Creating pseudo-Kondo resonances by field-induced diffusion of atomic hydrogen

Werner A Hofer¹, Gilberto Teobaldi¹ and Nicolas Lorente²

¹ Surface Science Research Centre, University of Liverpool, Liverpool L69 3BX, UK
² Centro de Investigación en Nanociencia y Nanotecnología (CSIC-ICN), Campus de la Universitat Autonoma de Barcelona, Bellaterra, Barcelona E-08913, Spain

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Abstract

In low-temperature scanning tunneling microscopy (STM) experiments a cerium adatom on Ag(100) possesses two discrete states with significantly different apparent heights. These atomic switches also exhibit a Kondo-like feature in spectroscopy experiments. By extensive theoretical simulations we find that this behavior is due to diffusion of hydrogen from the surface onto the Ce adatom in the presence of the STM tip field. The cerium adatom possesses vibrational modes of very low energy (3–4 meV) and very high efficiency (≥20%), which are due to the large changes of Ce states in the presence of hydrogen. The atomic vibrations lead to a Kondo-like feature at very low bias voltages.

(Some figures in this article are in colour only in the electronic version)

The goal of attaining full control of atomic-scale systems has driven much of the recent research in low-temperature scanning tunneling microscopy and spectroscopy (STM/STS). These experiments at very low temperatures have enhanced our understanding of single-atom contacts [1], Kondo resonances and their signature in the near-contact regime [2], spin-flip excitations of single atoms or atomic chains [3, 4] and vibrational excitations of single molecules [5]. Recently, the changes of electronic properties or atomic configurations due to field excitations were thoroughly investigated in STM experiments [6–8]. The salient feature in these experiments is the ability to modify the systems by varying the position and the field intensity of the STM tip. Hydrogen has only recently come into focus [9–12]; its effect on experimental data so far has not been studied in any great detail.

The aim of this paper is to analyze the ability of manipulating the position of atomic hydrogen at the nanometer scale by the field of an STM tip and to determine its effect in spectroscopy experiments at very low bias voltages. In this range, one typically detects a Kondo resonance for magnetic adatoms [13, 2], which is due to the interaction of a spin state at a magnetic impurity with the conducting electrons of the underlying metal. In recent low-temperature experiments Ternes [14, 15] found that adsorption of cerium atoms at Ag(100) surfaces leads to two different atomic species in low-temperature (4 K) experiments. Most of the Ce adatoms remained stable and showed an apparent height of 200 pm in all STM scans. However, 5–50% of the adatoms were not imaged in a unique fashion but showed two distinct appearances. STM scans below 90 mV bias voltage showed these atoms as large protrusions with an apparent height of 200 pm. Increasing the bias voltage to 90 mV in both polarities abruptly changed the contour of the adatom: in this case a vertical displacement of the STM tip toward the sample surface was observed by about 100 pm (see figures 1(a) and (b)). If the STM tip was positioned above such a switching object, the small feature was retained, even if the bias voltage was reduced after the flip. This apparent stability of the small object allowed comparing STS measurements of the bistable objects in their low-apparent-height state yielded a Fano function, characteristic for a Kondo resonance of magnetic impurities, while the curves remained perfectly flat for the objects in their large state (see figure 1(c)). The q value in the Fano fits was typically very low and, in some cases, even negative. A negative q value seems problematic, since q describes the ratio between the transition probability of direct tunneling and tunneling via a spin-flip process.

New experiments of the Lausanne group [16] confirm the original findings [14] in three important points: (i) the switching of Ce atoms at the silver surface upon crossing a bias threshold of ±100 mV, (ii) the change of the apparent height of the Ce adatom from 200 pm to about 100 pm as the bias is increased beyond the threshold and (iii) a Fano-like...
lineshape of the $dI/dV$ spectrum only for the small object. In addition, the experiments showed one more feature, the shift of the contour maximum laterally by about 100 pm in four perpendicular directions for the reverse switching from small to large. Experiments performed with La and Cr adatoms revealed that the same effect can also be observed for these systems and, furthermore, that the width of the Fano-like curve increases with decreasing mass of the adatom.

It is quite difficult to account for all aspects of the experiments in a consistent manner. Starting with the observed switching it is inconceivable that the field of the STM tip could change the tunneling current by one order of magnitude given the low bias (90 mV) and the low tunneling current (as low as 10 pA). The only other option is field-induced diffusion of atoms along the surface onto the Ce adatom. However, in this case the atomic species cannot usually be visible, because then an additional feature would be observed in one or both appearances of the adatom (see figure 1(a)). The only atomic species which is very rarely visible in STM experiments is hydrogen (for an exception see [10, 11]). Tentatively, one could therefore relate the two different appearances of the adatom to two different positions of atomic hydrogen. The observed Fano-like feature for the small adatom in this case would indicate an electronic effect: either a decreased conductance at zero bias voltage (Kondo resonance) or an increased conductance at a certain bias threshold (atomic vibrations). The $q$ value in a Fano fit of such a feature will be zero.

In figures 2(a)–(e) we show the ground-state configurations of the calculated systems. Single Ce and H adatoms can adsorb at the fourfold hollow site (figures 2(a) and (b)). Coadsorbed hydrogen at Ce is close to a bridge position of the silver surface (figure 2(c)). In addition, we simulated an enlarged unit cell containing Ce and H at separate hollow sites to determine whether the presence of hydrogen on the surface near the Ce adatom affects constant current contours in STM measurements (figure 2(d)). The adsorption energy of hydrogen at Ag(100) is $-2.84$ eV (configuration (b)); coadsorbed at Ce it is smaller and only $-2.43$ eV (configuration (c)). From these results it can be concluded that the ground state of the system is given by Ce and H, adsorbed at fourfold hollow sites. This result seems surprising at first view, because Ce is routinely used in ultra-high-vacuum chambers to remove hydrogen. One would thus expect that the coadsorption of Ce and H should be more favorable. To clarify this important point we also simulated H$_2$, CeH and CeH$_2$ in a vacuum, using the B3LYP functional. Here, we obtained a binding energy of $-4.10$ eV for H$_2$, in good agreement with experiments ($-4.51$ eV [17]), of $-1.68$ eV for CeH, and of $-3.50$ eV for CeH$_2$. For CeH, the corresponding value with standard functionals is $-1.65$ eV. This analysis leads to the unambiguous conclusion that coadsorbed hydrogen at Ce/Ag(100) is not the ground state of the system by $0.41$ eV.

This conclusion is in contrast to the interpretation of the Lausanne group published recently [16], where they infer from experimental data that 'the hydrogen atom is supposed to occupy a fourfold hollow site and the CeH molecule is lying on the surface', corresponding to the model shown in figure 2(e). This model is invalid for two reasons: (i) the total energy of local density contours at the distance determined by single-point calculations including the STM tip. For the tunneling parameters of the experiments (typically $-90$ mV and 100 pA) the maximum distance above the isolated Ce adatom is 5.3 Å. The phonon efficiencies were calculated using the theoretical method developed by Lorente and Persson [23, 31]. The ratio between the sum of elastic and inelastic contributions divided by the normal contribution, i.e. the ground-state density, at a bias-specific voltage gives the efficiency $\eta$ of a vibrational mode [23].
this configuration is higher by about 1.5 eV than the ground state (see figure 2(d)). (ii) In the experiments it was also found that the center of the protrusion for the large object is shifted by about 100 pm after reverse switching. Given that the Ce atom is only displaced by 20 pm from the fourfold hollow position in this upright configuration (figure 2(e)), the observed shift is not in line with the proposed model.

Calculating the total energy of H and CeAg(100) for hydrogen at an adjacent bridge site we find an energy barrier of +0.29 eV. The relative energies for hydrogen diffusion from its ground state at the Ag(100) surface to CeAg(100) are shown in figure 2(e). Figure 2(g) shows charge transfer due to hydrogen coadsorption. We find that CeH leads to the occurrence of a dipole moment in the vertical direction since charge is removed across the surface and coadsorb at Ce. Given that the field for an atomically sharp tip is confined to a radius of less than 1 nm [20], diffusion will occur only in the immediate vicinity of the STM tip and thus the position of the Ce adatom. We may thus conclude that the higher susceptibility of Ce compared to H leads to diffusion of hydrogen along the Ag(100) surface. However, once CeH is formed, the diffusion barrier of 0.29 eV will retain H at Ce, even if the bias voltage is decreased. This conclusion is also in line with experimental data. From the diffusion barrier of 0.29 eV we may finally conclude that a voltage pulse of +0.3 V should be sufficient for H to overcome the barrier and diffuse along the surface. Given the high mobility of H even at low temperature, the observed object will change again at higher positive bias voltages.

To determine the changes of the contours upon coadsorption of hydrogen we performed STM simulations as described in footnote 3. The adatom appears as a bright protrusion with an apparent height of about 2.5 Å (figure 3(b)) and a diameter of about 7 Å, in accordance with experimental images of the (i) large stable and (ii) large unstable atom. Subsequently, we simulated coadsorbed hydrogen at the Ce adatom and determined the ensuing constant density contours. Using the contour value for the bare adatoms, we find that the density contours on top of Ce are now 1.2 Å closer to the surface, in line with experimental findings (figures 3(c) and (d)) [14]. Figure 3(d) was obtained by superimposing the color-coded contours of the two separate simulations, retaining the color coding of the absolute distances in the simulations. The reason for the lower contour is the decrease of density at the position of the Ce adatom due to charge transfer. From the simulations we may thus conclude that the switching behavior of Ce adatoms is due to reversible diffusion and coadsorption of hydrogen. We also simulated the lateral shift of a contour maximum, which should in principle be detectable in STM scans, from an isolated Ce adatom to a system where H is adsorbed at a neighboring hollow site (figures 3(e) and (f)).

Here, we find that the contour is displaced laterally by about

\[ \Delta E = -P_0 E_{tip} - 4\pi \chi_e |E_{tip}|^2. \] (1)

Here, \( P_0 \) is the residual dipole moment of CeH and \( \chi_e \) is the electric susceptibility. Due to the much higher number of valence electrons in Ce it can be expected that \( \chi_e \) is much larger for CeH/Ag(100) than for H/Ag(100). The total charge accumulated in the surface dipole is less than 0.05 electrons; the residual dipole, and consequently the asymmetric changes of total energy with an applied tip field, will be rather small. The dominating term in the energy change should thus be due to induced dipoles (the second term in equation (1)), which is symmetric with the applied field intensity. In this case we expect that a certain threshold intensity in both polarizations will lower the total energy of CeH/Ag(100) enough, so that it becomes more favorable than the ground state Ce + H/Ag(100). In this case hydrogen will diffuse across the surface and coadsorb at Ce. Given that the field for an atomically sharp tip is confined to a radius of less than 1 nm [20], diffusion will occur only in the immediate vicinity of the STM tip and thus the position of the Ce adatom. We may thus conclude that the higher susceptibility of Ce compared to H leads to diffusion of hydrogen along the Ag(100) surface. However, once CeH is formed, the diffusion barrier of 0.29 eV will retain H at Ce, even if the bias voltage is decreased. This conclusion is also in line with experimental data. From the diffusion barrier of 0.29 eV we may finally conclude that a voltage pulse of +0.3 V should be sufficient for H to overcome the barrier and diffuse along the surface. Given the high mobility of H even at low temperature, the observed object will change again at higher positive bias voltages.

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Figure 2. Systems ((a)–(e)), diffusion barrier (f) and charge transfer ((g)–(h)). (a) Ce adatom on Ag(100). (b) H atom adsorbed close to the surface plane of Ag atoms. (c) Ce with coadsorbed H. (d) Ce with H at a neighboring lattice site in an extended unit cell. (e) Model of CeH proposed by Pivetta et al [16]. (f) Relative energy of coadsorbed hydrogen, hydrogen at a neighboring bridge site and hydrogen in a fourfold hollow site. (g) Charge accumulation due to coadsorption of Ce and H on Ag(100).
Figure 3. (a) Diffusion of hydrogen from an Ag lattice site to Ce (see arrow). (b) Constant density contour for Ce adatom and (c) for Ce adatom with coadsorbed hydrogen. (d) The contour changes its vertical distance by more than 100 pm due to diffusion of hydrogen onto Ce. (e) Constant density contour for Ce and H at separate hollow sites of the Ag lattice, calculated with the unit cell figure 2(d). (f) Lateral shift of the contour maximum by 0.1 nm due to hydrogen at a neighboring lattice site. The small cell refers to the calculation of Ce/Ag(100), shown in figure 2(a) (hydrogen: large circle, new contour maximum: small circle). Linescans (f) of the Ce and CeH feature. The linescans refer to the diagonal indicated in frames (b), (c) and (e). Note that the unit cell (figure 2(d)) of the simulation only possesses C1 symmetry; the current contour has been offset so that the position of the Ce atom is at the center of the calculated contour.

Figure 4. Efficiency of two low-energy vibrational excitations for Ce adatoms and coadsorbed hydrogen ((a) and (b)) and La with coadsorbed hydrogen (c). The colormap scale bar indicates the spatially resolved efficiency. The efficiency is positive in all cases. The mode with the highest efficiency, at 3.7 meV (frame (a)), is due to Ce motion constrained by coadsorbed hydrogen (see frame (d)). ((e) and (f)) High-efficiency mode of Ce/H. The inelastic efficiency is centered at the position of the Ce adatom (e) and is substantially larger than the elastic component (f).

0.1 nm due to the presence of hydrogen at a neighboring lattice site. The linescans along the diagonal of the unit cells (see wide lines in frames (b), (c) and (e)) are shown in figure 3(g). Given the symmetry of the system, we expect four equivalent shifts to occur in the experiments. Again, the expectation is verified by experiments [16].

An analysis of the f-states of Ce reveals that, due to their position at the Fermi level, the Kondo temperature should be well below the temperature in the experiments (4 K). In order to model low-energy vibrational excitations, we solved the dynamical matrix for ionic motion of the Ce adatom, the hydrogen adatom and the silver surface layer keeping the other ionic positions fixed. We find low-energy vibrational modes between 3 and 4 meV for both systems, Ce/Ag(100) and CeH/Ag(100). The reason for the very low excitation energy is the very high mass of cerium. The coupling to a vibrational mode of molecules depends on a superposition of elastic and inelastic contributions to the tunneling current, which yield a reduction and an increase in current, respectively [21, 22]. The total efficiency of a vibrational mode thus depends significantly on the superposition of these two contributions [23]. Due to this effect, the total efficiencies for the Ce/Ag(100) system in the low-energy range are close to zero for all calculated vibrational modes. However, this changes drastically for systems with coadsorbed hydrogen. In figures 4(a) and (b) we show the total efficiencies of two low-energy vibrational
modes as a function of position for CeH/Ag(100). At the position of the Ce atom the efficiency in this case is higher than 20% (figure 4(b)) or even 40% (figure 4(a)). Given that the efficiency determined from constant density contours is generally overestimated by a factor of about two, the results for vibrational efficiencies under the condition of hydrogen coadsorption agree very well with the experiments (about 20%, see figure 1(c)).

While the experimental signature of this effect is similar to a Kondo resonance, the physical picture is completely different. In the case of a Kondo resonance the dip at the Fermi level is due to interference of two different pathways for tunneling electrons, generally visible at the Fermi level as a reduction of the measured conductance. In the case of very-low-energy vibrations it is due to the opening of an inelastic pathway near the Fermi level, leading to an increase of the tunneling conductance above a certain threshold.

It is interesting to extend the analysis to hydrogen coadsorption at other metal adatoms. Ce possesses one electron in the 4f state, which is the reason for its rare-earth magnetic properties. Removing this electron, i.e. substituting Ce by La, removes the possibility of a Kondo resonance even at mK temperatures in the experiments. If, therefore, the same pseudo-Kondo resonance due to vibrational excitations can be found at LaH/Ag(100), an experimental observation of this feature would definitely exclude any contribution of magnetic properties. To predict the result of such a measurement we simulated the coadsorption of hydrogen on La/Ag(100). We find indeed a very-low-energy vibration at 3.5 meV, with a vibrational efficiency in the same range of 20–30% (figure 4(c)) as for CeH/Ag(100). Corresponding measurements in Lausanne confirmed this finding [16].

An analysis of the high-efficiency phonon mode at 3.7 meV reveals that it is due to a constrained vibration of cerium. The mode is shown in figure 4(d), with the inelastic and elastic efficiencies in figures 4(e) and (f), respectively. In the higher energy range above 5 meV we found several vibrational modes, both for Ce/Ag(100) and CeH/Ag(100). However, the amplitude of the coupling for vibrational excitations is inversely proportional to the excitation energy [24]. While a low frequency excitation with an efficiency of about 20% can therefore easily be detected at 3–4 meV, the ensuing increase in the dI/dV spectrum will be less than 10% for 8 meV, and below 5% for 16 meV, which corresponds roughly to the detection limit in the experiments. Considering, in addition, that the superposition of elastic and inelastic contributions in most cases makes these vibrations invisible by scanning tunneling spectroscopy, it is reasonable to assume that the higher energy modes will not leave a measurable signature in the experimental scans.

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