

# Magnetism of 3d transition metal atom on Au(110)-(1×2) and Au(111) surfaces

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We calculate the magnetism of 3d transition metals on Au(110)-(1×2) surface and Au(111) surface based on the Density Functional Theory. Our results show that the spin moments of the two-side elements of the 3d group such as Ti, V, Co and Ni decrease greater values than those of the middle elements such as Cr and Mn when they absorb on the surfaces. Our results also show the orbital moments of the left-end elements Ti and V increase if they relax together with surface and decrease for the left-end elements such as Co and Ni. The absorbed 3d atoms in the middle of this group still keep the large spin moment similar to their individual atoms due to the strong electronic correlation. PACS: 75.70.Ak, 75.70.Rf, 75.75.+a, 71.15.Mb

## I. Introduction

The magnetism of nano-structures on a surface is a current interesting topic in material science and surface science due to their potential application to the high-density magnetic recording and the memory devices. The magnetism of a single magnetic atom on a surface is important to understand the magnetism of the material with more complex structures. The reduced dimensionality and the reduced coordination for the surface enhance the magnetism of the surface and the absorbed atoms. The magnetism of the absorbed atoms have been studied in experiments<sup>1-5</sup>, the theoretical model and the density functional theory<sup>6-8</sup>. It is plausible that the structures of materials influence the magnetism of the embedded magnetic atoms. The magnetism of the magnetic atoms also influence the structures of material, such as the large magnetic moment stabilizes the structure of clusters doped with magnetic impurities<sup>9</sup>.

In this work we calculate the magnetism of a single absorbed 3d atom on Au(110)-(1×2) surface which reconstructs from the Au(110) surface by missing Au row every others. The reconstructed surface has one-dimensional troughs along the closed packed [110] direction. It is the winkled the Au(111) surface because the index of the side fact is [111]. As a comparison, we calculate the magnetism of 3d atoms absorbed on the Au(111) surface which has some common properties with the Au(110) missing row surface. Our results show that the spin moments of the two-side elements of the 3d group such as Ti, V, Co and Ni decrease greater values than those of the middle elements such as Cr and Mn when they absorb on the surfaces. Our results also show the orbital moments of the left-end elements Ti and V increase if they relax together with surface and decrease for the left-end elements such as Co and Ni. The absorbed 3d atoms in the middle of this group still keep the large spin moment similar to their individual atoms due to the strong electronic correlation.

## II. Computation Methods

We calculate the magnetism of the 3d transition metal atoms from Ti to Cu which are absorbed on Au(110)-(1×2) and Au(111) surfaces based on the Density Functional Theory<sup>12,13</sup> using the Methods of Projection of Augmentation Wave (PAW)<sup>14</sup> with the plane-wave base-set and the Perdew-Wang's exchanging-correlating potential<sup>15,16</sup>. The program is the VASP code written by the computational materials science group at Vienna university<sup>17-20</sup>. The initial structures are constructed by placing the 3d atom on the hollow sites of the Au(111) and Au(110)-(1×2) surface in the trough (Fig. 1). The initial surface constructs with 28 Au atoms with 4 atomic layers. The atoms in the layer of the slab bottom are unrelaxed. The sizes of the super-cell are (11.523Å×8.148Å×15.52Å). The initial structures are relaxed using the conjugate-gradient Methods with  $\Gamma$  points used as the Brillouin-zone sampling in the corresponding calculations of the electronic structure. Based on the relaxed structures, we calculate the electronic structures of Ni chains using the RMM-DIIS algorithm<sup>17</sup> with the (6×6×1) Monkhorst-Pack grids sampling the Brillouin zone. If the changes of the total energies are smaller than 0.0001eV between two electronic self-consistent (SC) steps the SC-loops break, and 0.001eV between two ion-steps the programs stop. The Wigner-Seize radiuses 1.323Å is set for Ti, V, Cr, Mn 1.302Å for Fe and Co 1.286Å for Ni 1.312Å for Cu to calculate the magnetic moments. The energy cutoffs of plane waves are set to 229.9eV for Ti, V and Cr, 269.9eV for Mn, 267.9eV for Fe, 268.0eV for Co, 269.6eV for Ni, 273.2eV for Cu atoms. We set the Methfessel-Paxton smearing width equal to 0.20eV to accelerate the speed of convergence. We choose the [110] direction as the quanta axis.

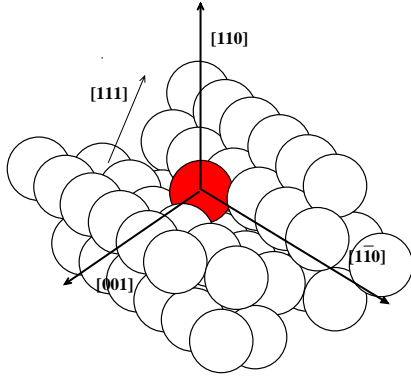


FIG. 1. The schematic diagram of a 3d transition metal atom absorbed on the Au(110)-(1 $\times$ 2) surface. The trough is along the  $[1\bar{1}0]$  direction. The normal of the facet of the trough is the  $[111]$  direction. The adatom absorbs on an hollow site in the trough. The white spheres are the Au atoms of the surface, the gray sphere the absorbed adatom.

### III. Results and Discussion

We calculate the magnetic moments of the absorbed 3d atoms on the Au(110)-(1 $\times$ 2) and the Au(111) surface with the spin-orbit coupling and non-collinear calculations. We also calculate the magnetism of the free standing 3d atoms by removing the surface atoms and keeping the other conditions unchanged. From Fig. 2, we can see that the spin moments reach the maximum in the middle of the group elements. The large spin moment of the absorbed Mn atom is about  $4.163\mu_B$  on the Au(110)-(1 $\times$ 2) surface. We can see from the left panel of the figure that the spin moment of the absorbed Cr atom is the second largest when including the spin-orbit coupling and non-collinear calculation, and almost zero without considering them.

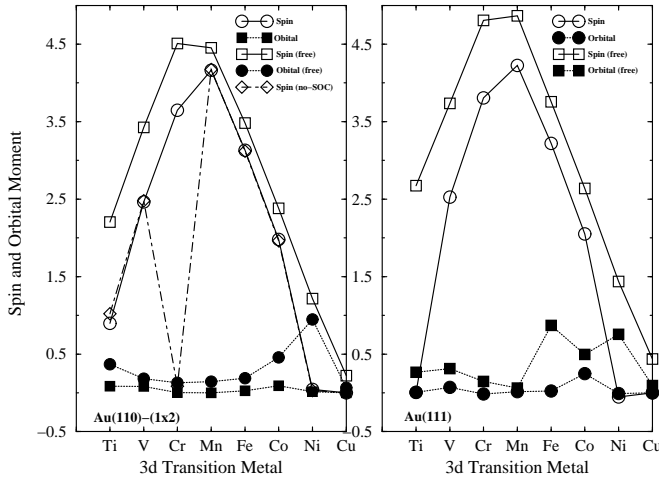


FIG. 2. The spin (solid lines) and orbital (dot lines) moments of the absorbed 3d atoms and the free standing 3d atoms. The left panel shows the results for Au(110)-(1 $\times$ 2) surface, the right panel for the Au(111) surface. The dot-dash line shows the collinear result for Au(110)-(1 $\times$ 2) surface.

Rooting on the Pauli principle and the electronic correlated interaction such as the coulomb interaction, the first Hund rule requires that the spin moments for the free standing 3d atoms reach their maximum. The magnetism of the absorbed 3d atoms are determined not only by the Hund rule but also the hybridization with the quantum states of the surface electrons. The hybridization makes the electrons redistribute in the system, that is, the electrons transfer from the surface to the absorbed atom or vice versa. The redistribution also includes the electron transferring among the s,p,d orbits of the same absorbed atom. Our results show that the spin moments of the absorbed atoms are smaller than those of the free standing atoms (Fig. 2) due to the hybridizing interaction with the surface. The magnetic moments of the absorbed atoms near the two ends of 3d elements group such as Ti,V,Cr,Ni decrease the larger values compared with the middle atoms of the group such as Mn,Fe,Co. Thus our results show that the hybridization with the surface weakens the efficient of the Hund rule. The localized 3d states of the absorbed 3d atoms will be delocalized when they embed in the environments of the extended surface states. The weakened coulomb interaction between electrons in the delocalized states will produce the more double-occupations and decrease the spin moments of the absorbed 3d atoms. Our results also show that the absorbed Cr and Mn atoms are more like the free standing atoms than the other 3d atoms because of the stronger correlation interactions. The decreases of their spin moments are smaller than those of the other 3d atoms. By comparing with the results on the Au(110)-(1 $\times$ 2) surface, we can find that the biggest difference is that the spin moment of the absorbed Ti atom decreases almost to zero when it absorbed on the Au(111) surface. The changes for the spin moments of the absorbed 3d atoms on the Au(111) surface are similar to those on the Au(110)-(1 $\times$ 2) surface when the absorbed atoms change from the left to the right end across the group.

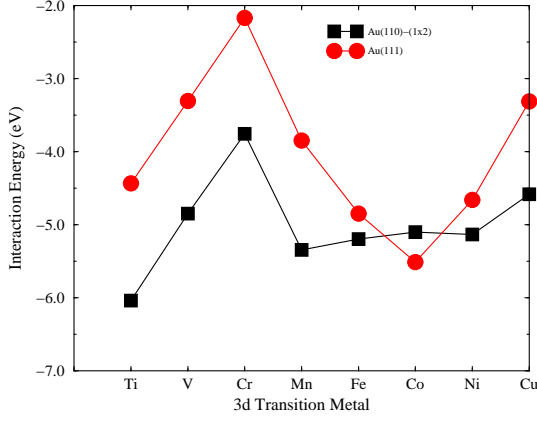


FIG. 3. The interaction energies of between the absorbed 3d atoms and Au(110)-(1 $\times$ 2) (the filled squares) and Au(111) (the filled circles) surface.

Rooting on the spin-orbit coupling and the correlations between electrons, the second rule of Hund requires that the orbit moments of the free standing 3d atoms reach their maximum. Just like the role of the hybridizing interaction for spin moment, the crystal fields in crystal and on surface have important influence on the orbital moments of the absorbed 3d atoms. The crystal fields with cubic symmetry will quench the orbital moment to very small value in bulk crystal due to the lift of the degeneracy of the ground state. For the absorbed atoms on surface the three dimensional cubic symmetries will be broken to two-dimensional cubic symmetries. The lost of the three-dimensional cubic symmetries will make the orbital quenching inefficient. It is plausible that the values of the orbital moments of the absorbed atoms are visible. Thus both the electronic correlations and the crystal field determine the orbital moments of the absorbed 3d atoms. If the electronic correlation is stronger than the crystal fields the orbital moment is large, otherwise small. The absorbed Ti, V, Co atoms have visible orbital moments  $0.086\mu_B$ ,  $0.082\mu_B$  and  $0.092\mu_B$  on the Au(110)-(1 $\times$ 2) surface, and  $0.071\mu_B$  and  $0.247\mu_B$  on the Au(111) surface respectively. The usual exchanged-correlated potentials (LDA or GGA) underestimate the electronic correlations such as the Coulomb correlation and the orbital polarization<sup>21-24</sup>, the calculated orbital moments are generally small compared with experimental values.

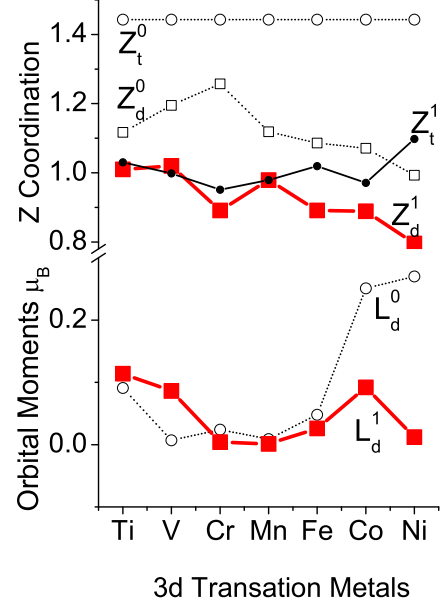


FIG. 4. The effects of relaxation on the orbital moments of the absorbed 3d atoms.  $L_d^0$  and  $L_d^1$  are the orbital moments before and after relaxations illustrated by the short dots line with open circles and the solid line with filled squares.  $Z_d^0$  and  $Z_t^0$  (superscript 0) are the average Z coordinates before relaxations, and  $Z_d^1$  and  $Z_t^1$  (superscript 1) after relaxations. The subscript 'd' represents the absorbed atoms and 't' the top-row atoms of the reconstructed Au(110) surface. The Z coordinates measure from the second surface layer.

Generally, the structures of materials are close related to the magnetism of materials. The smaller atomic nearest neighbor distance leads to the larger exchanged integral  $J$ . The strong magnetic correlation of different atoms enhances the magnetism of the materials. The distances of surface atoms are generally smaller than those in bulk. Thus the magnetism of surface are generally stronger than that in bulk. The supported atoms on the surface is in the environment similar to the surface atoms. Based on the same logic, the supported atoms on the surface have possibly strong magnetism. The interactions between the absorbed 3d atoms and the surface can be measured with the interaction energies  $E_I$  which are equal to the differences of the total energies of 3d atoms absorbed on the surface and the sum of the total energies of the free surface and the free standing 3d atoms. The values of the interaction energies are generally negative. The small absolute values of the interaction energies are indicative of the weak interactions between the absorbed atoms and the surface, otherwise the strong interactions.

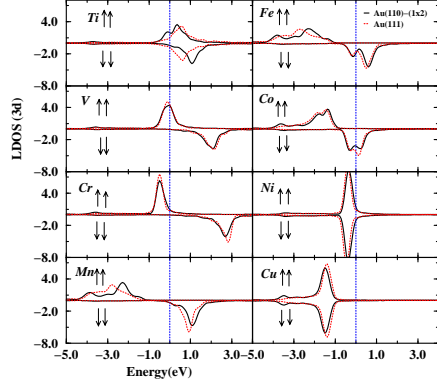


FIG. 5. The 3d densities of state (DOS) for the 3d atoms absorbed on Au(110)-(1×2) (solid lines) and Au(111) (dot lines) surface.

There is a simple rule which can estimate the influence of symmetry on the orbital moments of materials. The broken of global symmetries (Space Group) generally enhances the orbital moments such as the broken from three-dimensional translation symmetries in the bulk to the two-dimensional translation symmetries on the surface makes the orbital quenching uncompleted on the surface. The broken of local symmetries (Point group) generally quenches the orbital moments efficiently because the lost of local symmetries can efficiently lift the degeneracy of the ground state. The interactions between the absorbed atoms and the surface can deform the surface structure. The extra lost of local symmetries will has important influence on the orbital moments of the absorbed atoms which decreases or increases dependent on the degree of the deformation of the surface structure and the species of the absorbed atoms. The local deformation generally quenches the orbital moment. The large deformation with long range which possibly destroys the translational symmetry so it can enhance the orbital moments.

From the interaction energies Fig. 3 we can see that the absorbed Cr atom interacts weakly with the Au(110)-(1×2) and Au(111) surfaces. We can infer that the deformations of the surfaces are small when the Cr atom absorbs on the two surfaces. The small values of orbital moments of the absorbed Cr atoms in our calculation are not related to the crystal field but to its electronic structure. In the individual Cr atom, five 3d-electrons half-fill the 3d states, the total orbital moment is very small. The large spin moment, small orbital moment and the weak interaction with the surface all imply that the absorbed Cr atom is just like an individual atom. We also find from Fig. 3 that the absolute values of the interaction energies on the Au(111) surface are smaller than those on the Au(110)-(1×2) surface for all the 3d atoms except for the Co atom. The interaction favors the more neighbors for every atom below a maximum value about 12

in the bulk environment. The Au(111) surface is compact and doesn't desire to capture more atoms compared with the Au(110)-(1×2) surface. This is why these atoms weakly absorb on the Au(111) surface.

In order to illustrate the effects of the crystal deformations (or the cubic distortions), we also calculate the magnetism of the absorbed 3d atoms on the perfect reconstructed surface. The absorbed 3d atoms still modify their positions to reach their stable positions on the surface, although the surface atoms are fixed. By comparing with the pervious results including the surface relaxations, we find that the relaxations of the surface structure generally decrease the orbital moments of the absorbed 3d atoms except for the absorbed V and Ti atoms. The changes of the orbital moments in response to the relaxations are closely related to the changes of the depth of the 3d atoms in the trough of the reconstructed Au(110) surface. The absorbed atoms are deeper in the trough, their orbital moments are quenched to smaller values due to the stronger crystal field. The absorbed V atom evaluates above the top row of the trough after the relaxation and its orbital moment enhances, which opposes to the orbital quenching for the other 3d atoms except for the absorbed Ti atom. This is due to the weaker crystal field above the surface than that in the trough. The absorbed Ti atom has almost the same height as that of the top row after the relaxation, its orbital moment slightly increases. Thus our results indicate that the surface relaxation decreases the orbital moments of the absorbed 3d atoms with the excess half-filled 3d states and increases the orbital moments of the absorbed atoms with less half-filled 3d states.

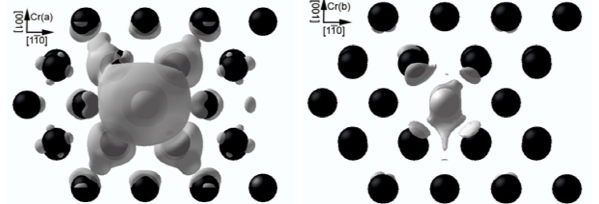


FIG. 6. The magnetic density of the absorbed Cr atom which is the components along the quanta axis [110] and perpendicular to the surface. The magnetic density is defined as  $\vec{m}(r) = \sum_{\alpha\beta} n^{\alpha\beta} \cdot \vec{\sigma}_{\alpha\beta}$ ,  $\vec{\sigma}$  is the Pauli Matrix. The figure shows the component along the quanta axis [110]. The contour values are  $0.002/\text{\AA}^3$  for the left panel and  $-0.002/\text{\AA}^3$  for the right panel

The 3d densities of states of the absorbed 3d atoms on the two surfaces are shown in Fig. 5. From this figure, the large spans between the spin-up and spin-down peaks imply the large electronic correlations for the Mn, and Cr, and Fe atoms. This is why the magnetism of the absorbed Cr, Mn, Fe atoms are similar to the magnetism of their individual atoms. The 3d DOS of the absorbed Fe has more contributions to the total DOS at Fermi energies. The electrons near Fermi energy from

a glue which sticks atoms in bulk together<sup>25,26</sup> and also dominates the electron transports of materials. The absorbed Ti, V, Fe and Co atoms with large 3d DOS at the Fermi energies all have strong interactions based on the calculations of the interaction energies. On the contrary, the absorbed Mn, Cr, Cu atoms with small 3d DOS at the Fermi energies have weak interactions with the two surfaces. Our results also show that the 3d DOS at Fermi energies are also closely related the orbital moments of the absorbed 3d atoms. The absorbed Ti, V, Co atoms on the Au(110)-(1×2) surface and V, Co atoms on the Au(111) surface with large 3d DOS at the Fermi energies have large orbital moments. We get the same arguments on the magnetism of Ni<sub>n</sub> (n=1-5) chains in our parallel research<sup>27</sup>. It is valuable to note that we can not infer the large orbital moment for the absorbed Fe atom based on our results. This is possible that at the current stage, it is difficult to calculate the orbital moment exactly based on the density functional theory with LDA or GGA approximations. It can be rescued by the introductions of the orbital-polarization term<sup>21</sup> or the correction of the on-site coulomb energy U.

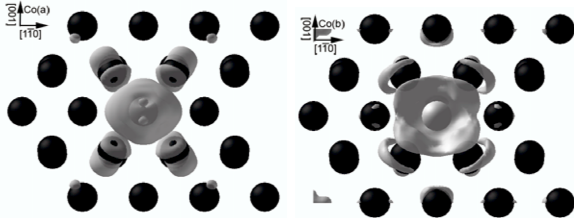


FIG. 7. The magnetic density of the absorbed Co atom which is the components along the quanta axis [110] and perpendicular to the surface. The magnetic density is defined as  $\vec{m}(r) = \sum_{\alpha\beta} n^{\alpha\beta} \cdot \vec{\sigma}_{\alpha\beta}$ ,  $\vec{\sigma}$  is the Pauli Matrix. The figure shows the component along the quanta axis. The contour values are  $0.002/\text{\AA}^3$  for the left panel and  $-0.002/\text{\AA}^3$  for the right panel

The STM<sup>11</sup> experiments of 3d atoms absorbing on Au(111) surface show that the elements (Ti, Co, Ni) near the two ends of the group have obviously Kondo resonances and for the middle elements not. The intense of STM spectrums at zero bias voltage are proportional to the local density of state (LDOS) at the Fermi energy. The STM experiments indicate the large LDOS near the Fermi energy for the absorbed Ti, Co and Ni atoms. The density functional theory with the LDA or GGA exchanged-correlation potential generally doesn't completely include the Kondo correlation. The Kondo resonance and Kondo effects origin from the screening of the conducting electrons on the local spin<sup>28,29</sup>. The ground state is the Kondo single state with total zero spin<sup>30</sup>. Thus, the screening effect is an important aspect for the Kondo resonance. Although the calculation of DFT can not show the completely screening to the local spin, we still hope to find the partial screening effect based on the DFT theory. Fig. 7 shows the partial screening effect to the local spin for the Co atom. From

Fig. 6 the screening effect for the Cr atom is weak, the experiment also don't show the Kondo resonance. In our calculations the large spin moment, the small orbital moment and the small interaction energy for the absorbed Cr atom show that the absorbed Cr atom likes an individual atom whose interactions with the surfaces and the screening of the conducting electrons to its local spin are weak. The middle elements of this group have large magnetic moments which need more electrons screening them to form the spin single state. The large re-organization of electrons is energetically unfavorable and prevents the formation of Kondo resonance.

## IV. Conclusion

In conclusion, we calculate the magnetism of 3d transition metals on Au(110)-(1×2) surface and Au(111) surface based on the Density Functional Theory with Project Argument Wave Methods and plane-wave base-sets. Our results show that the spin moments of the two-side elements of the 3d group such as Ti, V, Co and Ni decrease greater values than those of the middle elements such as Cr and Mn when they absorb on the surfaces. Our results also show the orbital moments of the left-end elements Ti and V increase if they relax together with surface and decrease for the left-end elements such as Co and Ni. The absorbed 3d atoms in the middle of this group still keep the large spin moment similar to their individual atoms due to the strong electronic correlation.

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