Relationship between magnetism, topology, and reactivity of Rh clusters

Saroj K. Nayak, S. E. Weber, and P. Jena

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

K. Wildberger, R. Zeller, and P. H. Dederichs
Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

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

(Received 31 March 1997; revised manuscript received 22 May 1997)

Self-consistent first-principles calculations based on the molecular-orbital theory and the Korringa-Kohn-Rostoker Green's-function method have been used to demonstrate that the magnetism of Rh clusters can be altered by either modifying their structure or depositing them on a suitable substrate. This ability to alter the magnetic properties of clusters can also have significant effect on their chemical reactivity, thus linking the field of magnetism and catalysis of atomically engineered materials. [S0163-1829(97)09337-5]

Atomic clusters constitute a unique class of matter.[1] The strong dependence of cluster properties on size and geometry and the existence of many isomers allow the possibility of designing clusters with tailored properties.[2] Two of the most interesting quantities in this regard are the magnetic property and reactivity since these are substantially modified by surfaces and almost all atoms in a small cluster are surface atoms. It has been well demonstrated that magnetic moments of clusters of traditional ferromagnetic elements can be enhanced over their corresponding bulk values,[3,4] while clusters of otherwise nonmagnetic elements can be magnetic.[5] It takes hundreds of atoms before the magnetic properties of clusters approach their bulk limit.[4] Similarly, the reactivity of small metal clusters (containing less than 30 atoms) with reagent molecules often varies by several orders of magnitude.[6] What has not been explored thus so far is whether isomers of a cluster exhibit different magnetic properties and if the magnetism of a cluster isomer is related to its chemical reactivity.

In this paper we report a calculation showing that a cluster in the gas phase can exist simultaneously in magnetic as well as nonmagnetic form. The different magnetic structures of these cluster isomers can lead to different chemical reactivities, thus providing a link between catalysis and magnetism. In addition, chemisorption of H_2 on clusters can substantially modify their underlying spin structures. This could be important since a new class of materials with clusters as building blocks is being envisioned.[2] In this context Rh clusters are particularly interesting. Rh clusters containing between 9 and 100 atoms have been found to be magnetic even though bulk Rh is nonmagnetic.[5] The ratio of (magnetic moments)/atom ranges from $0.8\mu_B$/atom to $0\mu_B$/atom. We find that the ratio of (magnetic moments)/atom of small Rh clusters such as dimers and trimers carries substantial moments, namely, $2\mu_B$/atom and $1\mu_B$/atom, respectively. The magnetic moment of a Rh atom is $3\mu_B$/atom. The most interesting case, however, is the Rh_4 cluster. It exists in two isomeric forms: a nonmagnetic tetrahedron structure and a magnetic square structure with a moment of $1\mu_B$/atom. More importantly,

the ratios of (binding energy)/atom of these two isomers differ only by 0.06 eV/atom; i.e., they are nearly degenerate. On the other hand, the Rh monomer, dimer, and trimer supported on a Rh(001) surface are nonmagnetic, while they become magnetic when supported on an Ag(001) surface.[7] These results, based on fully self-consistent state-of-the-art first-principles calculations, demonstrate the possibility that materials with tailored magnetic properties can be designed. In the following, we discuss these methods briefly and provide results on free and supported Rh clusters.

The electronic structure, binding energy, equilibrium geometry, and magnetic moments of Rh_n and Rh_4+H_2 clusters are calculated using the self-consistent-field (SCF) linear combination of atomic orbitals (LCAO) and molecular orbitals (Mo) method based on density functional theory. Here we have used two levels of approximations—the local spin density and the generalized gradient correction. While both the methods give the same ground-state geometries and magnetic moments of the clusters, their energetics differ. The gradient correction gives a better description of the energetics and ionization potential (IP's) of Rh atoms and dimers compared to the experimental values. We have examined the effect of basis sets by performing calculations using both numerical and Gaussian bases. For the former we have used DMOL software[8] and the nonlocal correction is treated at the BLYP level, while for the latter we have used GAUSSIAN94 software[9] where the exchange correlation potential is treated within the generalized gradient approximation (GGA) following the Becke-Perdew-Wang method.

First, we give details of our calculation. The basis functions that we have used in the GAUSSIAN94 software is the LanL2DZ effective core potential with $[Kr]4s4p4d5s5p$ atomic orbitals. In order to assess the accuracy of the effective core potential, we repeated the calculation of the energetics for small clusters such as Rh_2 and Rh_3 using all electrons, namely $1s2s2p3s3p3d4s4p4d5s5p$ atomic orbitals. The results obtained from both the methods are found to be essentially the same. For example, the ground-state binding energies of Rh_2 and Rh_3 obtained from the effective core
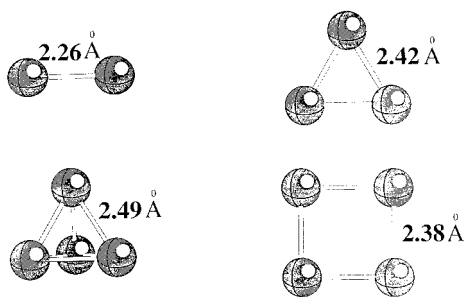
FIG. 1. Equilibrium geometries of free Rh_n ($n = 2-4$) clusters.

potential are 1.51 and 1.99 eV/atom, respectively. The corresponding values in all electron calculation are 1.55 and 2.28 eV/atom. Both the methods give the same multiplicity, namely, 5 and 4 for Rh_2 and Rh_3, respectively. In order to see the effect of basis sets, we have also used DMOL software with numerical basis sets and a polarization function (DNP) with a BLYP nonlocal correction.[8] The DMOL results agree quantitatively with the GAUSSIAN94 calculation. The binding energy difference, for example, between the two Rh_4 isomers (square and tetrahedron) is found to be 0.06 eV/atom in both the calculations. In the following, we present results obtained using the effective core potential given by Hay and Wadt[10] and the generalized gradient approximation of the density functional theory and GAUSSIAN94 software.

The equilibrium geometries of clusters for different spin multiplicities are calculated by computing the forces at each atomic site and relaxing the geometry by the method of steepest descent. Different starting configurations are used to ensure that the geometry of the cluster corresponds to the global minimum.The numerical accuracy of our method is tested by calculating the ionization potential and binding energies and comparing these results with available experiment. For example, our calculated binding energy and bond length of the Rh dimer are 3.03 eV and 2.26 Å, in good agreement with the corresponding experimental values of 2.92 eV and 2.28 Å.[11] The calculated ionization potential of the Rh atom is 7.68 eV, while the experimental value is 7.46 eV.[12]

In Fig. 1 we give geometries of the clusters corresponding to the global minimum configuration. Although the clusters were given the freedom to distort, their equilibrium geometries are very symmetric. For Rh_4 where isomers exist within a very narrow range of the ground-state structure, we provide both structures. The interatomic distances, ratio of (binding energy)/atom (defined as the ratio of energy/atom needed to dissociate the cluster to individual atoms), vertical ionization potential (i.e., energy needed to ionize the cluster without changing their neutral geometry), and ratio of (magnetic moment)/atom are given in Table I. Note that while the

nearest-neighbor distances evolve rapidly towards the bulk value of 2.9 Å, the ratio of (binding energy)/atom is much below the bulk cohesive energy of 5.75 eV. The dimers and trimers are magnetic with moments that are much larger than what have been observed in Rh_9 to Rh_{100} clusters.[5] The surprising result is, however, connected with the Rh_4 cluster: The two isomers, whose binding energies differ only by 0.06 eV/atom, have entirely different magnetic structures. The tetrahedral structure is nonmagnetic, while the square structure carries a moment of $1\mu_B$/atom. We should mention that a previous calculation by Jinlong *et al.*[5] based on local spin density and the discrete variational method (DVM) found the energy difference between the two isomers of Rh_4 to be 0.22 eV/atom, which is larger than the one reported here. To examine the source of this discrepancy, we repeated the calculation using both the GAUSSIAN94 and DMOL methods at the local spin density (LSD) level and have found the energy difference between the isomers to be 0.16 eV/atom. The small difference in energy between Jinlong *et al.* and our LSD calculation could arise due to the different integration techniques used in the calculation. Although both DMOL and the DVM code (which is used by Jinlong *et al.*) use numerical basis sets, the integration in the DVM is carried out with use of a diophantine grid. Improvements in the method of integration have been introduced into the DMOL code.[8] We should also point out that the effect of generalized gradient approximation (GGA) on the structural properties of the transition metal elements have been systematically investigated by Ozolins and Körling.[13] The authors have shown that gradient-corrected results give better agreement with the experiments than the corresponding local-density approximation results. Since both GAUSSIAN94 and DMOL with GGA give similar results, we believe that our result of 0.06 eV/atom as the energy difference between the two isomers is more accurate than that reported by Jinlong *et al.*

The effect of cluster topology on its spin multiplicity has been studied before. For example, in alkali-metal tetramers, the tetrahedral structure has a spin multiplicity of 3, while the rhombus structure has a spin multiplicity of 1.[14] However, these two structures are not degenerate: The ground state of the alkali tetramers is spin singlet with a rhombus geometry. Ni_4, on the other hand, has two isomers (tetrahedral and square) that are nearly degenerate, but the ratios of (magnetic moments)/atom in both these structures are the same.[15] In this regard Rh_4 presents a special case. The tetrahedral and square structures are nearly degenerate, but magnetically very different.

The magnetism of a cluster is influenced by a number of factors, such as symmetry, coordination, and interatomic distance. In general, decreasing coordination and increasing interatomic distance enhances magnetic moments as both fac-

TABLE I. Binding energies (eV/atom), ionization potential, and magnetic moment of Rh clusters.

Cluster	Binding energy (eV/atom)	Ionization potential (eV)	Spin multiplicity
Rh_2	1.51	7.86	5
Rh_3	1.99	7.44	4
Rh_4 (square)	2.35	6.99	5
Rh_4 (tetrahedron)	2.41	6.94	1
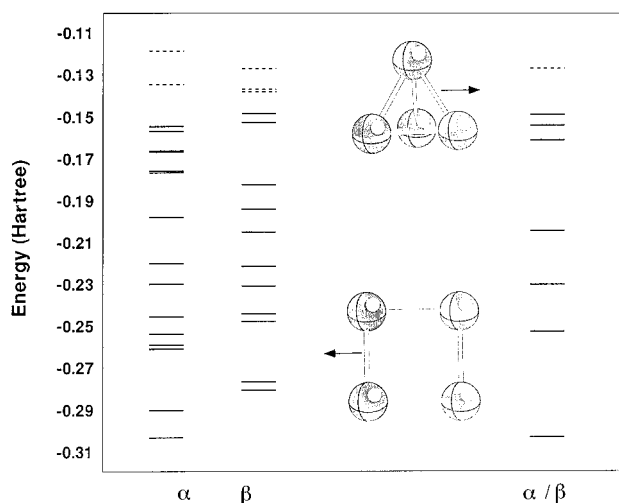
FIG. 2. Orbital energy levels of Rh_4 isomers.

FIG. 3. Geometries of Rh_nH_2 ($n = 1,2,4$) clusters.

tors tend to reduce electron overlap. In the tetrahedral structure, each atom has three nearest neighbors, while for the square structure there are two nearest-neighbor atoms. On the other hand, the interatomic distance in the tetrahedral structure is only 0.1 Å larger than that in the square structure. Thus, the vanishing magnetic moment in the Rh_4 tetrahedral cluster is due primarily to its enhanced coordination. The increasing symmetry of a cluster usually leads to higher spin multiplicity, but the situation is reverse in the present case. In this regard, it is interesting to recall that the magnetic moment of Ni_{13} (which is a perfect icosahedron) is smaller than that in Ni_{14} and Ni_{12} and the variation in the moment follows closely the systematics in the coordination number in Ni clusters.[16]

To gain further insight into the magnetism of Rh_4 clusters, we have examined the orbital energy levels for spin-up (α-spin) and spin-down (β-spin) states for the two isomers. Shown in Fig. 2 are the energy levels for Rh_4 isomers. One observes from Fig. 2 that for Rh_4 in the square geometry there are a large number of states in the vicinity of the highest-occupied molecular orbital (HOMO) compared to that in the tetrahedral structure. The close spacing in the energy levels gives rise to a large density of states, which invariably leads to magnetic structures as is known in extended systems. The orbital character of the HOMO is also very different between these two isomers. While the HOMO of the tetrahedral structure is marked by entirely d states, there is significant hybridization between s and d states in the square structure. This results in the small contraction of the bond length of the square structure compared to the tetrahedral structure.

The vertical ionization potentials (IP's) of the Rh_n clusters are given in Table I. Note that unlike in alkali clusters, the ionization potentials of Rh clusters are considerably large and do not decrease significantly from the value in the atom. Our results are in agreement with the experimental value of Zakin et al.[17] who were able to bracket the IP's by using two-photon ionization. They concluded that the IP's are <7.87 eV for Rh_{1-4} and <6.42 eV for Rh_{5-18}.

Although the nonmagnetic Rh_4 cluster with the tetrahedral geometry is the ground state, its binding energy is so close to its magnetic square isomer that under experimental condi-

tions both might be simultaneously present. Since the existence of isomers has been detected in reactivity experiments,[18] we have studied the reaction of H_2 with both isomers of Rh_4. It was hoped that such studies may demonstrate the relationship between the magnetism and reactivity of clusters. Indeed, this is what we find in our study of the reaction of H_2 with both the isomers of Rh_4. Starting with the initial geometry of each of the isomers, we allowed the H_2 to interact and varied the various bonds and bond angles until the forces at each site vanished. The corresponding geometries of Rh_4H_2 clusters starting with square and tetrahedral forms of Rh_4 are given in Fig. 3. The binding energies of the H_2 molecule in the cluster, defined as the energy difference between the Rh_nH_2 and dissociated $Rh_n + H_2$, and the corresponding spin multiplicities are given in Table II. There are several important features to be noted. (1) H_2 dissociates and binds atomically to both the isomers. (2) The spin multiplicity of both isomers changes as H_2 is chemisorbed. The spin-singlet tetrahedral Rh_4 assumes a spin-quintet configuration, while the spin-quintet square Rh_4 changes to a spin-triplet configuration. (3) The binding energy of the H_2 to the nonmagnetic Rh_4 is almost a factor of 2 larger than its magnetic counterpart. This implies that the reactivity of H_2 may depend on the underlying magnetic structure of the cluster. This observation is not only important from the point of view of providing a link between magnetism and reactivity, but can be used to prove experimentally our prediction of the existence of Rh_4 in two magnetic forms. Since one of the Rh_4 isomers is nonmagnetic, it cannot be detected in a Stern-Gerlach experiment. However, the mass-isolated Rh_4 clusters can be reacted with H_2 and then studied in a Stern-Gerlach experiment. Since both the forms of Rh_4H_2 have different spin multiplicities, they would deflect differently in a Stern-Gerlach field. The chemisorption of a H_2 on a Rh atom and

TABLE II. Binding energies of H_2 and spin multiplicities of Rh_nH_2 clusters.

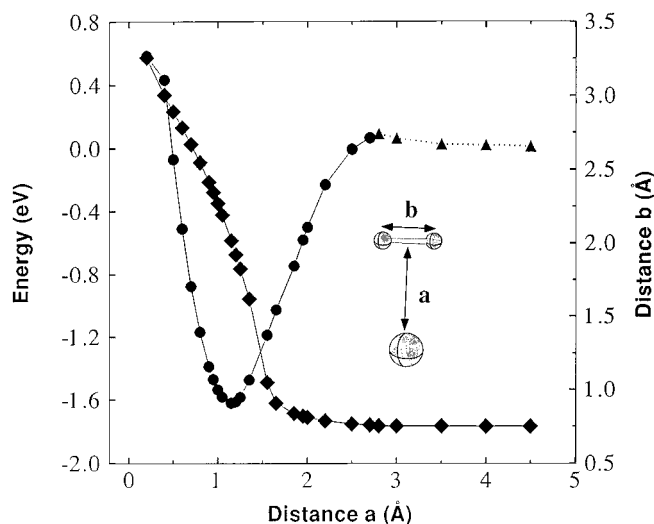| Cluster	H_2 binding energy (eV)	Spin multiplicity
RhH_2	1.62	2
Rh_2H_2	1.08	3
Rh_4H_2 (square Rh_4)	0.56	3
Rh_4H_2 (tetrahedron Rh_4)	1.04	5

FIG. 4. Binding energy of RhH$_2$ as a function of the distance between the center of mass of the H$_2$ molecule and the Rh atom.

FIG. 5. Energy levels of Rh atom, H$_2$, and RhH$_2$.

dimer also affects the spin structure as can be seen by comparing the results in Tables I and II.

To illustrate how the cluster spin changes upon chemisorption of H$_2$, we study in detail the interaction of H$_2$ with a single Rh atom as the geometry of RhH$_2$ is simple, namely, a triangle. Note that Rh atom has a moment of $3\mu_B$ but RhH$_2$ has a moment of $1\mu_B$. Clearly, when the H$_2$ molecule is far away from the Rh atom, the total moment of the RhH$_2$ cluster has to be $3\mu_B$. But as H$_2$ dissociates and atomically binds to the Rh atom, its moment changes to $1\mu_B$. To illustrate how this transition from a multiplicity of 4 to 2 occurs as H$_2$ is brought in towards the Rh atom, we have calculated the binding energy and bond stretching of H$_2$ as a function of distance a between the Rh atom and the center of mass of the H$_2$ molecule. The results are plotted in Fig. 4. The dotted line corresponds to the RhH$_2$ cluster in the quartet spin configuration. At a distance of 2.6 Å, the spin multiplicity changes to a doublet, and at about 2 Å from the Rh atom, the H$_2$ molecule splits and binds atomically. The energy needed for Rh atom to go from a quartet to a doublet structure is about 0.12 eV, and this is close to the energy barrier that H$_2$ needs to overcome before chemisorption in the atomic form. It is important to emphasize that the spin of Rh atom changes before H$_2$ breaks apart. This can be understood by examining the energy levels of the Rh atom in the quartet and doublet configurations and comparing it with the levels of H$_2$ in Fig. 5. For the quartet state of the Rh atom, the HOMO contains an electron on the s state which repels the H$_2$ molecule. The Pauli repulsion is reduced when the s electron reverts to occupy a hole in the d orbitals, converting the Rh atom into a doublet configuration. Interestingly, the HOMO of the doublet Rh atom is much closer to the antibonding orbital of H$_2$ than the HOMO of the quartet state, thus making electron transfer from the metal atom to the H$_2$ molecule easier. This causes the H$_2$ bond to break, making it possible for the eventual formation of the metal-hydrogen bond. The influence of H$_2$ chemisorption on the magnetism of Rh$_2$ is also seen where the spin multiplicity of Rh$_2$H$_2$ is 3, while that of Rh$_2$ is 5.
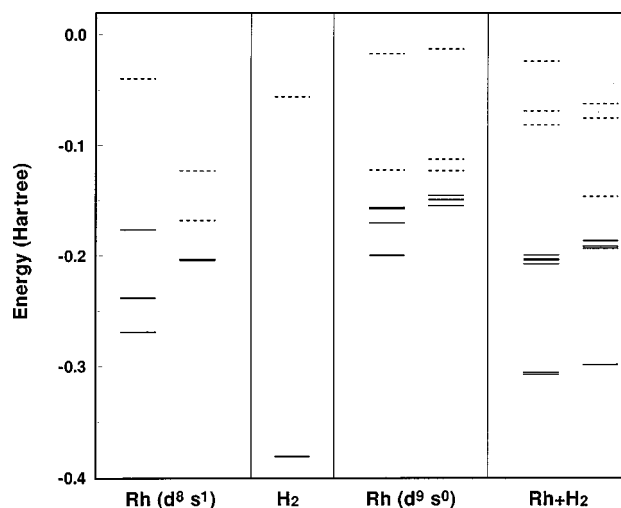
The magnetic properties of gas phase clusters can also be

affected when they are allowed to interact with substrate atoms.[7] The strength of the interaction between the cluster and substrate atoms determines the extent to which the properties of gas phase clusters can be altered. Earlier calculations of Rh$_n$ ($n \leqslant 4$) clusters deposited on Ag(001) revealed that these clusters remain magnetic.[7] We have studied this problem by carrying out calculations of Rh$_n$ clusters on a Rh(001) surface and find that both the Rh surface as well as the supported clusters are *nonmagnetic*. We first outline the method of our calculation. The calculations are based on the local spin density approximation in the density functional theory and the Korringa-Kohn-Rostoker (KKR) Green's-function method that enables us to investigate the electronic structure of single defects at surfaces. Details of the theoretical method, concerning the calculation of the unperturbed surface and the impurity, respectively, are described elsewhere.[7,19] Here we only provide the relevant details. In the construction of the potential, all angular momenta up to $l = 3$ are included. The full anisotropy of the charge density is taken into account by multipole expansion up to $l = 6$. In our supported cluster calculation we allow the potentials of all cluster atoms and neighboring reference sites to be perturbed. All atoms are fixed to their ideal lattice positions, and relativistic effects are described in the scalar relativistic approximation. The experimental bulk-lattice parameter was chosen ($a_{Rh} = 7.180\,96$ a.u., $a_{Ag} = 7.728\,98$ a.u.). The occupancy of states is described by a Fermi-Dirac distribution with an electronic temperature of 470 K.[20] A sufficient number of $\mathbf{q}_{\parallel}$ points, e.g., 465 $\mathbf{q}_{\parallel}$ points in the irreducible two-dimensional Brillouin zone for the two Matsubara poles closest to the real axis, is used to assure convergence. The densities of states are calculated with 55 $\mathbf{q}_{\parallel}$ points by assuming a complex energy with a small imaginary part of 5 mRy.

We first discuss the results of the Rh(001) surface. The magnetism of the Rh(001) surface has been a controversial issue since the first theoretical prediction that the surface could be magnetic.[21] While experimental investigations are inconclusive,[22] recent calculations have indicated that the earlier prediction of a magnetic surface is flawed due to the use of inaccurate pseudopotentials.[23] Our study shows that the Rh(001) surface is *not* magnetic and agrees with recent theoretical results.[24] The question of whether single Rh ad-
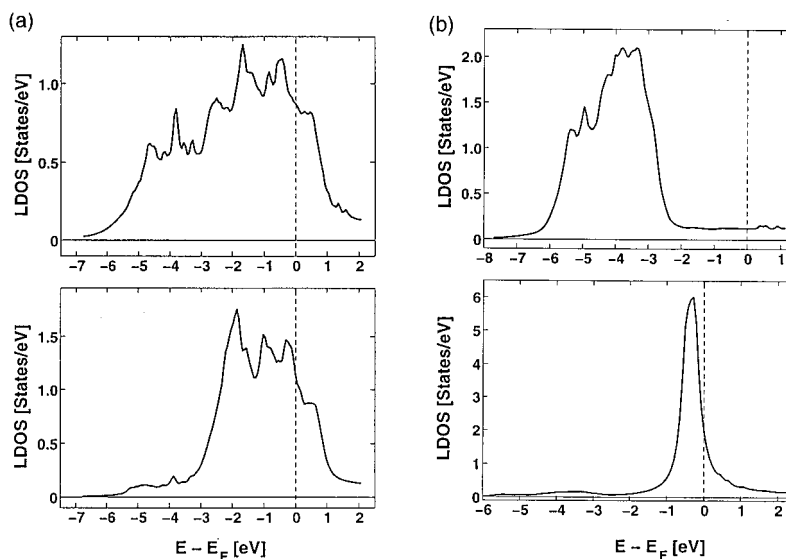
FIG. 6. Local density of states of Rh atom supported on (a) Rh(001) and (b) Ag(001) substrates. The upper panels give the density of the bare surfaces.

sorbatatom or small Rh clusters deposited on a Rh(001) substrate exhibit magnetism or not has not been studied. Therefore we performed calculations for a single Rh atom on a hollow site and small Rh clusters consisting of two, three, and four atoms in linear and compact geometry. The clusters, like the surface, are found to be nonmagnetic. To gain further insight into why the clusters are nonmagnetic on Rh(001), but magnetic on Ag(001), we plot the local density of states of the Rh surface and a single Rh adatom in Fig. 6(a). Near the bottom of the band the density of states (DOS) of the surface layer is reduced compared to that in the energy range between -3 eV and E_F. Consequently, there is a strong d-d hybridization of the $4d$ wave function of the Rh adatom with the d-like valence electrons of Rh. This leads to a broad local density of states (LDOS) of the Rh adatom [lower panel in Fig. 6(a)] with $n(E_F) = 1.19$ states/eV being substantially higher than the one for the bare surface (upper panel). Nevertheless, the Stoner criterion is not satisfied for the Rh adatom, since with an exchange constant I of about 0.65 eV,[25] the product $n(E_F)I < 1$. Also, for supported Rh dimers, trimers, and tetramers on nearest-neighbor sites, we do not find magnetic solutions. In addition to the d-d interaction with the substrate, the hybridization among the Rh adatoms leads to a further broadening of the LDOS. In order to clearly demonstrate the dramatic effect of the interaction with the substrate, we compare this result with a former calculation[7] for an Ag(001). The corresponding DOS for the Ag surface and the Rh adatom on Ag(001) are displayed in

Fig. 6(b). Since the Ag d band is filled and is therefore located well below E_F, the Rh $4d$ wave functions hybridize with the sp-like valence electrons of Ag. Due to the weaker hybridization with the substrate compared with the Rh surface, the LDOS of the Rh adatom [lower panel in Fig. 6(b)] results in a rather sharp virtual bound state which is located right below the Fermi level. The paramagnetic LDOS at E_F is, however, high enough to satisfy the Stoner condition,[25] and we find a moment of $0.3\mu_B$ for the single Rh adatom. Also, larger Rh nanostructures are found to be magnetic with an average moment varying from $0.6\mu_B$ to $0.8\mu_B$.

In conclusion we have shown that magnetic moments of Rh clusters are very sensitive to size, shape, and surroundings. Isomers of Rh$_4$, for example, can exhibit very contrasting magnetic behavior. Chemisorption of H$_2$ on Rh clusters profoundly affects their magnetic character and strong correlation exists between reactivity and magnetism. Interaction between cluster atoms and substrate atoms can also significantly change their magnetic behavior, thus allowing the possibility of altering the magnetism of clusters by design. The strong influence of H$_2$ chemisorption on cluster magnetism allows the possibility that the magnetic status of the Rh(001) surface can be altered by chemisorbing hydrogen. Both theoretical and experimental studies of this problem are highly desirable.

[1] Proceedings of Small Particles and Inorganic Clusters, edited by R. S. Berry, J. Burdett, and A. W. Castlemann, Jr., Z. Phys. D **26** (1993).

[2] S. N. Khanna and P. Jena, Phys. Rev. Lett. **69**, 1664 (1992).

[3] F. Liu, M. R. Pess, S. N. Khanna, and P. Jena, Phys. Rev. B **39**, 6914 (1989).

[4] I. M. L. Billas, A. Chatelain, and W. A. de Heer, Science **265**, 1682 (1994).

[5] B. V. Reddy, S. N. Khanna, and B. I. Dunlap, Phys. Rev. Lett. **70**, 3323 (1993); A. J. Cox, J. G. Louderback, and L. A. Bloomfield, *ibid.* **71**, 923 (1993); J. A. Cox, J. G. Louderback, S. E. Aspel, and L. A. Bloomfield, Phys. Rev. B **49**, 12 295 (1994); Y. Jin-

long, F. Toigo, and W. Kelin, *ibid.* **50**, 7915 (1994).

[6] R. L. Whetten, D. M. Cox, D. J. Trever, and A. Kaldor, Phys. Rev. Lett. **54**, 1494 (1985).

[7] K. Wildberger, V. S. Stepanyuk, P. Lang, R. Zeller, and P. H. Dederichs, Phys. Rev. Lett. **75**, 509 (1995).

[8] Computer code DMOL, Biosym Technologies, Inc., San Diego, 1994.

[9] M. J. Frish *et al.*, computer code GAUSSIAN94, Gaussian Inc., Pittsburgh, 1995.

[10] P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 299 (1985).

[11] K. A. Gingerich and D. L. Cocke, J. Chem. Soc. Chem. Commun. **1**, 536 (1972).

[12] D. L. Cocke and K. A. Gingerich, J. Chem. Phys. **60**, 1958 (1974).

[13] V. Ozolins and M. Körling, Phys. Rev. B **48**, 18 304 (1993); M. Körling and J. Häglund, *ibid.* **45**, 13 293 (1992).

[14] B. K. Rao, P. Jena, and A. K. Ray, Phys. Rev. Lett. **76**, 2878 (1996).

[15] F. A. Reuse and S. N. Khanna, Chem. Phys. Lett. **234**, 77 (1995).

[16] S. E. Apsel, J. W. Emmert, J. Deng, and L. A. Bloomfield, Phys. Rev. Lett. **76**, 1441 (1996); B. V. Reddy, S. K. Nayak, S. N. Khanna, B. K. Rao, and P. Jena (unpublished).

[17] M. R. Zakin, D. M. Cox, and A. Kaldor, J. Chem. Phys. **89**, 1201 (1988).

[18] M. E. Geusic, M. D. Morse, and R. E. Smalley, J. Chem. Phys. **82**, 590 (1985); E. K. Parks, L. Zhu, J. Ho, and S. J. Riley, *ibid.* **102**, 7377 (1995).

[19] V. S. Stepanyuk, W. Hergert, K. Wildberger, R. Zeller, and P. H. Dederichs, Phys. Rev. B **53**, 2121 (1996).

[20] K. Wildberger, P. Lang, R. Zeller, and P. H. Dederichs, Phys. Rev. B **52**, 11 502 (1995).

[21] I. Morrison, D. M. Bylander, and L. Kleinmen, Phys. Rev. Lett. **71**, 1083 (1993).

[22] S. C. Wu, K. Garrison, A. M. Begley, F. Jona, and P. D. Johnson, Phys. Rev. B **49**, 14 081 (1994).

[23] M. Weinert, S. Blügel, and P. D. Johnson, Phys. Rev. Lett. **71**, 4097 (1993).

[24] A. Eichler, J. Hafner, J. Furthmüller, and G. Kresse, Surf. Sci. **346**, 300 (1996).

[25] J. F. Janak, Phys. Rev. B **16**, 255 (1977).