Ferromagnetic properties of Pd monolayers

Ming J. Zhu, D. M. Bylander, and Leonard Kleinman
Department of Physics, The University of Texas at Austin, Austin, Texas 78712-1081
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Using a scalar-relativistic norm-conserving pseudopotential and a Gaussian-orbital expansion, we have calculated the magnetic moment and magnetic energy of a free-standing Pd(001) monolayer as a function of lattice constant a_0. They attain their maximum values when a_0 is close to the Ag nearest-neighbor distance. Nevertheless, we find that a Pd monolayer on Ag(001) is paramagnetic.

I. INTRODUCTION

There is substantial interest in finding the first paramagnetic metal which becomes ferromagnetic when grown epitaxially on the appropriate substrate, or which has a ferromagnetic surface in spite of being a bulk paramagnet. The first candidate was vanadium, which Rau *et al.*[1,2] using electron-capture spectroscopy (ECS), found to have a ferromagnetic (001) surface and also to have a ferromagnetic surface when any number of layers between one and seven were grown epitaxially on Ag(001). Moodera and Meservy[3] find somewhat indirectly that for thickness $d > 0.03$ monolayer (ML) V atoms on presumably polycrystalline 14-Å films of Au or Ag deposited over 90-Å lead films interact antiferromagnetically, but at $d \simeq 1.5$ ML the interaction becomes predominantly ferromagnetic. These results have been supported by theoretical calculations,[4,5] which found for monolayers that the ferromagnetic state lay below the paramagnetic, but which failed to consider the possibility of an antiferromagnetic ground state. Heine and Samson[6] have given a general proof, within the tight-binding approximation, that the beginning and end of a transition-metal series is ferromagnetic or paramagnetic, while the middle is antiferromagnetic or paramagnetic. *Ab initio* calculations[7] have proved to be consistent with this in that V, Cr, and Mn monolayers on Ag or Pd were found to be antiferromagnetic, while Fe, Co, and Ni were ferromagnetic. Spin-polarized photoemission[8] and magneto-optic Kerr-effect (MOKE) measurements[9] indicate V is not ferromagnetic on Ag(001), while magnetic-susceptibility measurements[10] of small V clusters indicate[11] surface antiferromagnetism. It is our opinion that the weight of experimental evidence favors V monolayers being paramagnetic or antiferromagnetic and, from the theoretical point of view, this is almost certainly the case.

Because of its strongly enhanced bulk paramagnetic susceptibility,[12] palladium appears to be the strongest candidate for two-dimensional ferromagnetism. Rau,[13] using ECS, finds up to 10 overlayers on Ag(001) are ferromagnetic, while the Pd(001) surface shows only very weak indications of ferromagnetism. Fink *et al.*[9] find no indication of ferromagnetism of Pd overlayers on Ag(001) in their MOKE measurements. Low-energy electron diffraction measurements of Lin *et al.*[14] indicate that the surface layer of Pd(001) relaxes outward by 3%, contrary to all other fcc metals, which contract; they find this to be consistent with the possibility of surface ferromagnetism. Several calculations find that Pd becomes a bulk ferromagnet with about a 6% expansion of the lattice constant. However, if one ignores the possibility of antiferromagnetism, V, Cr, and Mn also become ferromagnetic with expanded lattice constant;[15] thus one must invoke the theorem of Heine and Samson[6] to appreciate the significance of these results for Pd surfaces. Moruzzi and Marcus[16] find a first-order (i.e., the magnetization jumps discontinuously to a finite value at some lattice constant a) magnetic phase transition at $a = 7.83$ a.u., where the magnetic moment $\mu = 0.12\mu_B$. At $a = 8.44$ a.u. μ attains its maximum value of $0.36\mu_B$, falling to $0.25\mu_B$ at $a = 10.74$ a.u. and to zero at 14.59 a.u. (Unlike all other ferromagnetic elements, Pd with its d^{10} configuration is diamagnetic in the separated-atom limit.) Chen *et al.*[17] find μ jumps to $0.31\mu_B$ at $a = 7.735$ a.u. peaks at $0.35\mu_B$ when $a = 8.00$ a.u., and drops to $0.275\mu_B$ when $a = 10.0$ a.u. The largest discrepancy between these two calculations, the value of μ at the phase transition, may arise from the fact that Moruzzi and Marcus found a small range of lattice constants above the transition over which the paramagnetic state remained a local energy minimum, whereas Chen *et al.* did not. Fritsche *et al.*[18] performed calculations at the experimental lattice constant[19] $a = 7.3508$ a.u. and at 7.7183 and 8.0859 a.u. obtaining $\mu = 0\mu_B$, $0.117\mu_B$, and $0.225\mu_B$ with a scalar-relativistic Hamiltonian and $\mu = 0\mu_B$, $0.003\mu_B$, and $0.177\mu_B$ with a fully relativistic Hamiltonian. That the spin-orbit interaction reduces μ is not surprising; that the semirelativistic μ is smaller than the nonrelativistic μ's of Refs. 15 and 16 is.[20]

As far as we know, there have heretofore been no theoretical studies of Pd monolayers. In this work we study the properties of a free-standing Pd(001) monolayer as a function of lattice constant a_0 and then a five-layer Ag(001) slab with a (1×1) Pd overlayer on both sides. The monolayer calculation is essentially identical to that we[21] performed for Mo. We constructed a scalar-relativistic[22] norm-conserving pseudopotential,[23,24] used Kohn-Sham[25] exchange and Wigner[26] correlation, spin polarized in the manner of von Barth and Hedin,[27] and expanded in five s and p and four d Gaussians on each atom, plus two s and p floating Gaussians in the hollow sites on either side of the plane. The atomic Gaussians

were chosen in a harmonic sequence whose two parameters, along with the height and exponents of the floating Gaussians, were varied at each a_0 to minimize the energy calculated variationally using eigenfunctions of a non-self-consistent potential. The 56 Gaussians thus obtained were used in a self-consistent calculation at 21 points in the $\frac{1}{8}$ irreducible wedge of the Brillouin zone (BZ) (corresponding to 144 points in the full BZ). The charge density and exchange-correlation potentials were fitted at 4500 random points distributed as in the Mo calculation and using essentially the same set of Gaussian and plane-wave fitting functions.

The seven-layer slab was taken to have the experimental Ag(001) lattice constant, $a_0 = a_{\text{bulk}}/\sqrt{2} = 5.467$ bohrs, with $a_0/\sqrt{2} = 3.866$ bohrs, the spacing between Ag planes. The average of the Ag and Pd experimental spacings, 3.771 bohrs, was taken for the Ag-Pd interplanar spacing. The 144-point BZ sampling was again used. The atomic Gaussians obtained for the Pd monolayer at the Ag lattice constant were used on both Ag and Pd, but the longest-range s and p Gaussians caused numerical instabilities and had to be discarded, after which all the Gaussians were reoptimized. (This gives a total of 268 Gaussians per unit cell.) We fit at 20 000 random points, of which 208 are on a radial mesh[28] at random angles about the central-plane atom and 415 on each of the three atoms with $z > 0$. Another 300 points were taken in the selvage region $4a_0/\sqrt{2} \le z \le 5a_0/\sqrt{2}$, and the remaining 18 247 points between $0 \le z \le 4a_0/\sqrt{2}$.

II. RESULTS AND CONCLUSIONS

To make sure that our total-energy calculations were giving reasonable results, we calculated the cohesive energy of the paramagnetic Pd film over a large range of lattice constants, as shown in Fig. 1. The 4.8-bohr equilibrium lattice constant is somewhat larger than that calculated[21] for Mo. Also the 2.86-eV cohesive energy is essentially the same fraction of the experimental bulk cohesive energy as in the Mo calculation, although both are probably overestimates since bulk cohesive energies of transition metals calculated accurately in the local-density approximation are usually too large.[29]

We used the fixed-moment method[30] to evaluate the cohesive energy and magnetic moment in the ferromagnetic case at the set of a_0 shown in Fig. 2. Although bulk calculations have resulted in first- and second-order transitions for different metals, and even in cases in which there is a second-order transition to a low-magnetization state followed by a first-order transition to a high-magnetization state with increasing lattice constant,[15] we have found only simple second-order transitions in the two two-dimensional metals we have studied. The maximum difference between ferromagnetic and paramagnetic cohesive energies occurs at the Ag a_0 (5.467 bohrs) and is only 18.7 meV, while at the Pd a_0 (5.199 bohrs) this difference is 17.7 meV, and the magnetic moments at these two points are $0.45\mu_B$ and $0.42\mu_B$, respectively. This suggests that the (001) surface of Pd or a (1×1) monolayer of Pd on Ag(001) might be ferromagnetic. In Fig. 3 the s-p and d Löwdin[31] projection of the densities

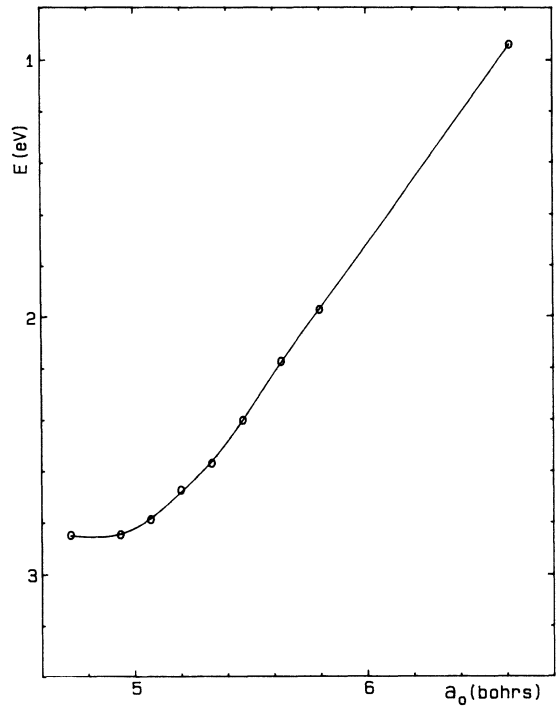

FIG. 1. Cohesive energy of a paramagnetic Pd(001) monolayer as a function of lattice constant.

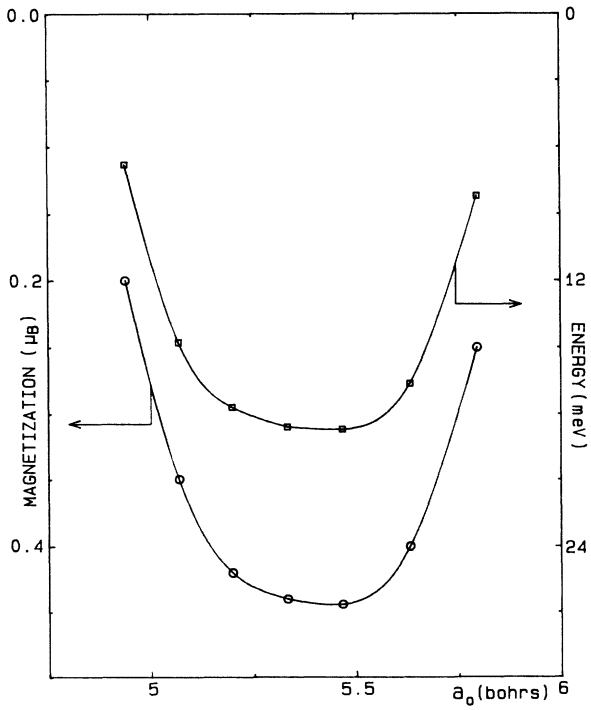

FIG. 2. Magnetic moment and magnetic energy (cohesive energy of the ferromagnetic state minus that of the paramagnetic) of a Pd(001) monolayer as a function of lattice constant.

of states (DOS's) are plotted for the paramagnetic and ferromagnetic states at the Ag a_0. We note that in the paramagnetic case the largest peak in the d DOS lies just below the Fermi energy, $E_F = -6.061$ eV (i.e., the work function is 6.061 eV), and that the DOS is still quite large at E_F, so that the ferromagnetic state becomes energetically favorable. In the ferromagnetic state the work function is 6.036 eV. This slight decrease relative to the paramagnetic state is simply a consequence of the DOS being larger below the paramagnetic E_F than above it. Experimental values of the work function are 5.6 eV for a (111) surface[32] and 5.55 eV for a polycrystalline film,[33] which implies about 5.50 eV for a (001) surface. Since a decrease of 0.4 eV in the calculated work function of V was obtained[34] in going from a monolayer to a seven-layer film, and since our work function was calculated for a Pd monolayer with a lattice constant 5% larger than the separation between (001)-surface atoms[35] on bulk Pd, our calculated value is just about what one would expect it to be relative to the experimental value. In order to get the minority- and majority-spin Fermi energies to be identical, we took our fixed-moment[30] results, released the moment, and iterated to full self-consistency. This lowered the magnetic moment to $0.40\mu_B$ and raised the magnetic energy to 19.8 meV. Thus the curves in Fig. 2 are not very accurate, but they suffice to show the range of lattice constants over which Pd(001) adlayers have a chance to be ferromagnetic. In any event, $\mu = 0.40\mu_B$ is 10% larger than the largest calculated bulk value at any lattice constant. Although the theorem of Heine and Samson[6] tells us that Pd will not be antiferromagnetic, we

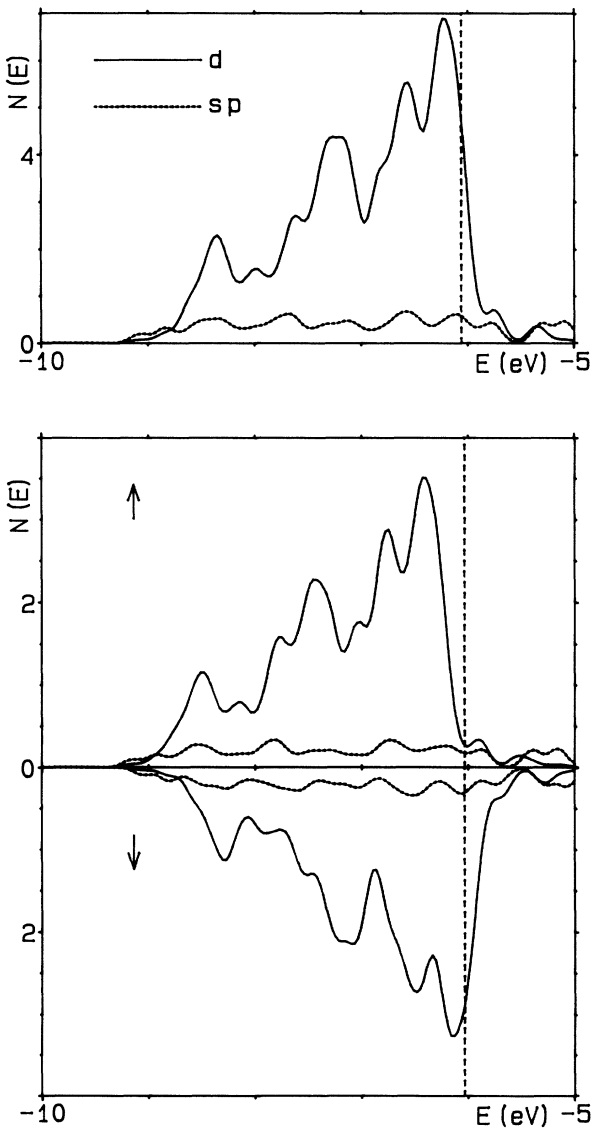

FIG. 3. Partial densities of states in electrons per atom per eV for a paramagnetic (top curve) and ferromagnetic (bottom curves) Pd(001) monolayer. Solid curves are d DOS's and dashed curves are s-p DOS's. The vertical line is at $E = E_F$.

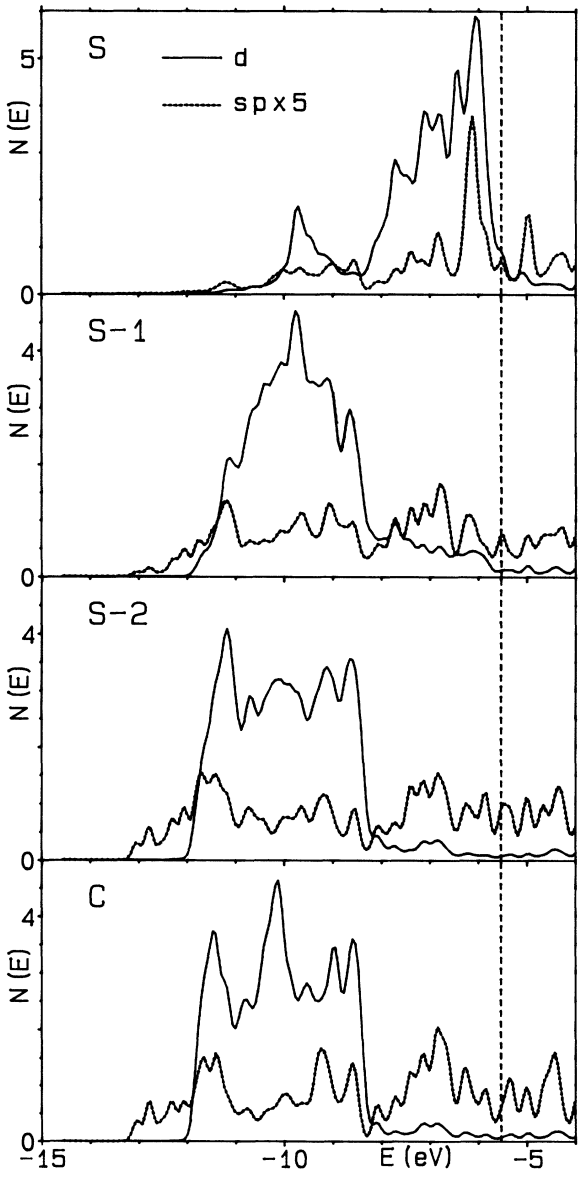

FIG. 4. Planar projected d DOS (solid curves) and s-p DOS×5 (dashed curves) for a five-layer Ag(001) film with (1×1) Pd monolayers adsorbed. S is the surface Pd plane, and $S-1$, $S-2$, and C the two subsurface and central Ag planes.

thought that an antiferromagnetic state might exist at an energy between the ferromagnetic and paramagnetic states. We attempted to calculate one at $a_0 = 5.467$ bohrs exactly as we[21] did for Mo, but found it converged to the paramagnetic state.

We performed a spin-unpolarized calculation for the five-layer Ag film with Pd monolayers on both sides. We then constructed a starting potential for the magnetic case by adding 1.5% of the Pd (d^9s) atomic charge density with spin up and subtracting 1.5% with spin down from the self-consistent unpolarized charge density. After iterating to self-consistency, the magnetic moment vanished. The reason for this can easily be understood with the help of the projected[31] DOS of Fig. 4. The peak in the Pd density of states in the surface plane now lies well below E_F, and the d bands are essentially filled, so that there is no way the surface can become ferromagnetic. The reason for this is that the work function of Ag(001) (according to Ref. 32, it is 4.64 eV) is well below that of Pd, and therefore electrons flow from Ag to Pd, filling the Pd d bands and forming a surface dipole which lowers E_F (relative to a clean Ag surface) to the value -5.538 eV shown in Fig. 4.

Thus we conclude that Pd monolayers have a strong propensity toward ferromagnetism. They fail to be ferromagnetic on Ag only because electrons flow from Ag to Pd, filling the d bands. Although the strong coupling between surface and bulk d bands could render the Pd(001) surface paramagnetic, nothing in this work indicates that it will not be ferromagnetic. Perhaps the best chance to observe a ferromagnetic Pd overlayer is on gold. The lattice constant is in the right range, the top of the Pd d bands should be fairly well decoupled from the gold d bands, and the Au(001) work function of[32] 5.47 eV is almost identical to that of Pd(001), so that the flow of electrons should be negligible.

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