

Au and Cu Atoms on NaCl(001): a single-atom based memory device prototype?

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Abstract. We present a first-principle study of gold and copper atoms adsorbed in NaCl(001) surfaces. Motivated by a recent STM experiment on this subject, the electronic and magnetic properties of Au and Cu atoms are investigated, as well as the modifications in these properties under charge injection. Similarities of these systems and the corresponding isolated atom are exploited. A discussion about the possibility of applying the studied systems on high-density memory devices is addressed.

1 Introduction

The recent advances in microscopy techniques have made possible the manipulation of isolated atoms on surfaces [1] and the measurement of their related magnetic properties [1–3]. These advances motivated the appearance of several theoretical [4–8] and experimental [1–3] studies involving adsorption of magnetic atoms on metallic surfaces. Besides the fascinating physics behind these systems, researchers have exploited the possibility of using them as building block of high density memory devices. These studies focus their attention on nanostructures like adatoms, dimers and small clusters built mostly from magnetic atoms belonging to the $3d$ series of the periodic table, deposited in non-magnetic metallic surfaces. As a general result, the theoretical studies have shown that the spin moments of small clusters are enhanced compared to their moments in the bulk phase due the reduction of the coordination [7]. The complex electronic interaction between the orbitals belonging to the adsorbed atom and the surface orbitals leads to effects that can extend quite far from the adsorption site [4,8].

When an atom is adsorbed on a surface, we expected the enhancement of its single atom characteristics compared to its bulk phase or when it is hosted in another material as a substitutional defect. The partial quenching of the adatom orbitals with a metallic substrate gives rise to a myriad of effects, like the long-range interaction between adatoms emphasized above. On the other hand, insulating surfaces like NaCl(001) can enhance even more the single atom character of an adsorbed atom. In fact, spontaneous magnetization in simple metal nanowires was theoretically

predicted for Al chains deposited on NaCl(001) surface [9] and for some free nanowires of simple (non-magnetic) metals [10].

In a recent article, Repp and collaborators [11] observed bi-stable charge states in a single gold atom adsorbed on NaCl. These atoms may be manipulated with STM tips, which enable also the addition or removal of a single electron on the adsorbed atom by inverting the bias voltage. The adsorption site was determined to be on top of Cl^- ions directly from the STM images, which are very sensitive to the Au charge state. First principles calculations (Plane waves + Projector-Augmented-Wave method, PAW) carried out by the authors confirmed the shape of STM images but they did not present any quantitative result about the magnetism of the system. In another article, Repp and collaborators [12] have shown that the STM images of the electronic states of a pentacene molecule adsorbed on NaCl(001) surface present no significant difference from the images obtained from theoretical calculations for a free molecule. This is a strong indication that the NaCl substrate does not exert a strong influence in the molecules adsorbed on top it. Merging these two results [11,12], we can expect a priori that the magnetic moments of the gold atoms on NaCl will be little affected by the substrate.

The experiments carried out by Repp et al. [11,12] suggest the usefulness of insulating substrates for studying the physical properties of adsorbed nanostructures, where the effect of the substrate is expected to be small and, as a consequence, these properties would exhibit values similar to the corresponding isolated atom limit, despite the charge localization in this kind of substrate. Within this picture, adding an extra electron in Au or

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Cu adatoms should, in principle, result in the vanishing of adatom magnetic moment, because the corresponding isolated atoms have a half-filled s valence orbital.

In the present work, we will report first-principles simulations focusing on the modification of the magnetic properties caused by extra charge injection in simple atoms (Au or Cu) adsorbed on NaCl. Quantifying the changes on the magnetic moments of the adsorbed atoms upon charge injection is essential if one wants to exploit the possibility of using this mechanism for producing ultra-high density magnetic memory devices.

2 Computational details

2.1 Formalism

We have performed spin-polarized *ab-initio* density functional theory (DFT) calculations as implemented in the Abinit package [13], with plane wave cutoff energy of 20 Ha and Troullier-Martins pseudopotentials [14]. The calculations were carried out using the local density approximation (LDA) as parameterization for the exchange-correlation potential. Although all results presented here were calculated utilizing Troullier and Martins pseudopotentials [14], available in the Abinit homepage, we checked the reliability of the results testing other pseudopotentials. All pseudopotentials utilized include non-linear core-valence corrections and the Teter-Pade exchange and correlation parameterization in the local spin density approximation (LSDA) [15]. The non-linear core-valence corrections are essential to reproduce correctly the properties of magnetic atoms, like Au and Cu. For the Na and Cl atoms, the inclusion of non-linear core-valence corrections in their pseudopotentials assures the correct reproduction of the charge transfer processes that occur in ionic compounds.

3 Studied structures and results

In reference [11], the application of a bias voltage was possible by depositing the NaCl layers on a Cu(001) substrate, being the metallic substrate itself the electric contact. We do not consider the inclusion of Cu layers below NaCl in our calculations, because their lattice parameters are incommensurate and thus the simulation of Cu/NaCl would require extremely large supercells or would lead to large strain in the system. In fact, the authors in reference [11] worked with a 4% mismatch between the Cu(001) and the NaCl(001) layers. NaCl is a face-centered cubic (FCC) array of anions with an interpenetrating FCC cation lattice (or *vice-versa*), that is, a FCC lattice with 2 atoms in the basis. Each ion is 6-coordinated and has a local octahedral geometry, the lattice parameter being $a = 5.65$ Å.

A previous DFT study on NaCl carried out by Hebenstreit and Scheffler [16] shows that the bulk properties of NaCl, like the equilibrium lattice parameter, can be well reproduced using a cutoff energy of 20 Ha for the expansion of the wave functions in plane waves and 10

k-points to sample the irreducible part of the Brillouin zone (ZB). We take these values as reference for our convergence studies. However, for the system ADATOM + NaCl substrate, the results do not change significantly when increasing the cutoff energy from 15 Ha to 20 Ha. This cutoff was used too to perform the study of the magnetic properties of the isolated Au and Cu atoms, and the values of the magnetization obtained from the calculations are in agreement with the Hund's rule for isolated atoms: $1.0 \mu_B$. Therefore, for all results concerning the ADATOM + NaCl(001) systems presented in the next section we have used the 15 Ha cutoff energy.

4 Results

4.1 First results: searching for the adsorption site of the adatoms

For single atoms adsorbed on NaCl(001), we restrict our studies to Au and Cu adatoms for two reasons: (*i*) to compare with previous experimental work [11] and (*ii*) to study the effects of increasing the atomic number, but keeping the similarity between the electronic configurations. In fact, the atoms belonging to the 1B family (Cu, Ag and Au) have their valence shell composed by fully occupied d orbitals and a singly occupied s orbital, implying that these atoms have a net magnetic moment equal to one Bohr magneton. If one considers an isolated atom, the effect of injection of an electron is clear: the atomic magnetism will disappear.

As pointed out in the previous section, we start our studies without considering metallic planes below the NaCl(001) substrate. The calculations were performed in supercells of dimensions $N_x = N_y = N_z = 2$, in units of NaCl lattice parameters, resulting a 65-atom system: 32 Na and 32 Cl in the NaCl structure, giving 4 NaCl planes, plus the adatom (Cu or Au). Periodic boundary conditions are applied in all directions, but the topmost NaCl plan is separated from the bottom plane by 10 Å vacuum layer, enough to prevent interactions between the planes. In order to mimic an infinite substrate, the atomic positions of the bottom most plane were constrained to be fixed at their bulk values. The lateral dimensions are sufficient large to avoid interactions among the adatom and their periodic images and, on the other hand, being NaCl a non-metallic compound, substrate mediated interactions are not expected to be relevant.

First we determine the most energetically favorable adsorption site of the adatom. Experimentally, it is known that Au adatoms on NaCl(001) adsorb over the Cl atoms [11]. In order to make additional tests on the used pseudopotential, we perform several calculations changing the adsorption position of the Au atom over the surface and allowing for full optimization of all atomic positions, except the bottommost layer, which remained fixed. Our calculations show that the NaCl substrate relaxes relatively little, with most of its atoms essentially keeping the original bulk positions. Taking as energy reference the system with the adatom over a Cl atom, in Figure 1 the total

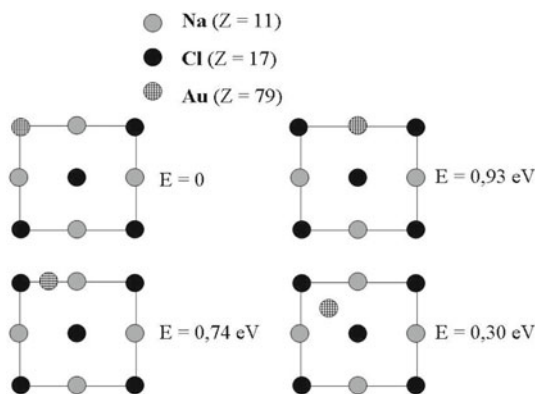


Fig. 1. Adatoms energies as function of the adsorption site.

Table 1. Properties of Au and Cu adatoms on NaCl(001).

Adatom properties			
Adatom	Global charge	Magnetization (μ_B)	d_{ad} (\AA)
Au	0	0.82	2.42
	-1	0.00	3.02
Cu	0	0.96	2.18
	-1	0.08	2.21

energy of the NaCl planes plus adatom is given as a function of the adsorption site, where it can be noticed that the present results yields the correct position of the adsorption site.

4.2 Au and Cu on NaCl(001)

The results concerning the magnetization and the adsorption distance d_{ad} are summarized in Table 1. In all calculations the adatom is positioned atop a Cl surface atom. The magnetization is defined as the difference between the spin up and down densities and d_{ad} is the difference between the final (relaxed) z coordinates of the adatom and the corresponding Cl atom below it (their respective x and y coordinates remain essentially the same). In the charged system, one extra electron is added to the unit cell, and the electronic density is determined self-consistently to minimize the total energy¹. As pointed out in the previous section, neutral adatoms do not disturb significantly the NaCl surface. The most significant change occurs in the Cl atom beneath the adatom, which is pushed downwards into the substrate by approximately 0.2 \AA relative to its four Na nearest neighbor atoms. It is worth noticing that the z coordinates of all Na surface atoms remain practically unaltered in the presence of the neutral adatom. However, when an extra electron is added to the Au/NaCl system, the Cl atom beneath the Au adatom is pushed down even further, and the Na atoms are pulled up, increasing the Na-Cl z -coordinate difference to approximately 0.7 \AA . For the Cu adatom, the the effect of

¹ Actually, the addition of a negative charge in the system is accompanied, in the Abinit code, by an addition of a jellium background of same value and opposite sign, in order to get a neutral cell for the calculation.

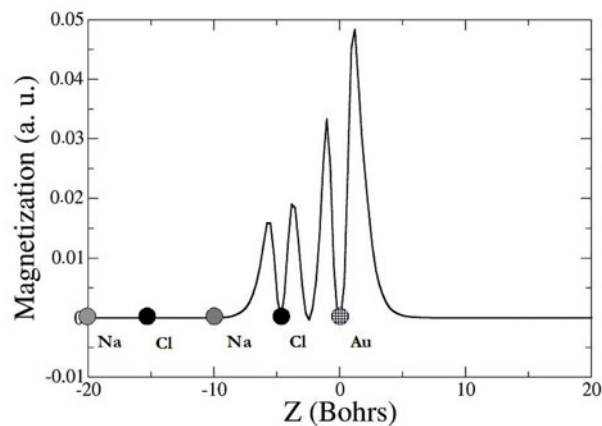


Fig. 2. Magnetization along the z direction in a line containing the adatom site for the Au/NaCl(001) system. The atomic species and their respective localization below the adatom.

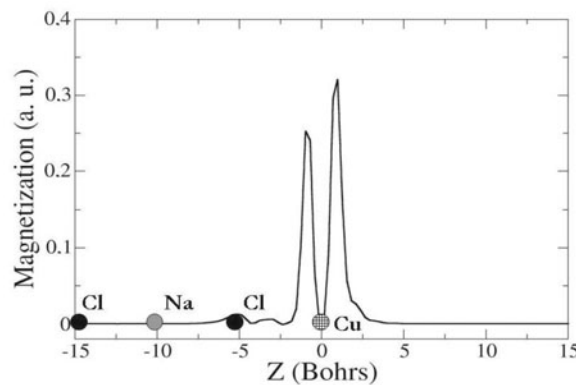


Fig. 3. Magnetization along the z direction in a line containing the adatom site for the Cu/NaCl(001) system. Notice the significant localization of the magnetization around the adatom site.

charge injection is not so strong, but it also leads to an increase of the Na-Cl z -coordinate difference to 0.4 \AA .

The interatomic distance between the adatom and the Cl atom beneath it (d_{ad}) is expected to change when an extra electron is added to the system, particularly if the excess charge localizes in the vicinity of the adatom. The results shown in Table 1 indicates that the extra charge most probably fills the s valence orbital of the Au and Cu adatoms. The calculated values of the magnetization confirm this picture: they are close to $1\mu_B$ for the neutral adatom, and zero for the charged systems. This is precisely what one would expect when the outermost electronic s shell of the noble metal adatom is filled by the extra electron added.

Concerning the spatial distribution of the magnetization, the calculated spin density was plotted along a line in the z direction passing through the adatom site. Figures 2 and 3 show, respectively, the magnetization along this line for the Au and Cu adatoms. Notice the significant concentration of the magnetization around the adatom sites: for the Au adatom the Cl atom below it retains only a small

Table 2. Properties of Au adatoms on NaCl(001)/Au(001) Systems.

Adatom properties			
NaCl planes	Global charge	Magnetization (μ_B)	d_{ad} (\AA)
	0	0.75	2.36
2 planes	-1	0.13	2.58
	0	0.81	2.39
4 planes	-1	0.00	2.62

portion of the magnetization whereas for the Cu adatom the magnetization is concentrated essentially around the adatom site.

Our results confirm the picture that Au and Cu adatoms adsorbed on NaCl(001) behave almost as isolated adatoms, in agreement with what has been reported by Repp et al. [11,12], who verified the weak influence of the NaCl substrate on the structures adsorbed over its surface. Another question needs to be addressed: the influence of the metallic substrate where the NaCl is grown, which serves as contact for the STM measurements.

4.3 Including a metallic substrate below the NaCl(001)

In order to simulate the effect of a metallic contact, a few atomic layers of Au(001) were included as a substrate to the NaCl film. Crystalline Au was chosen because it is possible to construct unit cells nearly commensurate with the NaCl unit cells. Choosing the translation vectors $\mathbf{b}_1 = a(1, 1, 0)$, $\mathbf{b}_2 = a(1, -1, 0)$ and $\mathbf{b}_3 = a(0, 0, 1)$, where a is the Au lattice parameter, a 10-atom unit cell of lattice parameter $a' = \sqrt{2}a = 5.77 \text{ \AA}$ is obtained. Since the lattice parameter of NaCl is 5.65 \AA , there is a relatively small mismatch between the two lattice constants, of $\approx 2\%$. As a consequence, a structure with rather low strain at the interface may be formed. The calculations in this section correspond to supercells of $N_x = N_y = 1$ lateral dimensions. The results from the last section assure the concentration of the magnetization around the adatom site, and then even for those lateral dimensions the interaction among the adatom and their periodic images is small.

Our results are summarized in Table 2 for the Au adatom, and in order to quantify the effect of the substrate, results for 2 and 4 NaCl planes, corresponding to one and two NaCl unit cells along z direction, are presented. Concerning the magnetization, the values in Table 2 suggest a weak interaction between both the NaCl and the metallic substrate and the Au adatom. Notice that for 4 NaCl planes we have essentially the same results for the magnetization presented in the Table 1, where the metallic substrate is absent, showing that the metallic substrate in this case has virtually no effect on the adatom. A similar behavior is obtained for the adsorption

distance d_{ad} : their values systematically approach the corresponding ones listed in Table 1.

5 Conclusions

The results presented in this article show that neutral Au and Cu adatoms on NaCl(001) interact weakly with the ionic substrate, exhibiting magnetization values close to those of the corresponding isolated atoms, with spatial distributions concentrated mainly around the adatoms. The magnetization comes from the unfilled s valence orbital of the adatoms, and its value drops to zero when a single electron is injected in the adatom and fills its s shell. The calculated values of the adsorption distance between the adatom and the Cl atom beneath it (d_{ad}) suggest that the interaction between the adatom and the NaCl substrate does not involve chemical bondings, besides the disturbance caused on the positions of the surface's atoms induced by the charge injection, mainly on the position of the Cl beneath the adatom. The inclusion of a metallic Au substrate supporting the NaCl thin film has little effect in the adatom, and does not change significantly the values of the magnetization and d_{ad} .

Experimental works [11,12] show the possibility of manipulating the adatom charge and magnetization with a STM tip. Our results show that the charge states interact weakly with the substrate and with their periodic images, suggesting the possibility of producing ultra-high density memory devices.

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