

Magnetism of 3*d*, 4*d*, and 5*d* transition-metal impurities on Pd(001) and Pt(001) surfaces

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We present systematic *ab initio* calculations for the magnetic moments of 3*d*, 4*d*, and 5*d* transition-metal impurities as single adatoms on the (001) surfaces of Pd and Pt. Large magnetic moments are found for all 3*d* adatoms except for Sc and Ti, which are nonmagnetic. Among the 4*d* and 5*d* adatoms Mo, Tc, Ru and W, Re, Os have large magnetic moments. Also the adatom-induced magnetization of the Pd and Pt surfaces is investigated. We compare our results with former calculations for adsorbate atoms on Cu and Ag surfaces and for monolayers on these substrates.

I. INTRODUCTION

In the past years, magnetism of transition-metal monolayers on nonmagnetic substrates, such as Cu, Ag, Au, and Pd has been investigated by different theoretical methods.¹⁻⁸ Ferromagnetic, as well as antiferromagnetic solutions, have been obtained for the monolayers of the 3*d* transition-metal series. As a general result, the 3*d* monolayer moments are strongly enhanced, compared to the moments of the elemental 3*d* metals.

Most unexpected was the prediction of magnetism for 4*d* and 5*d* monolayers.^{5,6} Recently, experimental evidence of 4*d* magnetism for Ru monolayers on a C(0001) has been reported.⁹ Until now no long-range magnetic order for 4*d* and 5*d* monolayers on noble metals could be detected. There are different reasons for this. Fully relativistic calculations¹⁰ have shown that the moments of the 5*d* monolayers are quenched by the spin-orbit coupling, which was neglected in the previous calculations. On the other hand, the 4*d* moments are slightly affected by the spin-orbit interaction. However, the real growth conditions can lead to a structure of the films, which cannot be described by the model of pseudomorphically grown monolayers used in the calculations.

Blügel¹¹ has shown that the magnetic moments of the 4*d* double layers are significantly reduced. Turek *et al.*¹² have demonstrated that structural imperfections strongly reduce the local magnetic moments of Ru and Rh films. Thus, the relation between the structure of the monolayers and magnetism is a very important question. In this sense, the magnetic properties of single adatoms and supported clusters are of considerable interest, because they show the development of magnetic moments from single adatoms to monolayers.

Our own studies¹³⁻¹⁵ have revealed the changes in magnetic moments from adatoms and small clusters to monolayers for 3*d*, 4*d*, and 5*d* elements on Cu(001) and Ag(001) surfaces. Experimental verification for Nb adatoms on Ag surfaces has been reported recently.¹⁶ We have shown that

due to the hybridization with the substrate and with the adatoms in the clusters, the maximum of the moment curve is shifted to large valencies and approaches for larger clusters the monolayer results. The investigated surfaces of Cu and Ag both have the electronic *d* bands located well below the Fermi energy and the influence on adatoms and clusters is given mainly through the hybridization with the *sp* electrons of the noble metals. The Pd and the Pt substrates represent the opposite limit. The *d* bands of these systems are crossing the Fermi level and are not completely filled. The *d* band of Pd is near the threshold of becoming ferromagnetic and the bulk Pd has the largest Stoner enhanced susceptibility among the 4*d* metals. Therefore, the main difference between the magnetic properties of *d* adatoms, clusters, and monolayers on Pd(Pt) and Ag(Au, Cu) surfaces should arise from the strongly increased *d-d* hybridization between electronic states of adsorbates and substrates.

In the past, first-principles calculations were performed for 3*d* impurities in Pd (Ref. 17) and for 3*d* monolayers on the Pd(001) surface.³ The results of these calculations show large magnetic moments for Cr, Mn, Fe, and Co. Among the 4*d* and the 5*d* elements, only for Ru impurities in Pd (Ref. 18) and Ru monolayers on Pd(001) (Ref. 19) appreciable magnetic moments ($\approx 0.2\mu_B$) were obtained by *ab initio* calculations. In this paper, we present a systematic series of first-principles calculations for the magnetic moments of 3*d*, 4*d*, and 5*d* adatoms on Pd(001) and Pt(001) surfaces and compare our results with those of Ag and Cu substrates.

II. METHOD OF CALCULATION

Our calculations are based on density-functional theory and the Korringa-Kohn-Rostoker (KKR) Green's function method. The impurities are calculated within a recently developed KKR Green's function method for defects at surfaces.^{13-15,20} We apply multiple-scattering theory to obtain the Green's function via a Dyson equation. First, we treat the surface as a two-dimensional perturbation of the

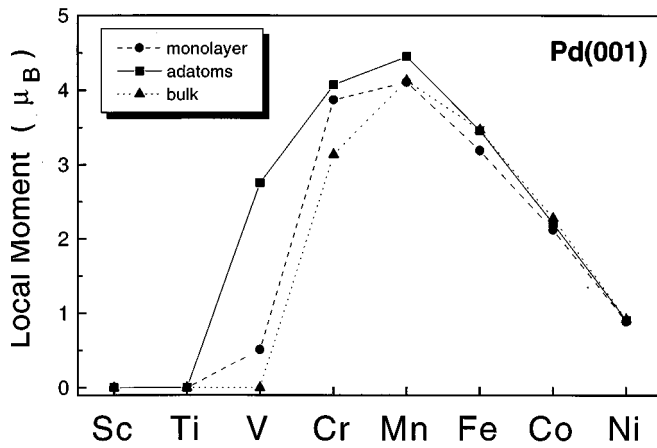


FIG. 1. Comparison between the magnetic moments per atom of 3d transition metals as adatoms on Pd(001), 3d monolayers on Pd(001), and 3d impurities in bulk Pd.

bulk. For the construction of the ideal surface the nuclear charges of seven Pd(Pt) monolayers are removed, thus creating two half crystals being practically uncoupled. The structural Green's function of the ideal surface is then used as the reference Green's function for the calculations of the impurities on the surface. We perform the calculations for impurity atoms at hollow sites, i.e., at a regular fcc site in the first "vacuum" layer. We allow the potentials of all adatoms and of all reference sites adjacent to the adatoms to be perturbed. Using a multipole expansion up to $l=6$, the full charge density is taken into account to calculate the Coulomb and exchange-correlation potential. For the latter we use the form of Vosko, Wilk, and Nusair.²¹ Only the spherically symmetric part of the potentials inside atomic Wigner-Seitz spheres is then used to calculate the Green's functions. This approximation is not important for the calculated local moments, as can be concluded from model calculations with our full-potential codes for impurities in the bulk, where we simulated the surface geometry by putting Ru atoms close to a void of 13 vacancies inside a Ag cube. At these "inner" surfaces the moments, calculated by full and spherical potentials, are nearly identical ($1.79\mu_B$ and $1.81\mu_B$, respectively). Relativistic effects are described in the scalar relativistic approximation. Details concerning the calculations of the surface Green's function can be found elsewhere.^{15,20} In our calculations, lattice relaxations are neglected, i.e., all atoms are fixed at ideal lattice positions. For single adsorbate atoms, having very large local moments, the spin polarization energy is sufficiently large so that the moments should not be appreciably changed by lattice relaxations.^{14,15,22}

III. RESULTS AND DISCUSSION

First, we discuss the results obtained for the Pd(001) surface and then we compare the Pd and Pt substrates. Since the 3d wave functions are well localized, the interaction of the adatoms with the 4d states of the Pd is strongly reduced, especially for the elements at the end of the 3d series. Figure 1 shows the calculated local moments for 3d adatoms on the Pd(001) surface together with the corresponding results for the monolayers³ and the impurities in the bulk.¹⁷ It is seen that, except for V and Cr, the moments of the 3d adatoms are

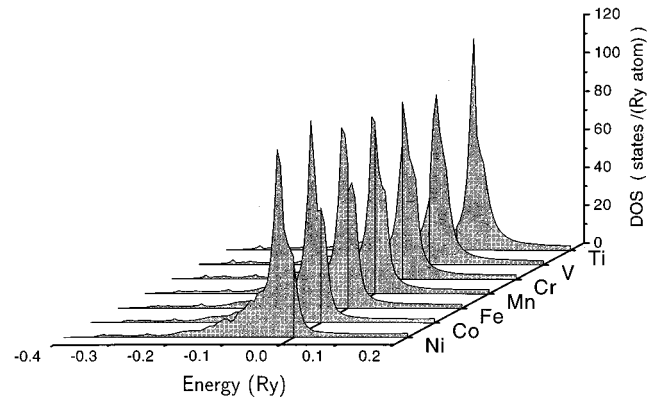


FIG. 2. Paramagnetic local densities of states of 3d adatoms on Pd(001). The vertical line indicates the position of the Fermi energy.

well saturated and are similar to the monolayers and the impurity moments. The impurity and adatom moments of Fe and Co are slightly larger than the corresponding monolayer ones. The moment of Ni is nearly the same for all cases. The more or less equal moments obtained for Fe, Co, and Ni for the three different environments are basically a consequence of the fact that in all these cases the majority band is practically filled, so that the moments are determined by the valence and increase by about $1\mu_B$ in the sequence of Ni, Co, and Fe. The effect of $sp-d$ interactions is relatively small, since, as discussed by Blügel *et al.*,⁴ the major trends are determined by the $d-d$ hybridization. Dramatic environmental effects are, however, found for V and, to a somewhat smaller extent, for Cr. For a V impurity in bulk Pd, the Stoner criterion is not satisfied, since the 3d-4d hybridization between the impurity 3d and the bulk 4d states shifts the virtual bound state above the Fermi energy, so that the density of states at the E_F is rather small.⁴ This can also explain the rather small moment obtained for the V monolayer on Pd(001). On the other hand, for the V adatom, the hybridization is sufficiently reduced so that a rather large V moment of $2.8\mu_B$ is obtained. The adatom moments in Fig. 1 follow essentially Hund's rule of isolated atoms with the largest moment at the center of the series (Mn). The paramagnetic local density of states (LDOS) for 3d adatoms on the Pd(001) surface are shown in Fig. 2. The peak of the LDOS is located above E_F at the beginning of the 3d series, resulting in a small LDOS at E_F and in a suppression of the moments of Sc and Ti adatoms.

A comparison of the magnetic moments of 3d adatoms on Pd, Ag, and Cu(001) surfaces is presented in Fig. 3. The lattice constant of Cu is about 10% smaller than the lattice constant of Ag, which increases the $sp-d$ hybridization with the substrate considerably. As a result, the magnetic moments of the adatoms on the Cu surface are always smaller than those on the Ag surface. Compared to the Ag and the Cu substrates, the whole curve for the 3d adatoms on the Pd substrate is shifted to the right. In fact, we obtain that the Ti adatom is nonmagnetic, the magnetic moments of V and Cr adatoms are slightly suppressed, while the moments of the adatoms at the end of the d series are enhanced and larger than the moments on the Ag(Cu) surface. Exactly the same trend was observed for the 3d monolayers on the Pd(001) surface and the 3d impurities in bulk Pd.⁴ It was shown⁴

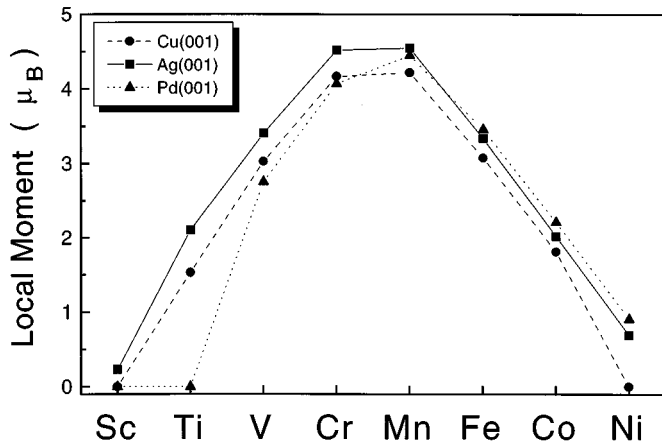


FIG. 3. Comparison of the local magnetic moments of 3d adatoms on different substrates [Ag(001), Cu(001), Pd(001)].

that due to the hybridization with the 4d band of Pd, the *d* states of the impurities and the monolayers at the end of the *d* series are shifted to higher energies, leading to an increase of the LDOS at E_F and thus to higher moments.

Due to the large extent of the 4d and the 5d wave functions, the differences between the Pd(001) and the Ag(001) substrates should be more pronounced for the 4d and 5d adatoms. This is clearly shown in Figs. 4(a),(b), where the results for the 4d and the 5d adatoms on the Pd, Ag, and the Cu surfaces are shown. Compared to the Ag surface, the magnetic moments of Ru and Os (isoelectronic to Fe) on the Pd surface are enhanced, but the moments of Mo and W (isoelectronic to Cr) are suppressed, while Nb and Ta (isoelectronic to V) are nonmagnetic.

Surprisingly, the moments of 4d adatoms Mo, Tc, Ru and of the isoelectronic 5d adatoms W, Re, Os are very large. For Ru and Os the moments are nearly the same. This is quite different from the usual assumption that the magnetism in 5d metals is more strongly suppressed than in the 4d ones. The same effect is seen for the Ag surface: the moments of Re and Os are larger than the corresponding 4d ones of Tc and Ru. This unexpected behavior is caused by relativistic effects, as was suggested by Blügel.²³ The 6s wave functions of 5d metals are “heavier” than 5c for 4d metals, due to the relativistic mass enhancement. Moving from 4d to 5d adatoms, the energy difference between the 6s and 5d states becomes larger. It means that, relative to the 4d states, 5d states are shifted up in energy. This leads to an enhancement of the magnetic moments at the second half of the 5d series.

A comparison of the magnetic moments on Pd(001) and Pt(001) surfaces is presented in Figs. 5(a),(b),(c). The magnetic moments of 3d adatoms [Fig. 5(a)] are similar for both substrates. Due to the more extended 5d functions of Pt, in comparison with the 4d ones of Pd, the interaction between adatoms and Pt surface is stronger than for the Pd surface. Therefore, the magnetic moments on the Pt substrates are, in general, decreased. This is a small effect for the 3d adatoms, since the moments are very large and more or less saturated. However, this is more pronounced for the 4d and 5d adatoms [cf. Figs. 5(b),(c)].

Analogously to the quenching of the local moments of the 5d monolayers, due to the spin-orbit coupling, one might argue that the moments of the 5d adatoms W, Re, and Os

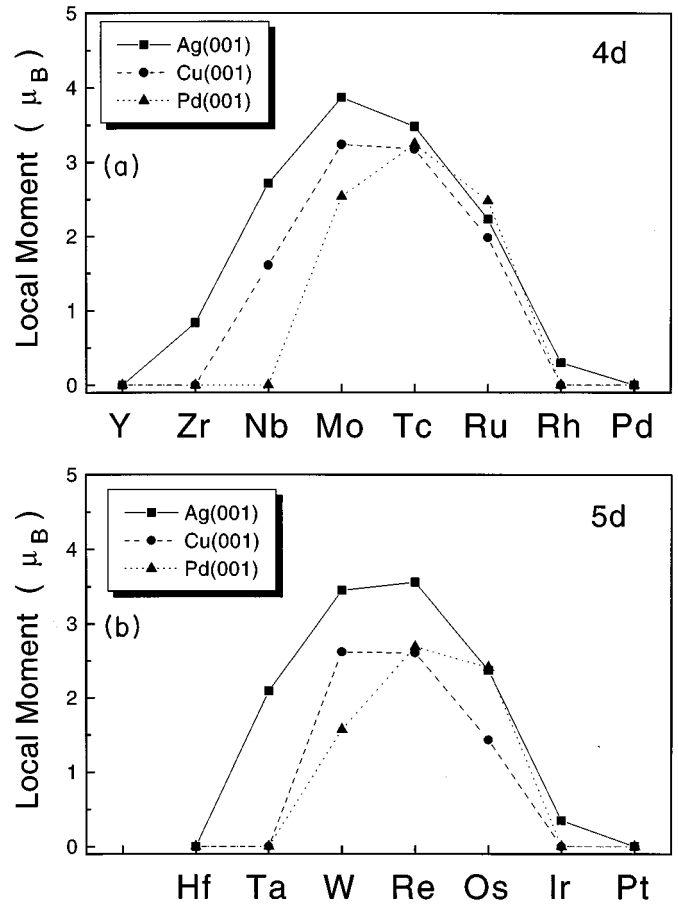


FIG. 4. Comparison of the local magnetic moments of 4d (a) and 5d adatoms (b) on different substrates [(Ag(001), Cu(001), Pd(001)].

might also be suppressed by spin-orbit interaction being neglected in our calculations. However, the calculated 5d moments of the adatoms and the resulting exchange splitting of the densities of states are much larger than in the monolayer case and the spin-orbit interaction should be less important for the moments of the adatoms. Future calculations should show if this is correct.

Let us shortly speculate about the importance of lattice relaxations for the calculated local moments being neglected in our method. For instance, in the case of a Mn adatom on Pd, we expect a strong inward relaxation similar to the value -8% calculated for a ferromagnetic Mn monolayer on Pd.²³ In direct analogy to this result the Mn moment, being practically saturated, should only be slightly reduced. In contrast to this, the volumes of the 4d metals Mo and Tc are about the same as the one of Pd, so that no large relaxation effects are expected, while for the isoelectronic 5d elements the W and Re one would expect a modest outward relaxation, leading to an increase of the moments. Due to the similar lattice constants of Pd and Pt, the relaxation effects are expected to be also similar for both surfaces. Thus, in total, we do not expect substantial changes of the present results, due to lattice relaxation. Nevertheless, calculations including these effects would be highly desirable.

Due to the large spin susceptibility of Pd and Pt, one expects that the magnetic adatoms induce magnetic moments

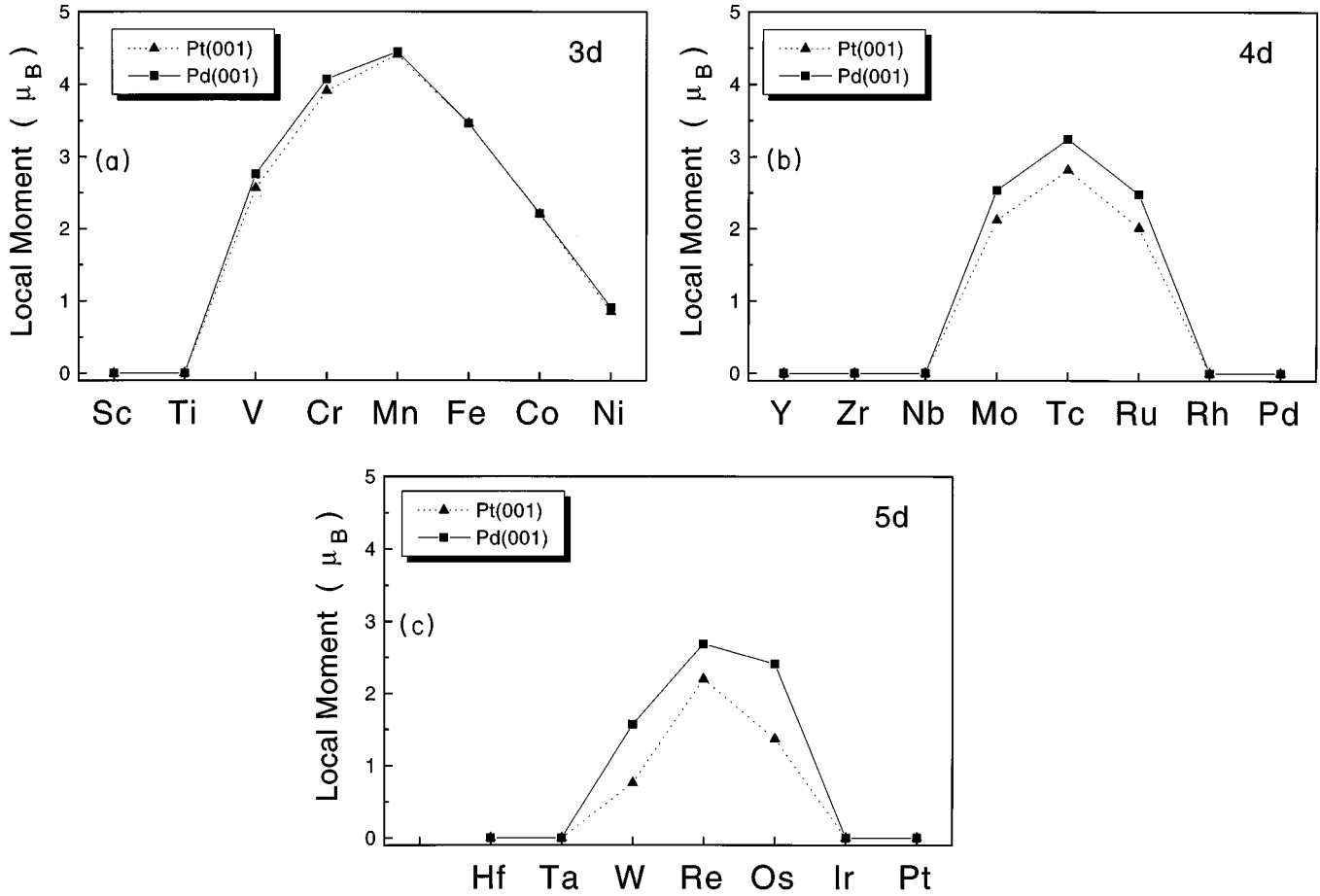


FIG. 5. Comparison of the local magnetic moments of $3d$ (a), $4d$ (b), and $5d$ (c) adatoms on Pd(001) and Pt(001).

on surfaces of these metals. This effect was extensively studied for the d impurities in Pd,²⁴ the Fe monolayers on the Pd (001) surface,^{4,25} and Fe-Pd interfaces.²⁶ Table I shows the magnetic moments of Pd and Pt atoms being nearest neighbors of the adatom in the first surface layer. For $3d$ atoms on

TABLE I. $3d$, $4d$ and $5d$ induced magnetic moments on Pd and Pt atoms.

	Pd(001)					
	V	Cr	Mn	Fe	Co	Ni
Adatoms	-0.09	-0.03	0.07	0.15	0.14	0.09
Imp.	0.00	-0.03	0.05	0.10	0.12	0.07
Monol.	-0.01	0.17	0.30	0.32	0.33	0.24
	Pd(001)					
	Nb	Mo	Tc	Ru	Rh	Pd
Adatoms	0.00	0.01	0.13	0.20	0.00	0.00
	Pd(001)					
	Ta	W	Re	Os	Ir	Pt
Adatoms	0.00	0.01	0.09	0.19	0.00	0.00
	Pt(001)					
	V	Cr	Mn	Fe	Co	Ni
Adatoms	-0.08	-0.05	0.05	0.12	0.11	0.00
	Nb	Mo	Tc	Ru	Rh	Pd
Adatoms	0.00	0.00	0.08	0.11	0.00	0.00
	Ta	W	Re	Os	Ir	Pt
Adatoms	0.00	0.00	0.05	0.07	0.00	0.00

the Pd surface, the results for monolayers and impurities are also presented. Among $3d$ adatoms, the largest moments on Pd and Pt surfaces are induced by Fe and Co. The moments induced by other $3d$ adatoms are small. The moments induced by adatoms and impurities are nearly the same for Pd with the adatom ones being somewhat larger. For the $3d$ monolayers, the increased coordination number strongly enhances the induced moments, since a Pd or Pt surface atom “sees” four magnetic adatoms. Surprisingly appreciable induced moments are found around $4d$ (Tc,Ru) and $5d$ (Os) adatoms on Pd(001). The magnetic moments induced by Ru and Os are even larger than the moments induced by Fe. On the Pt surface, Ru induces nearly the same moment as Fe does. While in the present calculation, we only calculate the induced polarization of the neighboring Pd and Pt surface atoms, we expect in analogy to the behavior in the bulk¹⁷ a longer-ranged polarization cloud extending into the Pd or Pt substrate. The form and extension of this cloud might be influenced by the half space boundary condition, as well as by the inhomogeneous enhancement at the surface and represents an interesting problem for future calculations.

IV. CONCLUSIONS

We have presented results of first-principle calculations of magnetic moments of $3d$, $4d$, and $5d$ adatoms on Pd and Pt(001) surfaces. Our calculations show that the $3d$, $4d$, and $5d$ adatoms from the middle of the d series have very large magnetic moments. Compared to the Ag and Cu surfaces, the

interaction between the adatoms and the Pd and Pt substrates suppresses the magnetic moments at the beginning of the d series and enhances the moments at the end of the d series. We have found similarities within the behavior of 3d adatoms and 3d monolayers, with respect to the different substrates. Our calculations reveal that magnetic 3d (Fe, Co), 4d (Ru), and 5d (Os) adatoms induce sizable magnetic moments ($0.15\text{--}0.2\mu_B$) on neighboring Pd and Pt atoms at the surfaces.

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