Imperfect magnetic nanostructures on a Ag(001) surface

V. S. Stepanyuk
Fachbereich Physik, Martin-Luther-Universität, Halle-Wittenberg, Friedemann-Bach-Platz 6, D-06099 Halle, Germany and Max-Planck-Institut für Mikrostrukturphysik, Weinbergweg 2, D-06120 Halle, Germany

W. Hergert and P. Rennert
Fachbereich Physik, Martin-Luther-Universität, Halle-Wittenberg, Friedemann-Bach-Platz 6, D-06099 Halle, Germany

K. Wildberger, R. Zeller, and P. H. Dederichs
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany
(Received 31 August 1998)

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 clusters[3] 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.[8] 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 $l_{\max}=12$. 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 investigations[3,11] 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

	Pure clusters	Mixed clusters ● - X ○ - Ag								
	C1	C2			C3			C4		
										
	A	B	C	A	B	C	A	B	C	A	B	C
Ru	1.12	1.50	1.61	0	1.90	1.74	2.14	0	1.89	1.45	1.71	0
Rh	0.16	0.62	0.64	0	0.86	0.70	0.45	0	0.10	0.73	0.30	0
Os	0	0	0	0	0	0	2.28	0	1.76	-0.23	0.67	0
Ir	0.17	0.33	0.34	0	0.65	0.63	0.67	0	0.12	0	0	0
Fe	3.11	3.17	3.22	0	3.22	3.22	3.26	0	3.27	3.11	3.23	0
Co	2.01	1.98	1.98	0	1.98	1.98	1.97	0	1.97	2.01	1.96	0

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.

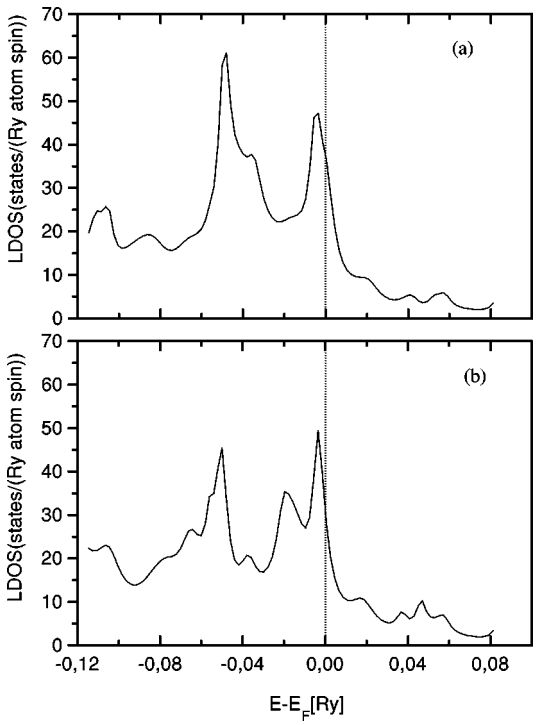

FIG. 2. Paramagnetic LDOS (d component only) of Rh atoms of position B in (a) a mixed Rh_8Ag cluster ($C2$); (b) a pure Rh_9 cluster ($C1$).

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 comparison with the results for a monolayer.[10] We consider the results for the $C2$ clusters with a single Ag impurity at the A side. Surprisingly, the magnetic moments of the Rh, Ru, and Ir atoms at the B and C sides are enhanced. The effect is particularly strong for Ru and Ir clusters. Contrary to the $4d$ and $5d$ clusters, the moments in the $3d$ clusters are only slightly changed, since they are almost saturated.

In order to get a deeper insight into the unusual behavior of clusters with nonmagnetic impurities, we performed calculations for the paramagnetic local densities of states (LDOS) of the pure and mixed clusters. As an example, we present in Fig. 2 the LDOS for Rh atoms at the position B in the mixed Rh_8Ag cluster $C2$ [Fig. 2(a)] and for the pure Rh_9 cluster $C1$ [Fig. 2(b)]. One can see that the substitution of the central Rh atom by an Ag atom leads to an enhancement of LDOS at the Fermi level for the Rh atom. Due to Stoner criterium the magnetic moment therefore increases. Results for more ''strongly'' mixed clusters X_5Ag_4 ($C3$ and $C4$) exhibit also a nontrivial magnetic behavior. One can see that for Ru_5Ag_4 a large enhancement of magnetic moments of all atoms compared to pure Ru_9 clusters is obtained for both configurations, especially for the configuration $C3$. In Rh_5Ag_4 clusters, Ag atoms increase the moment of the central Rh atoms very strongly. Nonmagnetic Os clusters become ferromagnetic with giant magnetic moments for the $C3$ configuration and antiferromagnetic for the $C4$ configuration. The moments of the Ir adatoms are enhanced in $C3$ configuration. Thus, even in the case of strong intermixing with the Ag substrate, small $4d$ and $5d$ clusters can be magnetic and in most cases the moments in mixed clusters can be larger than in pure ones.

Furthermore, one expects that $4d$ and $5d$ clusters to be very sensitive to changes in size. To demonstrate this, we performed calculations of pure Co, Rh, and Ir clusters for some selected sizes and geometries shown in Fig. 3. One can see that the magnetic moments in $4d$ and $5d$ clusters change much stronger than in $3d$ clusters. Also, 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

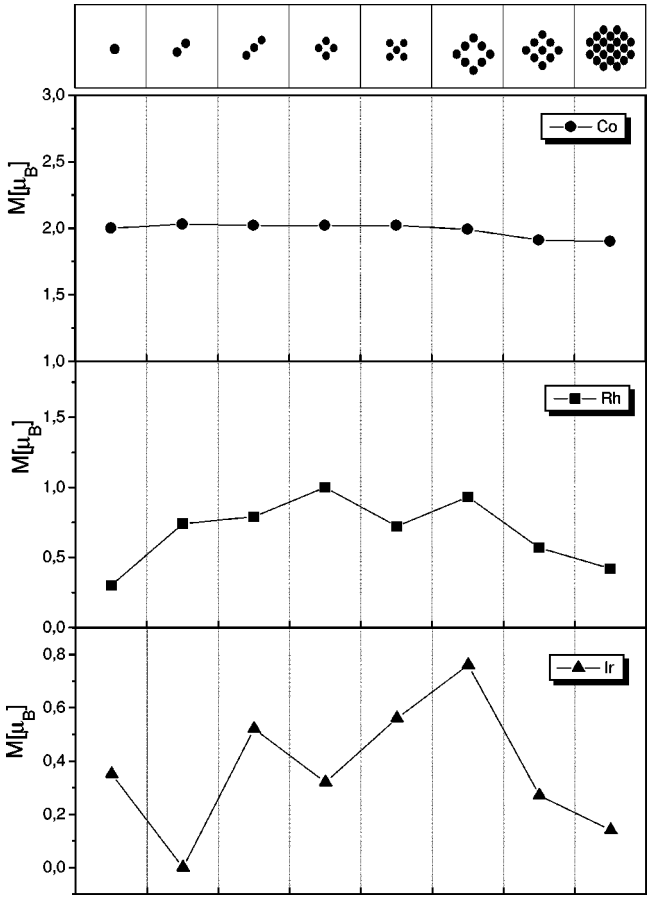

FIG. 3. Size dependence of the moments for some selected $3d$, $4d$, and $5d$ clusters. The average magnetic moments per atom are presented in Bohr magnetons.

moment of the local DOS at a certain site i (A,B,C) is given by

$$\mu_i^{(2)} = (n_1 + n_2\gamma^2 + n_3\beta^2 + n_4\beta^2\gamma^2)\,\delta^2 \qquad (1)$$

because we have to sum over all paths of length two hops from site i. δ is an effective nearest-neighbor hopping integral, $\gamma\delta$ is the next-nearest-neighbor hopping integral ($\gamma \approx 0.1$). The factor β 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 $\mu_A^{(2)} = 4(1+\gamma^2)\,\delta^2$ 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, and C in the structures (1)–(7) of Fig. 4,

$$M_A^{(1)} < M_A^{(6)} < M_A^{(2)}, \quad M_A^{(1)} < M_A^{(7)} < M_A^{(3)},$$

$$M_B^{(1)} < M_B^{(6)} < M_B^{(4)}, \quad M_B^{(1)} < M_B^{(7)} < M_B^{(5)},$$

$$M_C^{(1)} < M_C^{(4)} < M_C^{(2)}, \quad M_C^{(1)} < M_C^{(5)} < M_C^{(3)},$$

$$M_i^{(2)} > M_i^{(3)}, \quad M_i^{(4)} > M_i^{(5)}, \quad M_i^{(6)} > M_i^{(7)}. \qquad (2)$$

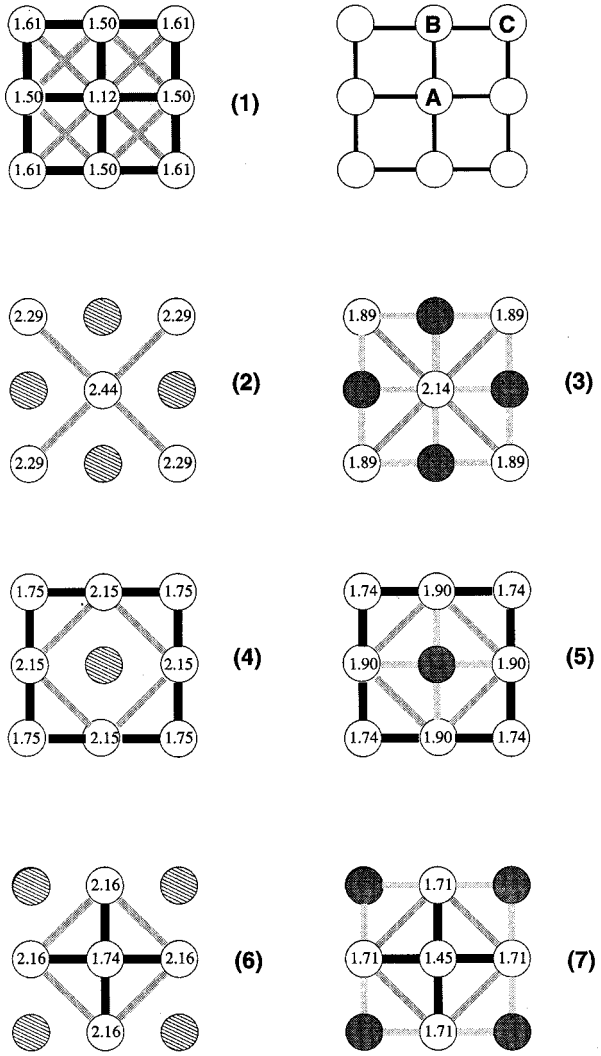

FIG. 4. Substitution of Ru atoms in the Ru_9 cluster by empty spheres or Ag atoms. The magnetic moments per atom of the Ru atoms are given in Bohr magnetons.

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 loose 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 looses 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 $4d$ ($5d$) monolayers on the Ag surface, exhibit unusual magnetic properties. In sharp contrast with results obtained for the

monolayer regime,[10] the moments of small supported clusters are enhanced due to the interdiffusion of Ag atoms into $4d$ and $5d$ adislands. The resulting local moments are considerably larger than the moments for the corresponding monolayers.

This project was supported by Deutsche Forschungsgemeinschaft (DFG) and the TMR-Network ''Interface Magnetism'' of the European Union. Calculations were performed on Cray computers of the German supercomputer center (HLRZ).

[1] M. J. Zhu, D. M. Bylander, and L. Kleinman, Phys. Rev. B **43**, 4007 (1991); O. Eriksson, R. O. Alders, and A. M. Boring, Phys. Rev. Lett. **66**, 1350 (1992); S. Blügel, *ibid.* **68**, 851 (1992); R. Wu and A. J. Freeman, Phys. Rev. B. **45**, 7222 (1992).

[2] B. V. Reddy, S. N. Khanna, and B. L. Dunlap, Phys. Rev. Lett. **70**, 3323 (1993).

[3] K. Wildberger, V. S. Stepanyuk, P. Lang, R. Zeller, and P. H. Dederichs, Phys. Rev. Lett. **75**, 509 (1995); V. S. Stepanyuk, W. Hergert, K. Wildberger, R. Zeller, and P. H. Dederichs, Phys. Rev. B **53**, 2121 (1996); V. S. Stepanyuk, W. Hergert, P. Rennert, K. Wildberger, R. Zeller, and P. H. Dederichs, *ibid.* **54**, 14 121 (1996).

[4] G. A. Mulhollan, R. L. Fink, and J. L. Erskine, Phys. Rev. B **44**, 2393 (1991); C. Liu and S. D. Bader, *ibid.* **44**, 12 062 (1991).

[5] A. J. Cox, J. G. Louderback, and L. A. Bloomfield, Phys. Rev. Lett. **71**, 923 (1993); A. J. Cox, J. G. Louderback, S. E. Apsel, and L. A. Bloomfield, Phys. Rev. B **49**, 12 295 (1994).

[6] R. Pfandzelter, G. Stecerl, and C. Rau, Phys. Rev. Lett. **74**, 3467 (1995).

[7] R. Schäfer and G. Bergman, Solid State Commun. **8**, 45 (1996); H. Beckmann, R. Schäfer, Wenqi Li, and G. Bergman, Europhys. Lett. **33**, 563 (1996); H. Beckmann and C. Bergman, Phys. Rev. B **55**, 14 350 (1997).

[8] H. Li, S. C. Wu, D. Tian, Y. S. Li, J. Quinn, and F. Jona, Phys. Rev. B **44**, 1438 (1991); E. I. Altman and R. L. Colton, Surf. Sci. Lett. **304**, L400 (1994); W. Hergert, P. Rennert, S. Bourab, C. Demangeat, and H. Dreysse, J. Magn. Magn. Mater. **126**, 310 (1993).

[9] S.-L. Chang, J.-M. Wen, A. A. Thiel, S. Günter, J. A. Meyer, and R. J. Behm, Phys. Rev. B **53**, 13 747 (1996).

[10] I. Turek, J. Kudrnovsky, M. Sob, V. Drchal, and P. Weinberger, Phys. Rev. Lett. **74**, 2551 (1995).

[11] V. S. Stepanyuk, P. Lang, K. Wildberger, R. Zeller, and P. H. Dederichs, Surf. Rev. Lett. **1**, 477 (1994); K. Wildberger, P. H. Dederichs, P. Lang, V. S. Stepanyuk, R. Zeller, Berichte des Forschungszentrum Jülich Report No. 3022 (unpublished).

[12] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).