Magnetism of 4*d* and 5*d* adlayers on Ag(001) and Au(001): Comparison between a nonrelativistic and a fully relativistic approach

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The magnetic properties of single and double layers of Ru, Rh, Pd, Os, Ir and Pt on Ag(001) and Au(001) are investigated using the scalar relativistic and the fully relativistic spin-polarized screened Korringa-Kohn-Rostoker method. It is shown that, in particular, for the case of the Ir monolayers and Pt double layers a nonrelativistic approach is no longer valid, since a magnetic ground state would be predicted, while a relativistic description yields a nonmagnetic ground state.

In the past three years, possible ferromagnetism of 4*d* and 5*d* overlayers grown epitaxially on noble metal substrates, such as Ag(001) and Au(001), has been explored in terms of *ab initio* electronic structure calculations within the local spin density approximation (LSDA). By using a scalar-relativistic norm-conserving pseudopotential, Zhu *et al.*[1] found a magnetic moment of 1.09 μ_B for a Rh monolayer on Au(001). A systematic study within the fixed spin-moment method by Eriksson *et al.*[2] predicted ferromagnetic ground states for Ru and Rh on Ag(001), while Tc and Pd were paramagnetic on the same substrate. The ferromagnetism of Ru and Rh on Ag(001) has been confirmed by Wu and Freeman[3] in terms of a full-potential linearized augmented-plane-wave method (FLAPW), finding magnetic moments of 1.57 and 0.96 μ_B, respectively. General trends for the magnetism of transition metal overlayers on noble metal (001) substrates were then established and discussed by Blügel,[4] who also used the FLAPW method.

Surprisingly enough, experiments mostly contradict the theoretical LSDA results. While the splitting of 4*s* levels of Rh on Ag(001), seen by photoemission,[5] seemed to indicate the existence of nonvanishing magnetic moments on the Rh atoms, measurements using the magneto-optic Kerr effect found no evidence of ferromagnetic order for Rh/Ag(001) (Ref. 6) or Rh/Au(001).[7] Among the possible reasons for this disagreement between theory and experiment, the occurring structural imperfections at the surface seem to be most likely. Attempts on different levels have been made to explore this effect theoretically. It was shown that for 4*d* and 5*d* transition metal interlayers in Ag(001) the magnetism is considerably decreased as compared to the corresponding overlayer: the large overlayer magnetic moment of Ru, Rh, and Ir is approximately halved, while Tc and Os are practically nonmagnetic as interlayer.[8] The ferromagnetism of Rh/Ag(001) is destroyed by covering with a Ag layer; however, the system Ag/Ru/Ag(001) remains magnetic with a slightly reduced magnetic moment.[3] Very recently, Blügel has found a dramatic reduction of magnetism for double layers of Ru, Rh, and Ir on Ag(001). He also predicted, however, weak magnetism for double layers of Pd and Pt on Ag(001), which are paramagnetic as monolayers.[9] Also very recently, Turek *et al.*[10] presented models for noninteger coverage and for interdiffusion in terms of the coherent-potential approximation (CPA) as combined with the tight-binding linear muffin-tin orbital method (TB-LMTO). They found that for Ru/Ag(001) a coverage larger than 1.5 monolayer (ML) completely destroyed the ferromagnetic ground state. A similar effect was found for Rh/Ag(001), nevertheless, the coverage, where the breakdown of magnetism occurred, was rather dependent on the surface relaxation.

In this paper a series of 4*d* (Ru, Rh, and Pd) and 5*d* (Os, Ir, and Pt) transition metal single and double layers on both Ag(001) and Au(001) substrates are investigated systematically, from a different theoretical point of view. For each of the monolayer and double layer systems, two types of self-consistent spin-polarized calculations were performed, namely, (i) solving the scalar-relativistic Schrödinger equation[11] separately for the up and down spin channels in the valence band, and (ii) solving the fully relativistic Dirac equation in the presence of the internal magnetic field.[12,13] Although, viewed in terms of the elimination method (see for example Ref. 14), in the first approach "only" the spin-orbit coupling is missing, this leads to an essentially different description of the magnetism as compared to the fully relativistic case. For matters of convenience, the first approach will be referred to as nonrelativistic, while the second one will be denoted simply as relativistic.

In order to perform multiple scattering calculations for a set of layers sandwiched by semi-infinite systems, the screened Korringa-Kohn-Rostoker (KKR) technique was applied.[15] Apart from the inherent differences with respect to single-site scattering,[16] all technical details apply equally well for both sets of calculations: the interface consisted of a total of nine layers of potentials, which were determined self-consistently, namely two empty sphere layers, one or two adlayers according to the monolayer or the double layer calculations and, subsequently, six or five Ag (Au) layers. It should be noted that these layers were embedded between a perfect semi-infinite bulk region from one side and a perfect semi-infinite vacuum region, represented by constant potential wells, from the other side. Due to the evaluation of the screened structure constants as described in Ref. 15, no lattice strain was included into the present calculations. A cutoff of $\ell_{max}=2$ in the angular momentum expansion was used. The Brillouin zone integrations were performed by sampling generally 45 $k_{\|}$ points in the irreducible segment of the surface Brillouin zone. The energy integrations were performed by using a 15 point Gaussian sampling along a semicircle in the upper complex energy semiplane starting below the valence band and ending at the Fermi level. Charge self-consistency in the interface was obtained within the atomic sphere approximation (ASA) by including the dipole moments into the lattice Madelung potential and by using the exchange-correlation functional of Vosko *et al.*[17] In each case, the self-consistent iterations were stopped at a convergency of better than 0.05 mRy for the interface total energy.

The results for the magnetic moments obtained from the nonrelativistic calculations are presented in Table I, in the left column of each element. As compared to previous film-FLAPW calculations,[4,9] in particular with respect to the dominating trends, the agreement is fairly satisfactory. Within the 4d monolayers, Ru and Rh show a clear onset of surface magnetism, while Pd is paramagnetic. The Os monolayer is found paramagnetic both on Ag(001) and Au(001). For Ag(001) this is in disagreement with the corresponding FLAPW result, which predicts a small magnetic moment of 0.31 μ_B.[9] The present results generally suggest that the onset of magnetism of the overlayers under consideration is fairly insensitive to a change of the substrate from Ag to Au. It should be noted that the calculated magnetic moments for the Ir monolayers are also considerably less than in Ref. 4. With the exception of the Pt double layer, in all cases a second adlayer leads to a paramagnetic ground state. The weakly ferromagnetic ground states found in Ref. 4 for Rh, Pd, and Ir double layers on Ag(001) are not reproduced in the present results. The discrepancies between the present results and the FLAPW results mentioned above are probably mostly due to the different exchange-correlation functionals used, a slightly different geometrical arrangement, but also due to the spherical shape approximation for the potentials used in the present approach.

Before moving on to the results of the relativistic approach, it seems to be worthwhile to discuss qualitatively the effects to be expected. For this reason, we investigated the d-like resonances for various different kinds of single-site scattering. Such a study is presented in Fig. 1, where the resonance energies corresponding to the scalar-relativistic potentials of Rh and Ir monolayers on Ag(001) are displayed. In this figure, panel (a) refers to the nonrelativistic spin-polarized case, and shows an exchange splitting that is approximately twice as large for Rh as for Ir. This explains in simple terms the difference in the calculated magnetic moments for these two monolayers (see Table I). In panel (b) the resonance energies corresponding to a fully relativistic nonmagnetic approach are shown. Quite clearly, the spin-orbit splitting of Ir, i.e., the splitting between the $d^{3/2}$ and $d^{5/2}$ resonance energy, is about three times larger than that of Rh. As compared to panel (a), the spin-orbit splitting of Rh amounts to only about 70% of the corresponding exchange splitting, while the spin-orbit splitting of Ir is more than four times larger than the corresponding exchange splitting. The fully relativistic spin-polarized case is shown in panel (c). Here, Rh represents the "strong magnetic case," in which the scattering channels corresponding to different j but to the same μ quantum numbers, namely $-3/2 \leq \mu \leq 3/2$ and $j = 3/2, 5/2$, are strongly coupled, while the two uncoupled resonances, $(j,\mu) = (5/2,-5/2),(5/2,5/2)$, are energetically separated approximately by the exchange splitting as shown in panel (a). For Rh this coupling obviously leads to an "upper" and a "lower" set of resonances, each of them

TABLE I. Calculated magnetic moments [μ_B] of 4d and 5d monolayers (ML) and double layers (DL) on Ag(001) and Au(001). For double layers, the surface layer and the first subsurface layer are denoted by S and S-1, respectively. For each element, the left and right columns refer to the nonrelativistic (NR) and the relativistic (R) calculations, respectively.

			4d overlayers						5d overlayers					
			Ru		Rh		Pd		Os		Ir		Pt	
			NR	R	NR	R	NR	R	NR	R	NR	R	NR	R
	ML		1.64	1.59	0.93	0.93					0.42		0.01	
Ag	DL	S					0.07						0.28	
		S-1					0.05						0.18	
	ML		1.62	1.55	0.96	0.88					0.35		0.02	
Au	DL	S	0.06										0.19	
		S-1	0.05										0.11	

consisting of five levels. By transforming the single-site t-matrices from the (κ,μ) representation to the (ℓ,m,σ) representation, as suggested by Staunton *et al.*,[18,19] one can rather safely associate the lower and the upper sets of resonances with the $\sigma=-\frac{1}{2}$ and $\sigma=\frac{1}{2}$ channels, respectively, although, the resonances corresponding to different values of the spin quantum number σ are still slightly coupled. In the case of Ir, the small exchange coupling results into an almost "classical" Zeeman-type splitting of the $d^{3/2}$ and $d^{5/2}$ levels (see also Ref. 20). Since here the levels corresponding to the same j but to the opposite μ quantum numbers, e.g., $(3/2,-3/2)$ and $(1/2,-1/2)$, are split only very weakly, a decreased magnetism has to be expected.

As a consequence of reduced symmetry, for very thin ferromagnetic systems an enhanced perpendicular magnetic moment might be expected.[21] In order to justify this general finding for the present type of overlayers, as an example for Rh/Au(001), self-consistent fully relativistic calculations were performed with a magnetic field perpendicular as well as parallel to the surface. As expected, for the perpendicular orientation the magnetic moment for Rh is about 0.015 μ_B larger than that for the parallel orientation. Concomitantly, in terms of the total energy, the perpendicular orientation of the magnetic field was found by about 0.1 mRy more favorable than the in-plane orientation. The calculated magnetic anisotropy energy is, as is well known, highly sensitive with respect to the number of $k_{\parallel}$ points used to perform the Brillouin zone integration.[22,16] According to our previous experiences in calculating the magnetic anisotropy energy of Fe multilayers on a Au(001) substrate,[16] the anisotropy energy of Rh/Au(001) has been recalculated within the frozen potential approximation by using 325 $k_{\parallel}$ points in the irreducible segment of the surface Brillouin zone. In satisfactory agreement with the result of the self-consistent calculations, we got an anisotropy energy $E_{\perp}-E_{\parallel}$, of -0.13 mRy, a value more than twice as large in magnitude as found for Fe/Au(001).[16] Therefore, for the present overlayer systems, the perpendicular orientation of the magnetic field is considered as the preferable one, and all the results within the fully relativistic approach presented in this paper correspond to this case.

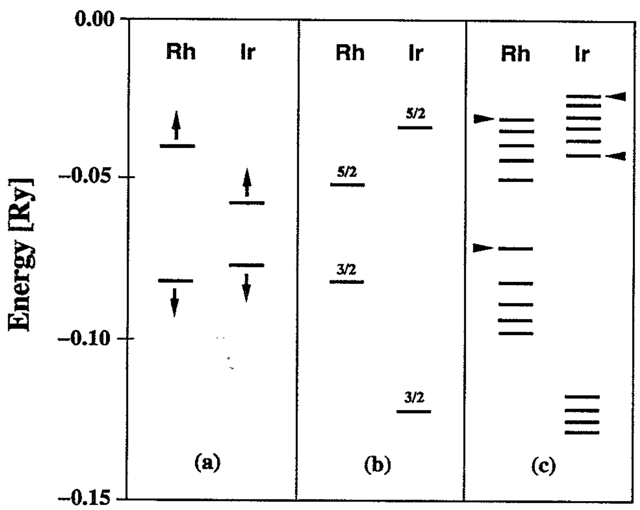

FIG. 1. Calculated positions of d-like resonances of a Rh and an Ir overlayer for the case of a Ag(001) substrate. The potentials from the scalar-relativistic spin-polarized calculations were used for the different single-site scattering schemes. Panel (a) refers to the scalar-relativistic spin-polarized case, where the spin-up and spin-down channels are denoted by up and down arrows. The relativistic nonmagnetic case is shown in panel (b) illustrating the spin-orbit splitting between the j=3/2 and 5/2 resonances. The relativistic spin-polarized case is displayed in panel (c) and shows a total of ten different resonance energies for each case. The uncoupled resonances corresponding to (j,μ) = $(5/2,-5/2)$ (upper ones) and $(5/2,5/2)$ (lower ones) are indicated by small horizontal arrows.

The magnetic moments, obtained from the self-consistent fully relativistic spin-polarized calculations, are listed in Table I in the respective right column. These moments follow remarkably well the above qualitative picture in terms of single-site resonance energies. As was to be expected from this picture, the magnetic moments of the strongly magnetic Ru and Rh monolayers are indeed slightly reduced. In order to compare to the nonrelativistic approach on the same footing, it is worthwhile to interpret the results in terms of the previously mentioned (ℓ,m,σ) representation. In this representation, one can define charges that correspond to the up- and down-spin channels, $Q_{\uparrow}$ and $Q_{\downarrow}$, respectively. In the nonrelativistic scheme, the magnetic moment is associated with the difference of these charges, $M'=Q_{\downarrow}-Q_{\uparrow}$. Within the relativistic picture, because of the coupling between different spin channels the (spin-only) magnetic moment M necessarily differs from M'. However, for Ru and Rh monolyers, we found that the deviation of M and M' is less than 0.01 μ_B, indicating that with the exception of the magnetic anisotropy, the spin-orbit coupling is of minor importance for the magnetic properties in these systems. Thus, in this case, the traditional picture of "up-spin" and "down-spin" electrons seems to be fairly well preserved. In all other cases, even in those where in the nonrelativistic approach a finite magnetic moment was found, the relativistic approach clearly yields a paramagnetic ground state. As discussed in the context of Fig. 1, in all these cases the spin-orbit splitting of d-like states dominates as compared with the exchange splitting found within the nonrelativistic calculations. As a final result of charge self-consistency, for the (nonrelativistically) weakly magnetic 4d and for all of the 5d overlayer systems the relativistically different hybridization within the d-band and/or backscattering to the substrate prevents the onset of magnetism.

In summary, we presented a study of magnetism for 4d and 5d single and double layers on Ag(001) and Au(001) in terms of a comparison of nonrelativistic (scalar-relativistic) and fully relativistic results. This comparison clearly indicates the limitation of the traditional nonrelativistic up-spin and down-spin picture, and strongly suggests, for example, the need of a relativistic study to describe the magnetism of $4f$ or $5f$ transition metal overlayers properly.

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