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Magnetic dimers of transition-metal atoms on the Ag(001) surface

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The magnetic properties of transition-metal dimers on Ag(001) are calculated in the local-spin-density approximation by means of a Korringa-Kohn-Rostoker Green's function technique. It is shown that many transition metals which are nonmagnetic in their bulk form are magnetic as dimers on the Ag(001) surface. The surface-dimer interaction is studied by comparing the magnetic moments of supported and free dimers. The increased sp-d hybridization with the substrate strongly decreases the magnetic moments of 4d and 5d dimers in comparison with the 3d ones. However, for these series magnetic dimers with large moments also exist. [S0163-1829(96)06043-2]

I. INTRODUCTION

The magnetic properties of small metal clusters are of interest for a wide range of surface science, catalysis, and magnetic recording applications.[1,2] For example, small magnetic particles can be used with advantage in the characterization of catalysts, in the identification of compounds, and in the determination of particle sizes.[2] Recent progress in the matrix-isolation method and the development of nanotechnology has enabled researchers to produce small metal clusters consisting of two to a few hundred atoms.[3] The results of experimental and theoretical investigations show that the magnetic properties depend strongly on the size and geometry of the clusters.

Using a molecular beam deflection experiment, Bucher *et al.*[4] have shown that magnetic moments of small Co clusters exceed the bulk value. Billas *et al.*[5] have recently reported that in Fe, Co, and Ni clusters ferromagnetism occurs already for small cluster sizes and that the magnetic moments approach the bulk value for approximately 700 atoms per cluster.

While 4d and 5d transition metals are nonmagnetic in the bulk phase, small clusters of such atoms may exhibit magnetism. For example, magnetism of small Rh clusters was predicted theoretically[6] and later confirmed experimentally.[7]

In many applications of clusters metal or semiconductor surfaces are used to fix the clusters. The interaction with surfaces can reveal many new interesting properties.[8] In fact, one can consider such supported clusters as a link between monolayers and single adatoms. There are quite a number of theoretical studies of the magnetic properties of transition-metal monolayers.[9] As a general result, it is found that the monolayer moments are enhanced compared to the moments of the bulk. Even magnetic monolayers of 4d and 5d elements have been predicted.[10] Recently experimental evidence of 4d magnetism for Ru monolayers on C(0001) has been reported.[11] Our own *ab initio* calculations have shown that many 3d, 4d, and 5d transition-metal adatoms have giant magnetic moments on the (001) surfaces of Ag, Cu, Pd, and Pt.[12,13] Also a rich variety of magnetic 4d nanostructures on Ag(001) has been predicted.[14] Experimental confirmation of the magnetism of 4d adatoms on noble metal surfaces has been reported recently. Using the weak localization method Beckmann *et al.*[15] found strong dephasing effects due to magnetism for Mo impurities on Au, while Schäfer and Bergmann[16] identified Nb on Ag(111) as a Kondo system.

However, there remain many questions about transition-metal clusters on metal surfaces. For example, what is the influence of metal surfaces on the magnetic properties of clusters? What is the relationship between magnetic properties of free clusters, supported clusters, and overlayers? The answers on these fundamental questions will depend on the type of substrate and the size and geometry of the supported clusters.

In this paper we study transition-metal dimers on the Ag(001) substrate. We consider this as a model system to answer some of the above questions. The 3d, 4d, and 5d dimers are chosen as the smallest metal-metal bonded systems which manifest the adsorbate-substrate interaction. There are many very important and interesting investigations[17] concerning the electronic structure and magnetic properties of free transition-metal dimers, but to our knowledge the effect of the dimer-substrate interaction on the magnetic properties has not been investigated. We compare the magnetic moments of supported dimers with those of free dimers and discuss the stability of the ferromagnetic and antiferromagnetic configurations. The comparison of the moments of free dimers, supported dimers, and monolayers allows one to see the ''development'' of the magnetic properties in metallic nanostructures. We also show that some transition-metal atoms induce a sizeable magnetic moment on Pd atoms in heterogeneous dimers Pd-X ($X=3d$, 4d, or 5d atom).

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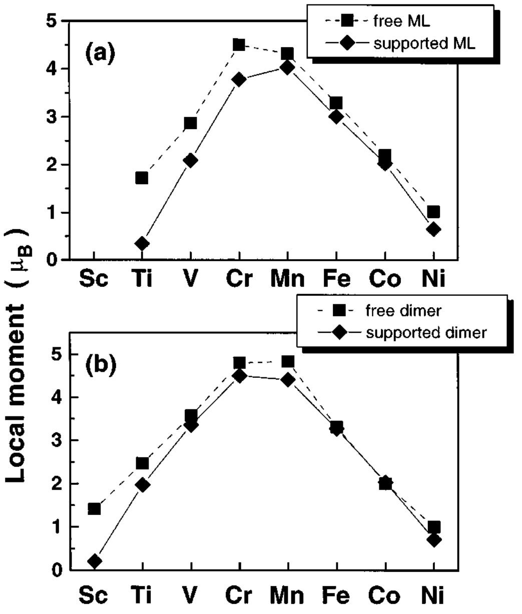

FIG. 1. (a) Local magnetic moments of unsupported 3*d* (001) monolayers with Ag lattice constant and 3*d* monolayers supported on Ag(001). (b) Local magnetic moments for free 3*d* dimers (bond length = nearest-neighbor distance of Ag) and of supported dimers on Ag(001). In all cases only the moments of the ferromagnetic configuration are given.

II. CALCULATIONAL PROCEDURE

We describe the calculational method used in this work only briefly, since the details can be found elsewhere.[12,13,18] The calculations are carried out with the Korringa-Kohn-Rostoker (KKR) Green's function method for surface defects and are based on density functional theory in the local-spin-density approximation (LSD).

By removing the atomic potentials of seven monolayers we create two half-crystals which are practically decoupled. In this way the surface can be treated as a localized two-dimensional perturbation of the bulk. Multiple scattering theory is applied to obtain the Green's function from the Dyson equation. The Green's function of the ideal surface is used as the reference Green's function for the calculation of the dimers on the surface, with the dimers atoms being positioned at hollow sites in the first ''vacuum'' layer. Nearest-neigbor dimers with (110) orientation are investigated. The potential perturbations of the dimer atoms and the first neighboring sites are taken into account, i.e., a cluster of 20 perturbed potentials is considered being perfectly embedded in an otherwise ideal surface.

The full charge density is taken into account using a multipole expansion up to $\ell_{\max}=6$. Coulomb and exchange correlation energies are evaluated using $\ell_{\max}=12$. For the latter ones the local functional of Vosko *et al.*[19] is used. Potentials are assumed to be spherically symmetric inside the Wigner-Seitz sphere. The influence of the approximation to the potential is tested by means of full potential calculations for 6 Ru atoms close to a void of 13 vacancies in an Ag cube. The moments calculated by full and spherical potentials are practically identical ($1.79\mu_B$ and $1.81\mu_B$). The calculations show that the moments are mainly determined by the *d* electrons of the dimers. The *s* moments are quenched due to the hybridization with the substrate. For example, the *s* contribution to the moment of 3*d* supported dimers is less than 0.1 μ_B. The *d* wave functions of the dimer atoms are well localized. Therfore the spherical approximation to the potential has also no strong influence on the magnetic moment in antiferromagnetic configurations.

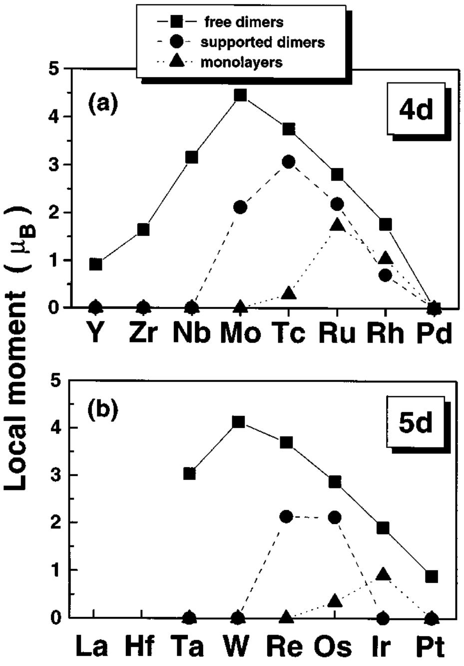

FIG. 2. (a) Local moments for free 4*d* dimers (bond length = nearest-neighbor distance of Ag), supported 4*d* dimers on Ag(001) and 4d monolayers on Ag(001). (b) Local moments for free 5*d* dimers (bond length = nearest-neighbor distance Ag), supported 5*d* dimers on Ag(001) and 5*d* monolayers on Ag(001). The moments refer to the ferromagnetic configuration.

Calculations for dimers in free space are performed for a dimer bond length equal to the nearest-neighbor distance in Ag. The Green's function of the central ''vacuum'' layer in the vacuum region between the two half-crystals is used as the reference Green's function in the corresponding Dyson equation. Due to a weak hybridization with the two half-crystals, the single particle levels are slightly broadened. This leads to a fractional occupation of the dimer levels. As is well known, the balance between kinetic and exchange energies or between chemical bonding and magnetism depends strongly on the interatomic spacing.[17] Since the equilibrium distance of the diatomic molecules is much smaller than the Ag nearest-neighbor distance, they do not represent a proper reference to discuss the effect of the substrate interaction. Therefore we fix the dimer bond length to the nearest-neighbor distance of Ag.

In this way magnetic moments for free dimers are compared with the moments of supported dimers to see the effect of the substrate. In our calculations the differences in the moments depend only on the electronic structure of the surface. Changes in bond lengths and surface relaxations are not taken into account in the present paper. Our calculations for spin-polarization energies[12,14] show that in most cases lattice relaxations (typical energies <0.1 eV) do not seriously effect the calculated moments.

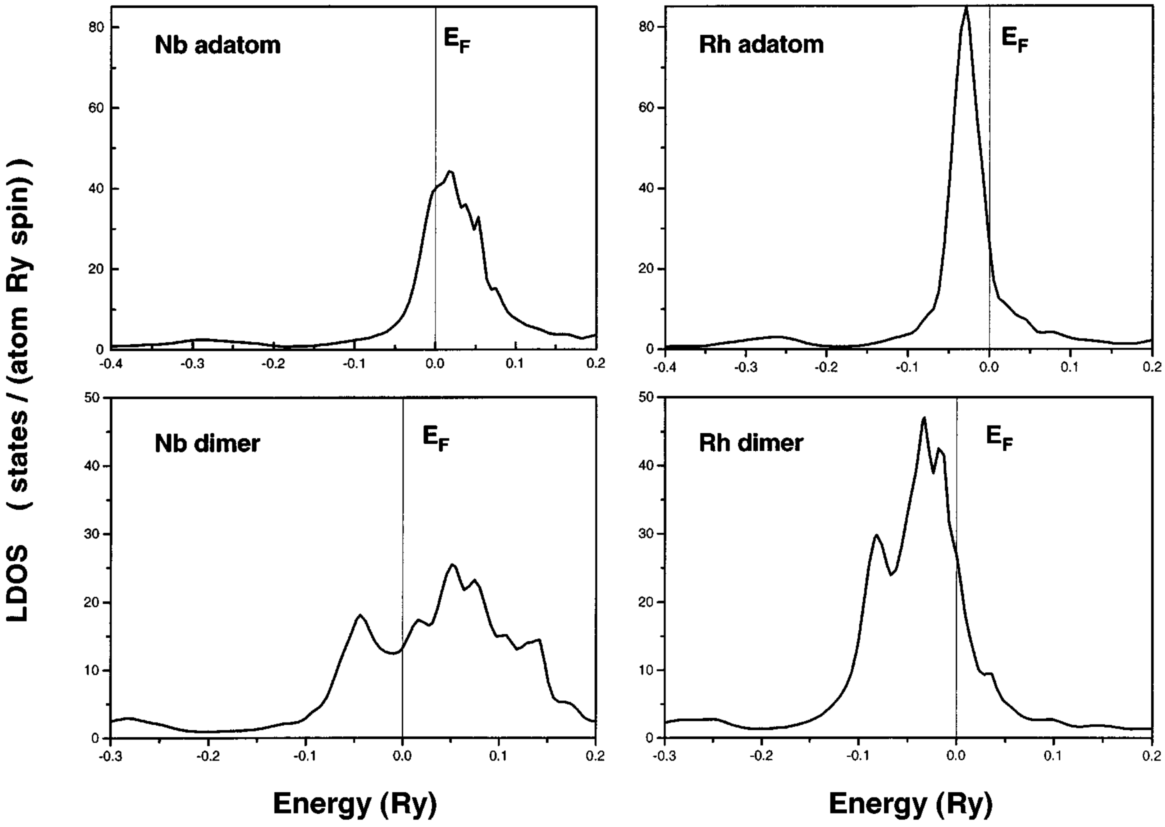

FIG. 3. Local densities of states of the Nb and Rh adatoms and the Nb and Rh dimers on Ag(001) from a non-spin-polarized calculation.

III. RESULTS AND DISCUSSION

Figure 1 shows the calculated local magnetic moments per atom for the free and the supported 3*d* dimers together with the results of Blügel *et al.*[20] for unsupported monolayers and overlayers on Ag(001). It is seen that the interaction with the substrate always reduces the moments. The main effect is determined by the *d*-*sp* interaction between the impurity *d* states and the *sp* states of Ag, which broadens the *d* density of states and reduces the moments. In the case of 3*d* dimers the interaction with the surface reduces the moments only slightly, because the 3*d* wave functions of the dimers are well localized. For instance, the moments for Fe and Co are nearly the same for the free and supported dimers. This is because the majority band is practically filled for these two elements. Exactly the same effect is seen for the 3*d* monolayers. For Ni dimers and Ni overlayers the reduction of the magnetic moment is larger. This effect has been discussed by Blügel.[20] It has been shown that for Ni overlayers the magnetism is stabilized by 3*d* holes rather than electrons. The small tailing-off of the local density of states of Ni on Ag at E_F reduces the moments. The increase of the coordination number in the monolayers in comparison to the dimers increases the *d*-*d* hybridization and broadens the *d* states of the monolayers. This effect is most important for the early transition metals Ti, V, Cr leading to considerably smaller moments of the monolayers.

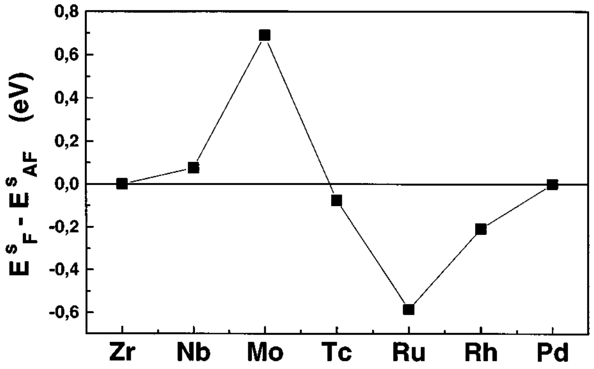

FIG. 4. Difference of the spin polarization energies for the ferromagnetic and antiferromagnetic state for 4*d* dimers. Positive (negative) energies mean that the antiferromagnetic (ferromagnetic) configuration is more stable.

The formation of dimers allows for two different configurations: ferromagnetic and antiferromagnetic. It is well known that around the center of the transition-metal series antiferromagnetic solutions are more stable.[21] It was confirmed for the 3*d* dimers in the bulk and for the monolayers.[20] Our calculations show that the antiferromagnetic moments for 3*d* dimers are the same or slightly smaller than the ferromagnetic ones. For instance, we obtained that V, Cr, and Mn dimers on the Ag(001) surface have the following magnetic moments in the antiferromagnetic state: $\mu_{\mathrm{V}} = \pm 3.16\mu_B$, $\mu_{\mathrm{Cr}} = \pm 4.38\mu_B$, $\mu_{\mathrm{Mn}} = \pm 4.46\mu_B$. These values are very close to the ferromagnetic solutions, cf. Fig. 1. The same trends have been obtained for the 3*d* monolayers.[20]

We have also performed calculations for dimers with 4*d* and 5*d* elements, being nonmagnetic as bulk metals. Figure

TABLE I. Magnetic moments of 4*d* and 5*d* dimers on Ag(001) for the antiferromagnetic configuration. Calculations for free dimers have only been performed for the some systems.

4*d* series	Free dimer (μ_B)	Supp. dimer (μ_B)	5*d* series	Free dimer (μ_B)	Supp. dimer (μ_B)
Zr	-	0.00	Hf	-	0.00
Nb	2.50	0.88	Ta	-	0.00
Mo	4.15	3.17	W	3.85	2.44
Tc	-	2.97	Re	3.86	2.74
Ru	-	1.47	Os	2.72	0.89
Rh	-	0.00	Ir	-	0.00
Pd	-	0.00	Pt	-	0.00

2(a) shows the local moments for ferromagnetic 4*d* dimers in free space, on the Ag(001) surface, and for the corresponding monolayers. Due to the larger extent of the 4*d* and 5*d* wave functions the influence of the substrate is much more pronounced. The moments of the early 4*d* dimers (Y,Zr,Nb) are totally quenched at the surface. This is particularly dramatic for Nb, where the free dimer has a moment of $3.16\mu_B$. Among the supported 5*d* dimers only Re and Os have magnetic moments at the surface, cf. Fig. 2(b). The maximum of the magnetic moment for 4*d* or 5*d* monolayers is shifted to higher valencies in comparison to the dimer curves. At the end of the series the magnetic moments for the monolayers (Rh and Ir) are even larger than the ones for the dimers. Thus at the end of the series the d-d interaction enhances the moment, while at the beginning and in the middle of the series this interaction suppresses magnetism. This effect can be understood from the characteristics of the paramagnetic density of states.[20]

To explain this behavior in more detail in terms of a Stoner-like picture the paramagnetic LDOS of Nb and Rh adatoms on Ag(001) are compared with the LDOS of the corresponding dimers (cf. Fig. 3). The Nb adatom has a moment of $2.72\mu_B$, while the moment of the Rh adatom is much smaller $(0.3\mu_B)$.[13] Figure 3 shows a strong decrease of the LDOS at the Fermi energy if one compares the Nb dimer with the single Nb adatom. Therefore the Nb dimer is nonmagnetic. Going through the 4*d* series, the peak of the LDOS moves through the Fermi energy so that the Rh adatom has a smaller LDOS at E_F than the Nb adatom and therefore a smaller moment. In contrast to the case of Nb, the LDOS at E_F of the Rh dimer is slightly increased compared with the Rh adatom. This leads to an increase of the moment of the Rh dimer $(0.74\mu_B)$. Along the same lines the further increase of the Rh moment of the monolayer can be understood.

We also investigated the antiferromagnetic solutions for 4*d* and 5*d* dimers. The results obtained for the moments are presented in Table I. Total energy calculations show that among the 4*d* dimers on the Ag(001) surface the antiferromagnetic solution for Nb and Mo is more stable than the ferromagnetic one. This can be seen from Fig. 4 giving the energy difference between the ferromagnetic and the antiferromagnetic configuration. The comparison of the moments obtained for free dimers with the moments for the supported dimers (Table I) shows that the antiferromagnetic configuration is less sensitive to the surface interaction than the ferromagnetic ones. This is due to the fact that for ferromagnetic dimers the majority states of both dimer atoms and the minority states of both dimer atoms hybridize with each other resulting in broad virtual bound states, which suppress magnetism. In the antiferromagnetic case the majority electrons of one atom hybridize with the minority electrons of the second one and due to the large energy difference between both states a rather weak covalent hybridization arises with narrow virtual bound states stabilizing antiferromagnetism. This effect is particularly important for 5*d* dimers, leading for Re and W to antiferromagnetic ground states with large moments of 2.7 and $2.4\mu_B$ (Table I).

LSD theory does not determine a well-defined many-electron state. Since the ground state of a diatomic molecule is either a spin singlet $^1\Sigma = 1/\sqrt{2}(\uparrow\downarrow - \downarrow\uparrow)$ or a triplet $^3\Sigma$, the antiferromagnetic solution cannot be the true ground state of the dimer. This problem of describing multiplet effects in density functional calculations has been discussed by von Barth.[22] Nevertheless calculations for the diatomic molecules Mo_2 and Cr_2 (Ref. 23) reveal that the antiferromagnetic solution describes the true (singlet) ground state quite well. This should be even more valid for the supported dimers, since in general multiplet effects are suppressed by the interaction with the substrate. A recent publication of Cheng and Wang[24] demonstrates also that LSD theory is applicable to antiferromagnetic Cr clusters.

There is also significant interest in Pd dimers, because it has been proven to be a challenging molecule in catalysis.[25] Similar to bulk Pd also the Pd dimer is nonmagnetic. However, due to the large spin susceptibility of Pd, one expects that in a mixed Pd-X dimer a magnetic moment can be induced on the Pd atom by a magnetic partner atom X. This is a known effect for d impurities in Pd bulk[26] and on the Pd(100) surface,[13] as well as for 3*d* monolayers on the Pd surface.[20] Therefore we have also calculated the magnetic properties of mixed Pd-X dimers ($X = 3d$, $4d$, or $5d$ atom) on Ag(001). The results obtained are presented in Table II. It is seen that many transition-metal atoms induce magnetic moments on the Pd atom. The moments induced by the 4*d* and 5*d* adatoms are even larger than the moments induced by Fe despite the fact that the corresponding 4*d* and 5*d* moments are much smaller. The same effect has been observed in our previous calculations for Pd(001) with transition-metal adatoms[13] and results from the stronger hybridization of these adatoms.

IV. CONCLUSIONS

We have performed *ab initio* calculations for $3d$, $4d$, and $5d$ transition-metal dimers on the Ag(001) surface and com-

TABLE II. Magnetic moments induced at the Pd atom in mixed Pd-X dimers on Ag(001). A vanishing Pd moment signals that also the X atom is nonmagnetic.

3d series	Moment (μ_B)	4d series	Moment (μ_B)	5d series	Moment (μ_B)
Ti	0.00	Zr	0.00	Hf	0.00
V	0.00	Nb	0.00	Ta	0.00
Cr	0.05	Mo	0.13	W	0.11
Mn	0.11	Tc	0.21	Re	0.22
Fe	0.12	Ru	0.17	Os	0.19
Co	0.09	Rh	0.05	Ir	0.13
Ni	0.00	Pd	0.00	Pt	0.00

pared with the results for free dimers and monolayers on Ag(001). For all d series many magnetic dimers exist on this surface. In general the interaction with the substrate reduces the moments. While this is a relatively small effect for the 3d dimers, the moments of the 4d and 5d dimers are more strongly reduced. Nevertheless also in these series magnetic dimers with sizable moments occur. For instance, in the 4d series the ferromagnetic T_c dimer has a moment of 3.07μ_B per atom, while the antiferromagnetic Mo dimer has local moments of 3.17μ_B. In the 5d series the antiferromagnetic Re dimer has the largest moments (2.74μ_B). We hope that the present calculations will motivate experimental efforts to study such dimers on surfaces.

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