Imperfect magnetic nanostructures on a Ag(001) surface

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Ab initio calculations are presented for magnetic properties of small islands of 3d, 4d, and 5d adatoms on the Ag(001) surface, intermixed with Ag substrate atoms. We show that the intermixing of small 4d and 5d clusters can lead to an unexpected enhancement of the local moments and is very different from the intermixing behavior found in the monolayer regime. [S0163-1829(98)05148-0]

Unusual magnetic properties of nonmagnetic in bulk 4d and 5d elements have been predicted for monolayers,1 free,2 and supported clusters3 in ab initio calculations within the local spin-density approximation (LSDA) of the density-functional theory. Naturally, these unexpected results attracted several experimental groups to test the possibility of the magnetism in new systems.4−7 Due to theoretical conclusions, the main possible candidates for new magnetic properties might be Ru and Rh among the 4d systems, and Os and Ir among the 5d systems. For monolayers and supported clusters, the surfaces of Ag and Au are interesting substrates due to the weak hybridization with the transition-metal atoms. Evidence of 4d magnetism has been found in experiments of Cox et al.5 for free Rh and Ru clusters. Experiments of Pfandzelter et al.6 have shown that Ru monolayers are magnetic on C(0001) surface. The confirmation of the magnetism of Nb adatoms and small Ru and Rh clusters on the Ag surface, which has been predicted in our group,3 has been recently reported.7 At the same time, the magnetism of 4d and 5d monolayers on noble metals has not been found in experiments.4 This seems to be connected with structural imperfections (islanding, surface roughness, interdiffusion) which exist in real experiments with noble metal surfaces.3 For example, recent scanning tunneling microscopy techniques revealed that for Rh on Ag(001) the direct exchange with Ag surface atoms and the growth of mixed Rh/Ag adislands are very important processes at the initial stage of epitaxial growth.9 Ab initio calculations of two-dimensional random alloys RhAg and RuAg on a Ag(001) performed by Turek et al.10 demonstrated that magnetic moments of Rh and Ru are strongly reduced and in some cases magnetism of Rh and Ru monolayers is totally suppressed due to the intermixing with the substrate. These results can be used to explain the null results in magnetic experiments with Rh and Ru monolayers on noble metal substrates. They also show that in the one- or two-monolayer regime the mixing of Rh and Ru with Ag atoms always leads to a reduction of magnetic moments.

The main goal of our paper is to show that at the initial stage of monolayer growth, when small mixed adislands are formed, the intermixing of small 4d and 5d islands with Ag substrate atoms has a very different effect and is determined by a cluster size effect, which can lead to an unexpected enhancement of magnetic moments in mixed adislands.

Our calculations are based on density-functional theory in the LSDA and the Korringa-Kohn-Rostoker Green’s-function method for impurities and clusters on metal surfaces developed in our group.3,11 We treat the ideal surface as a two-dimensional perturbation of the bulk. The Green’s function of the ideal surface and the Green’s function of clusters on the surface are calculated using the multiple-scattering theory. Exchange and correlation effects are included using the potential of Vosko et al.12 The full charge density is taken into account by a multipole expansion up to angular momenta of \( l = 6 \). Coulomb and exchange-correlation energies are calculated using \( l_{\text{max}} = 12 \). Details of the method can be found elsewhere.3,11

The discussion will be concentrated on isoelectronic 3d(Fe,Co), 4d(Ru,Rh), and 5d(Os,Ir) clusters on the Ag(001) surface. Our previous investigations3,11 showed that adatoms of these metals are magnetic on the Ag(001) surface with large magnetic moments (more than \( 1 \mu_B \)) except Rh and Ir, which have small moments (0.3\( \mu_B \) for Rh, and 0.35\( \mu_B \) for Ir). It is generally assumed that the hybridization of the d states of the magnetic adatoms with sp states of the Ag substrate reduces the moments. For example, a single Ag adatom on a first neighbor side suppresses the moments of Rh and Os adatoms. However, the interaction between adatoms in small supported clusters leads to a more complicated behavior, which cannot be easily explained by hybridization arguments.

To demonstrate this we performed ab initio calculations for the magnetic properties of pure transition-metal clusters (C1, first column in Fig. 1) on the Ag(001) surface and of clusters intermixed with Ag atoms (C2−C4, Fig. 1). With
three nonequivalent positions A, B, and C, four different configurations are considered. We choose plain islands of nine atoms. The structure and the magnetic moments of pure and mixed clusters are listed in Fig. 1.

In cluster C1, the inner atom has a nearest-neighbor coordination like atoms in a complete monolayer, therefore the difference in the magnetic behavior between this atom and atoms in a monolayer is determined by the size of clusters.

The main effect observed is an enhancement of the magnetic moments by intermixing. This is an unusual behavior in atoms in a monolayer is determined by the size of clusters. The structure and the magnetic moments of pure and mixed clusters are considered. We choose plain islands of nine atoms and the Ag impurities. If the exchange integral is fixed, the local magnetic moment increases with increasing density of states at the Fermi energy \( n(E_F) \) and the changes depend in a relative irregular way on the size and shape of the clusters and are somewhat larger in the 5d case, as one can see from the different behavior found for the isoelectronic Rh and Ir systems. In all these cases we expect that by substituting the transition-metal atoms with Ag atoms the moments of the Rh or Ir atoms will further increase thus leading to an enhancement of magnetism in the cluster. To understand more in detail which features in the atomic geometry lead to the enhancement of the moments, we introduced also empty spheres in the clusters instead of Ag atoms. The results for the Ru cluster are summarized in Fig. 4.

We use the Stoner model of ferromagnetism to explain in a simple model, how the magnetic moments at A, B, and C sites in the Ru cluster depend on the arrangement of the Ru atoms and the Ag impurities. If the exchange integral is fixed, the local magnetic moment increases with increasing density of states at the Fermi energy \( n(E_F) \). An increase of \( n(E_F) \) is coupled to a decreasing width of the d bands. In the framework of a tight-binding model the bandwidth is proportional to the square root of the second moment of the DOS. If we take into account next nearest-neighbor interactions and consider a model containing only one d orbital, the second

<table>
<thead>
<tr>
<th>Pure clusters</th>
<th>Mixed clusters</th>
<th>• - X</th>
<th>• - Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>C2</td>
<td>C3</td>
<td>C4</td>
</tr>
<tr>
<td>A</td>
<td>B</td>
<td>C</td>
<td>A</td>
</tr>
<tr>
<td>Ru</td>
<td>1.12 1.50 1.61</td>
<td>0.90</td>
<td>1.74</td>
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<tr>
<td>Rh</td>
<td>0.16 0.62 0.64</td>
<td>0.86</td>
<td>0.70</td>
</tr>
<tr>
<td>Os</td>
<td>0 0 0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ir</td>
<td>0.17 0.33 0.34</td>
<td>0.65</td>
<td>0.63</td>
</tr>
<tr>
<td>Fe</td>
<td>3.11 3.17 3.22</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>Co</td>
<td>2.01 1.96 1.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
</tbody>
</table>

FIG. 1. Magnetic moments of pure and mixed 3d, 4d, and 5d clusters C1–C4 on the Ag(001) substrate. The moments are given in Bohr magnetons.

FIG. 2. Paramagnetic LDOS (d component only) of Rh atoms of position B in (a) a mixed Rh₈Ag cluster (C2); (b) a pure Rh₉ cluster (C1).
moment of the local DOS at a certain site \(i\) (\(A, B, C\)) is given by

\[
\mu_{i}^{(2)} = (n_1 + n_2 \gamma_1 + n_3 \beta^2 + n_4 \beta^2 \gamma_1) \delta^2
\]

(1)

because we have to sum over all paths of length two hops from site \(i\). \(\delta\) is an effective nearest-neighbor hopping integral, \(\gamma_1\delta\) is the next-nearest-neighbor hopping integral (\(\gamma_1 = 0.1\)). The factor \(\beta\) is used to describe missing atoms (\(\beta = 0\)) or Ag atoms in the cluster (\(\beta < 1\)). \(n_1, \ldots, n_4\) describe the number of paths of the corresponding type. We get for example \(\mu_{A}^{(2)} = 4(1 + \gamma_1^2)\delta^2\) for the central atom (A site) of the pure Ru cluster [cf. Fig. 4(1)].

Assuming that the square root of the second moment of the local DOS is inverse proportional to the magnetic moment, we get the following relations for the magnetic moments at the sites \(A, B, C\) in the structures (1)–(7) of Fig. 4,

\[
\begin{align*}
M_{A}^{(1)} &< M_{A}^{(6)} < M_{A}^{(2)}, & M_{A}^{(1)} &< M_{A}^{(7)} < M_{A}^{(5)}, \\
M_{B}^{(1)} &< M_{B}^{(6)} < M_{B}^{(4)}, & M_{B}^{(1)} &< M_{B}^{(7)} < M_{B}^{(5)}, \\
M_{C}^{(1)} &< M_{C}^{(6)} < M_{C}^{(2)}, & M_{C}^{(1)} &< M_{C}^{(5)} < M_{C}^{(3)}, \\
M_{i}^{(1)} &< M_{i}^{(3)}, & M_{i}^{(4)} &> M_{i}^{(5)}, & M_{i}^{(6)} &> M_{i}^{(7)}.
\end{align*}
\]

(2)

This agrees very nicely with the results of the first principles calculations. If the edge atoms are substituted by empty spheres [Fig. 4(2)] the remaining Ru atoms interact as second nearest neighbors only. This leads to a narrowing of the local DOS and therefore to higher magnetic moments at the \(C\) sites. In Fig. 4(4), the central Ru atom is removed. The corner atoms lose only a second neighbor. Therefore, the moment at the \(C\) site is only slightly enhanced. The edge atoms lose a nearest neighbor, which leads to a stronger enhancement of the moment at site \(B\). In Fig. 4(6) the atoms at the corners are removed. Therefore, the central atom loses all next-nearest neighbors which enhances the moment also. The substitution of empty sites by Ag atoms leads to an increase of the second moments of the DOS in all cases. Therefore, the local moments are reduced with respect to the clusters containing empty spheres instead of Ag impurities. Nevertheless, the magnetic moments in the clusters with Ag impurities are still higher than in the pure Ru cluster due to a strong size effect similar to the discussion in Fig. 3.

In summary, we have shown that mixed adisland, which are formed at the initial stage of epitaxial growth of 4\textit{d} (5\textit{d}) monolayers on the Ag surface, exhibit unusual magnetic properties. In sharp contrast with results obtained for the
monolayer regime,\textsuperscript{10} the moments of small supported clusters are enhanced due to the interdiffusion of Ag atoms into 4\textit{d} and 5\textit{d} adislands. The resulting local moments are considerably larger than the moments for the corresponding monolayers.

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