Ferromagnetism of the Rh(001) Surface

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Ab initio pseudopotential calculations of a nine-layer Rh(001) film find the surface and first subsurface layers are ferromagnetic. The calculated surface energy lies within the range of experimental estimates and the discrepancy between LEED and an earlier calculation for the surface relaxation is greatly reduced.

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Feibelman and Hamann [1] (FH) have found a -5.1% (inward) surface relaxation of Rh(001) in their linearized augmented plane wave (LAPW) calculation. They compared this with the low energy electron diffraction (LEED) value [2] of $(+0.5\pm 1)\%$. They then calculated the reduction in the force on the outermost Rh layer [3] when a layer of hydrogen was adsorbed and estimated that this would reduce Δd_{12} to -1.4% (where Δd_{ij} is the percentage change in the spacing between the ith and jth planes, numbered inwardly from the surface, relative to the bulk spacing). This caused FH to speculate that the LEED data were collected from H covered surfaces. Li *et al.* [4] tersely mention that FH did not consider magnetic surface layers, the point being that the magnetic pressure would cause d_{12} to expand. It is well known that many magnetic materials have their magnetism enhanced at the surface because the narrower surface density of states allows more spins to be reversed at a lower cost in band energy. We [5,6] have previously determined that a layer of Rh on Au or Ag(001) is ferromagnetic; this result has been confirmed by many other calculations [7-9]. Experimental attempts to find this magnetic monolayer on Ag [10] and Au [11] have thus far been unsuccessful but it is quite clear [12] that a Rh monolayer cannot be grown on Ag while the quality of the monolayer on Au remains uncertain. We remain convinced that a perfect Rh monolayer on Ag or Au is ferromagnetic. The Ag and Au d bands lie well below the Fermi energy and the coupling to them of the Rh Fermi energy d electrons is negligible. On the other hand, d electrons at the surface of Rh couple strongly to the bulk d electrons. Thus there is no *a priori* reason to predict that the Rh(001) surface is ferromagnetic. There is recent experimental evidence [13] that the surface of a ferromagnetic metal can remain ferromagnetic well above its bulk Curie temperature [the Gd(0001) surface is magnetically ordered 60 K above the bulk Curie temperature] but that is not the same as a paramagnetic metal having a ferromagnet surface because the exchange splitting of ferromagnets exists and has been measured [14] above the Curie temperature. Thus a mechanism for surface magnetization that does not exist in the paramagnetic case could be the pinning of the magnetic fluctuations which destroy the bulk ferromagnetism above the Curie temperature. Hence the goal of this calculation is to determine whether or not the surface of Rh(001) is ferromagnetic and, if so, if this can account for the discrepancy between the previously calculated surface relaxation and the LEED measurements.

We here present the results of calculations of bulk Rh and nine-layer paramagnetic and ferromagnetic films, finding a ferromagnetic ground state and much improved agreement with the LEED results. This we believe is the first case reported of a paramagnetic crystal having a ferromagnetic surface. The local density approximation (LDA) for exchange causes an unphysical diminution of the magnetic energy. This is well known for Fe where the LDA ground state is paramagnetic fcc. Only by enhancing the magnetic energy with gradient corrections to the LDA has the correct bcc ferromagnetic ground state been obtained [15]. This unphysical diminution occurs in the core region where $(\rho_{\rm core}+\rho_{\rm val})^{1/3}\approx\rho_{\rm core}^{1/3}+\rho_{\rm val}/3\rho_{\rm core}^{2/3}$. Because $\rho_{\rm val}$ is small and $\rho_{\rm core}$ very large in the core region, $\rho_{\rm val}/3\rho_{\rm core}^{2/3}\ll\rho_{\rm val}^{1/3}$ but there is no physical reason for the core electrons to do more than minimally screen the exchange interaction between valence electrons. Note that it is also possible for the LDA to incorrectly yield a ferromagnetic ground state by misplacing the d bands relative to the sp bands. However, given a set of occupied states, it must always underestimate the exchange interaction between valence electrons in the core region. Our recent pseudopotential [16], which is based upon an atom in which all the electrons see a Hartree-Fock exchange potential arising from the core electrons and an LDA potential arising from the valence electrons, removes this difficulty. Using this, we calculated a norm-conserving [17] multiprojector Vanderbilt [18] pseudopotential for Rh in the $d^{8.5}$ configuration from $j=l\pm\frac{1}{2}$ averaged Dirac eigenfunctions and eigenvalues. (Although the true ground state is d^8s, the LDA ground state is known [19] to be d^9.) We had d projectors evaluated at the $4d$ and $5d$ eigenvalues. The s and p projectors were evaluated at the $5s$ and $5p$ eigenvalues. Attempts to add projectors at the $6s$ and $6p$ eigenvalues resulted in numerical instabilities because the $6s$ and p eigenfunctions do not differ sufficiently from the $5s$ and p within our pseudopotential cutoff radius of 2.22 bohrs; this implies that one projector is sufficient over that energy

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TABLE I. Present calculations (MBK) of the lattice constant, cohesive energy, and bulk modulus of Rh compared with values calculated by FH and with experiment.

	FH	MBK	Expt.
a_0 (bohr)	7.091	7.131	7.18
E_0 (eV)	⋯	5.972	5.75
B (10^{11} N/m^2)	3.31	3.014	2.704

TABLE II. Comparison of our calculated interplanar relaxation, work function, and surface energy for paramagnetic and ferromagnetic Rh(001) with those of FH for paramagnetic Rh(001).

	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}	φ (eV)	E_{surf} (eV)
para	−3.22%	−0.28%	+0.70%	−0.36%	5.57	1.1775
ferro	−1.52%	+0.98%	−0.12%	−0.06%	5.36	1.1534
FH	−5.1%	−0.5%	⋯	⋯	5.49	1.12

range. The ionic pseudopotential thus constructed was used in the Rh solids where only the valence pseudocharge density was used to obtain the self-consistent LDA exchange and Wigner correlation energies and potentials, with von Barth-Hedin [20] interpolation between the completely spin polarized and unpolarized limits.

We expand in plane waves (pw) up to $k^2=45$ Ry which requires up to 5593 pw in the film whose supercell is $a_0/\sqrt{2}\times a_0\sqrt{2}\times 6a_0$, where a_0 is the calculated bulk lattice constant. FH discuss the importance of using calculated rather than experimental transverse lattice constants in the thin film when calculating interplanar spacings. In Table I we compare our bulk Rh results with those of FH and with experiment. The fact that we obtain better agreement with experiment than they may be due to using different exchange and correlation functions or to the fact that we sample the Brillouin zone (BZ) at 4000 points compared to their 864 (110 to 28 in the $\frac{1}{48}$ th wedge) or it may be simply fortuitous. For the best comparison of bulk and thin film energies we sample the surface (S) BZ at points which are projected from the 4000 bulk BZ points. This results in a 200 point square array [21], compared to the 64 points used by FH in the SBZ (30 versus 10 points in the $\frac{1}{8}$ th wedge). Although we know of no studies of the dependence of surface relaxation on the SBZ sample density, it is known [8] that 10 **k** points are insufficient to determine surface magnetic properties.

In order to magnetically isolate the two surfaces we used a nine-layer film which is unusually thick and which resulted in a huge amount of charge sloshing between the surface and center of the film, making convergence to self-consistency the most tedious we have ever encountered. This sloshing was much more severe than for Rh on Ag or Au substrates because their d electrons lie well below the Fermi energy. The magnetic surfaces made the sloshing even worse and made it much harder to predict. Ordinarily the spin antisymmetric part of the potential sloshes up and down spin electrons in opposite directions resulting in a small net charge transfer, but here, because the majority spin surface d bands are below E_F, the cancellation did not occur [22].

A major advantage of pw expansions over LAPW is that the forces may be readily calculated at each atomic position and used as a guide in determining the next set of atomic positions to be tried. This is to be compared with FH who fit the total energy with a polynomial for ten different pairs of positions of only the first two planes to find their equilibrium positions. Since the d_{ij} are interrelated and since we found for the paramagnetic case that $|\Delta d_{34}| \gg |\Delta d_{23}|$ and even $|\Delta d_{45}| > |\Delta d_{23}|$, the neglect of Δd_{34} and Δd_{45} by FH must have caused small errors in their Δd_{12} and Δd_{23}. In Table II we compare our paramagnetic and ferromagnetic Δd_{ij}, work functions, and surface energies with those of FH. For reasons we do not understand, although we used the forces as a guide, we were unable to generate a good force constant model in the paramagnetic case and the results listed come directly from the last calculation. In the ferromagnetic case a nearest plane force constant model proved to be extremely consistent so the listed Δd_{ij} and E_{surf} are

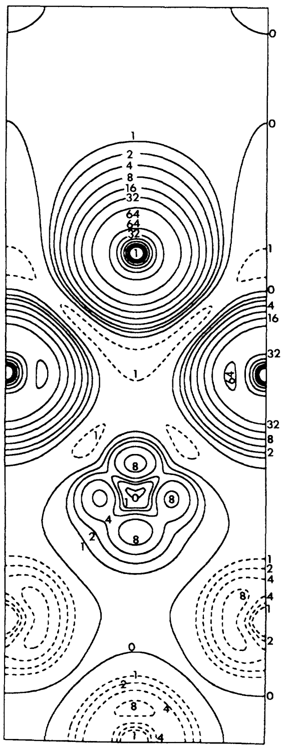

FIG. 1. Contour plot of spin polarization ($\rho_\uparrow - \rho_\downarrow$) of Rh(001) film in units of 10^{-4} electrons per cubic bohr. Dashed lines represent negative polarizations.

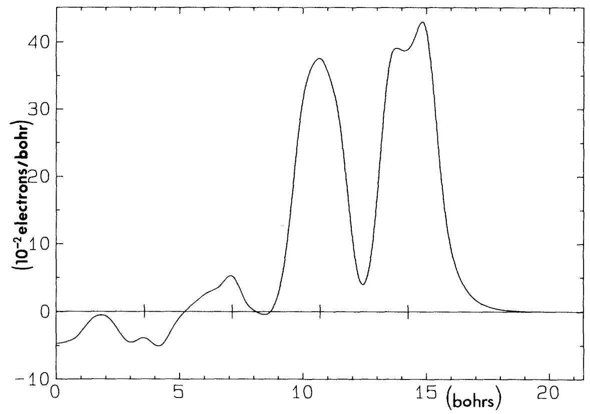

FIG. 2. Spin polarization per Rh(001) planar unit cell in units of 10^{-2} electrons per bohr. The center of the film is at the origin and the other atomic planes are represented by tick marks on the abscissa.

extrapolated from the last calculation. The Δd_{ij} and E_{surf} at exact equilibrium for the para (ferro) cases should differ from the listed values by no more than 0.1% (0.03%) and 0.0005 eV (0.0001 eV). The surface energy is the film energy minus the energy of nine bulk unit cells divided by 2. Although there are no direct measurements, three estimates obtained from experimental data are [23-25] 1.27, 1.22, and 1.12 eV/atom. The surface magnetic energy of 24 meV is the difference between the para and ferro E_{surf} and is small compared with the magnetic energy of 51 meV calculated [26] using the same pseudopotential for a monolayer of Rh on Ag(001). However, the surface magnetization of $1.797\mu_B$ is larger than the $1.225\mu_B$ of Rh on Ag(001) because it extends over two surface planes as seen [27] in Figs. 1 and 2. The only experimental value we can find for the Rh(001) work function is the unpublished 5.20 eV quoted by FH, in good agreement with our ferromagnetic value. Finally, comparing the para and ferro d_{ij} we see that the magnetic pressure caused d_{12} and d_{23} to increase by 1.70% and 1.26%, respectively. This relieved the kinetic pressure and allowed electrons to flow into the region from between planes 3 and 4 causing d_{34} to shrink by 0.82%, which in turn caused d_{45} to increase by 0.30%.

In summary, we have calculated that the surface and subsurface layers of Rh(001) are ferromagnetic. This can be checked experimentally using the magneto-optical Kerr effect [10,11] or electron capture spectroscopy [28]. We have also calculated the surface interplanar relaxation to be −1.52% compared with a previously calculated value [1] of −5.1% and an experimental value [2] of +0.5%. After receiving an earlier version of this paper, Begley *et al.* [29] analyzed some Rh(001) LEED intensity data they had previously collected. They argue convincingly, albeit without direct proof, that their samples did not suffer from hydrogen contamination. Although the fit was not completely satisfactory, they obtained $\Delta d_{12} = (-1.2 \pm 1.6)\%$, essentially in perfect agreement with our calculated value.

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must be chosen to be large to obtain rapid convergence of Δ_n^a to zero. Here because Δ_n^a contributes to charge sloshing we could not make β as large as otherwise desirable.

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