Quantum-well-driven magnetism in thin films

S. Mirbt and B. Johansson
Condensed Matter Theory Group, Physics Department, Uppsala University, S-75121 Uppsala, Sweden

H. L. Skriver
Center for Atomic-scale Materials Physics and Physics Department, Technical University of Denmark, DK-2800 Lyngby, Denmark
(Received 1 March 1996)

We have performed local spin-density calculations for an fcc (100) Ag substrate covered by 1 to 16 monolayers (ML) of Pd. We find that thin films of Pd are magnetic with a moment of the order of $0.3\mu_B$ except for films of 1–2 ML and 5–7 ML where magnetism is completely suppressed. We present a physically transparent explanation of this behavior in terms of the Stoner picture and magnetic quantum-well states. [S0163-1829(96)50520-5]

In the past there has been speculation[1] as to whether metallic elements that are paramagnetic as bulk materials may become magnetic as free standing monolayers or as overlayers on top of a metallic substrate. Obvious candidates for such a change in magnetic behavior are the late transition metals Rh, Pd, and Pt, which have the largest exchange-enhanced susceptibilities among the transition metals,[2] and which, on account of their large state density at the Fermi level, $D(E_F)$, are close to fulfilling the Stoner criterion,

$$ID(E_F)>1, \tag{1}$$

for ferromagnetism. The Stoner exchange parameter I in (1) depends only on atomic number, and the onset of magnetism in the late transition metals may therefore be induced by a small enhancement of the state density. Such an enhancement may be accomplished by a uniform lattice expansion, and in fact, local spin-density calculations[3–5] predict that at approximately 5% expansion Pd will be magnetic with a moment which reaches a maximum value of approximately $0.3\mu_B$ before decreasing towards the Hund's rule free-atom limit of $0\mu_B$ corresponding to the atomic $4d^{10}$ configuration.

The state density may also be enhanced by the reduction in coordination number that follows the formation of thin films on, for instance, a noble metal substrate. For a single layer, simple tight-binding theory predicts a 30% increase in the state density and, hence, a Stoner product (1) well above 1. The expectation is therefore that thin films, and in particular a single layer, of a late transition metal should be truly magnetic. In spite of this expectation, local- (spin-) density calculations show that the Stoner criterion is not satisfied for monolayers (ML) of late transition metals.[6–8] This result is, however, in agreement with magneto-optical Kerr effect experiments, which show that a Pd monolayer on the (100) surface of fcc Ag is nonmagnetic.[9] On the other hand, in recent local-density calculations one finds weak magnetism in bilayers of late transition metals[10,11] and this is interpreted as the onset of bulk magnetism.[10] Furthermore, unrestricted Hartree-Fock calculations on $\mathrm{Ag/Pd}_N$ beyond monolayer coverage indicate that while a monolayer is nonmagnetic, thin films of Pd on a Ag substrate may be magnetic in the range from $N=2$ to 6 ML.[12] As pointed out by Bouarab *et al.*[12] such an irregular behavior cannot be a surface effect but must be a property of the Pd film.

To clarify the situation we have investigated the magnetic behavior of thin films of late transition metals by means of local spin-density calculations on an fcc (001) surface of Ag covered by up to 16 ML of Pd. We demonstrate that the irregular onset of magnetism in this system is in complete agreement with the formation of highly localized quantum-well states of the kind discussed in connection with magnetic multilayers.[13,14] In the present case, these quantum-well states show little dispersion parallel to the interface and therefore govern the onset of magnetism through their contribution to the state density. They may be viewed as a third, so far neglected, way of manipulating the Stoner product (1). We believe that the present results as well as previous local spin-density calculations carry sufficient weight to warrant experimental investigations of magnetism in thin films of late transition metals.

In the calculations we have used a scalar-relativistic, spin-polarized Green's-function technique for interfaces[15] based on the linear-muffin-tin orbitals method[16,17] within the tight-binding,[18–20] frozen core, and atomic-sphere approximations together with the local spin-density approximation in the Vosko-Wilk-Nusair parametrization.[21] In contrast to slab calculations, the Green's-function technique takes proper account of the broken symmetry perpendicular to the interface and therefore deals correctly with the semi-infinite nature of the problem. It also allows one to see the effect of the quantum-well states in the thin Pd film directly in the spectral density. The number of $k_\parallel$ points was taken to be 528 special points[22] in the irreducible part of the two-dimensional Brillouin zone. Moreover, the Wigner-Seitz radii S for Ag and Pd were chosen to be 3.005 a.u. corresponding to the experimentally observed lattice spacing of fcc Ag. Thus, lattice relaxations were neglected. However, a surface relaxation, i.e., a tetragonal distortion, has little effect on the important parts of the Pd Fermi surface and is therefore expected to be unimportant for the quantum-well-determined magnetism.

Previous spin-polarized calculations for bulk Pd predict the onset of ferromagnetism to occur at $S=3.06$ a.u., Ref. 4, or $S=3.02$ a.u., Ref. 5, which should be compared with the

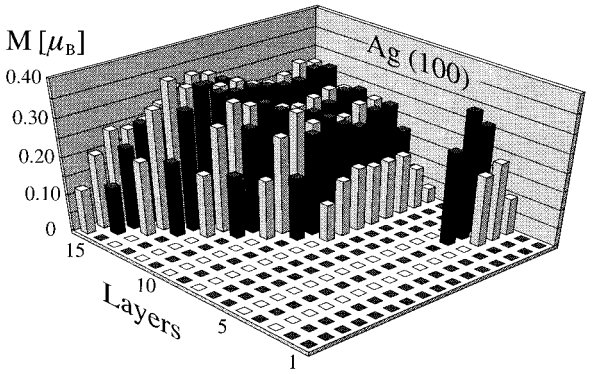

FIG. 1. Calculated magnetic-moment profiles for Ag/Pd_N as functions of Pd coverage N.

equilibrium value for Pd, $S_{\text{expt}} = 2.873$ a.u. Here, we find bulk Pd to be ferromagnetic with a moment of $0.29\mu_B$ already at the lattice spacing of Ag, i.e., for $S = 3.005$ a.u. This minor deviation from the earlier results may be attributed to the different exchange-correlation potentials used.[23] It dictates the asymptotic behavior of the Pd film but is otherwise unimportant for the physical picture we are going to present.[24] Finally, we find the Stoner exchange parameter I to be 0.65 eV, which is considerably larger than the value used by Bouarab *et al.*[12] but is in excellent agreement with earlier local spin-density calculations.[2,25]

The results of our interface calculations are presented in Fig. 1, where we show the calculated magnetic-moment profiles corresponding to from 1 to 16 ML of Pd on fcc (001) Ag. We find that 1 and 2 monolayers of Pd on Ag are nonmagnetic and that 3 and 4 ML are magnetic while 5, 6, and 7 ML again are nonmagnetic. Finally, at a coverage of 8 ML magnetism reenters and Pd remains magnetic with a magnetic moment that approaches the calculated bulk value. Thus, the present systematic study confirms the earlier local spin-density calculations for monolayers and bilayers[6–8,10,11] as well as the Hartree-Fock study[12] and shows that, contrary to the simplest expectations, Pd on Ag may exhibit a highly irregular magnetic behavior.

The question that must now be answered is not why thin Pd films may be magnetic but rather what physical effect causes the complete quenching of the magnetic moment for certain coverages. If we consider the Stoner picture for each individual coverage as presented in Fig. 2 we observe that for those coverages that have no magnetic moment the maximum state density at the Fermi level is reduced to a level where the Stoner criterion is not satisfied. It follows that the magnetism is suppressed by a reduction in the state density, but what causes the reduction? It is the main result of the present paper that the reduction in the state density and the resulting quenching of the magnetic moment are caused by quantum-well (QW) states in the Pd layers. Although our calculations are specific to Pd on Ag the physical effect may be operational in overlayer structures where both spin channels are confined to the overlayer and the exchange splitting is smaller than the separation of the quantum-well states.

To discuss the formation of quantum-well states in the Pd films we show in Fig. 3(a) the paramagnetic bulk energy bands for Ag and Pd in the direction perpendicular to the interface. In the energy range above the top of the Ag d

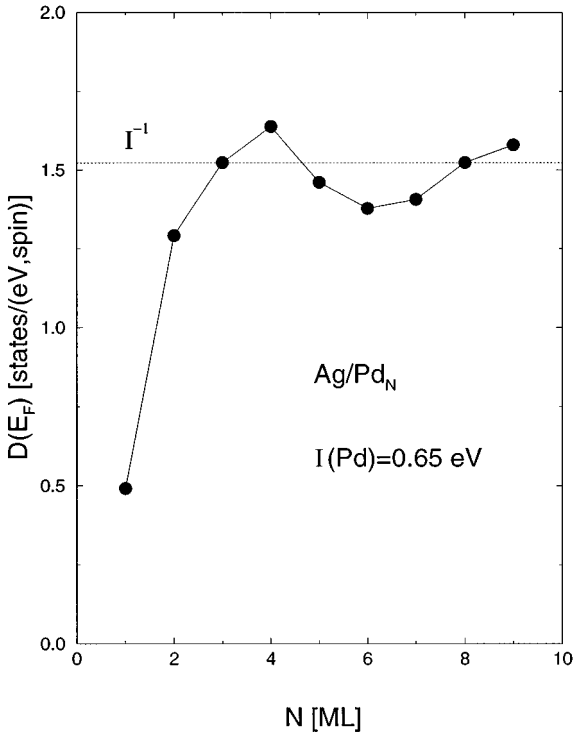

FIG. 2. Maximum Pd-layer–resolved state density at the Fermi level as a function of Pd coverage.

band, X_5(Ag), the band structure of Ag has a large degree of s character and as a result the Pd d states extending in energy up to X_5(Pd) cannot penetrate into the Ag host. Since they are also reflected at the vacuum interface, the work function being 5.7 eV, they are confined to a quantum well in the Pd film.[26] The continuum band structure of Pd is therefore discretized with the number of discrete QW states per band equal to the number of atomic layers in the film. One example of this discretization is shown as open squares in Fig. 3(a) but we stress that all d states in the energy range indicated by the arrow are discretized. We also note that the calculated exchange splitting in ferromagnetic Pd is only 0.2 eV and therefore the QW picture holds for both spin channels.

It is well known[27] that the shape of the state density in the immediate neighborhood of the Fermi level in Pd to a large degree is determined by the fifth band, which is the topmost of those ending at X_5 in Fig. 3(a). Note that the symmetry labels Δ_5 and X_5 refer to doubly degenerate states. The fifth band in Pd has essentially no dispersion along the XZW direction of the Brillouin zone and therefore the corresponding QW states have little dispersion as functions of $k_\parallel$. As a result, these QW states give a large contribution to the state density of the Pd film close to the Fermi level and may thereby govern the onset of magnetism.

The most characteristic feature of the Fermi surface of the late transition metals is the so-called $XW5$ open hole sheet which, because of the absence of dispersion along XZW, has the topology of cylinders along the $\langle 100 \rangle$ directions joined at X.[27] In the plot of the Fermi surface Fig. 3(b) these cylinders are seen as the rounded squares with the sides parallel to the boundaries of the Brillouin zone. It is the calipers of these Fermi-surface cross sections that determine the period with

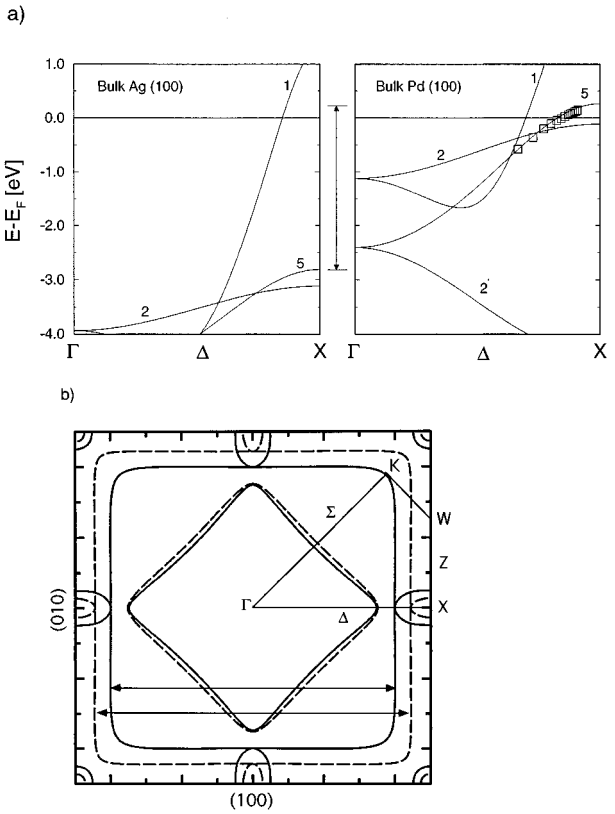

FIG. 3. (a) The energy bands for Ag and Pd at $S=3.005$ a.u. in the direction perpendicular to the Ag/Pd interface. The vertical arrow indicates the energy range of the Pd d-band quantum well. In the Pd panel we show by open squares as an example the topmost QW branch of Fig. 4 quantized according to the number of Pd layers (Ref. 28). (b) Exchange-split (001) cross sections of the Fermi surface of bulk Pd. Broken lines correspond to majority spin and solid lines to minority spin. The arrows indicate the nesting Fermi-surface calipers.

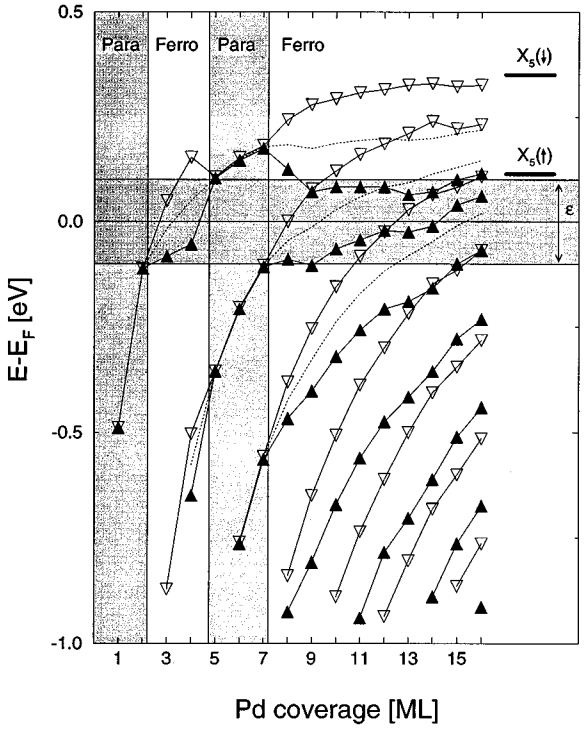

FIG. 4. Quantum-well states in Ag/Pd_N as functions of Pd coverage N. Open triangles correspond to minority-spin states and full triangles to majority-spin states. The dotted lines correspond to the paramagnetic QW states. The horizontally shaded area indicates the energy range ϵ where QW states must be present at a particular coverage in order to induce magnetism in the Pd film.

which the QW states move through the Fermi level as the number of atomic Pd layers increases. The arrows in Fig. 3(b) correspond to a period of 5 ML in the majority spin channel and 9 ML in the minority spin channel. The fact that these periods are independent of $\mathbf{k}_\parallel$ over large parts of the Brillouin zone means that many QW states will contribute to the state density at the same energy. We therefore conclude that the QW states in the fifth band of Pd give a major contribution to the state density of a Pd film. Depending on how close the QW states are to the Fermi level this contribution may, according to the Stoner criterion (1), either induce or suppress the onset of magnetism in the thin film.

The QW states in the Pd film are seen directly as narrow peaks in the spectral density,

$$D_s(E,\mathbf{k}_\parallel) = -\frac{1}{\pi}\mathrm{Im\ Tr}\sum_i G_{ii}(E,\mathbf{k}_\parallel), \tag{2}$$

calculated from the Green's-function matrix elements G_{ii} summed over the Pd layers i. We find that in the energy range close to the Fermi level all the calculated QW spectra exhibit two kinds of peaks, one that only exists at $\overline{\Gamma}$ and therefore is unimportant for the total state density and the other which exists at the same energy over an extended range in the two-dimensional Brillouin zone and thereby controls the state density. The latter we associate with the QW states in the fifth band of Pd described above.

In Fig. 4 we show as a function of the number of atomic Pd layers the position of those peaks in the spectral density at $\overline{\Gamma}$ that have essentially no dispersion in $\mathbf{k}_\parallel$. It is seen that the majority- and minority-spin QW states move through the Fermi level with periods of 9.8 ML and 4.6 ML, respectively, in good agreement with the Fermi-surface calipers shown in Fig. 3(b). Furthermore, one observes that the topmost exchange-split QW states move asymptotically towards the extrema of the Pd bulk bands at the X point, $X_5(\downarrow)$ and $X_5(\uparrow)$. Finally, if one plots the energies of the highest, paramagnetic QW branch in Fig. 4 as a function of $k_\perp$ one obtains the fit[28] to the Δ_5 band of Pd shown by squares in Fig. 3(a). We have thereby established the origin of the QW states in the Pd film and explained why they change with Pd coverage as shown in Fig. 4.

We may now answer the question as to why the magnetism in thin Pd films on Ag is quenched for certain coverages. To do so, we observe that at large coverages the layer projected state density at the Fermi level will approach the value for bulk Pd. Hence, for these coverages, here larger than 7 ML, the Stoner criterion will be satisfied and a magnetic moment of the order of the bulk value of $0.3\mu_B$ is obtained. As the energy separation of the discrete QW states increases with decreasing coverage one reaches a stage where there are no QW states close to the Fermi energy. Thereby, the state density at the Fermi level is reduced, the

Stoner criterion is no longer fulfilled, and, as a consequence, the magnetism is quenched. This happens for the Ag/Pd_N system for coverages of 1, 2, 5, 6, and 7. On the other hand, if a QW state is close to the Fermi level the state density will increase and magnetism may occur. This happens for coverages of 3 and 4.

Knowing the Stoner parameter, one may estimate how close to the Fermi level a QW state has to be to sustain a magnetic state. In fcc Pd the shape of the state density close to the Fermi level is such that the largest possible magnetic moment M is $\simeq 0.35\mu_B$. With $I = 0.65$ eV the associated exchange splitting of the QW state will therefore at most be

$$\epsilon = MI \simeq 0.2 \text{ eV}. \tag{3}$$

In order to maintain this exchange splitting, i.e., to keep the spin-up QW state occupied and the spin-down QW state unoccupied, it is necessary that the paramagnetic (nonexchange-split state) QW state lies less than 0.1 eV from the Fermi level. A comparison with Fig. 4 shows that this simple picture explains very well the magnetic behavior as a function of the film thickness.

In summary, we have used a leading edge first-principles computational technique to investigate the formation of magnetic moments in Pd overlayers on a Ag substrate. We find a situation in which the magnetic behavior for low coverages, less than 8 ML, is governed by quantum-well states in the Pd film. Although the calculations are specific to Ag/Pd_N, they lead to definite and unexpected predictions for the behavior of magnetism in thin films. Apart from the use of the local spin-density approximation and the Green's-function technique, the predictions are based on perfect conditions, i.e., we have not considered the many imperfections that in an experimental situation may prevent the formation of a magnetic moment. We therefore suggest that the search for the effect be extended also to the remaining group-8 transition elements.

We thank Lars Nordström and Anders Niklasson for helpful discussions. The support by the Swedish Materials Consortium No. 9 is acknowledged. The Center for Atomic-scale Materials Physics is sponsored by the Danish National Research Foundation.

[1] J. Mathon, Rep. Prog. Phys. **51**, 1 (1988).
[2] J. F. Janak, Phys. Rev. B **16**, 255 (1977).
[3] L. Fritsche, J. Noffke, and H. Eckardt, J. Phys. F **17**, 943 (1987).
[4] V. L. Moruzzi and P. M. Marcus, Phys. Rev. B **39**, 471 (1989).
[5] H. Chen, N. E. Brener, and J. Callaway, Phys. Rev. B **40**, 1443 (1989).
[6] S. Blügel, B. Drittler, R. Zeller, and P. H. Dederichs, Appl. Phys. A **49**, 547 (1989).
[7] S. Blügel, Phys. Rev. Lett. **68**, 851 (1992).
[8] O. Eriksson, R. C. Albers, and A. M. Boring, Phys. Rev. Lett. **66**, 1350 (1991).
[9] R. L. Fink, C. A. Ballentine, J. L. Erskine, and J. A. Araya-Pochet, Phys. Rev. B **41**, 10 175 (1990).
[10] S. Blügel, Phys. Rev. B **51**, 2025 (1995).
[11] B. Újfalussy, L. Szunyogh, and P. Weinberger, Phys. Rev. B **51**, 12 836 (1995).
[12] S. Bouarab, C. Demangeat, A. Mokrani, and H. Dreysse, in *Magnetic Surfaces, Thin Films, and Multilayers*, edited by S. S. P. Parkin, H. Hopster, J.-P. Renard, T. Shinjo, and W. Zinn, MRS Symposia Proceedings No. 231 (Materials Research Society, Pittsburgh, 1992), p. 317.
[13] D. M. Edwards and J. Mathon, J. Magn. Magn. Mater. **93**, 85 (1991).
[14] J. E. Ortega and F. J. Himpsel, Phys. Rev. Lett. **69**, 844 (1992).
[15] H. L. Skriver and N. M. Rosengaard, Phys. Rev. B **43**, 9538 (1991).
[16] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).
[17] H.L. Skriver, *The LMTO Method* (Springer-Verlag, Berlin, 1984).
[18] O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).
[19] O.K. Andersen, O. Jepsen, and D. Glötzel, in *Highlights of Condensed-Matter Theory*, edited by F. Bassani, F. Fumi, and M.P. Tosi (North-Holland, New York, 1985).
[20] O. K. Andersen, Z. Pawlowska, and O. Jepsen, Phys. Rev. B **34**, 5253 (1986).
[21] S.H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
[22] S. L. Cunningham, Phys. Rev. B **10**, 4988 (1983).
[23] Neither Moruzzi and Marcus (Ref. 4) nor Chen *et al.* (Ref. 5) explicitly state the exchange-correlation potential used in their calculations. However based on the authors previous publications in the field one may assume that they have used either the local spin-density potential given by U. von Bath and L. Hedin, J. Phys. C **5**, 1629 (1972) or the corrected form by J.F. Janak, Phys. Rev. B **12**, 1257 (1975).
[24] We have also performed interface calculations for the Ag/Pd_N system at the Pd lattice spacing where bulk magnetism is suppressed. The results are similar to those presented in Fig. 1 except for the fact that thick Pd films have no magnetic moment. However, the results at the Ag lattice spacing seem the most relevant ones for comparison with experiments.
[25] N.E. Christensen, O. Gunnarsson, O. Jepsen, and O.K. Andersen, J. Phys. (Paris) **49**, C8-17 (1988).
[26] For a transparent description of this point we refer to P. Bruno, Phys. Rev. B **52**, 411 (1995).
[27] O. K. Andersen, Phys. Rev. B **2**, 883 (1970).
[28] We have assumed that the width of the quantum well is $D_N = (N + \frac{1}{2})d$, where N is the number of Pd layers and d is the interlayer spacing.