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Magnetism of 4*d* and 5*d* transition metal adlayers on Ag(001): Dependence on the adlayer thickness

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We present results of *ab initio* calculations for the electronic structure and the magnetic moments of 4*d* (Ru, Rh, Pd) and 5*d* transition-metal bilayers (Ir, Pt) on the Ag(001) substrate. The bilayers of Rh, Pd, Ir, and Pt show ferromagnetism, but compared to the monolayers the moments are strongly reduced to less than $0.35\mu_B$. This indicates that the magnetism in the 4*d* and 5*d* metal films depends critically on the film thickness. These results put a severe upper limit on the experimental imperfections permitted to verify 4*d* and 5*d* magnetism.

In the past three years several groups presented *ab initio* calculations on the ferromagnetism of 4*d* and 5*d* transition-metal monolayers on Ag(100) and Au(100) substrates. Magnetism was predicted for Tc,[1] Ru,[1,2] and Rh (Refs. 1–4) monolayers on Ag and Au(001) substrates among the 4*d* metal monolayers and Os (Refs. 5) and Ir (Ref. 5) among the 5*d* metals, respectively. In summary, these calculations led to the general consensus that the magnetism of Tc and Os is rather subtle, but Ru, Rh, and Ir should show large magnetic moments of about $1.7\mu_B$,[2,5] $1.0\mu_B$,[2,3,5] and $0.93\mu_B$,[5] respectively. In addition, a systematic trend has been noticed by comparing the magnetic moments of 4*d* and 5*d* transition-metal monolayers on Ag and Au substrates with those of 3*d* metal monolayers:[5] The element with the largest moment among the 3*d*, 4*d*, and 5*d* monolayers is shifted from Mn to Ru (isoelectronic to Fe) and to Ir (isoelectronic to Co), respectively. This monolayer magnetism has been explained in terms of the Stoner model for ferromagnetism as a consequence of band narrowing due to the low coordination number for monolayers on noble-metal substrates accompanied by two-dimensional (2D) band structure effects. The trend results from different degrees of localization for the valence *d* wave functions[1,5] accompanied by different degrees of *d* band filling. Along this line, recently calculations have been extended to icosahedral Ru, Rh, and Pd clusters[6] for which moments of $1.02\mu_B$, $1.6\mu_B$, and $0.12\mu_B$ per atom, respectively, have been found. In light of the conventional wisdom that itinerant magnetism is limited to the 3*d* metals Cr, Mn, Fe, Co, and Ni, and alloys formed by those, all these predictions are quite unexpected, and show once more the potential inherent in the design of new materials. It has been speculated that these new ultrathin films, which combine large magnetic moments with large spin-orbit interactions, are useful for applications as high density storage materials and optical recording materials.

The above results have motivated a series of experiments, particularly of Rh adlayers on Ag (Refs. 7 and 8) and Au,[7,9] and more experiments are in progress.[10] Until now no long range magnetic order could be detected and all experimental results are at odds with the univocal theoretical predictions, which may be indicative of the beginning of a new controversy between theory and experiment. Various reasons may be said to be responsible for this discrepancy: the Curie temperature, coercivity, neglect of interlayer relaxation in the theory, many-body effects beyond the standard local spin density (LSD) approximation, or more complicated spin configurations. From the experiments it can be deduced that the Curie temperatures should be lower than 40 K (Ref. 8) and the coercivities of the films should be higher than 2.2 kOe (Ref. 9) to explain these null results, both of which are unlikely. The interlayer relaxation has been studied in detail for Ru and Rh by Wu and Freeman[2] with the result that the relaxation has little effect on the magnetic moments. We looked for more complicated spin configurations such as the $c(2\times2)$ antiferromagnetic order, but did not find any evidence for their existence. LSD usually underestimates magnetism; therefore any many-body improvement will contradict the experiments. Most likely the lack of experimental evidence comes from growth conditions leading to films that do not match the structural model of perfect monoatomic, pseudomorphic monolayers underlying the *ab initio* calculations. This view is supported by the experimental verification of 4*d* magnetism for substitutional Ru impurities in Pd (Ref. 11) and for Rh clusters in the gas phase,[12] which do not suffer from those growth problems.

In fact, investigations on the growth of Rh films on Ag or Au (Refs. 7 and 13) reveal different stages of the film quality depending on the substrate temperature: (i) intermixing of Rh with the noble metals, (ii) coverage of the Rh films by noble-metal films, and (iii) the formation of Rh clusters and islands. Previously we investigated the effect of Ag overlayers on the 4*d* and 5*d* monolayer magnetism.[14] We found in agreement with Wu and Freeman[2] a reduction of the magnetic moments roughly by a factor of 2 due to the doubling at the monolayer–noble-metal hybridization by the additional Ag cover layers, e.g., in the case of Rh/Ag(100) from $1.0\mu_B$ to $0.55\mu_B$ for Ag/Rh/Ag(100) and for Ru/Ag(100) from $1.73\mu_B$ to $0.93\mu_B$ for Ag/Ru/Ag(100), with moments remaining at least in the order of bulk Ni. Thus the noble-metal overlayers have no catastrophic effect on the presence of ferromagnetism in monolayers of 4*d* transition metals. Therefore we exclude the coverage of the Rh layers as an origin for the experimental absence of magnetism. In two recent theoretical investigations[15,16] the problem of intermixing was addressed. Both show a strong dependence of the magnetism on the degree of intermixing. Impurity calcula-

TABLE I. Local magnetic moments in μ_B/atom for $4d$ and $5d$ metal bilayers (BL) on Ag(001) compared with results for $4d$ (Ref. 1) and $5d$ (Ref. 5) monolayers (ML) on Ag(001) and interlayers (IL) (Ref. 14) in Ag(001). The results are obtained with 36 and partly with 78 k points (kpt) in the I2BZ. S denotes the moment of the atom at the surface of the bilayer, and $S-1$ the moment at the interface to Ag.

		$4d$ Metals				$5d$ Metals		
		Tc	Ru	Rh	Pd	Os	Ir	Pt
ML on 5L Ag	(36 kpt)	0.29	1.73	1.04	0	0.49	0.98	
	(78 kpt)	0.29		1.03		0.34	0.91	
ML on 7L Ag	(36 kpt)		1.76	1.02		0.38	0.99	0
	(78 kpt)					0.31		
IL in 5L Ag	(36 kpt)	0.07	0.91	0.59	0	0.03	0.40	
IL in 5L Ag	(78 kpt)	0.02	0.97	0.55	0	0.03	0.38	
BL (36 kpt)	S		0.05	0.32	0.20		0.11	0.30
	$S-1$		0.04	0.18	0.15		0.03	0.22
BL (78 kpt)	S		0.03	0.33	0.17		0.13	0.33
	$S-1$		0.01	0.18	0.11		0.05	0.23

tions of Lang *et al.*,[15] which simulate the low concentration limit of intermixing, reveal a total quench of the local magnetic moment for Rh impurities, but little effect on Ru impurities. Turek *et al.*[16] predict a dramatic concentration dependence for Ru/Ag films with suppression of magnetism at intermixing of around 50%.

In this paper we investigate the electronic structure and magnetic moments of $4d$ (Ru, Rh, Pd) and $5d$ metal bilayers (Ir, Pt) of the Ag(001) substrate. The bilayer results compared with the magnetism of the monolayers give a general idea of the possible effects of island growth and cluster formation on the magnetic properties of these films. A second purpose of this paper is the investigation of the thickness dependent crossover from the magnetic state of the $4d$ and $5d$ metal monolayers to the well-known nonmagnetic one for $4d$ or $5d$ bulk metals. Is there a sudden collapse of the magnetic moment at a certain film thickness? In any case it should be drastically different than the $3d$ metal films. For $3d$ metal films two scenarios are known: (i) Ferromagnetic monolayers Fe, Co, and Ni remain ferromagnetic upon deposition of additional layers, whereas the moments of the top layers change little and the moments of the atoms inside the film approach the bulk value. (ii) V, Cr, and Mn monolayers show an in-plane $c(2\times2)$ antiferromagnetic order which transforms after deposition of additional layers to a layered antiferromagnetic order along the surface normal. V becomes nonmagnetic.

The results are obtained with the full-potential linearized augmented-plane-wave (FLAPW) method[17] for film geometry. Nine-layer (001) films consisting of five layers of Ag and two $4d$ metal monolayers on each Ag surface are considered. Five layers of Ag are sufficient to obtain reliable overlayer moments as can be seen from the comparison with the films consisting of seven layers of Ag in Table I. A total number of about 2×50 symmetrized augmented plane waves per atom are used as variational basis set. Among the cutoff parameters inherent in the FLAPW method the magnetic moment depends most strongly on the accuracy of the Brillouin-zone integration. The convergence of the magnetic moment and the difference in the total energy between ferromagnetic and paramagnetic solutions were monitored by performing calculations with 3, 10, 36, and 78 special $k_{||}$ points[18] in the irreducible wedge of the 2D Brillouin-zone (I2BZ). Convergence of the moments was achieved with 36 $k_{||}$ points, as can be seen from Table I, where results for 36 and 78 $k_{||}$ points are collected. The accuracy achieved for the total energy differences were better than 10^{-4} Ry. Self-consistent iterations were continued until the total energy was stable within 10^{-5} Ry. We found in all cases that the total energies of the ferromagnetic states were lower than the corresponding paramagnetic ones. Metastable states have not been found. Thus the ferromagnetic state, if it exists, can be considered as being the ground state. All lattice constants a_0 were chosen according to Ref. 19. The monolayer-substrate interlayer spacing was taken to be the average of their bulk lattice spacings $a_0^{4d-\mathrm{sub}}=\frac{1}{2}(a_0^{4d}/2+a_0^{\mathrm{sub}}/2)$. The interlayer spacing between the transition-metal layers were taken to be half their bulk lattice constants. Thicker layers of Rh on Ag(001) were simulated by a nine-layer Rh(001) slab with the in-plane lattice constant of Ag and an interlayer spacing or c/a ratio determined so as to maintain the bulk volume of Rh. Core states are calculated full relativistically and valence states are treated scalar relativistically. The calculations apply density-functional theory using the LSD of von Barth and Hedin,[20] but with parameters as chosen by Moruzzi, Janak, and Williams.[19]

Our *ab initio* calculations predict ferromagnetism for Rh, and Pd among the $4d$ metals and Ir, and Pt among the $5d$ metal bilayers. The resulting magnetic moments are collected in Table I together with the moments of the $4d$ and $5d$ metal monolayers as overlayers on Ag(001) and as interlayers in Ag(001). Compared to the monolayer results the magnetic moments of the bilayers are strongly reduced in magnitude and the trend (see Fig. 1) has changed. The chemical element with the largest magnetic moment is shifted by one atomic number from Ru among the $4d$ and Ir among the $5d$ metal monolayers to Rh and Pt, respectively, for the case of bilayers. Pd and Pt, nonmagnetic as monolayers, became magnetic as bilayers with a surface moment of $0.17\mu_B$ and

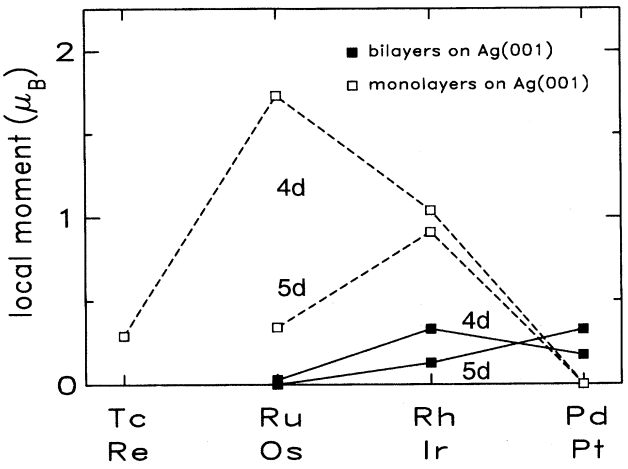

FIG. 1. Local magnetic moments calculated for ferromagnetic $4d$ and $5d$ metal bilayers on Ag(001) substrate (full squares connected by solid line) and as $4d$ and $5d$ monolayers on Ag(001) (open squares connected dashed line).

$0.33\mu_B$, respectively. The Ru moment of $1.73\mu_B$, the largest among the $4d$ and $5d$ metal monolayers, has completely collapsed in the bilayer state. The reduction of the magnetic moments of the bilayers is much stronger than for the interlayers and different in character leading to a different trend. As discussed in Ref. 14, the interlayer metals have a reduced magnetic moment by a factor of 2 as compared to the monolayers, but the trend remains the same. This indicates that the d-d hybridization between the transition-metal layers of the bilayer film is the basic source for this result.

Evidence for this view comes from the local density of states (LDOS) for nonmagnetic calculations, e.g., Pd on Ag(001) shown in Fig. 2. The major features in Fig. 2 arise from well-defined d bands of the Pd atoms. The bandwidth of the Pd bilayer is substantially wider than that of the monolayer. This is in line with the argument that the larger coordination number of $4d$ metal atoms in the bilayer film causes a wider bandwidth and a lower LDOS. The LDOS's of Rh and Ru look very similar to that of Pd except the bandwidth is wider and the LDOS is lower due to the decreasing localization of the $4d$ wave functions. Due to the smaller number of d electrons, the Fermi energy crosses the bands of Rh and Ru at about -0.5 eV compared to Pd. From Fig. 2 it becomes clear that for Rh and Ru bilayers the LDOS (n_{loc}) at the Fermi energy E_F is significantly smaller than that for the monolayers. With an exchange integral I of about 0.7 eV for $4d$ metals, the Stoner criterion for ferromagnetism $n_{\mathrm{loc}}(E_F)I>1$ becomes difficult to satisfy for the bilayers and the magnetism is drastically reduced. Thus the magnetism of the $4d$ and $5d$ metals alive for monolayers collapsed nearly in the range of the d-d hybridization, which means beyond one monolayer. This result shows that the large magnetism of $4d$ and $5d$ metal films is really a monolayer magnetism.

Within the bilayers, the moments in the surface layers, denoted by S in Table I and Fig. 2, are larger than the moments in the layers at the interfaces to Ag, denoted by $S-1$, because the atoms at the interfaces face the d-d hybridization with the surface layers and in addition the sp-d hybridization with the Ag substrates. This further reduces the LDOS at the Fermi energy, as can be seen from Fig. 2, which makes the onset of magnetism for interface atoms less likely or the magnetic moments smaller, respectively. If the surface atoms of a bilayer island are covered again by Ag cover layers due to the growth process, the surface atoms will become also interface atoms with moments similar to those of $S-1$. This means noble-metal cover layers on bilayer islands have an additional detrimental effect on the magnetism of $4d$ and $5d$ metal films.

The appearence of the weak magnetism of Pd and Pt deserves an additional comment. It is well known that Pd and Pt have the largest exchange enhanced susceptibilities[21] within the $4d$ and $5d$ transition-metal series, respectively, and for fcc Pd the onset of magnetism is predicted for a lattice expansion of 6% (Ref. 22) of the equilibrium value while for Rh the necessary lattice expansion is expected to be 16%.[22] Since the lattice constant of Ag is about 5% larger than those of Pd or Pt, Pd and Pt are favorable candidates for $4d$ and $5d$ metal magnetism. Despite the elevated lattice constants and despite the band narrowing due to the reduced coordination number, monolayer magnetism of Pd and Pt is absent. As demonstrated in Fig. 2 the sp-d hybridization, which is the dominating interaction between these monolayer atoms with the Ag substrate, pushes the d bands below the Fermi surface and the Stoner criterion for magnetism cannot be fulfilled anymore. Due to the d-d hybridization between the surface and interface layers the LDOS at the Fermi energy becomes

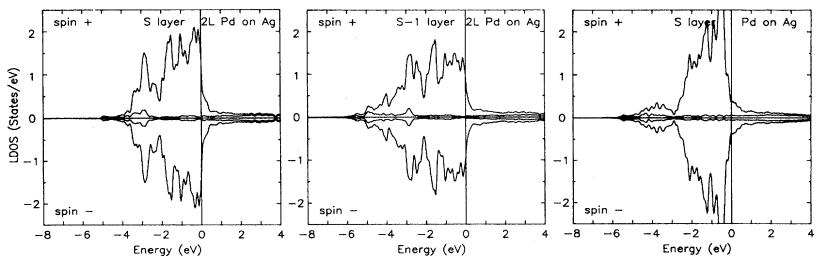

FIG. 2. Local densities of states together with the insignificant sum of $s+p+f$ contributions for Pd as bilayer (2L Pd on Ag) and monolayer on Ag(001) (Pd on Ag) resulting from paramagnetic calculations. Shown are only the LDOS of Pd and not those of Ag; S indicates the surface layer, and $S-1$ the layer underneath the surface layer. Fermi energy is the origin of the energy scale. [LDOS for the majority (+) and minority (−) spin direction is degenerate.]

bulklike and the magnetism of Pd and Pt bilayers can be viewed as the onset of bulk magnetism due to elevated lattice constants.

For $4d$ or $5d$ metal films thicker than two layers, the d-d hybridization within the film, as the dominating interaction, leads to bulklike LDOS. Rh and Ir films are expected to become nonmagnetic. Also, no surface magnetism of these films is expected. The existence of the Ag substrate becomes less important, with the exception of maintaining a lattice constant of the film different from the bulk. The lack of magnetism is derived from previous calculations of $4d$ metals on Pd(100),[1] which is, from the view point of d-d hybridization, a first approximation of thicker $4d$ metal films. No magnetism was found for these monolayer systems. Particularly for Rh, we have tested a nine-layer film with the in-plane lattice constant of Ag for magnetism, with no success. A recent theoretical prediction of the surface magnetism of Rh(100) by Morrison *et al.*,[23] based on a valence only approach, was not confirmed by Weinert *et al.*,[24] who performed calculations based on the LSD, and is also ruled out by a recent experiment of Wu *et al.*[25] Thicker Pd and Pt might remain magnetic as long as the lattice constant of Ag is maintained by the film.

In summary, detailed calculations on the electronic structure and magnetic moments for $4d$ (Ru, Rh, Pd) and $5d$ (Ir, Pt) transition-metal bilayers on the (001) surfaces of Ag have been performed. We found ferromagnetic solutions for Rh and Pd among the $4d$ bilayers as well as Ir and Pt among the $5d$ metals. When comparing the magnetism of $4d$ and $5d$ metal bilayers with that of the monolayers, one observes (i) that the magnetic moments of the bilayers are significantly reduced and (ii) that the chemical element, which supports the largest magnetic moment within the $4d$ or $5d$ series, respectively, is shifted by one atomic number, from Ru to Rh for the $4d$ series and from Ir to Pt for the $5d$ series. Increasing the thickness of the Rh layers magnetism is quenched. This means that the transition from the magnetic monolayer state to the nonmagnetic bulk state happens rather suddenly, just at the one-monolayer stage. The sudden collapse of the magnetic moments of the bilayers was explained with the onset of the d-d hybridization due to the existence of the second transition-metal layer. The appearance of the weak magnetism of Pd and Pt bilayers is the onset of a bulk effect, and the weak magnetism found is driven by the expansion of the Pd and Pt lattice constants due to the Ag substrate. From previous calculations[5] we can conclude that the magnetic behavior on Ag and Au substrates are very similar. This is very likely also true for Cu_3Au as substrate. Therefore the conclusions drawn for the Ag substrate are rather general and are not limited to the Ag substrate.

These results place a severe upper bound on the imperfections permitted to verify $4d$ and $5d$ magnetism of the films. The lack of layer by layer growth on the monolayer level has a detrimental effect on the presence of ferromagnetism in monolayers of $4d$ and $5d$ transition metals. Magnetism of Ru, Rh, and Ir should be detected in case of complete wetting or wetting above the percolation limit, respectively, of the Ag or Au surface by one monolayer, with or without a cover layer of the noble metals. Island growth largely suppresses magnetism and also superparamagnetism of islands below the percolation limit will be suppressed. This effect is amplified by noble-metal cover layers. Magnetism of Pd and Pt films may be realized only for films in a limited thickness range and pseudopmorphic growth conditions. The thickness of the layers should be larger than one monolayer to avoid the suppression of the magnetism due to the sp-d hybridization with the noble-metal substrate, and thin enough such that the Ag or Au lattice constant will be maintained. Due to the weakness of the magnetism of Pd and Pt against sp-d hybridization, intermixing of Pd and Pt with noble metals or noble-metal cover layers may have catastrophic effects for the magnetism.

The computations were performed on Cray computers of the Forschungszentrum Jülich and the German supercomputer center (HLRZ).

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