Prediction of Ferromagnetism and Metamagnetism in 4*d* Transition-Metal Overlayers on the (001) Surface of Ag (4*d* =Tc, Ru, Rh, and Pd)

Olle Eriksson, R. C. Albers, and A. M. Boring
Center for Materials Science and Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 22 October 1990)

We present the first theoretical evidence for ferromagnetism in 4*d* overlayers on a nonmagnetic substrate. These predictions are based on *ab initio*, spin-polarized, electronic-structure calculations within the framework of the local-spin-density approximation. For Tc, Ru, Rh, and Pd overlayers chemisorbed on Ag(001), only Ru and Rh exhibited ferromagnetism. Several metamagnetic spin states were found for the Ru overlayers.

PACS numbers: 73.20.At, 75.10.Lp, 75.70.Ak

Atoms for which the intra-atomic exchange interaction is sufficiently large to drive a magnetic transition in pure elements and their compounds are normally restricted to 3*d* transition-metal, rare-earth, and actinide systems.[1] Often, these atoms also induce magnetism in nonmagnetic systems; for example, Lu shows an induced moment in $LuFe_2$ and Sn shows an induced moment in $NpSn_3$. Magnetic compounds can also be formed from atoms that are nonmagnetic as pure elements (e.g., UCu_5), and the inverse situation exists as well; i.e., nonmagnetic compounds can be formed from atoms that are magnetic as pure elements (e.g., YNi_2). Breaking the crystal symmetry and forming a surface is also expected to result in new magnetic configurations, since nonmagnetic systems can become magnetic at surfaces.[2] Although the available parameter space for tuning magnetic properties seems, therefore, to be quite large, magnetism is rarely observed among the 4*d* or 5*d* transition-metal elements; only a few exceptions exist. For instance, bulk $ZrZn_2$ is ferromagnetic,[1] and magnetism has been theoretically predicted in a Au/Pd/Au sandwich system, although the predicted moment[3] is almost negligible (about $0.02\mu_B$). A Pd monolayer calculation also gave a ferromagnetic ground state,[4,5] although an experimental check of these results would require putting the monolayer on a substrate, which can destroy magnetism. For example, the calculations of Zhu, Bylander, and Kleinman[5] showed that a Pd monolayer is paramagnetic on a Ag(001) substrate. Thus, *we know of no realistic published calculations that predict magnetism of 4d overlayers on a nonmagnetic substrate.* This lack of magnetism (other than induced magnetism such as[4] Pd on Fe) among the 4*d* elements is surprising, since the late 3*d* isoelectronic transition-metal elements show magnetic ordering with atomic volumes that are nearly the same. The extra node in the 4*d* wave function (due to orthogonality to the 3*d* core wave function) must apparently increase the wave-function overlap enough to prevent magnetism.

This Letter represents a systematic search for magnetism in the 4*d* transition-metal elements. In this search it is natural to look at the very end of the 4*d* series, since these elements have the narrowest bands (e.g., Pd). However, although the susceptibility of Pd looks promising (it is strongly enhanced), band-structure calculations on bulk Pd show that the paramagnetic state is stable.[6] Only with a high magnetic field (~100 T) present in the calculations was a ferromagnetic state found to be stable[6] (with a moment of $0.19\mu_B$).

In our search we have tried to tune different parameters that might favor a 4*d* magnetic ground state. One possibility is geometries that favor narrow bands; this suggests a consideration of Tc, Ru, Rh, and Pd chemisorbed on Ag surfaces. The reduced coordination of the surface atoms as well as the increased interatomic distances of the chemisorbed atoms produces narrower bands. Moreover, because the lattice mismatch is never larger than 7%, it should be experimentally possible to grow these systems. To keep the search simple, we have not included surface-relaxation effects, since they are not known for these systems; the equilibrium Ag lattice constant has been used for all the calculations. Our theoretical approach is the restricted form of the density-functional theory, namely, the fixed spin-moment (FSM) method,[7] in a film-linearized muffin-tin orbital code.[8]

In ordinary band calculations, based on density-functional theory, the ground state is obtained by minimizing the functional

$$E(N)=\min\left[E(n(\mathbf{r}))+v\left(\int_V d^3r\,n(\mathbf{r})-N\right)\right]. \quad (1)$$

The number of electrons in the volume V is constrained to be exactly N. The factor v is a Lagrange parameter, $n(\mathbf{r})$ is the charge density, and $E(n(\mathbf{r}))$ is the usual energy functional. In the FSM method another constraint is imposed on the system, namely, that the magnetic moment of the electrons in the volume V is fixed to be M. This leads to minimizing the functional

$$E(N,M)=\min\left[E(n(\mathbf{r}),m(\mathbf{r}))+v\left(\int_V d^3r\,n(\mathbf{r})-N\right)+H\left(\int_V d^3r\,m(\mathbf{r})-M\right)\right]. \quad (2)$$

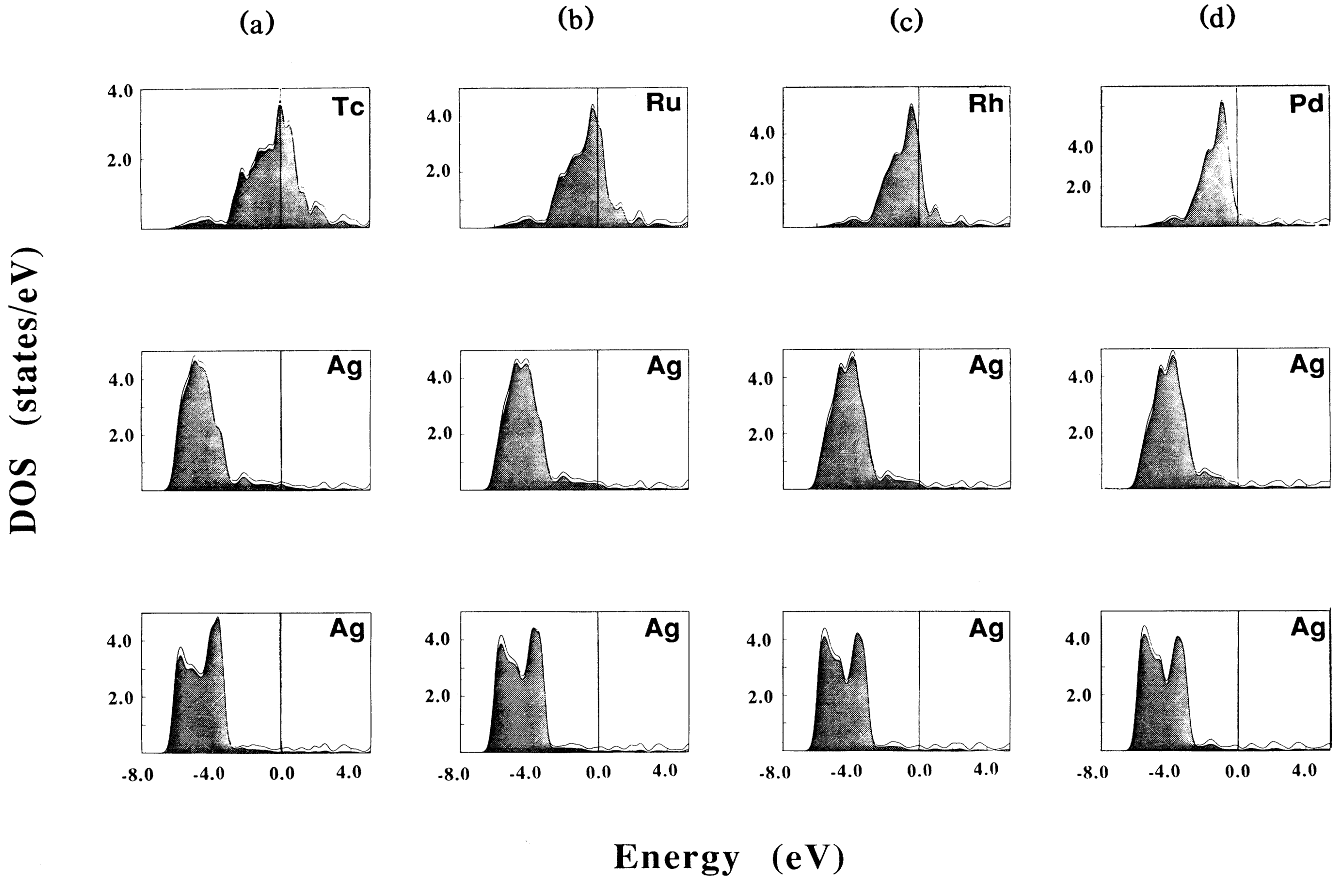

FIG. 1. Paramagnetic density of states (DOS) of a 4*d* monolayer on the Ag(001) surface for the 4*d* systems: (a) Tc, (b) Ru, (c) Rh, and (d) Pd. The hatched area represents the *d* partial DOS, and the DOS is projected on the center (bottom panel), subsurface (middle panel), and surface (top panel) atoms. Energies are in electronvolts; the Fermi level is at zero and is marked with a vertical line.

Here, H is another Lagrange parameter and $m(\mathbf{r})$ is the spin density. In this scheme for calculating the electronic structure and total energy for a given, constrained, spin moment,[7] the occupations of the valence electrons for the two spin channels are given by

$$N^{\uparrow}=\int_{-\infty}^{E_F^{\uparrow}} D^{\uparrow}(E)dE\,, \tag{3}$$

$$N^{\downarrow}=\int_{-\infty}^{E_F^{\downarrow}} D^{\downarrow}(E)dE\,, \tag{4}$$

where $M=N^{\uparrow}-N^{\downarrow}$ and $N=N^{\uparrow}+N^{\downarrow}$. The total energy can be calculated as a function of M, and, whenever a local minimum or maximum is found,[7] $E_F^{\uparrow}=E_F^{\downarrow}$. We have implemented this method in a film-linearized muffin-tin orbital method.[8] The calculations were performed for a five-layer slab and employed nine muffin-tin orbitals[9] per atom as well as eighteen plane-wave orbitals.[8] The warping of the potential was accounted for as described in Ref. 8 and the Vosko-Wilk-Nusair parametrization[10] of the local-spin-density approximation was used. Final self-consistency was obtained using ten special k points in the irreducible wedge of the two-dimensional Brillouin zone.[11] The calculations were done for a five-layer slab (three Ag layers with a 4*d* monolayer on each side). In order to check if the slab thickness was large enough, we also performed a seven-layer calculation for paramagnetic Pd/Ag(001). All calculated properties (charge-density contours, orbital occupation numbers, work functions, and density of states) differ very little between the five- and seven-layer calculations. This justifies using a five-layer geometry in the rest of the calculations.

In Fig. 1 we show our calculated densities of states (DOS) for the paramagnetic 4*d*/Ag(001) overlayers (4*d*=Tc, Ru, Rh, and Pd). Notice that the substrate DOS looks very similar for all the different chemisorbed atoms. This indicates that the interaction or hybridization between the bulk and surface atoms is quite small. This is because the Ag *d* band is located at low energies where the *d* band of the chemisorbed atom has very small spectral weight. Therefore, *these systems can be viewed as approximately two dimensional.* Nonetheless, we emphasize that approximating a 4*d* overlayer on Ag as a free-standing monolayer is insufficient, since the interaction between the surface and the substrate is sufficient to affect the magnetic properties of the monolayer. Notice also, due to incomplete screening, that the surface *d* band narrows going across the series (Tc to Pd). One would therefore expect Pd to be the best candidate for a magnetic instability. However, as seen in Fig. 1, most of the Pd *d*-DOS is located below the Fermi level (E_F), which leads to a low DOS at E_F, and hence is actually less likely to be magnetic; the calculated Stoner product for this system is less than 1. However, the situation is more promising for the lighter 4*d* elements (see Fig. 1), since these systems have an unfilled *d* band and a correspondingly high DOS at E_F. The Stoner products of Rh/Ag(001) and Ru/Ag(001) are slightly larger than 1, indicating that a ferromagnetic ground state is more favorable than a paramagnetic state.

In order to investigate the possibility of magnetic ordering or metamagnetic states, we have performed spin-polarized FSM calculations.[7] For the Pd/Ag(001) system there is no metastable state, since the total energy increases monotonically with the magnetic moment (see Fig. 2). However, the Rh/Ag(001) system exhibits magnetism with a magnetic moment that is almost entirely associated with the Rh atom. The total moment is $1.32\mu_B$/unit cell (which contains two Rh atoms), and the Rh moment is $0.62\mu_B$/atom. The Rh moment can be decomposed into orbital angular-momentum components, and, as expected, the *d* component dominates, $\mu_d(\mathrm{Rh}) = 0.61\mu_B$. The total energy is lowered by 2.4 mRy when the system spin polarizes. The Ru/Ag(001) system is somewhat more exotic. Although the Stoner product is larger than 1, the total-energy curve shows only a small drop with increasing magnetic moment. For a large range of magnetic moments the total energy is almost constant with small variations. We therefore find several local minima of the total energy. One minimum has a total moment of $0.29\mu_B$/unit cell [low spin (LS)], another has a total moment of $0.77\mu_B$/unit cell [medium spin (MS)], and another has a total moment of $3.42\mu_B$/unit cell [high spin (HS)]. The LS state is lowest in energy, although the energy difference between the paramagnetic state and the LS state is very small (see Fig. 2), and the other states are metamagnetic with the HS state 2.9 mRy higher in energy than the LS state. Also, for this system the moment is dominated by the chemisorbed atom, Ru. For the LS state the Ru moment is $0.14\mu_B$, for the MS state $0.36\mu_B$, and for the HS state $1.59\mu_B$.

To understand the magnetism in these systems, we note that a high DOS at E_F is required for the Stoner product to be larger than 1. The optimal situation to achieve this is a partially filled narrow *d* band (note that the DOS is usually highest somewhere in the middle of a band). While the late 4*d* elements (i.e., Pd) have the narrowest *d* bands, these *d* bands are almost completely filled, and they have a low DOS at the Fermi energy. The 4*d* elements to the left of Pd have slightly broader *d* bands, but since they have a nonfilled *d* band, the Fermi energy cuts the DOS where it is quite high (Fig. 1). Because the occupation effect on the DOS predominates, our calculations show that the spin polarization drops as we move from Rh to Ru. This raises the possibility that Tc might show a magnetic instability; unfortunately, Fig. 2 shows that this is not the case. Although the total-energy curve is initially very flat with increasing magnetic moment, the curve is monotonically increasing. Apparently, the *d* band has become sufficiently broad in Tc to prevent magnetic ordering.

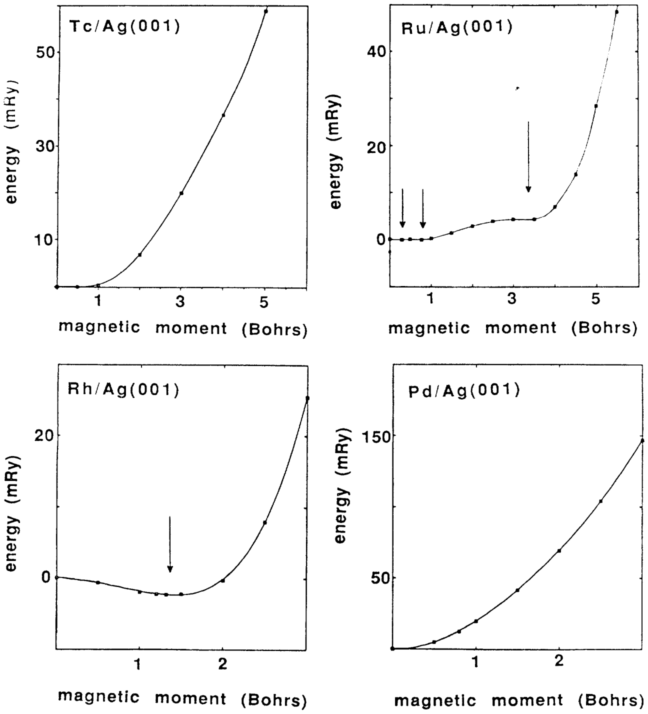

FIG. 2. Calculated total energy as a function of the constrained magnetic moment for the 4*d*/Ag(001) systems, 4*d* =Tc, Ru, Rh, and Pd.

Although this is not the main result of the present investigation, we have calculated the work functions to be 5.9, 6.0, 5.8, and 5.8 eV for Tc/Ag(001) to Pd/Ag(001), respectively.

In conclusion, we have predicted ferromagnetism and metamagnetism in 4*d*/Ag(001) overlayers. Experimental data to confirm or deny these possibilities would be useful. Ideally, monatomic overlayers would be best, in order to minimize the interaction (or hybridization) between the substrate and the chemisorbed atoms, even though this might complicate the experimental work. Although we have neglected the effects of surface-relaxation effects in our calculations, we expect that the bands would become even more narrow if the surface layer relaxed outward, and, hence, relaxation might enhance the tendency for magnetism in borderline systems. Finally, speculations on possible systems that might become magnetic at the surface lead us to expect that nonmagnetic narrow-band systems (such as U, Np, and Pu) chemisorbed on Ag might be "pushed" into a magnetic ground state; investigations of these systems are underway. For these systems orbital moments should be important, which would require a fully relativistic treatment. Also, since it seems that the substrate interacts weakly with the chemisorbed atoms, these effects might be found with substrates of Cu or Au, which are isoelectronic with Ag.

This work was supported by the Department of Energy. Valuable discussions with B. Johansson, Uppsala University, are acknowledged.

---

[1] See articles in *Ferromagnetic Materials,* edited by E. P. Wohlfarth and K. H. J. Buschow (Elsevier, Amsterdam, 1988).

[2] C. L. Fu, A. J. Freeman, and T. Oguchi, Phys. Rev. Lett. **54**, 2700 (1985); S. Ohnishi, C. L. Fu, and A. J. Freeman, J. Magn. Magn. Mater. **50**, 161 (1985).

[3] S. C. Hong, C. L. Fu, and A. J. Freeman, J. Appl. Phys. **63**, 3655 (1988).

[4] H. Huang, J. Hermanson, J. G. Gay, R. Richter, and J. R. Smith, Surf. Sci. **172**, 363 (1986).

[5] M. J. Zhu, D. M. Bylander, and L. Kleinman, Phys. Rev. B **42**, 2874 (1990).

[6] T. Jarlborg and A. J. Freeman, Phys. Rev. B **23**, 3577 (1981).

[7] A. R. Williams, V. L. Moruzzi, J. Kübler, and K. Schwarz, Bull. Am. Phys. Soc. **29**, 278 (1984); K. Schwarz and P. Mohn, J. Phys. F **14**, L129 (1984).

[8] H. Krakauer and B. R. Cooper, Phys. Rev. B **16**, 605 (1977); C. Q. Ma, M. V. Ramana, and B. R. Cooper, J. Vac. Sci. Technol. A **1**, 1095 (1983); C. Q. Ma, M. V. Ramana, H. Krakauer, and B. R. Cooper, Phys. Rev. B **34**, 3854 (1986); G. W. Fernando, B. R. Cooper, M. V. Ramana, H. Krakauer, and C. Q. Ma, Phys. Rev. Lett. **56**, 2299 (1986). The scalar relativistic code from which the present code was developed was supplied by the authors above.

[9] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); O. K. Andersen and R. V. Kasowski, Phys. Rev. B **4**, 1004 (1971).

[10] S. H. Vosko, L. Wilk, and N. Nusair, Can. J. Phys. **58**, 1200 (1980).

[11] S. L. Cunningham, Phys. Rev. B **10**, 4988 (1974).