Ferromagnetism of Imperfect Ultrathin Ru and Rh Films on a Ag(001) Substrate

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We present a systematic study of the influence of various types of structural imperfections on the magnetic properties of ultrathin transition-metal films on noble-metal substrates. As a case study, we show by means of *ab initio* electronic structure calculations that recently predicted ferromagnetism of perfect Ru and Rh monolayers on a Ag(001) substrate is highly sensitive to noninteger coverage by additional Ru or Rh atoms and overlayer-substrate interdiffusion. Both types of structural imperfections strongly reduce the local magnetic moments and lead, in some cases, to a complete extinction of the ferromagnetic state.

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Ultrathin transition-metal films which can be epitaxially grown on noble-metal substrates have recently attracted considerable attention due to their unusual magnetic properties. One reason for this interest is undoubtedly the fact that the two-dimensional (2D) itinerant magnetism of these systems need not be restricted to $3d$ transition metals only. *Ab initio* electronic structure calculations within the local spin density approximation (LSDA) predicted that monolayers of late $4d$ and $5d$ transition metals placed on Ag(001) or Au(001) substrates should exhibit ferromagnetism with sizable magnetic moments [1–3]. According to systematic studies by Blügel [3], the greatest local magnetic moments of the $4d$ and $5d$ monolayers on Ag(001) are expected for Ru ($1.7\mu_B$), Rh ($1.0\mu_B$), and Ir ($0.9\mu_B$). The obtained trends across the $3d$, $4d$, and $5d$ series can be viewed within a Stoner-type theory of itinerant magnetism as a consequence of different degrees of localization of the valence d orbitals accompanied by 2D band-structure effects [3,4]. Despite the unambiguous theoretical results predicting the magnetism of $4d$ and $5d$ monolayers (ML) on Ag(001) and Au(001), experiments using the surface magneto-optic Kerr effect failed to confirm this phenomenon [5,6] indicating thus a strong disagreement between theory and experiment. The most probable reason for this discrepancy seems to be structural imperfections of the real samples [4,7,8] which are far off from the perfect monolayers considered in the calculations. Ample experimental evidence demonstrates that islanding, surface roughness, or interdiffusion cannot be neglected in these systems [5,9,10].

Several theoretical studies addressed the problem of ferromagnetism of structural models different from the ideal $4d$ and $5d$ monolayers on a Ag substrate: monolayers covered by an extra Ag top layer [11], monolayers sandwiched in Ag [12], double layers [4,8,13], small Rh islands as well as an ordered $c(2 \times 2)$ $Rh_{50}Ag_{50}$ ML [14], and $4d$ and $5d$ surface impurities [15]. In spite of a general confirmation of the crucial effect of the perturbed 2D translational symmetry and of the overlayer-substrate hybridization on the magnetic moments, the existing theoretical studies solve the problem of magnetism in real samples only partially. The main reason is a huge number of possible atomic arrangements which can occur in these systems due to their inhomogeneity and nonequilibrium nature. The purpose of this paper is to present results of a new approach to this problem, namely to simulate the imperfect ultrathin films by means of 2D random alloys formed in several surface layers of a nonmagnetic metallic substrate. This model allows us to investigate systematically the influence of different types of structural imperfections on the magnetism in these films. It enables us to find out general trends and to relate them to real systems with more complicated structures. In the following we concentrate on Ru and Rh films on a Ag(001) substrate which are the best candidates for the 2D magnetism among all $4d$ and $5d$ elements.

Our calculations employ a recently developed *ab initio* approach based on the tight-binding linear muffin-tin orbital method combined with a surface Green's function and the coherent potential approximation [16]. This approach takes into account the true semi-infinite geometry of the system. LSDA self-consistency is achieved within the atomic sphere approximation but with the dipole moments of the nonspherical charge density included into the interatomic Madelung potentials [17]. Relaxation of interlayer spacings between neighboring layers in the surface-vacuum interface is optionally included by using screened structure constants that are calculated in real space similarly as for amorphous structures [18]. The results reported here were obtained in the scalar relativistic approximation, with the exchange-correlation potential of Vosko, Wilk, and Nusair [19], and with 21 $\mathbf{k}_\parallel$ points in the 2D irreducible Brillouin zone. Our values of the magnetic moments for perfect $4d$ monolayers on Ag(001) as well as for the $4d$ impurities in the same surface compare well with those obtained by the full-potential slab [3] and Green's function [15] methods, respectively.

We considered two types of structural imperfections occurring frequently in artificially prepared ultrathin mag-

netic films: (i) films corresponding to a noninteger coverage of the Ag(001) surface with Ru or Rh varying between 1 and 2 ML, and (ii) Ru and Rh films of 1 ML coverage affected by the interdiffusion with the Ag(001) substrate. In terms of our 2D random-alloy approach, the former case was simulated by surface layers of the composition $R_x\mathrm{Vac}_{1-x}/R/\mathrm{Ag}(001)$, $0 \leq x \leq 1$, where R stands for Ru or Rh and Vac denotes a surface vacancy. This model describes a continuous formation of the second R layer on top of the first perfect R layer on a Ag(001) substrate. Within this model, the effect of interlayer relaxation on magnetic moments was studied as well: The spacing between the perfect R and Ag layers was taken equal to the average of the bulk R-R and Ag-Ag interlayer spacings [1,3] while the spacing between the perfect and the incomplete R layers was taken to be the bulk R-R interlayer spacing [13]. This approximate treatment of interlayer relaxations is justified by recent full-potential calculations for perfect Ru and Rh overlayers on Ag(001) [11]. The results were then compared to those calculated with an unrelaxed geometry where all atoms (and surface vacancies) occupied the positions of the ideal bulk Ag lattice. The case of interdiffusion was treated only in the unrelaxed geometry and was simulated by the layer sequence $R_{1-x}\mathrm{Ag}_x/R_x\mathrm{Ag}_{1-x}/\mathrm{Ag}(001)$, $0 \leq x \leq 1$. This corresponds to a continuous transition of the R layer from the surface ($x = 0$) to the first subsurface ($x = 1$) position.

The average local magnetic moments in the films with noninteger coverage are shown in Fig. 1 for both the relaxed and unrelaxed geometry. In all cases we find a transition from the ferromagnetic state at coverages near 1 ML into the paramagnetic state at higher coverages. For the Ru films the moment in the complete Ru layer drops from its original value of $1.8\mu_B$ for 1 ML coverage to zero before the second Ru layer is half formed. The Ru moment in the incomplete Ru layer is much smaller and exhibits a certain degree of antiferromagnetic coupling to the perfect Ru layer. The values of both Ru moments are only slightly modified by the interlayer relaxation; this effect being more pronounced for higher coverages. For the Rh films at 1 ML coverage the moment in the complete Rh layer is twice as small than in the Ru case; the moments of the Rh adatoms, however, are of comparable size with pronounced ferromagnetic coupling between both layers. Contrary to the Ru films, the coverage dependence of the Rh moments is strongly influenced by interlayer relaxation: The critical coverage for an extinction of ferromagnetism is changed from 1.7 in the unrelaxed model to 1.2 ML using the relaxed geometry. It should be noted that this different sensitivity of Ru and Rh moments to the interlayer relaxation can be hardly anticipated on the basis of calculations for perfect 1 ML films: The relaxation-induced changes of the moments are nearly negligible for both elements (see Fig. 1).

The calculated average local magnetic moments for films with Ag interdiffusion are presented in Fig. 2.

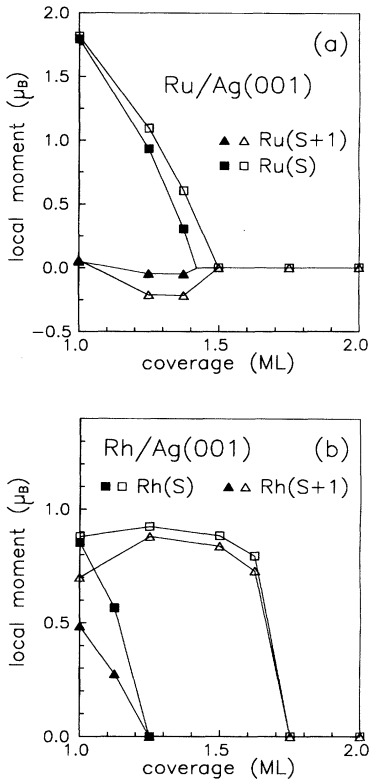

FIG. 1. Average local magnetic moments of Ru (a) and Rh (b) atoms in ultrathin films on a Ag(001) substrate as a function of the coverage. Squares and triangles refer to moments in the complete (S) and incomplete ($S + 1$) layer, respectively. Open symbols: unrelaxed geometry, full symbols: relaxed geometry.

The resulting trends demonstrate for both elements a nontrivial magnetic behavior which can be characterized by well-developed moments for systems where a perfect R monolayer is formed either on the surface or below. For intermediate values of x when interdiffusion strongly perturbs the structure of the thin film, the ferromagnetism is substantially reduced. This is manifested by a magnetic gap in the Ru case for $0.5 \leq x \leq 0.6$ and by a deep minimum of both local moments in the Rh case near $x = 0.6$ (see Fig. 2). In analogy to the films with noninteger coverage, we again find that magnetic properties of perfect monolayers cannot be simply extrapolated to imperfect films.

Figure 2 also shows an interesting difference in the behavior of Ru and Rh impurities near the perfect magnetic monolayers, naturally obtained in our model for $x \to 0$ or $x \to 1$. The Ru impurity has a moment of $0.2\mu_B$ in the first subsurface layer but this value is strongly enhanced to $1.2\mu_B$ in the surface layer. This enhancement is a surface effect as documented by the moments of a Ru impurity in bulk Ag (zero moment [20]) and in the surface layer of pure Ag(001) ($1.7\mu_B$ [15]). In contrast to missing

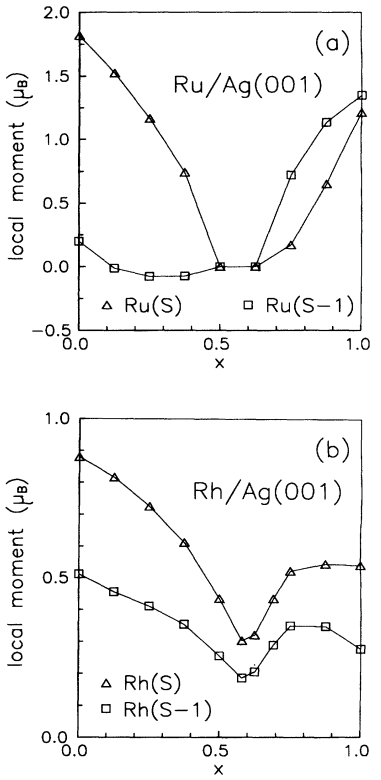

FIG. 2. Average local magnetic moments of Ru (a) and Rh (b) in films of 1 ML coverage on Ag(001) affected by interdiffusion with the Ag substrate. Triangles refer to moments in the surface (S) layer with the composition $R_{1-x}Ag_x$, squares refer to the first subsurface ($S-1$) layer with the composition R_xAg_{1-x} (R = Ru, Rh).

moments of a Rh impurity in bulk Ag [20] and on a pure Ag(001) surface [15], the moment of a Rh impurity near the perfect Rh ML amounts to $0.5\mu_B$, irrespective of its position [Fig. 2(b)]. Hence, our nonzero moments of Rh impurities are due to their ferromagnetic coupling with the neighboring Rh ML.

In order to get a deeper insight into the underlying electronic structure, spin-polarized local densities of states (LDOS) corresponding to the self-consistent potentials were studied as well. A typical example is presented in Fig. 3 for the Ru films with Ag interdiffusion. There is a common feature for all the systems considered here, namely a nearly complete separation of the d bands of Ag and Rh or Ru atoms and, therefore, a negligible d-d hybridization. This allows us to understand the concentration dependence of the LDOS widths discussed below. The LDOS of the Ru and Rh atoms near the Fermi level which are responsible for the magnetic properties are in all cases dominated by d electron contributions. For Ru and Rh in the perfect monolayers [see Figs. 3(a) and 3(c) for Ru], the LDOS show triangularlike shapes with high values at the top of the d band. This 2D band-structure

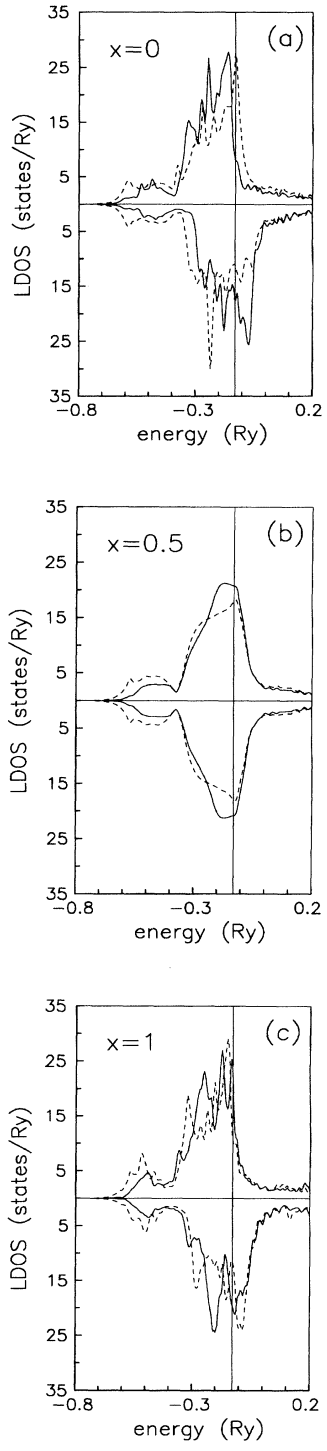

FIG. 3 Average spin-polarized Ru-projected densities of states in Ru/Ag(001) films affected by interdiffusion with the values $x = 0$ (a), 0.5 (b), and 1 (c). The solid line refers to the surface (S) layer with the composition $Ru_{1-x}Ag_x$, the dashed line refers to the first subsurface ($S-1$) layer with the composition Ru_xAg_{1-x}. Upper (lower) panels refer to the majority (minority) spin directions, the vertical lines denote the position of the substrate Fermi level.

effect and the narrowing of the d bands due to the reduced coordination in the surface are the main sources of the $4d$ and $5d$ ML magnetism [3,12]. For monolayers strongly affected by the Ag interdiffusion, the overall shapes of the Ru and Rh LDOS are significantly smeared out due to disorder [see Fig. 3(b) for Ru]. Note, however, that the bandwidths do not change with x as the average number of R nearest neighbors remains constant (compare the widths of all LDOS in Fig. 3). Near $x = 0.5$, the values of both the surface and the subsurface LDOS at the Fermi level are reduced and, in case of Ru, neither of them reaches the critical value necessary for a formation of moments as required by a simple Stoner model [3,4]. The maximal effect of disorder on the LDOS shape is at $x \approx 0.5$, which is in rough agreement with those compositions that correspond to a minimal magnetization in the films (see Fig. 2). The Ru and Rh LDOS in films with noninteger coverages exhibit also a disorder-induced smearing (most pronounced near 1.5 ML) which, in addition, is accompanied by an overall broadening gradually increasing with the coverage as the average number of R nearest neighbors increases. It is this combined effect of the smearing and broadening which reduces the LDOS at the Fermi level and leads to the extinction of the ferromagnetic state in this case.

The main features of the LDOS can be used to understand the different sensitivity of Ru and Rh monolayers with adatoms to the interlayer relaxation (see Fig. 1). The weak hybridization between the Ag d orbitals and the d orbitals of Ru or Rh explains the negligible influence of the Ag-R interlayer relaxation on the magnetic moments of the prefect 1 ML overlayers. The influence of the R-R interlayer relaxation is more pronounced, reflecting thus a stronger hybridization between the d orbitals of R atoms in the complete and incomplete R layers. This hybridization strength depends on the energy separation of the corresponding d orbital atomic levels (for both spin orientations) which consequently depends on the exchange splitting of the magnetic R atoms. The large magnetic moment of the perfect Ru ML together with the nearly vanishing magnetic moment of the Ru adatoms result in a small sensitivity of the Ru moments to the layer relaxation [Fig. 1(a)], while the comparable magnetic moments of the perfect Rh ML and of the Rh adatoms lead to a dramatic change of the Rh moments due to the layer relaxation [Fig. 1(b)].

In summary, we presented an *ab initio* LSDA approach to itinerant magnetism of imperfect ultrathin transition-metal films on a noble-metal substrate. The imperfect structures were systematically simulated by means of 2D random alloys at the noble-metal surface. The application of the formalism to the $4d$ transition-metal films on a Ag(001) substrate reveals a pronounced sensitivity of the ferromagnetic state of Ru and Rh monolayers with respect to noninteger coverage by additional transition-metal atoms, to interlayer relaxations between the complete and incomplete transition-metal layers, and to the interdiffusion of substrate atoms into the film. We found that the effects of alloying and structure imperfections are reflected in the widths and shapes of the transition-metal LDOS and contribute significantly to the reduction of the magnetization of the films. Our results indicate that only structurally perfect Ru and Rh ultrathin films with 1 ML coverage and without substrate interdiffusion are promising systems to obtain 2D itinerant magnetism of $4d$ transition metals.

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