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First principles investigations of 4d magnetism on C(0001)

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Possible 4d magnetism in X/C(0001) (X=Pd, Rh, and Ru) is investigated using the full potential linearized augmented plane wave method. We find that while small magnetic moments of 0.24 and 0.28 μ_B can survive for Rh and Ru on C(0001), the magnetism of Pd is completely diminished. Due to the unexpectedly strong interfacial interaction between the overlayer and the flat C(0001) substrate, the magnetic moment is very sensitive to changes in the interlayer distances. © 1997 American Institute of Physics. [S0021-8979(97)19408-7]

First principles predictions of magnetism in 4d transition metal monolayers on various inert substrates¹ have stimulated considerable experimental interest.^{2,3} So far, unfortunately, for most systems studied, no magnetic signal has been detected^{4,5} except for Ru/C(0001).⁶ The graphite C(0001) surface is very flat and thus is believed to be able to prevent interdiffusion and hybridization that occur at most metal/metal interfaces. A nonzero in-plane spin polarization was observed in Ru/C(0001) below 250 K, using spin-polarized secondary electron emission (SPSEE) technique.⁶

This first evidence of 4d monolayer magnetism is very encouraging and deserves theoretical verification. Several important issues need to be clarified for this system, such as: (i) the overlayer morphology; (ii) the Ru–C interlayer distance, (iii) the size of magnetic moments, and (iv) the role and strength of the interfacial interaction.

In this article, we report results of first principles investigations for the structural, electronic, and magnetic properties of Pd, Rh, and Ru monolayers on the C(0001) substrate using the full potential linearized augmented plane wave (FLAPW) method. Small magnetic moments (0.24 and 0.28 μ_B) are found for the Rh and Ru overlayers—a result which confirms the SPSEE observation. We find that the C(0001) substrate interacts strongly with the overlayers and, as a result, it completely diminishes the magnetism of the Pd monolayer.

The C/X(0001) systems (X=Pd, Rh, and Ru) are simulated by a four layer slab which consists of two graphite substrate layers with a 4d transition metal monolayer on each side. The lattice constant of bulk graphite is adopted for the two-dimensional lattice in the lateral plane and also for the interlayer distance between the carbon layers. The X–C interlayer distance is optimized through both total energy and atomic force approaches.

In the FLAPW approach, there is no shape approximation for charge density, wave function and potential. The single particle Kohn–Sham equation is solved self-consistently with an energy cutoff of 13 Ry for the variational plane wave basis set. Within the muffin-tin (MT) spheres ($r_X=2.30$ a.u. and $r_C=1.15$ a.u.), lattice harmonics with angular-momentum l up to eight are employed to expand the charge density, potential, and wave functions. Con-

FIG. 1. Schematic geometries for the 4d transition metal overlayers (black circles) on the C(0001) substrate (open circles).

TABLE I. The calculated magnetic moments, M (in μ_B) for the 4d free monolayers in the three structures.

Structure	Ru	Rh	Pd
(1)	0.93	0.79	0.06
(2)	1.15	0.12	0.68
(3)	2.48	1.35	0.14

TABLE II. The calculated magnetic moments of $4d$ transition metal atoms, M (in μ_B), and equilibrium overlayer/substrate interlayer distances, d (in a.u.), for Ru, Rh, and Pd on C(0001) in the third structure in Fig. 1.

System	d	M	ϕ
Ru/C(0001)	3.17	0.28	4.49
Rh/C(0001)	3.30	0.24	4.23
Pd/C(0001)	3.60	0.00	4.05

vergence is assumed when the mean-root-square distance between the input and output charge and spin densities is less than $1.0 \times 10^{-4} \text{ e/(a.u.)}^3$.

The calculated magnetic moments of $4d$ transition metal monolayers in the three geometries shown in Fig. 1 are listed in Table I. Surprisingly, we find that the magnetic moment of a free monolayer exhibits a monotonic trend with the interatomic spacing only for Ru as the lateral lattice expands on going from structure (1) to (3). By contrast, the magnetic moments of Pd and Rh free monolayers show very peculiar behavior. In the first geometry, which is obviously overpacked (the Ru–Ru interatomic distance is 8.5% smaller than that in the bulk hcp Ru), the magnetic moments for Pd, Rh, and Ru are 0.06, 0.79, and $0.93 \mu_B$, respectively. When the atomic density is reduced by a factor of 2 in the second structure, unexpectedly, the magnetic moment of Rh decreases to $0.12 \mu_B$, whereas the magnetic moment of Pd reaches its maximum value of $0.68 \mu_B$, the largest magnetic moment ever reported for Pd atoms. When the atomic density is reduced further in structure (3) the Rh magnetic moment increases to $1.35 \mu_B$, but the magnetic moment of Pd decreases to only $0.14 \mu_B$.

For Pd, this phenomenon can be understood from the fact that Pd is nonmagnetic in compact lattice and in a free atom. Thus, the magnetic moment of Pd peaks when the strength of interatomic hybridization is appropriate. The peculiar behavior for Rh can also be explained in terms of the local density of states (DOS). We find high antibonding peaks in the DOS just at the Fermi level for nonmagnetic Rh monolayers in structures (1) and (3), which induces a strong Stoner instability and results in larger magnetic moments. For the nonmagnetic Rh monolayer in structure (2), the ma-

FIG. 2. The calculated magnetic moment of Ru/C(0001) as a function of the interlayer distance.

FIG. 3. The charge density difference for Ru/C(0001), $\Delta\rho = \rho_{\text{Ru/C}} - \rho_{\text{Ru-ML}} - \rho_{\text{C}}$. Contours start from $\pm 5 \times 10^{-4} \text{ e/a.u.}^3$ and increase successively by a factor of $\sqrt{2}$. Solid and dashed lines indicate positive and negative differences, respectively.

jor peak in the DOS is just below the Fermi level and thus a much smaller magnetic moment is induced. Similar results were found also by Wildberger *et al.* for Rh clusters on Ag(001).⁷

As listed in Table II, none of the Pd, Rh, and Ru monolayers can sustain their magnetic moments in structure (1) on the C(0001) substrate. In structure (2), a very small magnetic moment of $0.1 \mu_B$ is found only for Ru on C(0001). Pd/C(0001) is not magnetic even in the expanded structure (3), which indicates the sensitivity of the $4d$ magnetism on the change of local environment, and also the strong overlayer/substrate interfacial interaction. Surprisingly, the magnetic moments of Rh/C(0001) and Ru/C(0001) are found to be very small in structure (3) (0.24 and $0.28 \mu_B/\text{adatom}$, respectively). Furthermore, the magnetic moments are found to depend strongly on the overlayer/substrate interlayer distance. As can be seen in Fig. 2, interestingly, the calculated magnetic moment of Ru jumps discontinuously to a value as large as $1.1 \mu_B$ just slightly away from the equilibrium position. It can even reach a value of $1.5 \mu_B$ if the interlayer distance is 10% larger than the equilibrium one. Such a discontinuous behavior suggests the coexistence of several high- and low-spin moment states. Thus, a well optimized interfacial structure is essential for the determination of the magnetic ground state.

We find that the equilibrium overlayer/substrate interlayer distances for Ru, Rh, and Pd on C(0001) are 3.17, 3.30, and 3.60 a.u., respectively. In addition, this distance depends also on the lateral structure of the overlayer. For example, the equilibrium Ru–C interlayer distance increases to 4.02

and 3.58 a.u. for structures (1) and (2), respectively. To understand the mechanism of this dependence, we plot in Fig. 3 the charge density difference for Ru/C(0001). Clearly, electrons deplete from the C sites and transfer to the Ru sites. Stronger lateral metal/metal interaction [as in structure (1)] or higher band filling (as in Pd) leads to an increase of the energy of the unoccupied antibonding metal states. Therefore, it is energetically favorable to have a larger interlayer distance so as to reduce the energy cost resulting from the C-X charge transfer.

In conclusion, we have studied the possible magnetism of Ru, Rh, and Pd monolayers on C(0001). We find that small magnetic moments ($<0.3 \mu_B$) can be sustained in Ru and Rh overlayers with a small coverage, confirming the experimentally observed magnetic signal in Ru/C(0001).⁶ The strong dependence of the magnetic moment on the interlayer distance indicates the sensitivity of $4d$ magnetism on the overlayer/substrate interaction.

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¹R. Q. Wu and A. J. Freeman, Phys. Rev. B **45**, 7222 (1992); S. Blugel, Phys. Rev. Lett. **68**, 851 (1992); M. J. Zhu, D. M. Bylander, and L. Kleinman, Phys. Rev. B **43**, 4007 (1991); O. Eriksson, R. C. Albers, and A. M. Boring, Phys. Rev. Lett. **66**, 1350 (1991); R. Q. Wu and A. J. Freeman, Phys. Rev. B **51**, 17 131 (1995).

²G. A. Mulhollan, R. L. Fink, and J. L. Eeskine, Phys. Rev. B **44**, 2393 (1991).

³C. Liu and S. D. Bader, Phys. Rev. B **44**, 12 062 (1991).

⁴P. J. Schmitz, W.-Y. Leing, G. W. Graham, and P. A. Thiel, Phys. Rev. B **40**, 11 477 (1989).

⁵T. J. Reaker, D. E. Sanders, and A. E. DePristo, J. Vac. Sci. Technol. A **8**, 3531 (1990).

⁶R. Pfandzelter, G. Steierl, and C. Rau, Phys. Rev. Lett. **74**, 3467 (1995).

⁷K. Wildberger, V. S. Stepanyuk, P. Lang, R. Zeller, and P. H. Dederichs, Phys. Rev. Lett. **75**, 509 (1995).