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A first-principles study of the magnetism and electronic structure of Cr clusters supported on a Au(111) surface

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Abstract

We have studied clusters of Cr on a Au(111) surface by means of a first-principles method that allows for non-collinear magnetic ordering. We find that the Cr atoms possess a large magnetic moment, of order $4 \mu_B$ /atom, and have essentially antiferromagnetic interatomic exchange interactions. This leads to collinear magnetic arrangements in linear clusters (dimers and trimers) and non-collinear ordering in clusters where antiferromagnetism becomes frustrated, such as in triangular geometries.

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

1. Introduction

The electronic structure and magnetic properties of clusters supported on top of a surface, or buried deeper within the surface, are of great interest, not only because of their technological applications, but also due to the fact that such systems challenge our understanding of magnetism in general. It is well known that magnetism is a property that is particularly sensitive to the details of the atomic environment. Therefore, the possibility of novel magnetic behaviour in these systems has been extensively explored in the last few years. For instance, a magnetic phenomenon that has recently attracted attention is the possibility for magnetic cluster atoms to couple their spin moments in a non-collinear way. Several theoretical studies have addressed this question, investigating non-collinear nanostructures on ferromagnetic [1, 2] and non-magnetic surfaces [3–8]. In particular, regarding non-magnetic substrates, *ab initio* electronic structure calculations have been employed to study the magnetic properties of V, Cr, Mn and Fe clusters of various sizes and shapes on a Cu(111) surface [3–5]. The Fe clusters studied are found to order ferromagnetically regardless of the cluster geometry. For V, Mn and Cr clusters, antiferromagnetic exchange interactions between nearest neighbours are found to cause either collinear antiferromagnetic ordering or non-collinear ordering. The

non-collinear ordering occurs when the cluster geometry is such that an antiferromagnetic arrangement becomes frustrated, and this is in particular true for a triangular cluster with equal bond lengths. In this paper, we determine the complex magnetism of Cr clusters (monomers, dimers and trimers) deposited on a Au(111) surface, making use of the real-space linear muffin-tin orbital method (RS-LMTO-ASA), a first-principles order- N method that has recently been extended to the treatment of non-collinear magnetism [3]. Since the Au(111) surface has a triangular geometry, the expected antiferromagnetic interaction between Cr atoms is likely to result in non-collinear spin arrangements for some of the clusters. Therefore it is of importance to study magnetic Cr clusters, allowing for non-collinear magnetic structures, and this is what we explore in the present paper. Finally, we note that recent experimental results for Cr clusters in Au(111) suggest that the Kondo effect may be present for some of these systems [9].

The next section gives a brief description of the theoretical method used in our study. In section 3 we then present the results for the electronic structure and the magnetic properties of various Cr cluster configurations, including geometries in which the clusters are localized on and in the Au(111) surfaces, as well as in the sub-surface layer. For Cr dimers we have also investigated the magnetic properties as a function of the distance between the Cr atoms. Finally, we give our conclusions in section 4.

2. Computational details

The self-consistent non-collinear real-space method used in this study is based on the Haydock recursion method [10] and the LMTO-ASA technique [11]. The method is essentially an extension of the RS-LMTO-ASA method [12, 13], generalized to handle non-collinear arrangements of the magnetic moments. Details of the Hamiltonian and the procedure used in the implementation of the non-collinear approach can be found elsewhere [3–5]. As in the case of the collinear RS-LMTO-ASA, all calculations are fully self-consistent and the spin densities are treated within the local spin density approximation (LSDA) [14]. Structural relaxation has not been included in this study, so surface and cluster sites have been placed on a regular fcc lattice with the experimental lattice parameter of Au. The clean Au(111) surface was modelled by a large (>5000) slab of atoms, and the continued fraction that occurs in the recursion method was terminated with the Beer–Pettifor [15] terminator after 30 recursion levels. Relativistic effects, very important in the case of Au, were included within the scalar relativistic approximation. It is well known that orbital moments can be very significant for some of the 3d elements on, and even in, Cu, Ag and Au [13, 16, 17] hosts. The method used here, being an extension of the RS-LMTO-ASA, can in principle treat spin–orbit coupling and orbital moments. However, due to a reminiscence of Hund’s rule [17], the orbital moments of Cr sites in Cu, Ag and Au or on their surfaces are expected to be small, and all existing calculations in the literature confirm this fact. Here, we have calculated the orbital moment at the Cr sites for a few of the clusters. These orbital moments (of order of $0.02 \mu_B/\text{atom}$) were negligible when compared to the spin moment of Cr and not likely to significantly influence the magnetic structures of the Cr clusters studied. With this in mind, orbital moments were not considered in the present calculations.

3. Results

3.1. Cr atoms

In figure 1 we show the geometry of a single Cr atom (a) on a Au(111) surface, (b) in the first surface layer and (c) in the first sub-surface layer. From the figure one can see that the

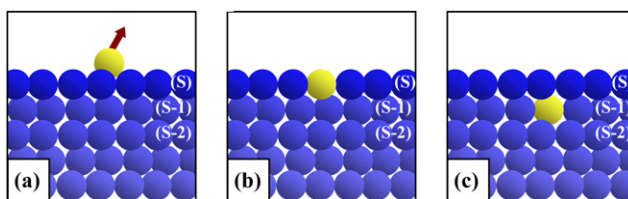


Figure 1. Geometry of a single Cr atom (a) on a Au(111) surface, (b) within the first surface layer (S) and in the sub-surface layer (S-1). The Au atoms are shown in blue (dark grey) and the Cr atoms in yellow (light grey).

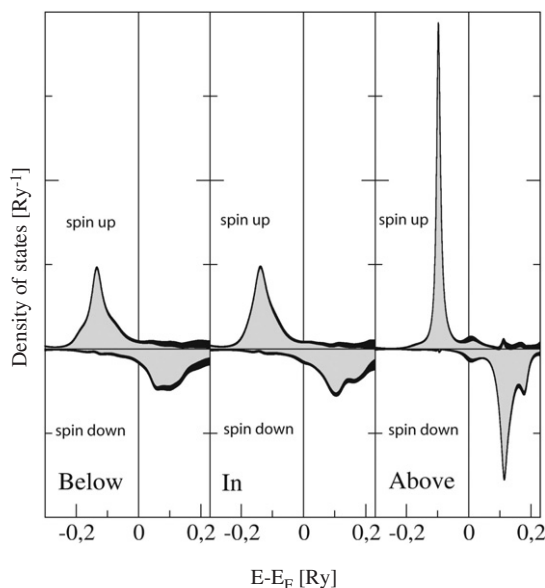


Figure 2. Local density of states (LDOS) of atomic Cr. The LDOS is for a cluster located on top of a Au(111) surface (right panel), in the first surface layer (middle panel) and in the sub-surface layer (left panel). The total LDOS is shown in black and the 3d partial LDOS in grey. The Fermi energy is at zero.

top, surface and subsurface Cr sites have very different local environments with 3, 9 and 12 Au first neighbours, respectively. The magnetic moment of the Cr atom in configuration (a) is $4.31 \mu_B/\text{atom}$, in (b) it is $3.85 \mu_B/\text{atom}$ and in (c) the Cr atom has a moment of $3.59 \mu_B/\text{atom}$. The very large Cr moments are dominated by the contribution from the 3d orbitals, but small contributions of order of $0.03 \mu_B/\text{atom}$ from 4s and 4p states are also present. We note that the moment of the Cr sites gets smaller as the Cr atom is buried deeper within the Au host. This trend is the result of an increase of the hybridization, and therefore of the resonance width of the Cr 3d states, due to the increased number of Au neighbours. The same trend for the local moments, the correlation with the hybridization, as well as the relevance of the number of neighbours, has been observed for Co atoms in Cu(001), as discussed in detail in [21]. To further analyse this behaviour, we show in figure 2 the calculated local density of states (LDOS) for the three geometries shown in figure 1. It can be seen that Cr atoms atop the Au surface have extremely sharp resonances, which get broader when the Cr atoms are in the surface or sub-surface layers. We note that the very sharp LDOS of Cr adatoms on Au surfaces leads to values of the moment close to saturation in these systems. Therefore, it is no surprise that our

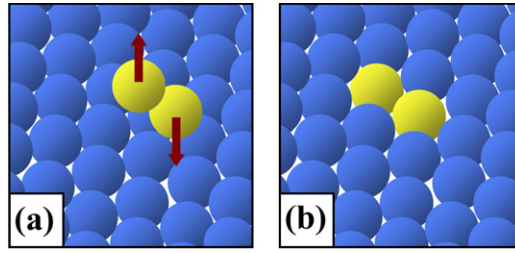


Figure 3. Geometry of the Cr dimer. The dimer is located on a Au(111) surface (a) or within the first surface layer (b). The Au atoms are shown in blue (dark grey) and the Cr atoms in yellow (light grey).

moment of $4.3 \mu_B$ for the adatom (configuration (a)) is in good agreement not only with the value of $3.93 \mu_B$ obtained by Gotsis *et al* [6] for the Cr adatom on Au(111), but also with the value of $4.3 \mu_B$ reported by Cabria *et al* [18], for the Cr adatom on the Au(001) surface. The slightly smaller value of the magnetic moment of the Cr adatom in [6] is probably due the fact that lattice relaxation was included there, bringing the Cr site closer to the Au neighbours in those calculations. The moment of $3.59 \mu_B$ for the Cr atom in the sub-surface layer, with 12 Au first neighbours (configuration (c)), is already very similar to the moment of $3.64 \mu_B$ obtained using a fully relativistic approach for Cr impurities in bulk Au [17].

3.2. Cr dimers

Here, we investigate the magnetism and the nature of the exchange interactions when a Cr dimer is placed on top of the Au(111) surface or within the surface layer. We also analyse the magnetic properties as a function of distance between the Cr atoms. The geometry of the Cr dimers in the first-neighbour (NN) configuration is given in figure 3. We note that the position of the Cr atoms in the dimer is assumed to be in registry with the underlying Au(111) substrate. We find that the exchange interaction between two Cr atoms positioned as nearest neighbours is antiferromagnetic. The energy differences between the antiferromagnetic (AF) and the ferromagnetic (FM) solution is $\Delta E_{AF-FM} = -125.8$ meV/atom for the atop geometry and $\Delta E_{AF-FM} = -156.4$ meV/atom for the Cr dimer within the first Au(111) surface layer. In this geometry, the calculated moments are $4.29 \mu_B$ /atom (atop geometry) and $3.79 \mu_B$ /atom (within the surface layer). Again we observe that the magnetic moment is reduced when the Cr atoms are moved down into the Au surface. We also note that the magnetic moments of the dimer atoms are only marginally reduced compared to the moments of single Cr atoms in a similar geometry (figure 1). When the Cr atoms are moved apart so that they are located at a next-nearest-neighbour (NNN) distance, the coupling is antiferromagnetic when the dimer is on the Au surface, $\Delta E_{AF-FM} = -1.3$ meV/atom, and ferromagnetic when the Cr dimer is within the surface layer, $\Delta E_{AF-FM} = +6.8$ meV/atom. The magnitude of the magnetic moments is $4.32 \mu_B$ /atom for the dimer on top and $3.84 \mu_B$ /atom for the dimer within the surface layer. If the distance is increased further, so that the Cr atoms are located one more neighbour distance away (a geometry to which we refer as next to next-nearest neighbour—NNNN), the coupling becomes antiferromagnetic both for the dimer on top and within the surface layer, with energy differences of $\Delta E_{AF-FM} = -1.0$ meV/atom and $\Delta E_{AF-FM} = -9.6$ meV/atom, respectively. The magnitude of the magnetic moments is $4.31 \mu_B$ /atom for the Cr atoms on top and $3.83 \mu_B$ /atom for the Cr atoms within the Au surface layer. It is to be expected that Cr atoms in a dimer that has a large separation between the atoms will have magnetic properties that are essentially similar to those of isolated Cr atoms in a similar geometry. This is what we

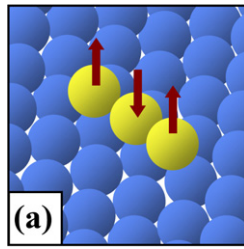


Figure 4. Geometry of the linear Cr trimer. The trimer is located on a Au(111) surface. The Au atoms are shown in blue (dark grey) and the Cr atoms in yellow (light grey).

Table 1. Calculated exchange parameters J_{ij} (in meV/atom) for Cr dimers located on top of the Au(111) and within the first surface layer. NN, NNN and NNNN denote the Cr dimers as nearest neighbour, next-nearest neighbour and next to next-nearest neighbour, respectively.

	(J_{NN})	(J_{NNN})	(J_{NNNN})
(Above)	-95.9	-0.1	-0.9
(In)	-87.0	+5.6	-5.0

observe when comparing the moments of the NNNN dimer with those of the Cr atoms shown in figure 1.

In order to examine the size and range of the exchange interactions, we have calculated exchange coupling parameters J_{ij} for the Cr dimers as nearest neighbour (J_{NN}), next-nearest neighbour (J_{NNN}) and next to next-nearest neighbour, shown in table 1. The exchange coupling parameters have been calculated by using the Liechtenstein formula [19] as implemented in the RS-LMTO-ASA [20], on a collinear solution. It may be observed that the exchange interactions are strongest and antiferromagnetic between nearest neighbours, with a smaller long-range interaction that oscillates between antiferromagnetic and ferromagnetic coupling as the distance between Cr atoms is increased, for Cr dimers positioned in the surface layers of the Au(111) surface. Nevertheless, Cr dimers located on top of the Au(111) surface were found to be antiferromagnetically coupled for all distances considered here.

3.3. Linear Cr trimers

Linear 3d trimers on surfaces have been studied in the literature, and different magnetic arrangements have been observed. While Fe [4] and Co [22] trimers on Cu surfaces show ferromagnetic ordering, Mn linear trimers exhibit antiferromagnetic arrangements [3]. Here, we investigate the magnetic behaviour of linear Cr trimers on Au(111) surfaces. We consider only linear trimers atop the Au(111) surface and with Cr atoms at the nearest-neighbour distance in the geometry shown in figure 4. The coupling is found to be antiferromagnetic between nearest neighbours and the calculated spin moment is $4.24 \mu_B/\text{atom}$ for the atom in the centre of the linear trimer, and $4.29 \mu_B/\text{atom}$ for the atoms on the ends. The latter value is actually the same as the magnetic moment of the dimers in the atop geometry, which is consistent with predominant nearest-neighbour interactions for the electronic structure and magnetism.

3.4. Cr triangles

We also investigated triangular clusters (figure 5) on top of the Au surface and within the surface. For both geometries, the coupling of the magnetic moments is non-collinear with 120°

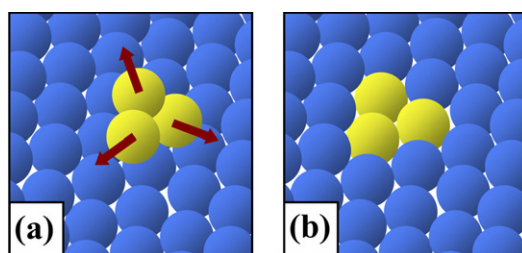


Figure 5. Geometry of the triangular Cr cluster. The triangle is located on a Au(111) surface (a) and within the first surface layer (b). The Au atoms are shown in blue (dark grey) and the Cr atoms in yellow (light grey).

between moments of different atoms. The magnitude of the moment for the atop configuration is $4.25 \mu_B/\text{atom}$, while the triangular clusters within the surface exhibit a Cr moment of $3.77 \mu_B/\text{atom}$. The non-collinear coupling of the atoms in the triangular cluster can be understood from antiferromagnetic nearest-neighbour interactions with a frustrated geometry. Similar examples are Cr or Mn triangular clusters on Cu(111) surfaces, as reported in [3, 4].

The stability of the non-collinear structure, compared to collinear solutions for the same cluster geometry, was examined by total-energy calculations. It was found that the non-collinear solution was the most stable configuration. The energy difference between the non-collinear solution and a collinear antiferromagnetic solution, with the magnetic moments of two of the atoms being parallel to each other and anti-parallel to the third atom, is $\approx 29 \text{ meV/atom}$ for the Cr triangular cluster on top of the Au surface, and $\approx 18 \text{ meV/atom}$ for the Cr cluster within the Au(111) surface. The collinear ferromagnetic solution has a total energy that is $\approx 245 \text{ meV/atom}$ above the non-collinear solution for the Cr cluster on top of the Au surface, and $\approx 234 \text{ meV/atom}$ for the Cr cluster within the Au surface.

The LDOS of the triangular clusters is shown in figure 6. It is interesting to compare the LDOS of the triangular trimer with that of the Cr atom given in figure 2. It is noteworthy that the LDOS of the atop triangular trimer is much broader than the LDOS of the single Cr atom in the atop geometry. This broadening is caused by the hopping of electrons within the triangular cluster and the fact that atomic orbitals centred on different Cr atoms overlap rather strongly with nearest-neighbour Cr atoms. The interaction (hybridization) between the Cr atoms and the Au atoms is strongest when the triangular cluster is within the surface layer, and for this reason the LDOS of this geometry is somewhat broader than for the Cr cluster in the atop geometry. But in contrast with the case of figure 2 for Cr sites with no Cr neighbours, the difference in width between the LDOS of the atop and the in-surface geometries is not very pronounced, since the strong hybridization between Cr sites within the cluster is present in both cases.

4. Conclusions and summary

In this work, using an extension of the RS-LMTO-ASA approach that allows for non-collinear magnetism, we have studied the magnetic ordering of Cr clusters placed on or in the Au(111) surface. Non-collinear ordering is important, since nearest-neighbour interactions in bcc Cr are antiferromagnetic, suggesting that complex magnetic structures may be present in these clusters. Our results show that Cr sites placed at the nearest-neighbour distance can indeed be analysed in terms of antiferromagnetic interactions. As a result of these interactions, linear structures (dimers and trimers) show, in most cases, collinear antiferromagnetic arrangements, whereas the triangular cluster, due to magnetic frustration, exhibits non-collinear ordering. In

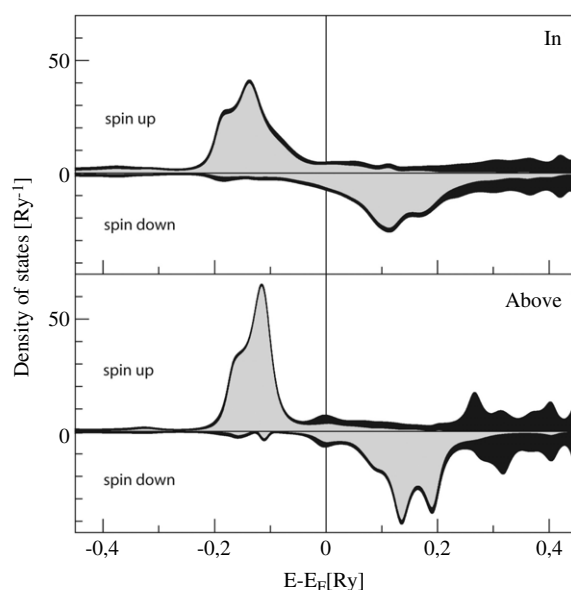


Figure 6. Local density of states (LDOS) of the triangular Cr cluster. The LDOS is shown for a cluster located on top of a Au(111) surface (lower panel) and within the first surface layer (upper panel). The total LDOS is shown in black and the 3d partial LDOS in grey. The Fermi energy is at zero.

an equilateral triangular cluster it is not possible to find a configuration in which the moments of all the nearest neighbours have antiferromagnetic alignment, and as a result, non-collinear ordering with 120° between the Cr magnetic moments evolves.

In the case of Cr dimers, as expected due to the Ruderman–Kittel–Kasuya–Yosida (RKKY) [23, 24] character of magnetic interactions in metallic systems, we find that the exchange interaction between two Cr atoms positioned in the surface layers of a Au(111) surface tends to oscillate between antiferromagnetic and ferromagnetic coupling as the distance between Cr atoms is increased. Nevertheless, Cr dimers located on top of the Au surface were found to couple their magnetic moments antiparallel for all distances considered here.

We find that the Cr adatom on Au(111) shows a virtual bound state, due to its reduced coordination. In fact, the calculated local density of states at Cr sites shows rather narrow features compared to those of bulk Cr. As a consequence, the magnetic moments of the systems presently studied are enhanced compared to the bulk. The Cr moment here is close to saturation, which explains why the variations in moment values between different clusters or between different atoms within one cluster are quite small. In a few cases we obtained orbital moments at the Cr sites and found that they are rather small. This behaviour is expected for Cr sites in noble metals, due to a reminiscence of Hund’s rule, as discussed in detail in [17], a study of orbital moments of 3d sites in Cu, Ag and Au. The calculations show that hybridization with the magnetic Cr sites induces a magnetic moment on the neighbouring Au atoms, but these moments are quite small, of order $0.01\text{--}0.02 \mu_B/\text{atom}$.

Compared to experimental observations on these systems, our calculated magnetic structure for the triangular cluster is not inconsistent with the scanning tunnelling microscope (STM) study of [9], but we note that a direct measurement of the magnetic structure was not performed in that experiment. In regard to other theoretical work, our calculation for a single Cr atom on top of a Au(111) surface is in good agreement with [6], whereas we do not reproduce

the non-magnetic (spin-degenerate) configuration of a Cr dimer in the atop geometry found there [6]. Given the fact that the calculated LDOS of the dimer is rather narrow, it is likely that an exchange-split configuration should be the ground state. Further experimental studies of such systems would hence be very valuable to resolve this issue.

Acknowledgments

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