Rhodium monolayer on gold: A 4*d* ferromagnet

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Using a scalar-relativistic norm-conserving pseuopotential and a Gaussian-orbital expansion, we have calculated the magnetic moment of a free-standing Rh(001) monolayer to be $1.56\mu_B$ and that of the epitaxial monolayer on Au(001) to be $1.09\mu_B$. This is a case of a paramagnetic element forming a ferromagnetic epitaxial monolayer.

In this paper we present the results of an electronic-structure calculation of an ideal five-layer Au(001) film with epitaxial Rh monolayers on both sides. We find the monolayers are ferromagnetic; this is a case of a paramagnetic element forming a ferromagnetic epitaxial overlayer. Electron capture spectroscopy has indicated[1] that V on Ag(001) is ferromagnetic but theory[2,3] is quite unequivocal in stating that it is antiferromagnetic and other experimental techniques[4,5] fail to find any sign of ferromagnetism. Furthermore, magnetic-susceptibility measurements[6] of small V clusters indicate[7] surface antiferromagnetism. We[8] recently calculated the magnetization of a free-standing Pd monolayer as a function of lattice constant and found that it obtained a maximum value of $0.40\mu_B$ at $a=5.467$ bohrs, which is identical to the Ag(001) surface lattice constant (i.e., $a=a_0/\sqrt{2}$). However, we found that epitaxial monolayers of Pd on both sides of a five-layer Ag(001) film were paramagnetic, which is consistent with the magneto-optical Kerr effect results of Ref. 5. We suggested that this might be due to a flow of electrons from the Ag into the Pd since Figs. 3 and 4 of Ref. 8 show a Löwdin[9] projection of the Pd *d* density of states (DOS) to have its leading edge well below the Fermi energy in the epitaxial case but not for the free-standing paramagnetic monolayer. We suggested that gold with its similar lattice constant and larger work function might serve as a substrate on which Pd would be ferromagnetic. Thus the first thing we looked at here was a five-layer gold film with paramagnetic Pd monolayers on both sides. We found the Pd *d* DOS was only negligibly closer to E_F than it was with the Ag substrate and so abandoned the idea of performing a ferromagnetic calculation. It is likely that the relative shift of the overlayer *s* and *d* bands due to interacting with the substrate is more important than the flow of charge between substrate and overlayer in determining whether or not a ferromagnetic free-standing monolayer will remain ferromagnetic as an epitaxial overlayer.

We will only present results here since our scalar-relativistic norm-conserving pseudopotential, Gaussian-orbital-expansion method is described in Ref. 8 as well as in an earlier publication[10] in which we found that a free-standing Mo monolayer was antiferromagnetic for $a>5.14$ bohrs and paramagnetic for smaller lattice constants.

We first calculated paramagnetic and ferromagnetic free-standing monolayers of Rh at the Ag lattice constant in order to have a direct comparison with Pd. The *sp* and *d* Löwdin[9] projected DOS are displayed in Fig. 1. Each energy level, calculated at 21 points in the irreducible wedge of the two-dimensional Brillouin zone, was given a

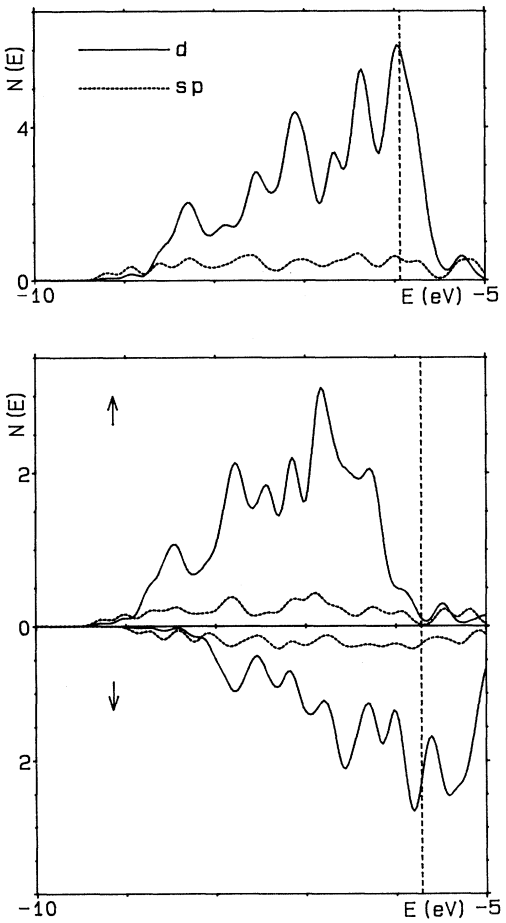

FIG. 1. The partial densities of states in electrons per atom per eV for a paramagnetic (top curve) and ferromagnetic (bottom curves) Rh(001) monolayer. The vertical lines are at $E=E_F$.

0.188-eV full width at half maximum broadening.[11] The paramagnetic work function is 5.94 eV and the ferromagnetic is 5.72 eV and the magnetization is $1.56\mu_B$, almost four times that of Pd. The ferromagnetic and paramagnetic cohesive energies are 3.890 and 3.718 eV, respectively, giving a magnetic energy of 0.182 eV, which is over nine times larger than the 19.8 meV obtained[8] for Pd.

We next calculated a five-layer Au film ($a_0/\sqrt{2}=5.454$ bohrs) with Rh epitaxial monolayers on both sides. The Rh-Au interplanar spacing was taken to be 3.724 bohrs, the average of their $a_0/2$. The minority- and majority-spin planar *sp* and *d* projected DOS are displayed in Figs. 2 and 3, respectively. The work function is 5.545 eV, compared with experimental values[12,13] of 5.47 and 5.18 eV for Au(001) and polycrystalline Rh, respectively, and the magnetic moment per Rh atom is $1.09\mu_B$. We have not calculated the paramagnetic state and therefore cannot give a magnetic energy. We did not feel it necessary to check for an antiferromagnetic ground state since the theorem of Heine and Samson[2] which states that the beginning or end of a transition-metal series will be ferromagnetic or paramagnetic while the middle will be antiferromagnetic or paramagnetic has held up in every two-dimensional case in which it has been tested.[3,8,10] Figure 4 is a contour plot of the charge density of the film. Although the Au and Rh contours look very similar, the two extra electrons associated with the gold are accounted for by the fact that the gold contours enclose a larger area than do the Rh. Had the contours been plotted in steps of 10 rather than factors of $\sqrt{2}$, the gold would peak at 500 and the Rh at 470. Figure 5 is a contour plot of the spin density $\rho_\uparrow-\rho_\downarrow$. Note that the units are $\frac{1}{10}$ those used in Fig. 4 for $\rho_\uparrow+\rho_\downarrow$. We see a non-negligible spin density exists on the first layer of gold atoms and a negative spin density exists in the interstitial regions. As is well known, this occurs because the majority-spin *sp* electrons see a more attractive exchange potential in the region where the *d* electrons are dense and thus do not extend with as great an amplitude into the interstitial region as do the minority-spin *sp* electrons.

When this calculation was nearly completed we became aware that the (001) surface of Au reconstructs into

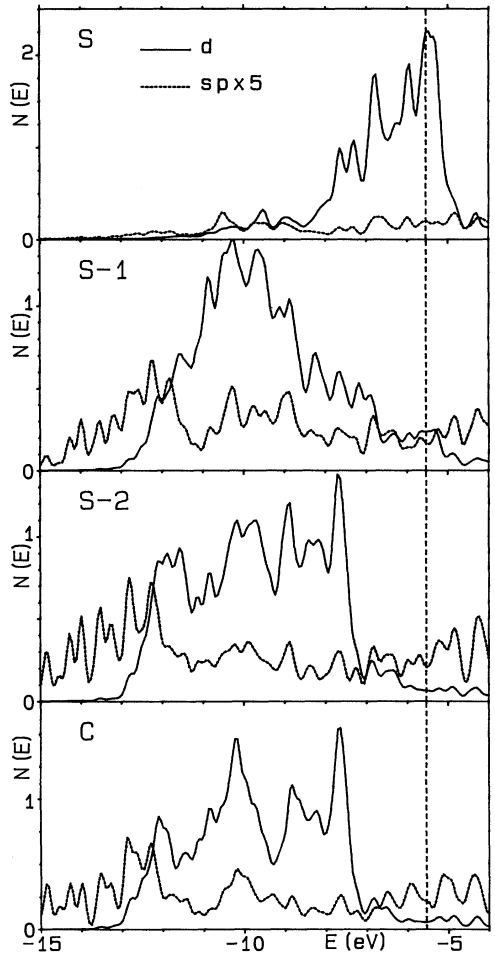

FIG. 2. The planar projected partial minority spin DOS for a five-layer Au(001) film with (1×1) Rh monolayers adsorbed. *S* is the surface Rh plane and *S*-1, *S*-2, and *C* the two subsurface and central Au planes. The vertical line is at $E=E_F$ and the units are electrons per atom per eV.

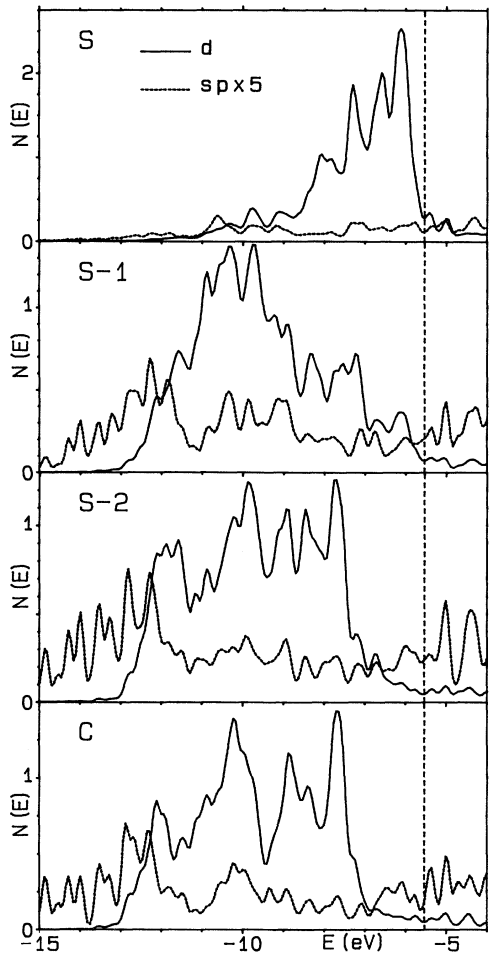

FIG. 3. Same as Fig. 2 but for majority spin.

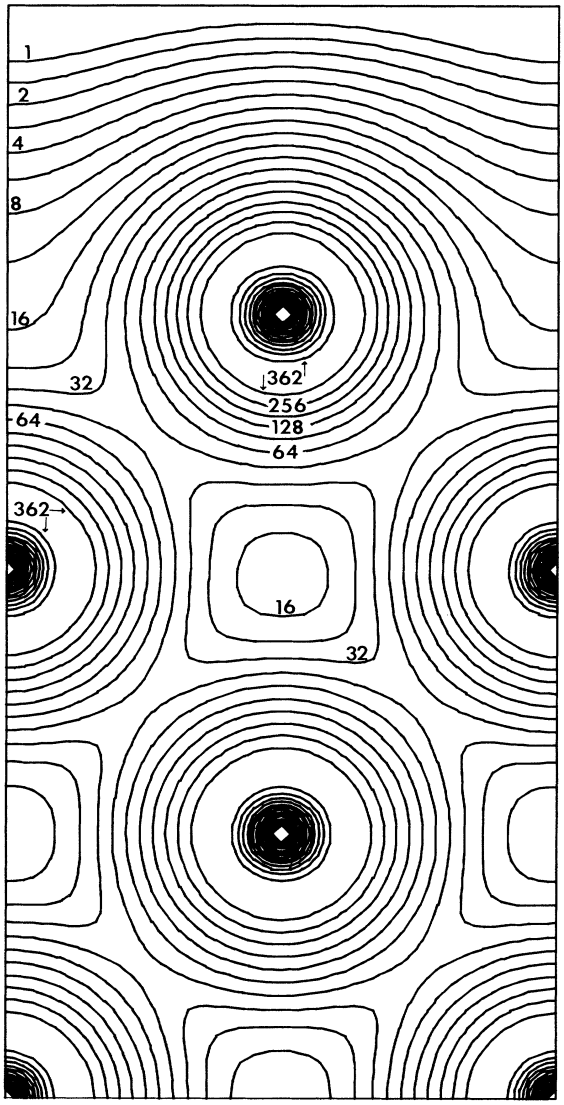

FIG. 4. Contours of constant charge density of half of five-layer Au(001) film with Rh monolayers adsorbed in units of millielectrons per cubic bohr. The contours increase by factors of $\sqrt{2}$.

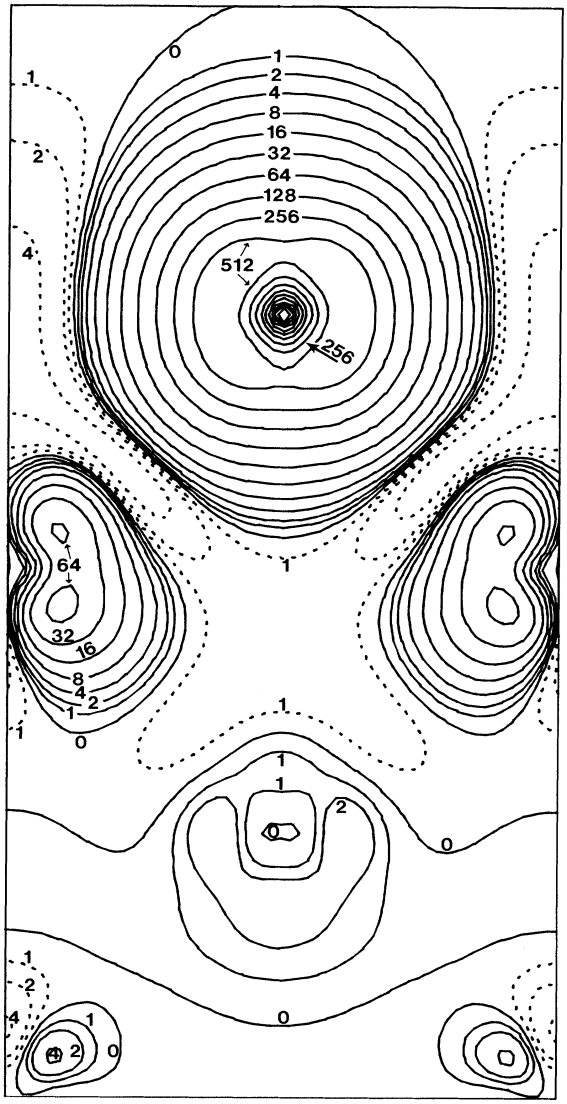

FIG. 5. Contours of constant spin-density polarization, $\rho_\uparrow - \rho_\downarrow$, in units of 10^{-4} electrons per cubic bohr. The dashed contours represent negative spin densities.

a tightly packed structure more dense than the unreconstructed (111) surface.[14,15] [This is consistent with the (001) work function being the largest.[12]] It is not clear whether a Rh overlayer will cause the Au substrate to remain ideal or if the Rh overlayer will grow epitaxially on the reconstructed surface. A denser overlayer will have less propensity to ferromagnetism but will be less strongly coupled to the substrate. Nevertheless, since we have found that Ag(001), which does not reconstruct,[15] and ideal Au(001) substrates have nearly identical effects on the leading edge of the Pd d DOS, we suggest that anyone seeking to find the first example of 4d ferromagnetism experimentally, try Rh on Ag(001). We expect some reduction of the magnetic moment below the $1.09\mu_B$ we have calculated due to the spin-orbit interaction. An estimate of the size of this effect can be obtained from a calculation[16] for bulk Pd with a 10% lattice expansion whose scalar relativistic value of $0.225\mu_B$ was reduced to $0.177\mu_B$ with the inclusion of the spin-orbit interaction.

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