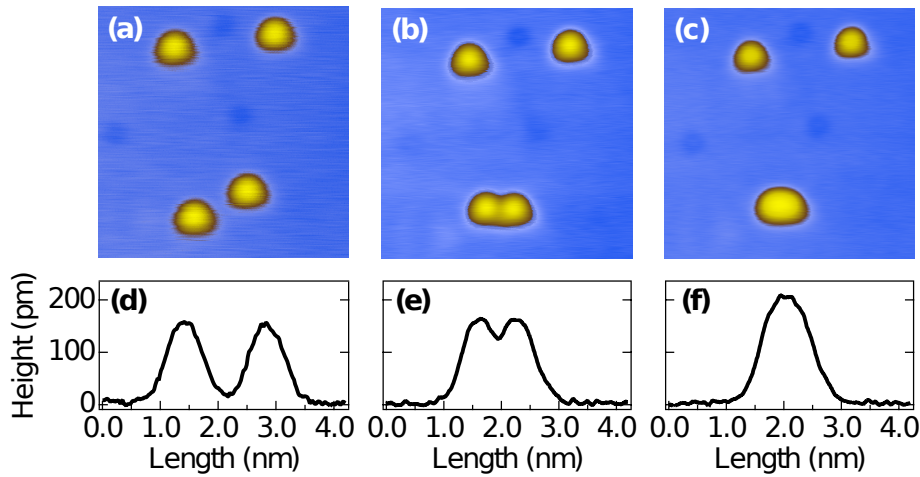


FIG. 1: STM images of (a) Co single atoms, (b) manipulated Co single atoms and (c) a created Co dimer on Pt(111). The sizes of STM images are 6.0 nm \times 6.0 nm. (d), (e) and (f) show the STM height profiles corresponding to (a), (b) and (c).

of the atoms and dimer are determined in this study by detecting the so-called inelastic spin-flip excitations with ITS. In these excitations, the magnetization direction of magnetic atoms or clusters can be changed through the exchange of spin angular momentum with the tunneling electrons. In the relativistic model, the spin-flip of tunneling electrons excites the ground state of magnetic clusters with $J_z = \pm J$ to the state with $J_z = \pm(J-1)$, where the total angular momentum is denoted by J . The inelastic spin-flip excitation energy E_{sf} corresponds to the energy difference between these two states. For the out-of-plane uniaxial system including Co single atoms and clusters on Pt(111) [1], the MAE is described quantum mechanically as DJ_z^2 ($D < 0$) and classically as $K\cos^2\theta$ (θ : the magnetization direction from the surface normal). These descriptions are linked by the corresponding principle $\cos\theta = J_z/J$. Hence, one can estimate the classical MAE K as $E_{sf} \times J^2/(2J-1)$ with known J [5, 6]. E_{sf} is shown as a kink in tunneling current I as a function of the bias voltage V in the low bias regime. However, this feature is usually too weak to be identified [7]. Hence, d^2I/dV^2 showing a peak is recorded in this study. The spin-flip excitation occurs for both tunneling directions, resulting in a positive (negative) peak structure at positive (negative) bias.

The d^2I/dV^2 spectra were recorded for the Co atoms, the dimer and Pt(111) surface of Fig. 1(c). The genuine excitation spectrum of the atom was obtained by subtracting the Pt background spectrum from the Co atom spectrum (Fig. 2(a)). The spectrum is almost anti-symmetric with a minimum and a maximum at the energy of 10.3 meV, reflecting an inelastic excitation. The same procedure gives the E_{sf} of 8.2 meV for the Co dimer on Pt(111) as shown in Fig. 2(b). Assuming $J = 2$ [8] for the atoms and ferromagnetic coupling between them ($J = 4$ for the dimer), K is estimated to be 13.7 and 9.4 meV/atom for the atom and dimer, respectively. It should be noted that the evaluated MAEs with the relativistic models slightly shift from those with the effective spin model [6]. The drop of the MAE per atom by forming a dimer would be attributed to the quenching of the orbital moment according to the broken symmetry with

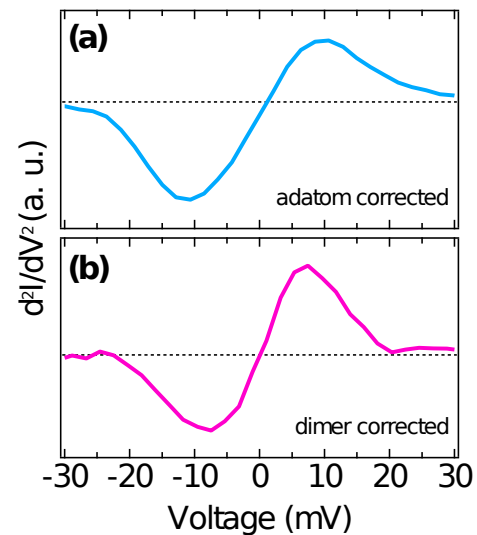


FIG. 2: Background-corrected d^2I/dV^2 spectra of Co (a) atom and (b) dimer on Pt(111).

respect to the surface normal. The obtained values are in good agreement with those by XMCD [1], confirming the magnetic origin of the observed inelastic excitations.

One might notice that not only the excitation energy but also the width of the spectrum differs between the atom and dimer. The intrinsic width of the spectrum W_{in} is linked to the lifetime τ of the excited state via the uncertainty principle $\tau W_{in} \geq \hbar/2$. W_{in} is given by $[W^2 - (5.4kT)^2 - (1.7eV_{mod})^2]^{1/2}$, where W is the measured width, T is the temperature and V_{mod} is the modulation voltage [7]. After subtracting experimental broadening, the lifetimes of the atom and dimer are found to be 20 and 45 fs, respectively. Considering the comparable MAEs of magnetic atoms in our case (metallic structures) and insulating films [9], one can exclude the spin-orbit interaction as the origin of these short lifetimes. This is because the evaluated lifetimes of the order of femtosecond in our case are considerably shorter than those of the order of picosecond or even nanoseconds on insulating films in spite of the fact that the strength of the spin-orbit interaction corresponding to the magnitude of MAE is similar.

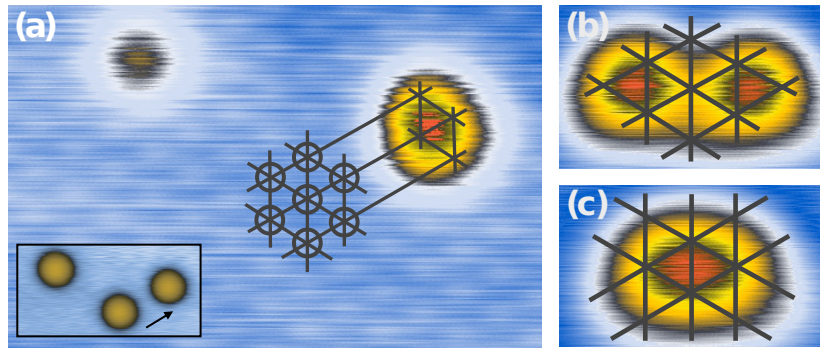


FIG. 3: (a) STM image with atomic resolution of Pt(111) with a Co atom and a dimer. The size of the STM image is $2.3 \text{ nm} \times 3.5 \text{ nm}$. Inset shows the STM image of three Co atoms on Pt(111), where the lower two atoms are manipulated to create a dimer in (a). (b) and (c) show the zoomed STM images of the manipulated Co atoms in Fig. 1(b) and the Co dimer in Fig. 1(c). The sizes of the STM images are $0.9 \text{ nm} \times 1.5 \text{ nm}$. The Pt(111) lattice (black grids) is superimposed on the STM images.

A most likely reason is the hybridization-induced spin-flip scattering of conduction electrons of the Pt substrate by an electron of the Co atom or dimer. Such a scattering transfers $\Delta J_z = \pm 1$ and energy from magnetic impurities to conduction electrons, relaxing the excited state back to ground state efficiently [10, 11]. To first order, the lifetime of an excited state is proportional to its excitation energy. In the case of dimers, however, the lower excitation energy does not fully account for the longer lifetime. Note that the excited dimer state is an entangled state of two spins of the form,

$$\Psi = \sqrt{1/2} |J, J-1\rangle + \sqrt{1/2} |J-1, J\rangle$$

The matrix element for the transition to the ground state by spin-flip scattering for the dimer is a factor of $(1/2)^{-1/2}$ smaller than that for the single atom, resulting in a twice as large lifetime.

The STM study of Co dimers on Cu(100) has revealed that their electronic and magnetic properties are strongly affected by the distance between two atoms [12]. In the case of Pt(111), two types of adsorption sites (fcc and hcp sites) exist, giving rise to more possible configurations of the dimer. The high lateral resolution of STM can determine the exact dimer configuration [13, 14]. Figure 3(a) shows an atomically resolved STM image of Pt(111) with the Co atom and dimer. The dimer is created with the atomic manipulation (inset of Fig. 3(a)). The circles and triangles represent the Pt atoms and adsorption sites. The fcc and hcp sites are distinguishable as triangles pointing right and left. Considering the slightly elongated shape of the dimer, two atoms are found to sit on the adjacent triangles pointing to opposite directions, i.e., nearest-neighbor fcc and hcp sites (Fig. 3(a)). Note that other dimer configurations can be excluded from the direction of the dimer axis and the distance between the two atoms (see Fig. 3(b)). We confirm that the cluster in Fig. 1(c) is a dimer by the increased height and the d^2I/dV^2 spectrum, which differ from those of separate adatoms only when two atoms sit in nearest-neighbor fcc and hcp sites (Fig. 3(c)).

The exchange interaction of the dimer can be investigated with ITS as well. Recently, we have shown that two excited states exist for an Fe dimer on Pt(111), i.e., the collinear and non-collinear excited states [6, 10]. While

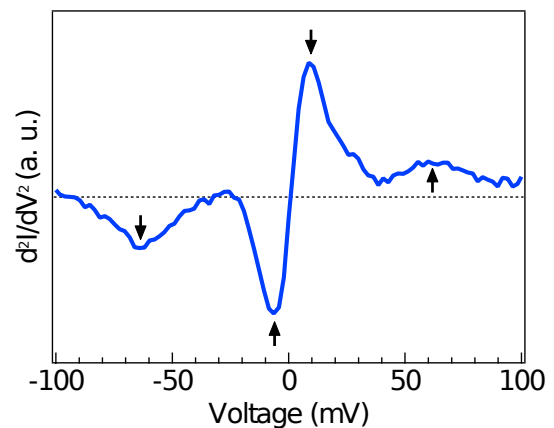


FIG. 4: The d^2I/dV^2 spectrum of a Co dimer showing two inelastic excitations positioned at $\sim \pm 8 \text{ meV}$ and $\sim \pm 60 \text{ meV}$ indicated by arrows.

the collinear state is related to the MAE, the energy cost of the non-collinear state is the sum of the MAE and the exchange energy, which is given by $4J_{ex} - 7D$ in the case of the Co dimer on Pt(111). Since the exchange constant J_{ex} is of the order of tens of meV/\hbar^2 in bulk Co [15], the excitation energy of the non-collinear state can be expected around 100 meV. Such an excitation indeed exists in the d^2I/dV^2 spectrum of the dimer as shown in Fig. 4. The observed excitation energy of $62 \pm 4 \text{ meV}$ gives J_{ex} of $14 \pm 1 \text{ meV}/\hbar^2$, in good agreement with XMCD study [16]. The broad peaks of the non-collinear state result in its extremely short lifetime of $\sim 10 \text{ fs}$. This could be attributed to the doubling of the scattering probability of the non-collinear dimer, which can relax into the ground state (spin-flip relaxation) or into the collinear excited state (non spin-flip relaxation).

IV. CONCLUSION

We have studied the magnetic stability of Co single atoms and dimers on Pt(111) using STM. The information on the MAE and magnetization dynamics of small clusters can be deduced from ITS. In good agreement with XMCD study, the MAE is found to decrease with

the size of the cluster. The estimated short lifetimes of the excited states are explained from efficient electron-electron scattering processes induced by the strong hybridization of the impurity state and the substrate. The difference of the lifetime between the atom and dimer can be interpreted by the entanglement of the excited state. We investigated inter-atomic exchange between nearest-neighbor fcc-hcp atoms and found large exchange interaction of $14 \text{ meV}/\hbar^2$. This exchange is most likely due to the direct exchange, in contrast to the indirect exchange interaction of Ruderman-Kittel-Kasuya-Yoshida (RKKY)

character [17].

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- [1] P. Gambardella, S. Rusponi, M. Veronese, S. S. Dhesi, C. Grazioli, A. Dallmeyer, I. Cabria, R. Zeller, P. H. Dederichs, K. Kern, C. Carbone, and H. Brune, *Science* **300**, 1130 (2003).
 - [2] D. M. Eigler and E. K. Schweizer, *Nature* **344**, 524 (1990).
 - [3] A. J. Heinrich, J. A. Gupta, C. P. Lutz, and D. M. Eigler, *Science* **306**, 466 (2004).
 - [4] P. Bruno, *Phys. Rev. B* **39**, 865 (1989).
 - [5] T. Schuh *et al.*, to be published.
 - [6] T. Balashov, T. Schuh, A. F. Takács, A. Ernst, S. Ostanin, J. Henk, I. Mertig, P. Bruno, T. Miyamachi, S. Suga, and W. Wulfhekel, *Phys. Rev. Lett.* **102**, 257203 (2009).
 - [7] B. C. Stipe, M. A. Razaee, and W. Ho, *Science* **280**, 1732 (1998).
 - [8] A. Ernst (private communication).
 - [9] C. F. Hirjibehedin, C.-Y. Lin, A. F. Otte, M. Ternes, C. P. Lutz, B. A. Jones, and A. J. Heinrich, *Science* **317**, 1199 (2007).
 - [10] T. Schuh, T. Balashov, A. F. Takács, T. Miyamachi, S. Suga, and W. Wulfhekel, *J. Appl. Phys.* **107**, 09E156 (2010).
 - [11] D. L. Mills and P. Lederer, *Phys. Rev.* **160**, 590 (1967).
 - [12] P. Wahl, P. Simon, L. Diekhöner, V. S. Stepanyuk, P. Bruno, M. A. Schneider, and K. Kern, *Phys. Rev. Lett.* **98**, 056601 (2007).
 - [13] Y. Yayon, Xinghua Lu, and M. F. Crommie, *Phys. Rev. B* **73**, 155401 (2006).
 - [14] F. Meier, L. Zhou, J. Wiebe, and R. Wiesendanger, *Science* **320**, 82 (2008).
 - [15] M. Pajda, J. Kudrnovský, I. Turek, V. Drchal, and P. Bruno, *Phys. Rev. B* **64**, 174402 (2001).
 - [16] P. Gambardella, A. Dallmeyer, K. Maiti, M. C. Malagoli, W. Eberhardt, K. Kern, and C. Carbone, *Nature* **416**, 301 (2002).
 - [17] L. Zhou, J. Wiebe, S. Lounis, E. Vedmedenko, F. Meier, S. Blügel, P. H. Dederichs, and R. Wiesendanger, *Nature Physics* **6**, 187 (2010).