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# A First-principles Calculation of Surface Magnetism of Half-monolayer Ru on Pd(001)

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**In order to investigate the magnetism of Ru submonolayer on Pd(001), we have performed first-principles calculations for half-layer of Ru on Pd(001) using the full-potential linearized augmented plane wave (FLAPW) method. We have found that the magnetic moment of Ru for 0.5 layer is 2.21 $\mu_B$. It is found that substrate Pd layers are polarized by the 0.5 Ru overlayer to have significant magnetic moments. Our results are compared with those obtained by the anomalous Hall effect. The calculated electronic structures, i.e., the spin densities and density of states are presented and discussed in relation with magnetic properties.**

## 1. Introduction

Recently, the magnetism of transition metal overlayers on nonmagnetic metallic substrates has been investigated by various theoretical methods [1, 2]. The theoretical calculations predicted large enhancement of the magnetic moment of 3*d* transition metal monolayers (ML) on inert substrates, and it was verified experimentally for some systems [3].

Theoretical studies for 4*d* free standing monolayers, such as Ru and Rh, also predicted ferromagnetism [4]. But, the experimental realization of free standing monolayer can not been accomplished. Thus similar calculations for monolayers of Ru and Rh on noble metals, such as Ag and Au, have been carried out and predicted to be ferromagnetic (FM) [5-7]. However, the experimental investigations to test these predictions failed to observe the FM order [8-10]. Several different reasons for this disagreement between theoretical and experimental results have been proposed and discussed [11-14]. The 4*d* monolayer bands are wider [15] than 3*d* ones, indicating that the in-plane 4*d*-4*d* hybridization is significantly larger than the 3*d*-3*d* one.

Magnetism of 4*d* and 5*d* monolayers depends strongly on the substrate. It has been reported [15] that changing the substrate from Ag or Au to Pd causes drastic reductions of the 4*d* magnetic monolayer moments. The electronic *d* bands of noble metals are located well below the Fermi energy, thus the influence by substrates on overlayers is given mainly through the hybridization of the 4*d* electrons of Ru or Rh overlayers with the *sp* electrons of substrate noble metals. On the other hand, the Pd and Pt have the *d* bands crossing the Fermi energy. Therefore, for Pd or Pt substrate, we expect the strongly increased *d*-*d* hybridization between electronic states of overlayer and substrate. It is well known [15] that the *d*-*d* hybridization increases when moving from 3*d* to 5*d* metals and decreases within a transition metal series from the beginning to end. We can find that Ru has the largest magnetic moment [15] within 4*d* transition metals for monolayers on Ag or Au.

There were some first-principles calculations for 3*d* impurities in Pd [16], for 3*d* monolayers on Pd(001) surface [17], and for 3*d*, 4*d*, and 5*d* transition metal impurities on Pd(001) and Pt(001) surfaces [18]. These calculations show large magnetic moments for 3*d* transition metals in or on Pd, which implies that Pd enhances the magnetism of surface metals. The appreciable magnetic moments were obtained for bulk Ru impurities in Pd [19] and Ru monolayers on Pd(001) [15, 18]. There is also a report that the maximum magnetization is found for a coverage of about 0.1 atomic layers of Ru on the thin Pd films by means of the anomalous Hall effect and weak localization [20].

In this work, motivated by the above-mentioned experimental result [20] about submonolayers of Ru on Pd substrate, we have calculated the total energies for nonmagnetic and ferromagnetic states of Ru in 0.5 monolayer Ru on Pd(001) systems by using the highly precise full-potential linearized augmented plane wave (FLAPW) energy band method. We investigate this system to study the effect on magnetism due to the in-plane 4*d*-4*d* interaction and the overlayer-substrate interaction. We have also calculated the magnetic moments, charge densities, spin densities, density of states, and work functions and have compared our results with those of noble metal substrates and those of experimental investigations.

## 2. Methods

We model the Pd(001) substrate as an ideally constructed 5-layer slab with the lattice constant taken from experiment ($a = 3.89$ Å) [21]. For the Ru overlayer, adatoms are put pseudomorphically over the fourfold hollow sites (alternatively for 0.5 layer) on both sides of the substrate slab. The Ru overlayer-substrate interlayer spacing is taken to be the average of the bulk lattice spacings. Overlayer relaxation is not considered.

To determine the total energies of the 0.5 ML Ru/Pd(001) system, we have solved the one-particle Kohn-Sham (KS) equations [22] based on the density functional theory (DFT) [23] within the LSDA [24]. These equations are solved self-consistently by means of the FLAPW energy band method [25]. No shape approximations are made to the charge densities and the potentials. The core states are treated fully relativistically, and the valence states are treated semirelativi-stically without considering spin-orbit coupling [26]. The Hedin-Lundqvist [27] and the von Barth-Hedin [28] forms for the exchange-correlation potentials are employed for the nonmagnetic and spin-polarized calculations, respectively.

About 2 × 70 augmented plane waves per atom are used as a variational basis set. Within the muffin-tin spheres, lattice harmonics with $l$ up to 8 are used to expand the charge density, potential, and wave functions. Integrations over **k** space are replaced by summations over 21 special **k** points in the irreducible wedge of the two-dimensional Brillouin zone. Convergence is assumed when the average root-mean-square difference between the input and the output charge and spin densities is less than $1 \times 10^{-4}$ electrons/(a.u.)$^3$.

## 3. Results and Discussion

The calculated magnetization energy $\Delta E = E_{\mathrm{FM}} - E_{\mathrm{PM}}$ (defined as the difference between the total energies of the FM and the PM states) for the 0.5 monolayers (ML) Ru on Pd(001) is found to be $-6.35 \times 10^{-2}$ eV, which means that the FM state is the ground state. This value is comparable to one for 1ML Ru on Ag(001) or Au(001) but much larger than one for 1 ML Ru on Pd(001) [15].

The spin density contour plot for the 0.5 ML coverage of Ru on Pd(001) is presented in Fig. 1. The solid and broken lines denote the positive and negative spin polarizations, respectively. We can see that a large eruption at the surface Ru layer toward the vacuum region which reflects an enhanced magnetic moment of the surface Ru atoms. As can be seen from Table 1 and Fig. 2, we can also find that Pd layers have considerably large polarizations. We are tempted to attribute these polarizations due to the strong

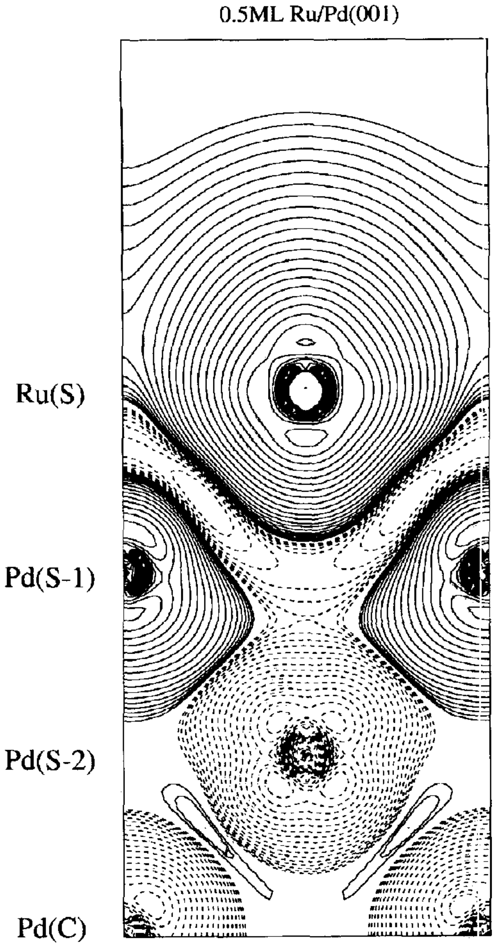

Fig. 1. The spin density contour plot for the 0.5 ML Ru coverage on Pd(001) on the (110) plane. The solid and the dashed lines denote the positive and the negative spin polarizations, respectively. The subsequent lines differ by a factor of 2.

Table 1. The $l$-decomposed majority (↑) and minority (↓) spins, total electrons, and magnetic moments ($\mu_B$) inside each muffin-tin spheres

| Layer | spin | s | p | d | Total | Magnetic Moment |
|---|---|---|---|---|---|---|
| Ru(S) | ↑ | 0.015 | 0.039 | 3.864 | 4.024 | 2.21 |
| | ↓ | 0.096 | 0.032 | 1.683 | 1.817 | |
| Pd(S-1) | ↑ | 0.141 | 0.098 | 3.984 | 4.237 | 0.19 |
| | ↓ | 0.147 | 0.104 | 3.780 | 4.045 | |
| Pd(S-2)I | ↑ | 0.140 | 0.109 | 3.750 | 4.015 | –0.29 |
| | ↓ | 0.143 | 0.111 | 4.033 | 4.302 | |
| Pd(S-2)II | ↑ | 0.142 | 0.109 | 3.763 | 4.030 | –0.26 |
| | ↓ | 0.145 | 0.108 | 4.109 | 4.288 | |
| Pd(C) | ↑ | 0.142 | 0.110 | 3.688 | 3.956 | –0.40 |
| | ↓ | 0.144 | 0.110 | 4.082 | 4.352 | |

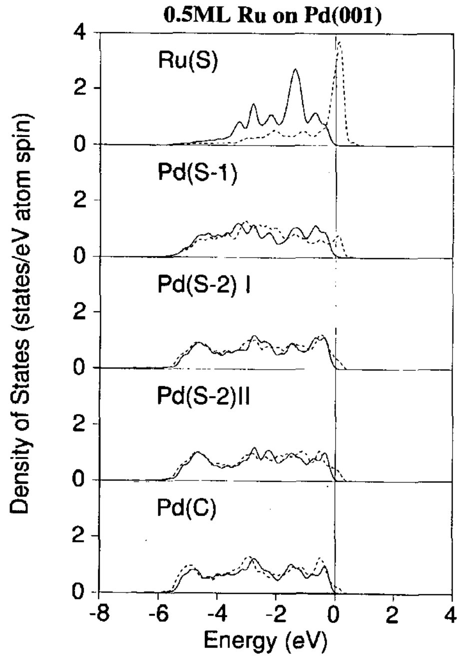

Fig. 2. The layer-projected density of states (LDOS) of the ferromagnetic 0.5 ML Ru/Pd(001) in each muffin-tin spheres. The solid and the dashed lines denote the majority and the minority spins, respectively.

perturbations from the large magnetic moments of 0.5 Ru layer which triggers the spin fluctuation to enhance susceptibility of Pd.

The calculated magnetic moments and *l*-decomposed number of majority and minority spin electrons inside the muffin-tin (MT) sphere for the 0.5 ML Ru/Pd(001) are given in Table 1. We can see that the surface Ru layer has a large moment (2.21 $\mu_B$), which is much greater than one for 1 ML Ru on Ag(001) or Au(001) (1.73 $\mu_B$) [15]. As mentioned before, the substrate Pd layers have significant magnetic moments, 0.19 [Pd(S-1)], −0.29 [Pd(S-2)I], −0.26 [Pd(S-2)II], and −0.40 $\mu_B$ [Pd(C)]. Our results are consistent with those obtained by the anomalous Hall effect [21].

The layer-projected density of states (LDOS) for each atom type in the 0.5 ML Ru system is plotted in Fig. 2, where the solid and broken lines denote the majority and minority spins, respectively. From the DOS curve, we can see that the minority bands of surface Ru are changed very much compared with 1 ML Ru on Ag(001) [15], which means that there is very strong *d-d* hybridization between Ru overlayer and Pd substrate. We can also find that the peak about −5 eV from the Fermi energy in the interface Pd layer is much depressed compared with that of central Pd layer.

## 4. Conclusion

We have investigated the magnetism of Ru submonolayer on Pd(001), by performing the first-principles calculations for half-layer of Ru on Pd(001) using the FLAPW method. We have found that the magnetic moment of Ru 0.5 layer is 2.21 $\mu_B$. It is found that the substrate Pd layers are appreciably polarized by the 0.5 Ru overlayer to have significant magnetic moments from the results of the calculated electronic structures, i.e., the spin densities and density of states. Our results are comparable with those obtained by the anomalous Hall effect [21].

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