PHYSICAL REVIEW B **73**, 100405(R) (2006)

Surface magnetism of Rh(001) from LDA+U calculations

N. Stojić,[1] N. Binggeli,[1,2] and M. Altarelli[1,3]
[1]*Abdus Salam International Centre for Theoretical Physics, Trieste 34014, Italy*
[2]*INFM Democritos National Simulation Center, Trieste I-34014, Italy*
[3]*European XFEL Project Team, DESY, Notkerstraße 85, 22607 Hamburg, Germany*
(Received 2 November 2005; revised manuscript received 24 January 2006; published 15 March 2006)

We report calculations indicating the presence of a surface magnetic moment for Rh(001), motivated by the detection of a finite moment by magnetic linear dichroism experiments. We show that, while the density functional with the local density or generalized gradient approximations (GGA) for exchange and correlation yields a nonmagnetic ground state, the application of the GGA plus on-site Coulomb interaction U method predicts surface magnetism, thus offering a solution to the long-standing discrepancy between experiment and theory. The calculated moment on the outermost Rh atom increases with the strength of the effective on-site parameter $U_{\text{eff}}=U-J$, for $U_{\text{eff}}\geqslant 1.2$ eV, and is as large as 1.24 μ_B for $U_{\text{eff}}=2.5$ eV.

DOI: 10.1103/PhysRevB.73.100405 PACS number(s): 75.70.Rf, 71.20.Be, 71.15.Ap, 71.15.Mb

The finding of a surface moment for a material which is non-magnetic in the bulk could have far-reaching consequences. It would give valuable directions for design of novel nanostructured materials and could have technological implications for the magnetic storage industry in the future. So far, the only experimental evidence of a magnetic surface on a nonmagnetic material has been obtained for the rhodium (001) surface.[1] Goldoni *et al.*[1] measured the linear magnetic dichroism in 3*d* core-level photoemission of Rh(001) surface. They applied an external magnetic field and reversed it by 180°, which caused a difference in the core-level intensity and shape, indicating the presence of a magnetic moment. In a later study,[2] the same authors concluded that the rhodium (001) surface displays either a weak ferromagnetic ordering or superparamagnetism at 100 K. The conclusion is based on their finding that a small residual magnetic field is necessary for the dichroic signal, but, at the same time, the intensity of the effect does not depend on the magnitude of the applied residual field. Earlier spin-polarized photoemission study by Wu *et al.*[3] found a weakly ferromagnetic Rh(001) surface at room temperature with an estimated moment per surface atom between 0.1 μ_B and 0.2 μ_B.

The experimental findings are in line with the expectation that the tendency toward magnetism increases near metal surfaces, because of the narrowing of the density of states which yields a Stoner enhancement in the susceptibility. The elements which are close to satisfy Stoner criterion in the bulk phase are likely to form magnetic ordering in a reduced dimensionality. In particular, there are theoretical and experimental efforts directed toward investigation of surface magnetism in some 4*d* and 5*d* transition metals. For a few decades now, many theoretical studies have examined the properties of rhodium surfaces[4] and possibilities of surface magnetism in rhodium.[5–8] Rhodium clusters have been investigated theoretically[9–11] and experimentally.[12] Overall, it has been found that the moment depends on the size and the geometrical structure of the cluster, with the calculated values of the moments somewhat larger than the measured value of 0.8 μ_B per atom for a ten-atom cluster.[12] Rh monatomic wires have also been shown theoretically to be magnetic.[13] Calculations of rhodium overlayers on Ag and Au (Refs. 14 and 15) yielded a moment on Rh atoms. Recently, ferromagnetic order has been found theoretically in bulk Rh at the optimum lattice constant in the body centered cubic lattice.[16] So far, no realistic *ab initio* study has found a ferromagnetic solution for the rhodium (001) surface. Cho and Scheffler[5] found a nonmagnetic ground state which was practically degenerate in energy with the ferromagnetic state, obtained as a solution of the constrained, fixed spin-moment calculations, for moments below 0.5 μ_B. Similar results have been obtained more recently,[7] with an imposed moment limited to the surface layers. These calculations indicate a high susceptibility on the rhodium surface and suggest that surface structures with defects might be magnetic. Cho and Scheffler[5] also solved a long-standing problem of anomalously large theoretical surface relaxations compared to the experimental data, by taking into account the thermal expansion of the surface, within the quasi-harmonic approximation.

In this paper, we explore the possibility for magnetism in rhodium (001) surface within the framework of the density-functional theory (DFT), using the generalized gradient approximation (GGA) of the exchange-correlation potential, and the GGA plus on-site Coulomb interaction approach [denoted as local density approximation (LDA)+U from this point on]. As the discrepancy between theoretical and experimental results on the surface magnetism of rhodium persists for all previously attempted band-structure approaches, it seems likely that the approximation used for exchange and correlation may be the reason for the nonmagnetic solution. There are various examples in the literature, not limited to strongly correlated systems, for which the LDA+U was originally designed, where application of this method corrected the DFT solutions by yielding results in agreement with experiments.[17] The LDA+U is a method going beyond the LDA by treating exchange and correlation differently for a chosen set of states, in this case, the rhodium 4*d* orbitals. The selected orbitals are treated with an orbital dependent potential with an associated on-site Coulomb and exchange interactions, U and J. In the LDA, the electron-electron interactions have already been accounted for in a mean field

TABLE I. Magnetic moments on the surface (m_5) and subsurface (m_4) layers, and difference of surface energies between magnetic and nonmagnetic solutions, ΔE_{surf}, as a function of effective Coulomb parameter U_{eff}.

U_{eff} (eV)	m_5 (μ_B)	m_4 (μ_B)	ΔE_{surf} (meV/surf unit cell)
0.5	0	0	
1.0	0	0	
1.2	0.07	0.01	−1.8
1.5	0.55	0.16	−5.0
2.0	0.86	0.37	−21.0
2.5	1.24	0.89	−57.1

way, and, therefore, one needs to apply a double counting correction. There are several existing versions of this correction.[18–20] We apply the most commonly used one, introduced by Anisimov *et al.*[18] which satisfies the LDA atomiclike limit to the total energy. It is known as the self-interaction corrected (SIC) LDA+U method.

We solve the DFT equations using the WIEN2K implementation[21] of the full potential linear augmented plane wave (FLAPW) method in a supercell geometry. We model the surface using an 11-layer slab with a vacuum thickness corresponding to six layers. For the surface layer relaxation, we applied the previously calculated result[5] of −1.4%, compatible with the experimental finding of $-1.16\pm1.6\%$.[22] We used the optimized lattice constant of 3.84 Å, sphere radius of 1.28 Å, energy cutoff equal to 13.8 Ry, and k-point sampling with $(22\times22\times1)$ k-points mesh in the full Brillouin zone (66 k-points in the reduced Brillouin zone). The calculations have been performed utilizing the GGA in the form given by Perdew, Burke, and Ernzerhof.[23] From convergence tests with the number of k-points and energy cutoff, we estimate the numerical accuracy of the energy difference between magnetic and non-magnetic solution to be 2 meV and of the surface magnetic moment to the 0.02 μ_B. We have also assessed the effect of the topmost layer relaxation on the energy difference and the surface moment. Changing the relaxation to −2.8%, changes the surface magnetic moment by 0.05 μ_B and the difference between magnetic and nonmagnetic surface energy by 6 meV per surface atom within the LDA+U.

Considering the fact that the Stoner criterion for bulk rhodium is close to being fulfilled, we first checked for the effects of the inclusion, within the GGA, of the spin-orbit interaction in Rh(001) surface calculations, which was not included in previous calculations. It did not result in a surface moment. A similar conclusion was obtained by checking the influence of steps and line defects on the surface, within the GGA. The removal of every other line, or a pair of lines of surface atoms, parallel with the [110]-direction, gave only a nonmagnetic solution. Structures with a few lines of surface atoms removed, simulating a step, also yielded no magnetic moment.

In contrast, the LDA+U method did induce a magnetic moment on the clean defect-free surface. Table I gives the information on how the magnetic moments in the surface and subsurface layers change as a function of the strength of the on-site parameter U_{eff}, given by: $U_{\text{eff}}=U-J$.[24,25] We estimated the values of the Coulomb and exchange parameters for bulk rhodium utilizing the tight-binding linear muffin-tin orbital code[26] in the atomic sphere approximation (TB-LMTO-ASA) and obtained $U\approx3.4$ eV and $J\approx0.6$ eV, i.e., $U_{\text{eff}}=2.8$ eV. Solovyev *et al.*[27] calculated U and J using the same TB-LMTO code for rhodium impurities in Rb. They obtained a value of $U=3.6$ eV, $J=0.6$ eV, and $U_{\text{eff}}=3.0$ eV for the monovalent Rh^{1+} impurity, which is not too different from the value we find. It is known that the calculated values of U and J tend to depend somewhat on the method used to calculate them and consequently have relatively large error bars (of the order of 1 eV). Therefore, the calculated values are to be used as guidance toward a reasonable physical range of U values and an effort should be made to observe and analyze trends as a function of U. In Table I, we reported the magnetic moments calculated for U_{eff} up to 2.5 eV, together with the corresponding difference between the magnetic and nonmagnetic surface energies: $\Delta E_{\text{surf}}=E_{\text{surf}}^{\text{FM}}-E_{\text{surf}}^{\text{NM}}$. The nonmagnetic energies were obtained using fixed-spin calculations with moment set to zero.

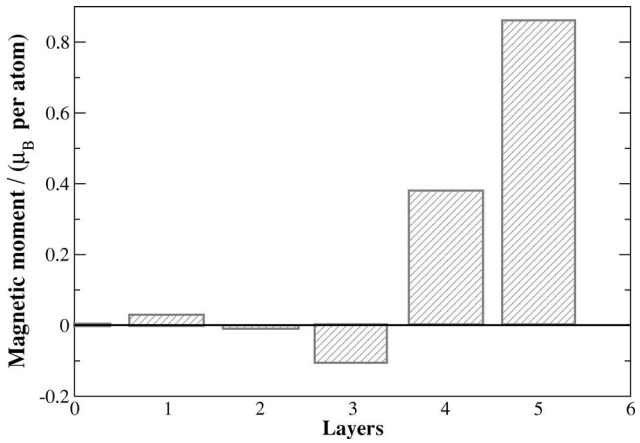

FIG. 1. Distribution of magnetic moments per atom inside a 11-layer Rh(001) slab. Layer 0 is the center and layer 5 the surface of the slab.

For values of U_{eff} below 1.2 eV, there is no ferromagnetic solution. Starting with U_{eff} of 1.2 eV, the ferromagnetic solution has lower energy than the nonmagnetic state. The surface energy difference for the case with $U_{\text{eff}}=2.5$ eV is significantly larger than thermal-fluctuation energy at room temperature, thus indicating that the effect could be observable even at higher temperatures. With the increase of U_{eff} up to 2.5 eV, the magnetic moment on the surface and subsurface layers increases, and the ferromagnetic solution becomes more stable. We note that already for $U_{\text{eff}}\approx1.5$ eV, our calculated magnetic moments are one to two orders of magnitude greater than those obtained by Niklasson *et al.*[28] from LDA calculations for Rh overlayers of comparable thickness on Ag(001), and do not disappear with increasing thickness.[29]

The magnetic moments per atom are presented in Fig. 1 as a function of the layer position inside the slab for the case $U_{\text{eff}}=2$ eV. The center of slab (denoted as layer 0) has a vanishing magnetic moment and the values of the moment

are clearly increasing toward the subsurface and surface layers (layers 4 and 5). We have also performed LDA+U calculations on bulk rhodium and found that, for all values of U_{eff} used in this work, the nonmagnetic solution is the stable state for the bulk. Considering the fact that the Rh 4d orbitals are not very localized, we performed a test using a different basis for the LDA+U in a pseudopotential plane-wave code.[30] In this case, the localized-orbital basis consisted of the orthonormal atomic tight-binding orbitals, while in the FLAPW approach, the orbitally dependent potential was applied to the atomic truncated orbitals (and was zero outside the muffin-tin radius). In the plane-wave scheme, we used an ultrasoft pseudopotential[31] with a nonlinear core correction and Perdew–Burke–Ernzerhof exchange and correlation potential.[23] The calculations gave similar results, with the values of magnetic moments somewhat larger than in the FLAPW code. For the sake of completeness, we did tests using the LDA for exchange and correlation and keeping all the other parameters of the FLAPW calculation the same. Just like in the case of GGA, the magnetic moment on the surface atom increases and the ferromagnetic solution becomes more stable with increasing U_{eff}, albeit with slightly smaller value of the moment on the surface Rh atom.[32] Finally, we also checked for the robustness of the Rh surface magnetism using another version of the LDA+U, with a different double counting correction, implemented in the WIEN2K code, the so-called mean-field correction.[19] For somewhat higher values of U_{eff} it also resulted in a ferromagnetic solution.[33] Hence, in all cases, we obtain a stable surface magnetic solution, with a significant moment on the outermost atomic layer, for values of U_{eff} smaller than, or comparable to the calculated U_{eff}. Larger values of the on-site interaction U_{eff} induce thicker magnetic surface regions, requiring the use of thicker slabs.

To gain further insight into the microscopic arrangement of magnetic moments, in Fig. 2 we show the spin density difference map within a (100) atomic plane perpendicular to the surface for the case U_{eff}=2 eV. The spin density is very localized on the atoms of the surface and subsurface layers and is vanishing toward the center of the slab (bottom line of atoms in Fig. 2). The spin polarized density on the outermost atoms derives mostly from d_{xy}, $d_{3z^2-r^2}$, d_{xz} and d_{yz} orbitals, with a contribution of $\sim$30% from the d_{xy} orbitals and of 21–22% from each of the other three types of d orbitals. In fact, these four types of d orbitals dominate the local density of states on the Rh surface atoms at energies around the Fermi energy (with comparable weights), both when U_{eff} =0 and at finite U_{eff} (2.5 eV). Inspection of Fig. 2 also indicates that the states which contribute to the spin density map have predominantly antibonding character, which is consistent with the character of the d states found near the Fermi energy in bulk Rh.

Intuitively, the magnetic ground state of the LDA+U method in this system can be understood by considering the effect of the on-site Coulomb interaction: It tends to favor the solution in which two spin states of the same d-orbital are separated in energy, with an energy separation roughly equal to U. To additionally check the reliability and stability of this method and its implementation, we applied it to (001) [or (0001) for hexagonal systems] surfaces of some 4d and 5d elements, namely Mo, Ru, W, and Ir. All of these surfaces were found to be nonmagnetic. We used a relaxed geometry for all systems and, where appropriate, we took into account the surface reconstruction (Mo and W). In all cases, we used the $U-J$ values estimated in Ref. 27 which should be an upper bound for U_{eff}.

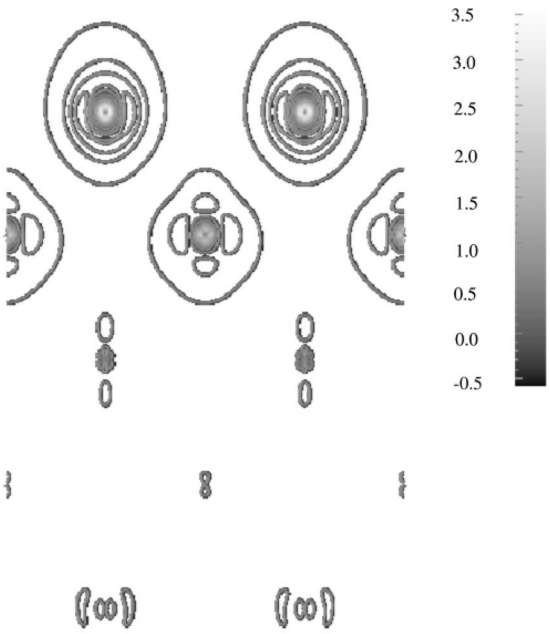

FIG. 2. Spin density difference map (in e/Å^3), for the case U_{eff}=2 eV, within a (100) atomic plane perpendicular to the surface.

At present, a truly quantitative comparison between the experimental results and theory is not possible. Our solution, for which energy difference is greater than room-temperature fluctuations (U_{eff}=2.5 eV), has a magnetic moment on the outermost Rh atom of 1.24 μ_B at 0 K. Goldoni *et al.*[1,2] could not give a measure of surface moment, but concluded that their results are consistent with weakly ferromagnetic or superparamagnetic surface. The only other experiment[3] estimated the surface moment to be between 0.1 and 0.2 μ_B. Experiments were done at 100 K and room temperature, respectively. As we are unable at present to include the temperature effects in our calculations, numerical comparison is not justified. It is also possible that a stronger ferromagnetic ordering in the experiment of Goldoni *et al.*[1] would be detected, had the 4d states been probed directly. Their 3d core-level photoemission experiment probed the 4p polarization induced by the 4d moment.

In summary, we have shown that a magnetic ground state for the rhodium (001) surface is obtained by using the LDA+U approach. A stable solution with a significant magnetic moment on the outermost Rh atom is obtained for U_{eff} smaller than, or comparable to the calculated U_{eff}, with a trend of increasing moment and stability of the magnetic solution with increasing U_{eff}. We believe that our results on the rhodium (001) surface prove that the corrected nonlocal exchange and correlation in the LDA+U method is the key ingredient toward an accurate solution in density functional formalism and in agreement with experiment for this rela-

tively weakly correlated system. It is our hope that similar approaches could be applied to other problems related to magnetism, even in the cases of relatively weakly correlated materials and including systems of lower dimensions,[34] in situations where the DFT method itself cannot fully reproduce the experimental results.

We would like to thank M. Komelj, G. Paolucci, and G. Comelli for helpful and stimulating discussions. Calculations in this work have been done using, among other codes, the PWSCF package.[30] We acknowledge support for this work by the INFM within the framework "Iniziativa Trasversale Calcolo Parallelo".

[1] A. Goldoni, A. Baraldi, G. Comelli, S. Lizzit, and G. Paolucci, Phys. Rev. Lett. **82**, 3156 (1999).
[2] A. Goldoni, A. Baraldi, M. Barnaba, G. Comelli, S. Lizzit, and G. Paolucci, Surf. Sci. **454**, 925 (2000).
[3] S. C. Wu, K. Garrison, A. M. Begley, F. Jona, and P. D. Johnson, Phys. Rev. B **49**, R14081 (1994).
[4] See, for example: A. Eichler, J. Hafner, J. Furthmuller, and G. Kresse, Surf. Sci. **346**, 300 (1996).
[5] J.-H. Cho and M. Scheffler, Phys. Rev. Lett. **78**, 1299 (1997).
[6] J.-H. Cho and M.-H. Kang, Phys. Rev. B **52**, R13805 (1995).
[7] G. Cipriani, PhD thesis, International School for Advanced Studies (SISSA), Trieste, *Ab-initio study of oxygen adsorption on selected transition metal surfaces* (2000), URL http://www.sissa.it/cm/phd.php.
[8] C. Barreteau, R. Guirado-López, D. Spanjaard, M. C. Desjonquères, and A. M. Oles, Phys. Rev. B **61**, 7781 (2000).
[9] K. Wildberger, V. S. Stepanyuk, P. Lang, R. Zeller, and P. H. Dederichs, Phys. Rev. Lett. **75**, 509 (1995).
[10] B. V. Reddy, S. N. Khanna, and B. I. Dunlap, Phys. Rev. Lett. **70**, 3323 (1993).
[11] F. Aguilera-Granja, J. L. Rodríguez-López, K. Michaelian, E. O. Berlanga-Ramírez, and A. Vega, Phys. Rev. B **66**, 224410 (2002).
[12] A. J. Cox, J. G. Louderback, S. E. Apsel, and L. A. Bloomfield, Phys. Rev. B **49**, R12295 (1994).
[13] A. Delin and E. Tosatti, J. Phys.: Condens. Matter **16**, 8061 (2004).
[14] O. Eriksson, R. C. Albers, and A. M. Boring, Phys. Rev. Lett. **66**, 1350 (1991).
[15] S. Blügel, Phys. Rev. Lett. **68**, 851 (1992).
[16] E. Hüger and K. Osuch, Solid State Commun. **131**, 175 (2004).
[17] See, for example: P. Mohn, C. Persson, P. Blaha, K. Schwarz, P. Novák, and H. Eschrig, Phys. Rev. Lett. **87**, 196401 (2001).
[18] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16929 (1993).
[19] M. T. Czyzyk and G. A. Sawatzky, Phys. Rev. B **49**, 14211 (1994).
[20] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).
[21] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave + Locals Orbitals Program for Calculating Crystal Properties* (Karlheinz Schwarz, Technical Universitat Wien, Austria, 2001).
[22] A. M. Begley, S. K. Kim, F. Jona, and P. M. Marcus, Phys. Rev. B **48**, 12326 (1993).
[23] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[24] H. Sawada, Y. Morikawa, K. Terakura, and N. Hamada, Phys. Rev. B **56**, 12154 (1997).
[25] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B **57**, 1505 (1998).
[26] O. Jepsen, G. Krier, A. Burkhardt, and O. K. Andersen, *Tight-Binding LMTO Vers. 4.7* (MaxPlanck-Institut für Festkörperforschung, O. K. Andersen, Stuttgart, Germany, 1994).
[27] I. V. Solovyev, P. H. Dederichs, and V. I. Anisimov, Phys. Rev. B **50**, 16861 (1994).
[28] A. M. N. Niklasson, S. Mirbt, H. L. Skriver, and B. Johansson, Phys. Rev. B **56**, 3276 (1997).
[29] We calculated a 13-layer slab and found its surface carries a magnetic moment similar to the moment at the surface of an 11-layer slab.
[30] S. Baroni, A. D. Corso, S. de Gironcoli, and P. Giannozzi, URL http://www.pwscf.org.
[31] A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, Phys. Rev. B **41**, R1227 (1990).
[32] For $U_{\mathrm{eff}}=2$ eV, the magnetic moment on the surface Rh atom, m_5, equals 0.44 μ_B and the ΔE_{surf} is −9.4 meV. For $U_{\mathrm{eff}}=2.2$ eV, $m_5=0.62$ μ_B, and $\Delta E_{\mathrm{surf}}=-15.2$ meV.
[33] The first magnetic solution was observed for $\sim U_{\mathrm{eff}}=3$ eV, with $m_5=0.10$ μ_B, but with virtually degenerate energies of magnetic and non magnetic solutions. For $U_{\mathrm{eff}}=3.5$ eV, the moment on the outermost Rh atom raised to 0.18 μ_B, and $\Delta E_{\mathrm{surf}}=-5.4$ meV.
[34] M. Wierzbowska, A. Delin, and E. Tosatti, Phys. Rev. B **72**, 035439 (2004).