Magnetic Nanostructures: 4*d* Clusters on Ag(001)

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We perform *ab initio* calculations for the electronic structure of 4*d* transition-metal clusters at the (001) surface of Ag and determine the magnetic moments. Dimers, linear chains, and plane islands are investigated, all showing a strong tendency for magnetism. We also compare our results with calculations for free clusters. Because of the hybridization with the substrate and with the adatoms in the clusters, the maximum of the moment curve is shifted to large valences. For all investigated structures Ru and Rh clusters are magnetic.

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Atomic clusters have special properties which often differ very much from those of bulk materials [1]. In particular, the properties strongly depend on the size and geometry of the clusters [1,2]. In the last few years considerable progress has been made concerning the magnetic properties of small free clusters [3]. Most unexpected was the theoretical prediction of magnetic clusters of 13 Ru, Rh, and Pd atoms [4]. It is well known that these elements are nonmagnetic in bulk geometry [5]. Recently, experimental evidence of the magnetism of clusters of Rh_n (for n between 12 and 32) has been reported [6].

The deposition of clusters on surfaces is of much technological importance for the development of new catalytic compounds, nanoscale electronics, and magnetic devices. Recently such supported clusters have been extensively investigated by experimental methods. The modern scanning tunneling microscopy technique [7] allows one to manipulate the structure of small clusters on surfaces and to produce one- or two-dimensional nanostructures. Field ion microscopy (FIM) investigations show that small metal clusters on a metal surface form linear chains and island-type configurations at low temperatures and low coverages [8,9]. Mass-selected Pt and Pd ($n = 1-15$) clusters on the Ag(110) surface have been generated by ion bombardment [10], and their geometry has been determined using the embedded atom method (EAM). It has been reported that linear chains of these clusters are preferred to plane islands. Oscillations between chain and island-type geometries have been observed by FIM for Pt clusters on Pt(001) [8] and also been predicted by the EAM for small Pt and Pd clusters on Pt(001) [11]. Thus, linear chains and plane islands are frequently observed as stable (or metastable) structures on metal surfaces.

The interaction of surfaces with clusters can lead to many interesting properties of cluster materials [12]. It can be speculated that some of these properties are strongly changed by the formation of local moments, and therefore the study of magnetism in these nanostructures seems rather desirable. Our own studies [13,14] predict that some of the 4*d* and even 5*d* adsorbate atoms on the Ag(001) and Cu(001) surfaces have giant magnetic moments. It has also been suggested by tight binding calculations [15] that small Rh clusters should be magnetic on the Ag(001) surface. Thus clusters of 4*d* elements could present a new class of magnetic materials with interesting properties.

To our knowledge the occurrence of magnetism of small clusters of 4*d* elements on metal surfaces has not been investigated by *ab initio* methods. One can consider such nanostructures as the missing link between the extensively studied magnetic monolayers on surfaces [16–18] as one extreme and single magnetic adatoms studied recently [13,14] as the opposite limit. The aim of the present paper is to provide theoretical information in this gap. We calculate the magnetic properties of several linear chains (*C*) and plane islands (*I*) of 4*d* adatoms which are shown in Fig. 1. In particular, we consider linear chains of 2 (dimers, *C*2), 3, and 4 adatoms (*C*3 and *C*4), being oriented in the (110) direction as well as three compact islands with 4, 5, and 9 adatoms (*I*4, *I*5, and *I*9). We will concentrate on the effect of the interaction with the substrate as well as on the role of the interaction within the cluster. Because of the limited space available we restrict ourselves to ferromagnetic configurations despite the fact that many antiferromagnetic solutions also exist. For the

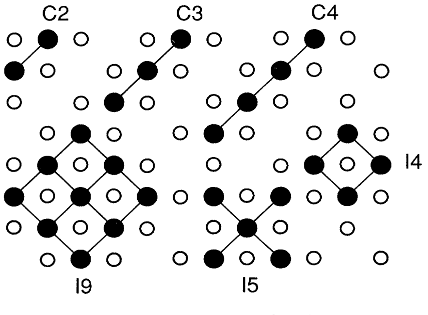

FIG. 1. Magnetic nanostructures of adsorbate atoms: linear chains in the (110) direction of two adatoms (dimers, *C*2), three and four atoms (*C*3 and *C*4), as well as compact islands (*I*4, *I*5, and *I*9). The lines indicate nearest neighbor bonds. The open circles denote surface atoms of the supporting Ag substrate.

same reason a discussion of the binding energetics and stability of these clusters has to wait for a more extended paper.

Our calculations are based on density functional theory and a newly developed Korringa-Kohn-Rostoker (KKR) Green's function method for defects at surfaces [13,14]. We apply multiple-scattering theory to obtain the Green's function in an angular-momentum representation from an algebraic Dyson equation given by

$$G^{nn'}_{LL'}(E) = G^{0\,nn'}_{LL'}(E) + \sum_{n''L''} G^{0\,nn''}_{LL''}(E)\Delta t^{n''}_{L''}(E) G^{n''n'}_{L''L'}(E)\,. \qquad (1)$$

Here $G^{nn'}_{LL'}(E)$ is the energy-dependent structural Green's function matrix and $G^{0\,nn'}_{LL'}$ the corresponding matrix for the ideal surface, serving as a reference system. The summation in (1) is over all lattice sites n'' and angular momenta L'' for which the perturbation $\Delta t^{n''}_{L''}(E) = t^{n''}_{L''} - t^{0\,n''}_{L''}(E)$ between the t matrices of the real and the reference system is significant. All angular momenta up to $l = 3$ are included.

The potentials are assumed to be spherically symmetrical within the Wigner-Seitz spheres. We construct the ideal surface by removing seven Ag monolayers, thus creating two practically uncoupled half crystals. The potentials of these vacuum layers and of four Ag layers on each side are calculated self-consistently. For the defect calculation we allow the potentials of all adatoms and of all adjacent reference sites to be perturbed. Equation (1) is then solved using group theory. Exchange and correlation effects are included using the local-spin density approximation with the exchange-correlation potential of Vosko, Wilk, and Nusair [19]. By multipole expansion up to $l = 6$ we take the full charge density into account. As a result, the spherical approximation for the potentials is not important for the magnetic behavior. We conclude this from model calculations with our full-potential codes for impurities in the bulk where we simulated the surface geometry by putting six Ru atoms close to a void of 13 vacancies inside a Ag cube. At these "inner surfaces" the moments, calculated by full and spherical potentials, are nearly identical ($1.79\mu_B$ and $1.81\mu_B$, respectively). Relativistic effects are described in the scalar relativistic approximation. Details about the calculations can be found elsewhere [14,20].

In our procedure lattice relaxations are neglected; i.e., all atoms are fixed at the corresponding positions in the ideal crystal. We do not believe that this approximation will seriously affect the results. The late transition-metal atoms from Mo to Pd have a similar, though smaller, size than the Ag atoms. For Ru and Rh overlayers on Ag(001) Wu and Freeman [17] found that lattice relaxations have a negligible effect on the moments.

Figure 2 shows the calculated local moments per adatom for 4d dimers ($C2$) on the Ag (001) surface. In order to see the effect of the Ag substrate, calculations for 4d dimers in free space are also performed for which the molecular separation has been fixed to the nearest neighbor distance in Ag. In fact, the "free" dimer atoms are positioned on the central vacuum layer, thus allowing a weak hybridization with the two half crystals. Because of this the single particle levels of the dimer are slightly broadened, which results in fractional occupancies. As a reference also the recently calculated moments of single adatoms [13,14] are given. The comparison of the dimers on Ag with the free dimers shows a strong decrease of the moments due to the hybridization with the substrate. This is particularly dramatic for Nb, where the moment of $3.16\mu_B$ for an atom of the free dimer is totally quenched at the surface. In addition to the reduction of the moments, the peak of the moment curve is shifted from Mo to Tc. Both effects arise from the strong hybridization of the 4d wave functions with sp-like valence electrons of Ag, which broadens the local density of states and reduces the moments. Since the 4d wave functions of the early transition elements have an especially large spatial extent, these moments are much more strongly reduced than the ones of the later transition elements leading to the observed shift of the peak position to Tc. Calculations for 4d dimers in the Ag bulk show no or negligible magnetism [21]. Thus only at the surface is the hybridization weak enough so that the 4d magnetism survives.

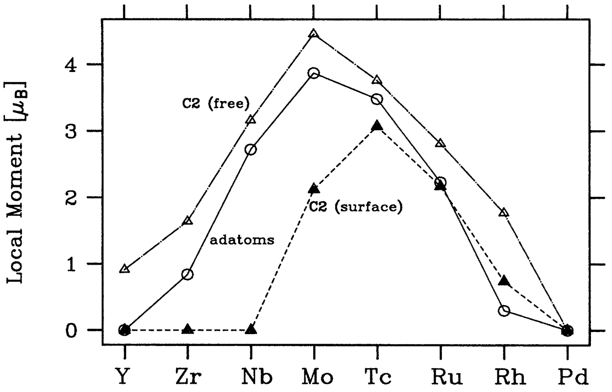

FIG. 2. Local moments per adatom for 4d dimers ($C2$) on the Ag(001) surface and for free 4d dimers in free space (with Ag nearest neighbor distance). For comparison the local moments of single 4d adsorbate atoms are also given [14].

It is interesting to compare the present calculations for 4d dimers with analogous results for 3d dimers on Ag(001). The important difference is that the 3d wave function is much better localized. As a consequence, the hybridization with the substrate reduces the moments only slightly. For instance, for Mn the moment per atom for a free Mn dimer is $4.83\mu_B$, which is reduced to $4.41\mu_B$ for a dimer on Ag(001) and to $4.13\mu_B$ for a Mn dimer in bulk Ag. Only at the beginning and end of the 3d series do important differences occur. For instance, a Ni dimer in bulk Ag is nonmagnetic, whereas at the Ag(001) surface the Ni dimer has a moment of $0.71\mu_B$ per atom.

Now we discuss the results for the different $4d$ clusters. Figure 3 shows the calculated moments per adatom for these nanostructures. Since several nonequivalent atoms exist for the clusters $C3$, $C4$, $I5$, and $I9$, only the average moment is given. For the linear chains quite large moments are obtained, but the behavior with size is nonregular. While the $C2$ and $C4$ moments are very similar, the $C3$ moments of Mo and Tc are much smaller. In this context it is interesting to compare the moments of the inner and outer chain atoms. For Mo and Tc the outer atoms of $C3$ and $C4$ have larger moments than the inner ones. In the $C4$ chain, for instance, the two inner Mo atoms have moments of $1.85\mu_B$, while the outer atoms carry $3.00\mu_B$. Moving to Ru and Rh the situation changes. In the Ru chains both types of atoms have about the same moments, whereas in the case of Rh the inner atoms carry larger moments. In the Rh $C4$ chain the inner atoms have moments of $0.96\mu_B$ but the outer ones only $0.76\mu_B$. This is because the higher coordination of the inner atoms tends to enhance the moments for Rh while Ru is an intermediate case being insensitive to environmental changes. The large moments obtained for all three chain structures indicate that infinite chains of these atoms should also show appreciable moments.

For the linear structure considered we also obtain antiferromagnetic solutions being the most stable configurations in the middle of the series. The moments can be quite large. For instance, for the Mo chains $C2$, $C3$, and $C4$ the atomic moments are larger than $3\mu_B$. More details will be given elsewhere.

For the compact islands ($I4$, $I5$, and $I9$) the hybridization effects within the cluster are even larger. Similar to magnetic monolayers [16–18] we find only appreciable moments for the Ru and Rh nanostructures, but no or very small moments for Mo and Tc. This is a consequence of the large spatial extent of $4d$ wave functions being more important for the compact islands than for the chain structures. Within the Ru structures $I5$ and $I9$ we observe that the outer atoms carry a larger moment than the inner ones, the same effect as found above for the linear structure of Mo and Tc. For Rh the situation is more complicated. For the $I5$ island the inner moment ($1.00\mu_B$) is larger than the outer one ($0.66\mu_B$), in agreement with the above rule, while the central atom in the $I9$ cluster has a very small moment of $0.16\mu_B$, and the outer atoms have moments of $0.62\mu_B$ and $0.64\mu_B$. Thus by comparing the islands with the chain structures, not only the peak of the moment curve is shifted to even larger valences, i.e., from Tc to Ru, but also the transition from surface enhancement of the moments to surface suppression is shifted: For the chains this turnover occurs at Ru, but for the more compact islands at about Rh. The very small moment obtained for the central atom of $I9$ seems to be in conflict with the results of Blügel and others [16–18] for a Rh overlayer on Ag (001) which should have a moment of about $1\mu_B$. We have therefore performed calculations for larger Rh islands and for a complete Rh monolayer on Ag(001) also. For the largest island $I21$ considered, we obtain for the inner Rh atoms considerably larger moments ($0.66\mu_B$). For the complete Rh monolayer a moment of $0.88\mu_B$ is obtained, which is compatible with the above results. Thus we conclude from these calculations, as well as from the strong difference obtained for the different linear chains $C2$, $C3$, and $C4$, that the moments of the $4d$ clusters show an unusual and oscillatory dependence on the cluster size. This is different from the behavior found in the $3d$ series and a consequence of the larger spatial extent of the $4d$ wave function causing a greater structural sensitivity.

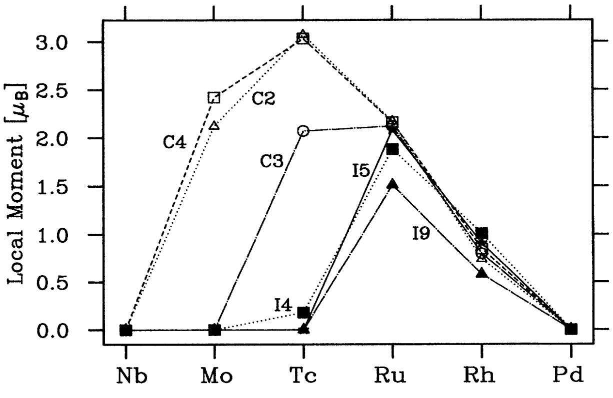

FIG. 3. Average magnetic moment per adatom for different $4d$ clusters (Fig. 1) on Ag(001).

The occurrence of magnetism for the $4d$ adatoms and $4d$ monolayers on Ag(001) [16–18] can be explained from the local density of states (LDOS). For instance, for the Rh monolayer the paramagnetic LDOS shows a strong peak at the Fermi level, so that the Stoner criterion is satisfied. For our $4d$ clusters this criterion requires the calculation of the nonlocal cluster susceptibilities which is involved since the clusters are nonhomogeneous. Nevertheless, the paramagnetic LDOS represents a reasonable indicator of magnetism also in this case. As an illustrative example Fig. 4 shows the paramagnetic LDOS for the Rh cluster $I5$ of Fig. 1. For the central atom an antibonding peak is located at E_F, while the strong peak of the outer atoms is centered below E_F. Consequently, the central atom has a larger moment ($1.00\mu_B$) than the outer atoms ($0.66\mu_B$). For the corresponding Ru cluster the LDOS of both atoms are shifted by about 0.26 eV to higher energies so that the central atom has a smaller LDOS at E_F than the outer atoms and consequently also a smaller moment ($1.74\mu_B$ compared to $2.16\mu_B$ for the outer atoms).

In summary, we have presented *ab initio* calculations for the magnetic properties of small $4d$ clusters on the Ag(001) surface. The calculations are based on local density functional theory and apply a KKR Green's function method. For these adsorbate systems we find a rich

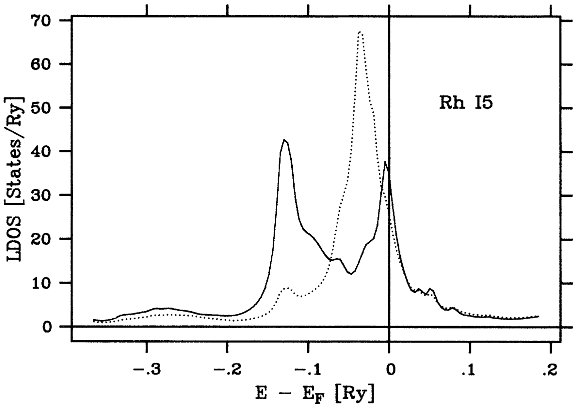

FIG. 4. Paramagnetic LDOS for the Rh cluster *I*5. Full line: central atom. Dotted line: outer atoms.

variety of magnetic nanostructures. Because of the strong hybridization of 4*d* wave functions with the substrate and with the neighboring adsorbate atoms the moments of the early transition elements are quenched and the maximum is shifted to larger valences. Contrary to small 3*d* clusters the moments of 4*d* nanostructures depend strongly on the geometry of the cluster, so that nonlocal effects are very important. While their moments are quenched in the bulk, the hybridization at the surface is nevertheless small enough that 4*d* elements show a similar behavior to 3*d* elements in the bulk. Because of the similarities in the electronic structures of Au and Ag we expect similar results to those obtained here for the Ag(001) surface as well as for the Au(001) surface. We hope that the present calculations encourage experimental efforts to study the magnetic properties of such nanostructures.

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