Surface Relaxation and Ferromagnetism of Rh(001)

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The significant discrepancy between first-principles calculations and experimental analyses for the relaxation of the (001) surface of rhodium has been a puzzle for some years. In this Letter we present density-functional theory calculations using the local-density approximation and the generalized gradient approximation of the exchange-correlation functional. We investigate the thermal expansion of the surface and the possibility of surface magnetism. The results throw light on several, hitherto overlooked, aspects of metal surfaces. We find that when the free energy is considered density-functional theory provides results in good agreement with experiments. [S0031-9007(97)02410-1]

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The significant discrepancy between first-principles calculations [1–5] and low-energy electron diffraction (LEED) analyses [6–8] for the relaxation of the (001) surface of rhodium has been a puzzle for some years. The earlier LEED studies [6,7] concluded that the interlayer spacing of the surface layer (d_{12}) is nearly identical to that in the bulk (d_0), i.e., the top-layer relaxation was determined to be $\Delta d_{12}/d_0 = +0.5 \pm 1.0\%$. A recent LEED study [8] found $\Delta d_{12}/d_0 = -1.16 \pm 1.6\%$. On the other hand, first-principles calculations showed a large top-layer relaxation ranging from -3.2% to -5.1%, depending on the calculational scheme and/or the employed numerical accuracy [1–5]. Inward relaxations are indeed the expected behavior of transition metals surfaces (see, e.g., Ref. [2]), and the practical zero relaxation determined by LEED is at least unexpected.

In order to reconcile this disagreement between their calculations and experiment, Feibelman and Hamann [1] proposed that in the experimental study the metal surface may be contaminated by residual hydrogen adsorption (see also Ref. [9]). Indeed, hydrogen is not easy to detect and quite soluble in transition metals, such as Ru, Rh, and Pd. Furthermore, it is known that adsorbed hydrogen significantly reduces the inward relaxations at metal surface as it increases the bond coordination of the surface atoms, making them, to some extent, more bulklike. However, the possibility of hydrogen contamination was strongly rejected by later experimental papers (e.g. [8,10]).

Morrison *et al.* [3] investigated an alternative possibility [11], namely, that the presence of surface magnetism could increase the first interlayer spacing, i.e., reducing the large inward relaxation they had obtained in their nonmagnetic calculation by "magnetic pressure." In fact, bulk Rh is already close to fulfilling the Stoner criterion of ferromagnetism, and the narrower density of d states at the surface might stabilize a magnetic state at the surface. Density-functional theory (DFT) together with the local-density approximation (LDA) gives a nonmagnetic ground state for Rh(001), but this might be due to the LDA. For example, for bulk iron, which is studied in greater detail, the LDA falsely puts the bcc magnetic ground state at a higher energy than the nonmagnetic hcp and fcc states [12,13]. To get around this LDA problem Morrison *et al.* [3] employed a pseudopotential 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 only from the valence electrons. Then in the surface calculations the valence exchange potential was taken proportional to $n_{\text{valence}}^{1/3}$. As a consequence, they found that their Rh(001) surface is ferromagnetic. The magnetic moment is $M = 1.8\mu_B$/surface atom, and the resulting magnetic pressure reduced the surface relaxation $\Delta d_{12}/d_0$ from -3.22% (in the nonmagnetic equilibrium state) to -1.52% in the magnetic ground state. Thus these authors concluded that the surface ferromagnetism is the driving force giving rise to the small surface relaxation deduced experimentally. Subsequently performed theoretical work, however, did not accept their approach and conclusions [4,14]; and also experimental studies provided no convincing support [15]. In their spin-polarized photoemission experiment Wu *et al.* [15] found only a weak indication of surface magnetism with a small magnetic moment of about $M = 0.2\mu_B$/surface atom.

In this Letter we present a new theoretical study which extends the previous work by considering the generalized gradient approximation (GGA) [16], and by taking zero-point effects and the thermal expansion as well as surface magnetism into account. Such a study is desirable since all previous DFT calculations [1–5] were performed with the LDA which does not describe the magnetic state reliably; furthermore, in all previous work zero-point and thermal vibrations were ignored, while the LEED data were taken at room temperature [6–8]. We will show that the above noted discrepancy between theoretical and measured results is mostly due to the unjustified neglect of vibrational contributions to the free energy. It is argued that the vibrational effects will typically play a much bigger role than hitherto anticipated. Furthermore, we find that surface magnetism has a very small effect on the surface interlayer distance.

We employ the full-potential (LAPW) method [17,18] together with norm-conserving pseudopotentials [19]. The

nonlinear core-valence exchange-correlation interaction is treated using the correct core-electron density as obtained in the atomic calculation [20]. The method gives an accurate and at the same time computationally efficient description of the interatomic interaction, total energies, and stable or metastable geometries. Our GGA calculations are performed consistently by creating the pseudopotential from first-principles DFT-GGA calculations. The Rh(001) surface is modeled by a periodic slab geometry consisting of nine layers of Rh and a vacuum thickness corresponding to five such layers. The geometry is optimized by a damped molecular dynamics [18], allowing the top two layers on both sides of the slab to relax. The remaining atoms are kept at the bulk lattice sites. The parameters describing the LAPW basis set are $(\mathbf{K}_{\max}^{\mathrm{wf}})^2 = 14$ Ry and $l_{\max}^{\mathrm{wf}} = 8$. For the $\mathbf{k}$ summation we use 28 points of the irreducible part of the surface Brillouin zone.

Since all previous calculations [1–5] for Rh(001) were performed with the LDA, we also performed LDA calculations, which together with our GGA results allow us to examine the effect of the GGA on the surface properties of Rh(001). Using DFT-LDA our bulk lattice constant is 3.81 Å, which is in good agreement with previous calculations [2,5]. The experimental results, which unlike the quoted calculated value contains the influence of zero-point vibrations, is 3.79 Å [21]. Were the zero point vibrations to be included in the theory, the calculated lattice constant would increase by about 0.5% [22].

Using the GGA we find that the bulk lattice constant is expanded with respect to the LDA value by 2.2%, giving it a value of 3.89 Å. For hcp Ru [23] and fcc Pd [24] a similar trend was found when comparing LDA and GGA lattice constants (see also Ref. [25]). However, we find that the GGA affects the surface relaxation of Rh(001) only little (see Table I), although the cohesive energy, the surface energy, and the work function are affected noticeably compared to the LDA values.

Table I summarizes the results for surface relaxations, work functions, and surface energies as obtained by different calculations and experiments. With respect to the surface relaxation it is immediately evident that the LAPW calculations by Feibelman and Hamann [1] give an exceptionally large value. The present LDA calculations, those of Cho and Kang [4], and those of Methfessel *et al.* [2], who did not relax the second layer, are in good agreement with each other. Also the result of the nonmagnetic study of Morrison *et al.* [3] (quoted above) agrees well with our value. As previously pointed out by Morrison *et al.* [3], the too large top-layer relaxation in Feibelman and Hamann's calculations may be attributed to the use of the poor $\mathbf{k}$-point sampling [29].

The difference between our DFT-LDA results for the surface relaxation ($\Delta d_{12}/d_0 = -3.0\%$) and the previous LEED analyses [6–8] is decreased significantly compared to the results of Refs. [1,29] (see Table I); the DFT-GGA calculations give a result ($\Delta d_{12}/d_0 = -2.8\%$) which is even closer. We will now show that the physics of Rh(001) is much more interesting than previous studies had anticipated. At first we will address the influence of lattice vibrations of the Rh(001) surface and show that the restriction to the $T = 0$ K *total energy* falsely neglects some important physical aspects, which clearly affect the free energy and as a consequence the surface properties. Then we analyze the possibility of surface magnetism.

It is well known that the zero-point vibrations give rise to a recognizable effect on the bulk lattice constant. Moruzzi *et al.* [22] had systematically included this effect in their studies of metals. Typically, however, this effect has been ignored. It is plausible that vibrational effects may be even larger at surfaces than in the bulk. In a correct treatment the equilibrium structure at a given temperature is determined by the minimum of the free energy. At not too high temperatures this differs from the total energy of the rigid lattice mainly by the contributions from atomic vibrations to the internal energy (including the zero-point vibrations) and the vibrational entropy. In the quasiharmonic approximation the free energy for the surface is $F(T) = Min_{d_{12}} F(d_{12}, T)$ with

$$F(d_{12}, T) = V(d_{12}) + k_B T \sum_i \left\{ \frac{\hbar\omega(d_{12})}{2k_B T} + \ln\left(1 - \exp\frac{-\hbar\omega_i(d_{12})}{k_B T}\right)\right\}, \quad (1)$$

TABLE I. Surface relaxations $\Delta d_{12}/d_0$ and $\Delta d_{23}/d_0$ (d_0 is the bulk interlayer spacing), work functions ϕ (eV), and surface energies γ (eV/atom) for Rh(001) as obtained by different calculations and experiments.

	$\Delta d_{12}/d_0$	$\Delta d_{23}/d_0$	ϕ	γ
LDA [1]	−5.1%	−0.5%	5.49	1.12
LDA [2]	−3.5%	⋯	5.25	1.27
LDA [4]	−3.8%	⋯	⋯	1.29
LDA [5]	−3.8%	+0.7%	⋯	1.44
This - LDA	−3.0%	−0.2%	5.26	1.29
this - GGA	−2.8%	−0.1%	4.92	1.04
Experiments	+0.50 ± 1.0% [7]	0 ± 1.5% [7]	4.65 [21]	1.12 [26]
experiments	−1.16 ± 1.6% [8]	0 ± 1.6% [8]	4.98 [27]	1.27 [28]

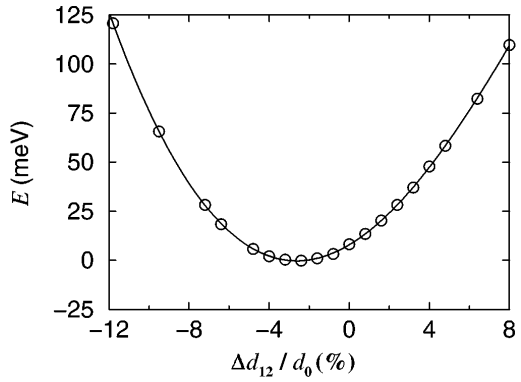

FIG. 1. Total energy per surface atom as a function of the top-layer relaxation for Rh(001). The minimum of the fitted curve is set to be the energy zero.

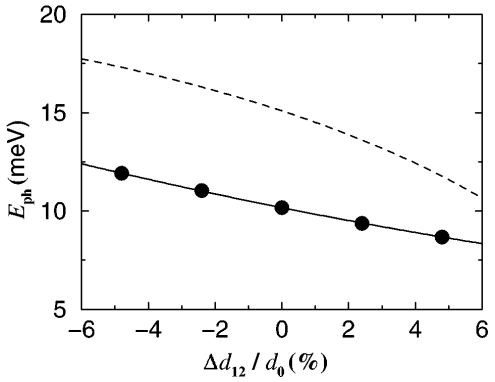

FIG. 2. Phonon energies $\hbar\omega_i$ of the in-plane (solid line) and out-of-plane (dashed line) modes of Rh(001) as a function of the top-layer relaxation.

where $\hbar\omega_i(d_{12})$ denotes the vibrational frequencies and the sum goes over all bands and **k** points. The first term in Eq. (1) is the first interlayer potential and the second term is the vibrational energy and entropy. We note in passing that such a quasiharmonic description had been used successfully in DFT calculations of the anomalous thermal expansion of covalent semiconductors [30]. For Ag, Cu, and Al surfaces Eq. (1) has been recently evaluated by Narasimhan and Scheffler [31]. We note that the equilibrium distance d_{12} is shifted away from the minimum of $V(d_{12})$ towards a larger interlayer spacing and that this shift is determined by the *slope* of the $\hbar\omega_i(d_{12})$ but not their actual values. To a first approximation this dependence of ω_i on d_{12} depends only weakly on the band index and **k**. We therefore replaced the sum in Eq. (1) by three surface-phonon wave packets. Only the top layer is moved and deeper layers are kept fixed. Figure 1 provides our DFT-GGA result for the potential energy $V(d_{12})$; its curvature gives the frequencies for the perpendicular vibrational mode. For the parallel vibrations we use two "modes" along $[1\bar{1}0]$ and [110], which are actually degenerate. The calculated phonon energies $\hbar\omega_i$ of the in-plane and out-of-plane vibrations are shown in Fig. 2. Our results for the temperature dependence $\Delta d_{12}(T)/d_0$, considering the three above discussed phonon modes, is given by the full dots in Fig. 3. Our approximation of the phonon contribution is crude but yields the correct order of magnitude. It is obvious that thermal vibrations have a noticeable effect. In our approximate approach they change the surface relaxation from the value given by the minimum of the total energy, -2.8%, to $\Delta d_{12}/d_0 = -1.4\%$ at 300 K. This result is now in excellent agreement with that of the room-temperature LEED analysis [8] which determined a value of $-1.16 \pm 1.6\%$.

It is interesting to note that the motion of the surface layer parallel to the substrate yields the most important contributions (compare Ref. [31]). If we would neglect the contributions of the parallel motion and use only the perpendicular vibration the resulting top-layer relaxation would be much smaller. This result, displayed by the open dots in Fig. 3, reveals that the anharmonicity of the interlayer potential of Rh(001) does not have a very pronounced influence on the top-layer relaxation.

Our DFT-GGA calculation predict that the ground state of Rh(001) is nonmagnetic. This result remains even if we intentionally increase d_{12} to the unrelaxed geometry, thus offering a bigger volume per surface atom which typically helps to stabilize a magnetic state. Despite this apparently clear result of a nonmagnetic ground state, we asked how far away in energy the ferromagnetic state actually might be. For this purpose we performed spin-polarized calculations employing the fixed-spin-moment method [32]. Figure 4 shows the total energy versus magnetic moment for a given relaxed surface of $\Delta d_{12}/d_0 = -2.4\%$. We find that the total energy monotonically increases with increasing magnetic moment. This behavior is similar to that of a previous fixed-spin-moment study of Cho and Kang [4], who used the LDA. The present DFT-GGA result for the energy difference ΔE between the nonmagnetic and ferromagnetic states is, however, reduced significantly compared to the previous LDA one [4], and Fig. 4 shows that ΔE remains almost constant until the magnetic moment reaches a value of $0.5\mu_B$/surface atom [33] In the fixed-spin-moment method [32], spin-up and spin-down

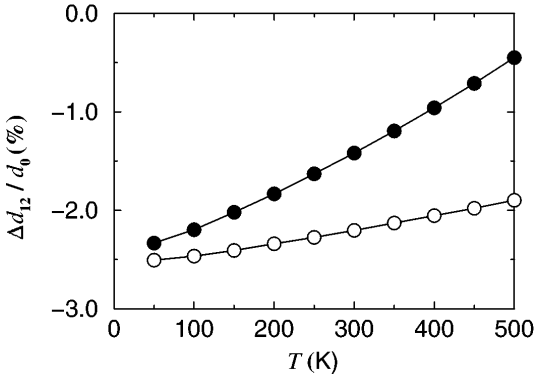

FIG. 3. Top-layer relaxation of Rh(001) as a function of temperature. Full dots represents results obtained using Eq. (1) with the results of Figs. 1 and 2. Open dots show results obtained if the parallel vibrations are neglected.

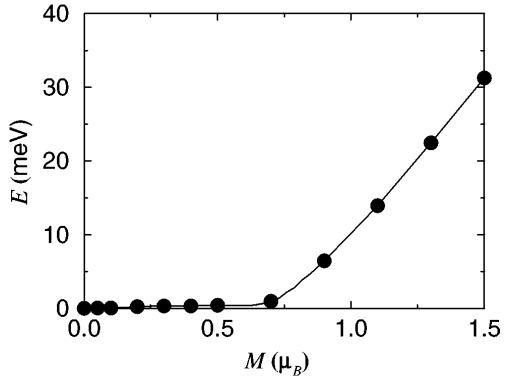

FIG. 4. Total energy per surface atom as a function of the magnetic moment per surface atom for a surface relaxed by $\Delta d_{12}/d_0 = -2.4\%$. The nonmagnetic state defines the energy zero.

eigenvalues are calculated for different Fermi energies. For a magnetic moment of $M = 0.5\mu_B$/surface atom we find that the difference between the two Fermi energies is only 25.9 meV; the total-energy difference at $M = 0.5\mu_B$/surface atom is only 1 meV. In other words, our calculations show that the ferromagnetic state is practically degenerate with the nonmagnetic one, and we expect that a weak ferromagnetic state will occur on Rh(001) possibly stabilized by surface imperfections. This result is consistent with the room temperature spin-polarized photoemission experiments by Wu *et al.* [15], who observed a rather weak ferromagnetism with the surface magnetic moment of about $0.2\mu_B$/surface atom. To some extent our results support the motivation behind the study of Morrison *et al.* [3], although their treatment predicted a rather strong and stable ferromagnetic state. In contrast to them we find that the magnetic state is very close to the critical point, the magnetic moment should be very small, and thus the magnetism has practically no effect on the surface relaxation, or vice versa.

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