Ferromagnetism in 4*d* (Tc, Ru, Rh, Pd) and 5*d* (Ir, Pt) transition-metal monolayers on a Cu(001) substrate

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We have studied the magnetic activity of transition metal monolayers of the 4*d* (Tc, Ru, Rh, Pd) and 5*d* (Ir, Pt) series on a Cu(001) substrate. Rh and Ir monolayers present ferromagnetism with magnetic moments 0.52 and 0.17 Bohr magnetons, respectively. We find that the Tc, Ru, Pd, and Pt monolayers are nonmagnetic. A Ru monolayer is magnetic on Ag(001) and Au(001) substrates with a comparatively high magnetic moment of 1.73 Bohr magnetons in both cases. The loss of its magnetic moment appears to be mainly due to the influence of inward tension. Cu has a smaller lattice constant than any of the monolayers considered here and therefore we are looking at the opposite effect as compared to Ag or Au. If we artificially enhance the Cu lattice constant we recover the high magnetic moment of Ru/Ag(001). We make use of the surface Green's function matching method together with tight-binding Hamiltonians to calculate the paramagnetic local density of states projected onto the monolayer or the substrate atomic layers and calculate the magnetic moment from the minimum of the total energy as a function of the magnetic band splitting. We obtain good agreement with the known results for the same set of monolayers on Ag(001) and Au(001) substrates. [S0163-1829(99)06509-1]

I. INTRODUCTION

For most of the elements, magnetism is found in isolated atoms as shown by Hund's rules.[1] In solids, magnetism is found within elements of the 4*f* and 5*f* series. But the electrons responsible for their magnetic ordered phases do not participate at the Fermi surface and give rise to localized spins. Itinerant magnetism in three dimensions (3D) is observed in the 3*d* transition metal series, in particular, in Fe, Co, and Ni. On the other hand, Sc, Ti, and V are not magnetic.[2,3]

In the 4*d* transition metal series, itinerant magnetism in 3D was studied by Gunnarsson[4] and Janak[5] using the qualitative Stoner criterium for ferromagnetism, $N(\varepsilon_F)J \geqslant 1$, where $N(\varepsilon_F)$ is the density of states (DOS) at the Fermi energy ε_F and J is the exchange integral. They used $J_{4d} \approx 0.65$ eV for all the 4*d* transition metals. The single spin local density of states varies from 0.32 eV^{-1} for Mo to 1.15 eV^{-1} for Pd and therefore the Stoner criterium is never satisfied for any metal of the 4*d* series.[2]

The 5*d* transition metal series has never been considered for itinerant magnetism. The general trend is that the conduction band *d*-wave functions are less localized when moving from the 3*d* to the 4*d* and 5*d* series. This means that the band width increases and a reduction of the density of states at the Fermi level follows. The exchange integral J does not vary very much from the 4*d* to the 5*d* series (see Tables II and III below) and, consequently, itinerant magnetism becomes less and less probable.

Electronic structure calculations using state-of-the-art methods reveal the exciting perspective that more elements might be forced to conserve their atomic magnetism, if properly synthesized at the nanometer scale.[1] In 2D, the coordination number is reduced and this factor diminishes the *d*-band width and increases the local density of states (LDOS) at the Fermi level $N(\varepsilon_F)$.[6,7] Furthermore, the exchange integral J might, in general, not be lower in 2D as compared to 3D.[8] For these reasons, itinerant magnetism is not restricted to the elements that exhibit it in 3D.[9–11]

Indeed, in the past few years, several groups presented *ab initio* calculations on the ferromagnetism of 4*d* and 5*d* transition metal monolayers on Ag(001) and Au(001) substrates. For the 4*d* transition metals, monolayer magnetism was predicted for Tc, Ru, and Rh.[2,9,12,13] Within the 5*d* series Os and Ir (Refs. 2,3) were found magnetic. These calculations lead to the consensus[2] that magnetism of Tc and Os monolayers is a subtle problem. But for Ru, Rh, and Ir monolayers a rather large magnetic moment was predicted. In units of Bohr magnetons, the predicted magnetic moments are 1.7 (Ru),[2,14] 1.0 (Rh),[2,13,14] and 0.9 (Ir).[2] The maximum magnetic moment found for a monolayer on Ag(001) and Au(001) is Mn (3*d*), Ru (4*d*) and Ir (5*d*). Notice that it is shifted by one element to the right in the Periodic Table as one moves from one *d* series to the next.

In spite of the state-of-the-art calculated predictions, experiments of Rh adlayers on Ag(001) (Refs. 15,16) and on Au (001) (Refs. 15–17) failed to detect magnetism. For small clusters, nevertheless, the prediction was confirmed by Cox *et al.*[18] who found that small Rh clusters consisting of some tens of atoms show magnetic ordering of the 4*d* atoms. Subsequent experiments have been done for Rh on Ag(001) as well as Rh and Pd on Au (001), but failed to find any evidence for the existence of spontaneous, long-range ferromagnetic order[16,17] or were inconclusive.[15] Disagreement between theory[7–11,19–23] and experiment[24–29] prevails with respect to the magnetic activity of the V(100) surface as well.[30,31]

Various reasons are discussed by Blügel[2] as being the possible source of discrepancy between theory and experiment. Among them he mentions the neglect of interlayer relaxation in the theory, many-body effects beyond the standard local spin density (LSD) approximation, or more com-

TABLE I. The lattice constants and the relative deformation involved in the systems that we are studying are presented in this table. Except for Pd and Pt, the deformation does not exceed 5% by much. The minus sign in Eq. (9) emphasizes that the monolayer suffers a contraction compared to the bulk. The tight-binding parameters can still be scaled meaningfully for deformations up to 10%. So even for Pd and Pt the use of a tight-binding description is meaningful.

Element	Lattice constant [Å]	ϵ_{xx}
Tc	3.81	0.052
Ru	3.81	0.052
Rh	3.80	0.050
Pd	3.89	0.072
Ir	3.84	0.056
Pt	3.92	0.079

plicated spin configurations. Wu and Freeman[14] have studied in detail the influence of interlayer relaxation for Ru and Rh adlayers and found that it has little effect on the magnetic moments. Blügel[2] looked at the $C(2\times2)$ antiferromagnetic order as an example of more complicated spin configurations but found no evidence for magnetism. Also many-body improvements in the calculation would only rise the disagreement with experiment since LSD usually underestimates magnetism. So, the situation points to the poor quality of the deposited films as the source of the controversy between theory and experiment as stated by Pfandzelter, Steierl, and Rau in a recent paper.[1] These authors reported the first observation of 4*d* two-dimensional ferromagnetism in a Ru monolayer grown by epitaxy on a $C(0001)$ substrate.

In this paper we want to report the results of our calculation of the magnetic moment of monolayers of the 4*d* (Tc,Ru,Rh,Pd) and 5*d* (Ir,Pt) transition metal series on a Cu(001) substrate. This substrate has been used in recent experiments with monolayers of Fe and good agreement with the theory was found.[32]

For magnitudes of the relative lattice mismatch less than 0.1 (10% lattice mismatch) coherent epitaxial growth might be possible under suitable conditions. The usual situation is that the monolayer adopts the substrate lattice parameter value[33,34] and, as a consequence, it is, in general, under stress. The lattice constants of Ag (4.09 Å) and of Au (4.08 Å) are bigger than the one of any of the monolayers considered here. The atoms are, therefore, split off as compared to the bulk. For Cu we have the opposite situation (the atoms are brought together) since its lattice constant (3.61 Å) is smaller. Table I (above) contains all the lattice parameters used in this work. In all the calculations that we have performed here, the lattice mismatch is less than 6%. We will come back to this point.

Ab initio calculations such as full potential linearized augmented plane waves (FLAPW) and full potential linear muffin-tin orbitals (FP-LMTO) based on local spin density functional theory were developed to calculate the electronic magnetic structure of transition metals.[35] The computational cost involved in the study of surfaces, interfaces, quantum wells, or superlattices with *ab initio* methods is high. In certain more subtle situations, where a big number of configurations are to be analyzed, the degree of complexity demands for a simple but accurate enough method of calculation that establishes the trends and give quantitative estimates that serve as a guide either to more elaborate *ab initio* calculations or inspires new experimental situations to search for new results. Although obviously less accurate, such methods can be implemented in codes of comparatively very low computational cost.

Tight-binding Hamiltonians have been parametrized to fit the *ab initio* bulk band structure calculation results.[36] These bulk tight-binding parameters are transferable to other atomic environments only if proper account is taken of the perturbation caused by a surface, an interface or any other configuration. Otherwise wild charge transfers take place, usually from the *s-p* to the *d* band,[37] and the calculation becomes meaningless. To avoid this unphysical charge transfer many authors have traditionally required local orbital charge neutrality.[38] Alternative ways of using the tight-binding method, avoiding these wild charge transfers, have been proposed by Fabricius *et al.*,[39] Riedinger *et al.*,[40] and by Dorantes–Dávila *et al.*[41]

In this paper, we want to present results using the known surface Green function matching (SGFM) method to calculate the local density of states (LDOS) for monolayers. The formalism presented here can be readily adapted for adlayers, or monolayers with an extra coverage. We use it here in the form specifically adapted to the use of bulk tight-binding-Hamiltonian parameters as input.[42]

To calculate the magnetic moment, we used both the Stoner method and a Hubbard Hamiltonian. Both lead to the same result for ferromagnetism. Antiferromagnetic configurations were studied with the Hubbard Hamiltonian but will not be discussed in this paper since none of the monolayers studied is antiferromagnetic.

The rest of the paper is organized as follows. In Sec. II, we present the substrate-monolayer Green's function. In Sec. III, we show the paramagnetic band structure calculations results and discuss them. Section IV is devoted to the calculation of the ferromagnetic moment of a monolayer from the minimum of the total energy as a function of the magnetic band splitting. We applied the method to the 4*d* and 5*d* monolayers on Ag(001) and Au(001) and compared our results with the ones calculated previously by other authors.[2,3] This is to check the accuracy of the method. The agreement is very good. Here we also present the new results and discuss them. Section V, contains our conclusions.

II. THE GREEN'S FUNCTION

We will make use of the known surface Green's function matching method[42] to calculate the Green's function for the semi-infinite system (surface) configuration. This formulation can be readily adapted to the substrate-monolayer problem. Since the method has been widely discuss in the literature, we omit here the details.

The SGFM surface Green's function $\mathcal{G}_s$ is given by[43–45]

$$\mathcal{G}_s^{-1}=\Omega I-H_{00}-H_{10}T, \tag{1}$$

where H_{00} and H_{01} are the in-layer (surface) and interlayer interaction Hamiltonians, respectively, in the customary description in terms of principal layers.[46–48] The T matrix is defined as $G_{10}=TG_{00}$. G_{10} is the propagator from the prin-

cipal layer 0 to the first one. $G_{00} \equiv \mathcal{G}_s$ is the propagator within the surface principal layer. I is the unit matrix and Ω is the energy. A quickly converging algorithm[49–51] for the T matrix allows a very effective use of this and other SGFM formulas.

We will use Eq. (1) for the calculation of the local density of states (LDOS) for a Cu(001) free surface. We will compare later on the first under-surface layer LDOS of a Cu(001) surface with the corresponding one (first atomic layer of the substrate) for the different monolayers considered in our work. Their differences show the influence of the monolayer on the substrate LDOS.

The substrate-monolayer Green's function. The SGFM surface Green's function, Eq. (1), has been used to describe substrate-monolayer systems.[52–55] Several adlayers have also been considered.[54,56]

Here we use the following formula for the Green's function of the substrate-monolayer system:

$$\mathcal{G}_{\mathrm{ML}}^{-1}(\Omega,\mathbf{k}) = \mathcal{G}_{S(A)}^{-1}(\Omega,\mathbf{k}) + [\Omega - H_{00(B)}(\mathbf{k})] - \mathcal{I}_A H^X \mathcal{I}_B - \mathcal{I}_B H^X \mathcal{I}_A . \quad (2)$$

In this supersupermatrix form, the expression is very transparent. The supersupermatrix is labeled with the indices describing the two media A and B. The upper diagonal part describes a semi-infinite medium A with a surface [see Eq. (1)]; the lower part a free-standing monolayer of B atoms. Both interact through the supermatrix Hamiltonian $\mathcal{I}_M H^X \mathcal{I}_N$, $(M,N=A,B)$. These matrices $H_{00(B)}$ and $\mathcal{I}_M H^X \mathcal{I}_N$ are readily written in the tight-binding Slater-Koster language.

A very important quantity for our application here is the local density of states (LDOS) projected onto the different atomic planes of physical interest. This is obtained from the density of states for the entire monolayer-substrate system, given by

$$N(\epsilon) = -\frac{1}{\pi}\int \mathrm{Im}[\mathrm{Tr}\mathcal{G}_{\mathrm{ML}}(\Omega,\mathbf{k})]\,\mathbf{dk}. \quad (3)$$

We use the method by Cunningham[57] to perform the numerical integration in the 2D FBZ. This method of integration together with the SGFM method has been used successfully in previous work.[42] We now proceed to show the results of our paramagnetic calculations which constitute the basis for our estimates of the monolayer magnetic moments.

III. THE SUBSTRATE-MONOLAYER LOCAL DENSITY OF STATES

In this section, we will present, first, our results for the semi-infinite free surface Cu(001) system and compare them with the bulk ones. Next, we will show the LDOS for the monolayer (ML)-Cu(001) system for the different $4d$ and $5d$ transition metals that we have considered. These results are presented in Figs. 1, 2, and 4. In all these figures we show, first, the LDOS for the surface or the monolayer, respectively, for the atomic layer under it (S-1), for the next atomic layer (S-2), and for the bulk-projected in the (001) direction (bottom). The three LDOS curves on each part of the figures correspond to the d band (dashed curves), the s-p band (dotted curves), and the total contribution (full line curves). Most of the total contribution comes from the d band in all cases. The Fermi level ϵ_F is at the origin in all the curves.

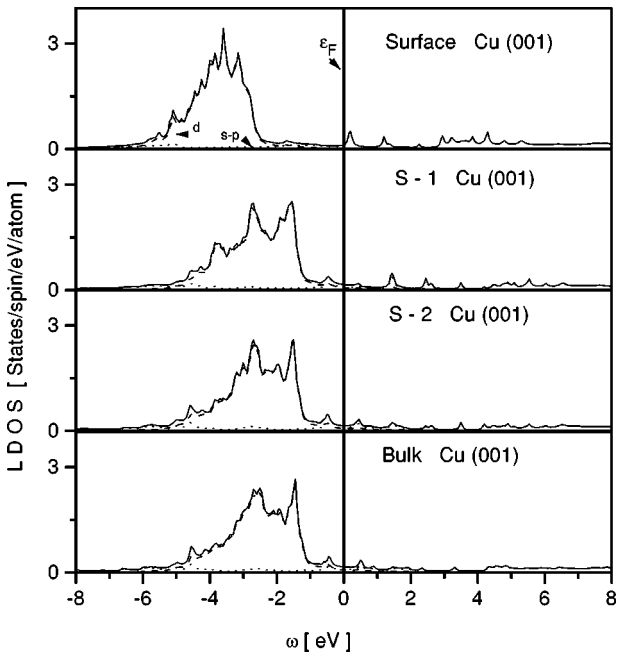

FIG. 1. The Cu(001) surface. We present the LDOS projected at the surface atomic layer (top), at the next atomic layer under the surface (S-1), at the next one (S-2), and at a (001) oriented bulk atomic layer. The three LDOS curves on each part of the figure correspond to the d band (dashed line), the s-p band (dotted curve), and the total contribution (full line curves). Most of the total contribution comes from the d band in all cases. The Fermi level ε_F is at the origin in all the curves.

A. The Cu(001) surface

The formalism described before was used to calculate the LDOS of the Cu(001) surface. We have assumed an ideal, nonreconstructed surface. The surface layer LDOS is on the top of Fig. 1. The d-band width is about 4 eV. The bulk one is roughly 5 eV. The LDOS is more intense at the surface than in the bulk, as a consequence. The atomic layer under the surface (S-1) LDOS looks much more similar to the bulk than the surface LDOS. The d-band width broadens and the LDOS is less intense as compared to the surface one. The (S-2) layer LDOS is almost similar to the bulk. It shows how the LDOS tends rapidly to the bulk one for atomic layers below the surface. From the fourth atomic layer on (not shown) the LDOS is essentially the bulk one. Notice how the top of the d band evolves towards the Fermi level in the LDOS curve from the surface to the bulk. At the surface layer, the top of the d band is about 2 eV below the Fermi energy while in the bulk it is only about 0.5 eV. Also notice that when a monolayer is grown on Cu(001), there is a strong influence of the monolayer on the LDOS curve projected at the topmost Cu-atomic layer (Compare S-1 in Figs. 1, 2, and 4).

B. The monolayer-Cu(001) system

Now we show the density of states for the ML-Cu(001) system. The bulk crystal structure of all the elements that

constitute the monolayers studied here is fcc. Their lattice constants appear in Table I. The lattice constant for bulk metallic fcc Cu is 3.61 Å. The epitaxial growth will impose this lattice constant a_{Cu} to the monolayer atoms a_{ML}. This situation will prevail until a critical thickness is reached and the tension that the difference in the lattice constant imposes to the adlayer atoms, will be sufficient to generate dislocations that free out this built-up energy. From this distance on, the material grows with its own crystal lattice constant.

We use the bulk tight-binding parameters of the transition metals as input to set our Hamiltonians to calculate the ML-Cu(001) system Green's function. Since the monolayer atoms are under tension, we have to modify the parameters correspondingly. First, let us check how big the deformation ϵ_{xx} defined by the equation

$$a_{\mathrm{ML}} = a_{\mathrm{Cu}} = a_X(1-\epsilon_{xx}) \tag{4}$$

is. Here a_X is the lattice constant of the corresponding $4d$ or $5d$ bulk transition metal X with no tension. Table I shows the values for ϵ_{xx} that we obtained.

For the interatomic-plane distance ML-Cu, $a_\perp$, we take one half of the average of the two lattice constants[2,3]

$$2a_\perp = (1/2)(a_{\mathrm{Cu}} + a_X). \tag{5}$$

To scale the tight-binding Slater-Koster parameters (SKP's), $H^m_{\alpha\beta}(r)$, we use[58]

$$H^m_{\alpha\beta}(r) = H^m_{\alpha\beta}(r_0)(r_0/r)^{-n_{\alpha\beta}}, \tag{6}$$

where r_0 and r are the zero-tension and tensioned interatomic distances, respectively. For $n_{\alpha\beta}$ we use the known Harrison rule.[59] The index m stands for the transition metal element SKP. For the interface (i) SKP we use the simple average of the corresponding ones from Cu and the ML, following Shore and Papaconstantopulos,[58] i.e.,

$$H^i_{\alpha\beta}(0) = [H^{\mathrm{Cu}}_{\alpha\beta}(0) + H^{\mathrm{ML}}_{\alpha\beta}(0)]/2, \tag{7}$$

Finally, α and β run over the basis of atomic states considered in the calculation.

1. The 4d monolayers

We will show the spin-dependent LDOS in the next section for some of the monolayers studied. We will consider here, as an example, Ru, which is the $4d$ monolayer with the highest predicted magnetic moment[3] when grown on Ag(001) as well as on Au(001). In contrast we get for Ru on Cu(001) a zero magnetic moment, a very interesting result to look at in some detail. We will comment on it below.

In Fig. 2, we present our results for the paramagnetic LDOS projected, successively, on the Ru monolayer, the first and second Cu(001) atomic layers and, in the figure at the bottom, the Cu bulk LDOS projected onto the (001) direction. The three LDOS curves on each part of the figure are the *d* band, the *s*-*p* band, and the total contribution, respectively, as we wrote above. Most of the total contribution comes from the *d* band in each case. The Fermi level ϵ_F is at the origin in all the curves.

In the monolayer projected LDOS (first curve), we can observe that the *d* band dominates strongly around the Fermi energy. This band is responsible for the magnetic properties

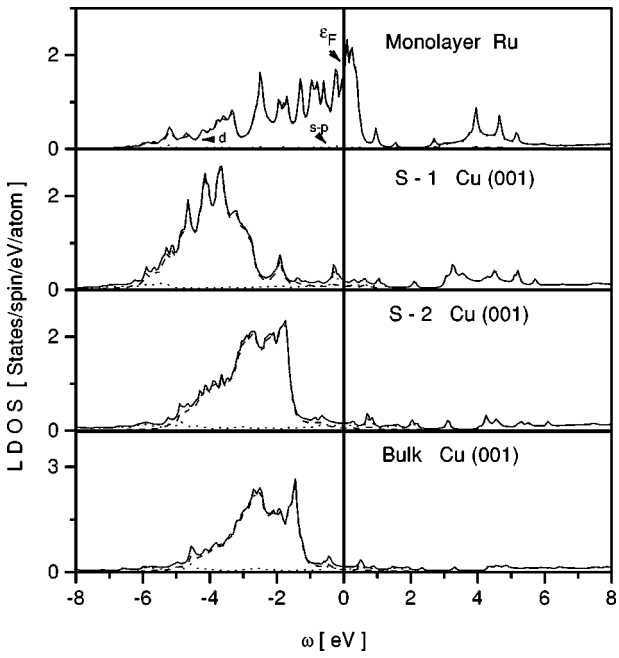

FIG. 2. The Ru-Cu(001) monolayer. The top part of the curve shows the LDOS projected on the Ru-atomic layer. For the rest of the curves see caption of Fig. 1.

of the monolayer. Its width is about 7 eV. The highest peak of *d*-band states occurs just above the Fermi energy. There are much more electrons at the Fermi energy on this monolayer than on the next Cu(001) atomic plane as we can see from the second curve in the same figure. This LDOS shows a *d*-band width of only about 5 eV, which is mainly located well below the Fermi energy. A minor *s*-*p* band contribution extends over all Ru conduction band which is about 20 eV wide.

The third curve (S-2) is the second Cu-atomic layer. Its LDOS resembles a bit more the bulk-projected one which is the curve at the bottom. The *d* band on the second atomic plane (S-2) LDOS is far away from the Fermi level as well. The width of the *d* band is slightly smaller (about 4 eV) and the structure that develops is more bulklike than the one of the previous atomic layer. From the fourth Cu atomic layer on (not shown) we get the bulk projected LDOS. It is very interesting to compare the behavior of a Ru monolayer on a Cu(001) substrate with its behavior on a Ag(001) or Au(001). In Fig. 3, we present the *d*-band LDOS projected onto the Ru monolayer when on a Ag(001) substrate (dotted line) and on a Cu(001) one (full line). We recall that the Ag(001) substrate expands the Ru interatomic distance as compared to the bulk, while Cu(001) contracts it. The expansion of the lattice shrinks the *d* band substantially and as a consequence the *d*-band LDOS intensity increases (see dotted line in Fig. 3) otherwise the opposite effect takes place (full line in Fig. 3). The *d*-band LDOS at the Fermi level $N_d(\varepsilon_F)$ is 3.12 eV^{-1} on Ag while it is only 1.45 eV^{-1} on Cu, i.e., half the value. It is expected, therefore, that the magnetic moment of the Ru monolayer will be quite smaller on Cu(001) than on Ag(001) or Au(001). This fact is general for all the monolayers studied here because they all have lattice constants that lie in between the Cu (3.61 Å) and the Ag (4.09 Å) or Au (4.08 Å) one. But the degree of sensitivity

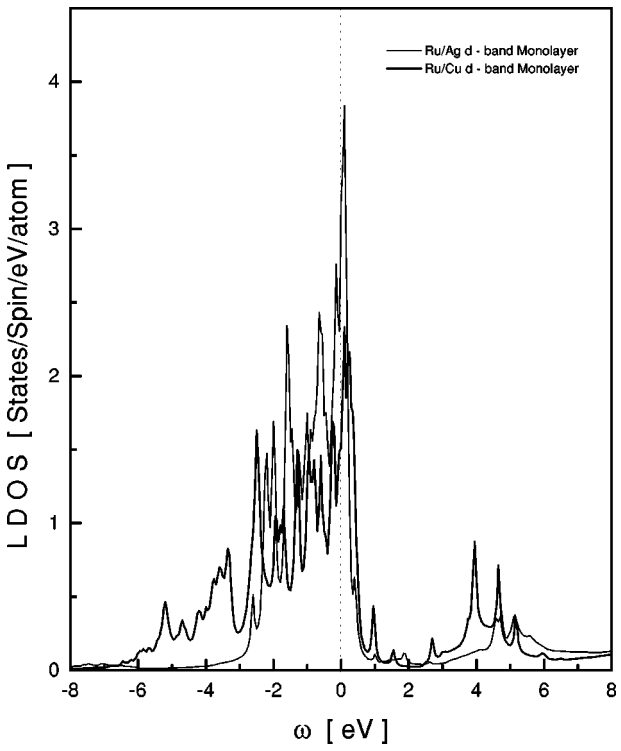

FIG. 3. The substrate has a very strong influence on the resulting monolayer density of states. In this figure we show the *d*-band LDOS projected on a Ru-atomic layer which lies on a Ag(001) substrate (dashed line) and on a Cu(001) (full line). The difference in the width of the *d* band and its density of states at the Fermi level is very important. The main factor determining this difference is the distance between the Ru atoms imposed by the substrate. See text.

of the magnetic moment to tension varies from one monolayer to another as we shall see in the rest of the paper.

2. The 5d monolayers

A monolayer of Ir on Cu(001) is presented in Fig. 4 as an example of our calculation for the $5d$ series. Although with noticeable differences, the LDOS curves have the same gross characteristics and trends as for the $4d$ series. Again the main weight of the *d*-band LDOS for the monolayer atomic layer is around the Fermi level. A high peak is here at the Fermi energy rather than above it as for Ru. This could be an important difference for the magnetic properties of the monolayer. The LDOS varies very quickly around ε_F, a common characteristic with Ru. The first Cu(001) atomic layer below the monolayer appears with similar characteristics as for Ru although in this case the LDOS is more intense. The (S-1) *d*-band LDOS remains quite below the Fermi level. The third curve (S-2) in Fig. 4, represents the second Cu-atomic layer. Its LDOS is different from the one above and resembles the bulk projected LDOS that appears as the bottom curve. The presence of a different monolayer on the top influences strongly at least the first two atomic layers below it. For example, the LDOS projected onto the first Cu-atomic-substrate layer under a monolayer of Ru differs all along the energy interval considered from the corresponding Cu-LDOS under a monolayer of Ir atoms. We need to project the LDOS onto at least the fourth atomic layer (not shown) to get essentially the bulk one, according to our results. The bulk LDOS projected onto the (001) direction is obtained independently in each calculation. It coincides exactly in all these. This constitutes a way of self-consistent checking.

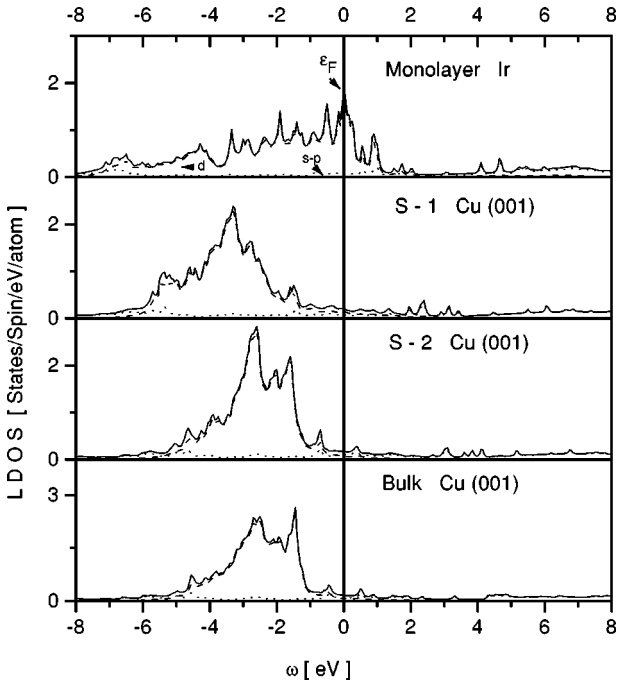

FIG. 4. The Ir-Cu(001) monolayer. See caption of Fig. 2.

IV. THE MAGNETIC MOMENT

For the ferromagnetic case, a Hubbard tight-binding Hamiltonian and the Stoner model gave us, essentially, the same results. We have studied antiferromagnetic configurations with a Hubbard Hamiltonian. None of the monolayers discussed here turned out to be antiferromagnetic. We describe in the following our calculation with the Stoner model[60] which has been widely used, for example, in finding the ferromagnetic phases of fcc iron.[61] In the Stoner model, the magnetization, in units of a Bohr magneton μ_B is given by[62]

$$\mu(\Delta)=\int_{-\infty}^{\varepsilon_F}[n_d^+(\varepsilon)-n_d^-(\varepsilon)]d\varepsilon=\int_{\varepsilon_F-\Delta/2}^{\varepsilon_F+\Delta/2}[n_d(\varepsilon)]d\varepsilon, \tag{8}$$

where Δ is the magnetic band splitting. We check that the total *d*-band electronic occupation n_d is conserved at each step:

$$n_d=\int_{-\infty}^{\varepsilon_F}[n_d^+(\varepsilon)+n_d^-(\varepsilon)]d\varepsilon, \tag{9}$$

$n_d^+(\varepsilon)$ and $n_d^-(\varepsilon)$ indicate $n_d(\varepsilon+\Delta/2)$ and $n_d(\varepsilon-\Delta/2)$, respectively. $n_d(\varepsilon)$ is the paramagnetic density of states per spin in the *d* band.

The total energy E of the magnetic system is given by

$$E(\Delta)=\int_{-\infty}^{\varepsilon_F}[n^+(\varepsilon)+n^-(\varepsilon)]\varepsilon d\varepsilon+\frac{J\mu^2}{4}, \tag{10}$$

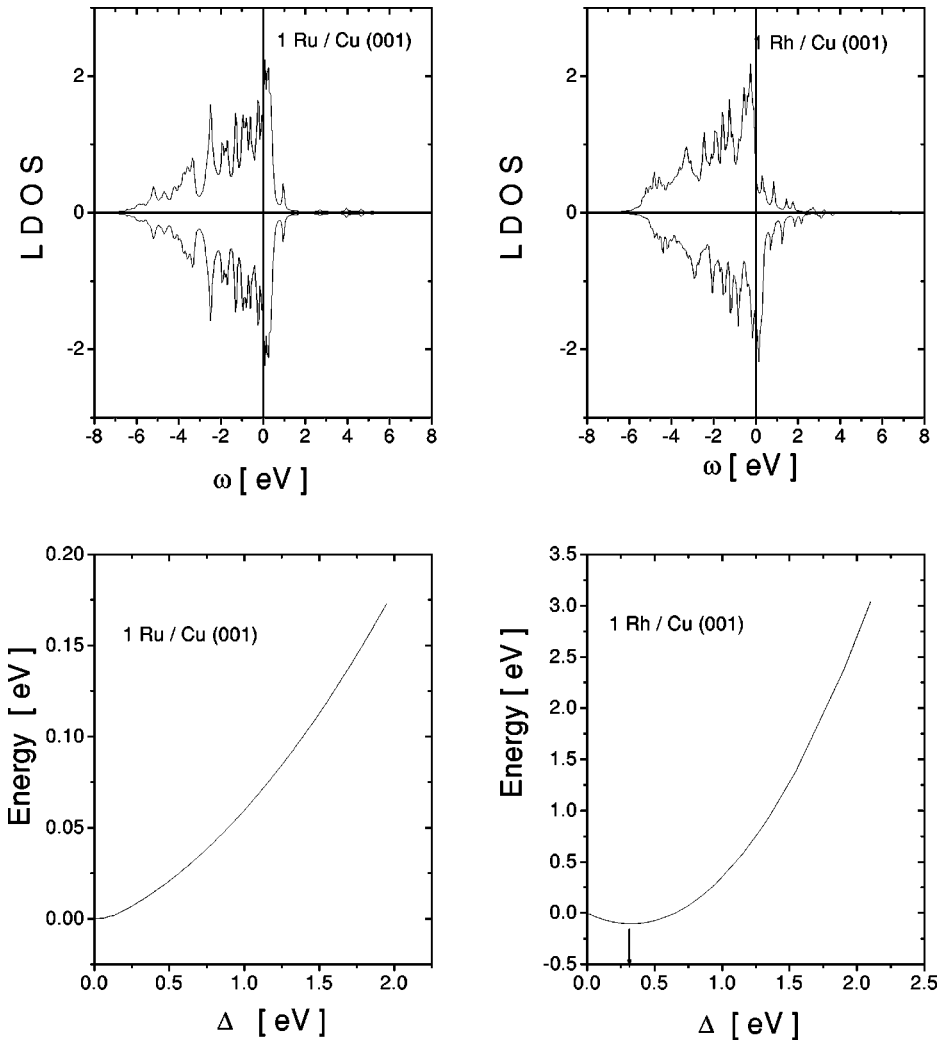

FIG. 5. Our results for the ML-Cu(001) system (ML=Ru, left and ML=Rh, right). At the top of the figure, we present the spin discriminated LDOS projected onto the monolayer atomic layer. At the bottom part, the total energy as a function of the magnetic band splitting $E(\Delta)$ is shown. We get Ru nonmagnetic (an interesting result to look at in more detail, see text) and Rh magnetic. See text for more details.

where $n^{\pm}(\varepsilon)=n_s(\varepsilon)+n_p(\varepsilon)+n_d^{\pm}(\varepsilon)$, with $n_s(\varepsilon)$ and $n_p(\varepsilon)$ the contribution to the LDOS from the *s* and *p* states, respectively.

In these equations the only independent variable is Δ. *J* is the Stoner parameter. Extensive calculations of this parameter were done by Sigalas and Papaconstantopulos[63] as well as by Janak.[5] The magnetic moment assigned in each case, corresponds to a minimum of the $E(\Delta)$ curve. At the minimum, the magnetic moment μ is related to the Stoner parameter through the relation $\mu=\Delta/J$. We have checked that our method reproduces well the predicted values for the same monolayers on Ag(001) and Au(001) substrates[2,3] using for *J* the values given in Ref. 63. The agreement is very good.

A. The magnetic moments for the 4*d* monolayers

Our results for the 4*d* series ML-Cu(001) systems (ML =Tc, Ru, Rh, and Pd) are presented here and shown in Fig. 5 for Ru and Rh. The top part of the figure shows the spin-dependent LDOS projected onto the corresponding monolayer atomic layer. The bottom series of curves show the total energy $E(\Delta)$ as a function of the magnetic band splitting Δ. For Tc and Pd, we find a single minimum at $\Delta=0$. Those monolayers are not ferromagnetic according to our calculations. This is an expected result since on Cu(001) the magnetic moment should be lower than on Ag(001) or Au(001). Let us now consider the Rh monolayer. The result is shown in the right half of Fig. 5. In this case we do find a minimum for $\Delta\neq 0$. Notice that the minimum is below the paramagnetic value of the total energy $E(\Delta)$, which means that the energy of the paramagnetic state is higher than the magnetic one, i.e., the magnetic phase is more stable and is therefore the ground state. To translate the value of Δ at the minimum of the total energy $E(\Delta)$ into a magnetic moment value, we have used the *J* values given by Sigalas and Papaconstantopoulos.[63] These values allow us to reproduce the results of Refs. 2,3 as we already pointed out. Using the *J* values given in Ref. 5 (which are different) the magnitudes of the magnetic moment change accordingly. For a Rh monolayer on Cu(001) we get at the minimum of $E(\Delta)$, a

TABLE II. We summarize our results in this table. The substrate for all the monolayers here considered is Cu(001). The first column refers to the monolayer. In the second we quote our value for the paramagnetic LDOS per spin at the Fermi level, projected onto the monolayer atomic layer. In the third column, the magnetic *d*-band splitting at the minimum appears. Next, we compare the value of the magnetic moment μ in three different substrates. They are given in units of Bohr magnetons. μ_Y (Y=Cu, Ag, Au) means the magnetic moment of the corresponding monolayer on a Y substrate grown in the (001) direction. The data for Ag and Au are taken from the Refs. 2,3. We have reproduced them with very good agreement.

Element	$N(\varepsilon_F)$ [eV^{-1}]	Δ [eV]	μ_{Cu}	μ_{Ag}	μ_{Au}	J
Tc	1.20	0.0	0.0	0.0	0.0	0.552
Ru	1.45	0.0	0.0	1.73	1.73	0.560
Rh	1.78	0.325	0.524	1.0	1.1	0.617
Pd	0.54	0.00	0.00	0.0	0.0	0.625

magnetic band splitting $\Delta=0.325$ eV. We use a Stoner parameter $J=0.617$ eV (Ref. 63) and get a magnetic moment $\mu=0.524\mu_B$. For Rh on Au(001) we get 1.10 and on Ag(001) 1.0 (See Table II).

In Table II, we summarize some data concerning our results. The first column refers to the $4d$ element, their atomic number grows from top to bottom. The second column refers to the LDOS at ϵ_F projected onto the monolayer atomic layer. Notice that it goes through a maximum. The two extreme monolayers in Table II (Tc, Pd) are nonmagnetic. The LDOS at ϵ_F for Pd is only about one third of the Rh one (the maximum). The LDOS for Tc is comparatively high (see Table II). Nevertheless, we do get a zero magnetic moment, as it is to be expected. The rest of the columns are explained in the Table II caption.

The Ru-Cu(001) system. Let us look now at the very interesting Ru-Cu(001) case. Our result is shown in the left part of Fig. 5; we get a zero magnetic moment. This result is, in principle, surprising since a Ru monolayer gives on Ag(001) and Au(001) the highest magnetic moment within the whole $4d$ and $5d$ series (See Tables II and III).

The main factors that intervene in this result are the interatomic distance imposed by the substrate, the ML-substrate interatomic distance that should, in principle, vary from one system to the other, the Ru *d*-wave functions of the electrons at the Fermi level, and the degree of hybridization of the ML substrate wave functions around the Fermi energy. These factors are actually inter-related. We will try to analyze them by isolating them artificially.

The LDOS of a particular monolayer can differ by much when on different substrates (see Fig. 3). Let us look first at the influence of the interatomic distance in more detail. In Fig. 6 we show this result. We have artificially enhanced the

TABLE III. The data for the $5d$ series. The entries are the same as in Table II.

Element	$N(\varepsilon_F)$ [eV^{-1}]	Δ [eV]	μ_{Cu}	μ_{Ag}	μ_{Au}	J
Ir	2.048	0.099	0.173	0.91	0.94	0.574
Pt	1.298	0.0	0.0	0.0	0.0	0.590

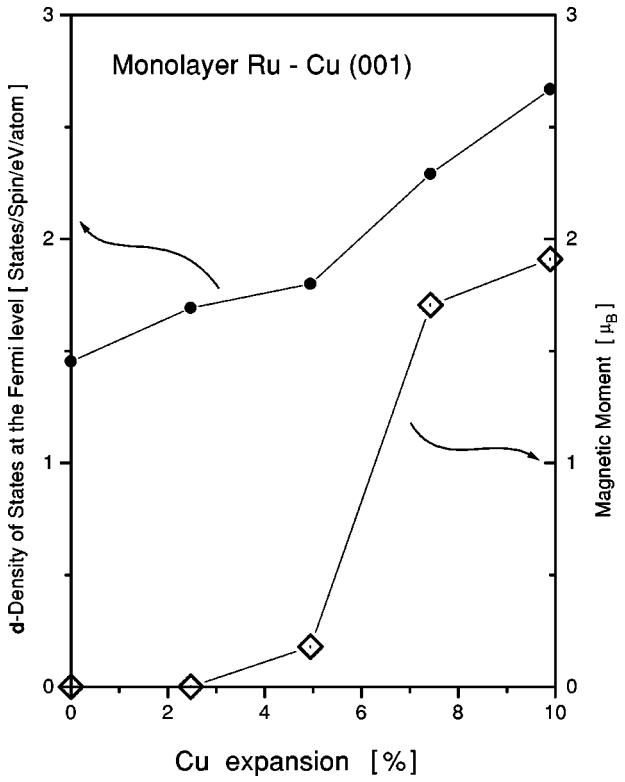

FIG. 6. The magnetic activity of a Ru-Cu(001) system is considered as a function of the percentage of expansion of the Cu lattice constant. The expansion gets up to the corresponding value for Ag. A magnetic moment different from zero is set from about 2.5% expansion on. To the Ru lattice constant value there corresponds a magnetic moment of $0.179\mu_B$. The Ru(001) surface is nevertheless, nonmagnetic. Therefore, the distance between the atoms of the monolayer imposed by the substrate, although perhaps an important factor, is not the only parameter to be considered. See text for details.

Cu(001) substrate lattice constant from the Cu value (3.61 Å) to the Ag one (4.09 Å) and calculated the change in the *d*-band LDOS at the Fermi level and the corresponding magnetic moment. When we reach the Ag lattice constant value, we get $\mu=1.9\mu_B$ which is slightly higher than $1.73\mu_B$, calculated for Ru-Ag(001). From a 2.5% expansion of the Cu lattice constant, Ru-Cu(001) becomes magnetic. The *d*-band LDOS at E_f enhances steadily with the Cu lattice expansion. Stating this the other way around, we can say that as the ML atoms approach each other and the *d* LDOS at E_f shrinks. Also the *d* band broadens according to our results. So it looks to be an important factor for the Ru-ML to lose on Cu(001) the magnetic moment it has on Ag(001), that the Ru atoms are closer together. One may speculate that the stronger interaction of the *d* electrons plays a crucial role, but this point has to be looked at in more detail before arising to a sharp conclusion.

Let us try to analyze this point further. Let us ask the following question: Is the interatomic distance the determining factor for magnetism to appear in a Ru monolayer? If it is so, a Ru(001) surface should be magnetic with a magnetic moment of $0.5\mu_B$ since the Ru bulk lattice constant (3.81 Å) corresponds to a 5.5% expansion in Fig. 6. Nevertheless, we find an ideal Ru(001) surface nonmagnetic. So the answer is

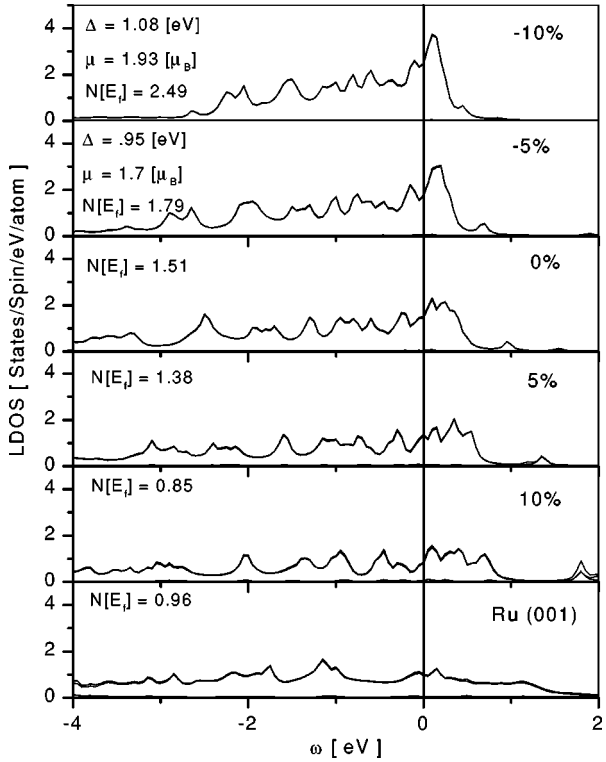

FIG. 7. We present here the effect of expansion and contraction of the monolayer-substrate distance on the magnetic activity of the Ru-Cu(001) system. As a general trend expansion [which points towards the Ru(001) surface situation, in this case] dimishes the LDOS and, as a consequence, the magnetic activity. On the contrary, contraction turns it on. In this figure we quote, for the magnetic active cases, the magnetic band splitting Δ (in eV) and the magnetic moment μ (in Bohr magnetons). For all cases, we quote the LDOS at the Fermi level. Here 0% means that the interlayer distance is given as the algebraic mean of the bulk Ru and Cu lattice constants. We show our results for $\pm 5\%$, $\pm 10\%$, and the Ru(001) surface which is not magnetic. Notice that the result seems to indicate that uniaxial (normal) pressure might turn a Ru-Cu(001) system magnetic. See text.

no. Then let us look at the influence of the ML-substrate interaction by changing this distance.

Following this idea, we have considered the effect of up to a 10% expansion and contraction. More explicitly, we have enhanced the ML-substrate normal distance by up to 10% (expansion) and have diminished it also by up to 10% (contraction). Our results are presented in Fig. 7. As a general trend, expansion shrinks the LDOS at the Fermi energy and leads to no magnetic moment. The trend is opposite for contraction. Magnetism does appear at about -2%. At -5% (contraction) the LDOS at the Fermi energy is enhanced up to 1.8 $\mathrm{eV}^{-1}\,\mathrm{atom}^{-1}$ with a resulting magnetic moment of $1.70\mu_B$. The trend follows up with further contraction as it is shown in Fig. 7. It is interesting to speculate that this result seems to suggest that a Ru monolayer on Cu(001) could become magnetic under uniaxial (normal to the surface) pressure. This effect, if confirmed experimentally, could possibly have a certain (as a sensor) technological interest, as well. So, in conclusion it is not possible to say from this analysis whether the most important factor for magnetism to appear is the Ru-Ru interaction or the Ru-Cu one. It is not even clear that a general material-independent conclusion is possible. Notice that these conclusions are independent of the fact that an *ab initio* calculation could give different numbers with obviously higher precision. The general picture and the trends would not essentially vary the relative importance of the factors leading to a monolayer magnetic moment as we have analyzed it here.

B. The magnetic moment for the 5*d* monolayers

Our results for the 5*d* series ML-Cu(001) systems (ML = Ir and Pt) are shown in Fig. 8. The top part of the figure shows the spin-dependent LDOS projected onto the corresponding monolayer. The bottom curves show the total energy $E(\Delta)$ as a function of the magnetic band splitting Δ. For Pt, we find a single minimum at $\Delta=0$. This monolayer should not be ferromagnetic according to our calculations. For Ir, the situation is different. We do find a minimum below the paramagnetic value and the Ir monolayer should be ferromagnetic. We have used the Stoner parameter $J=0.574$ eV for Ir and $J=0.590$ eV for Pt from Ref. 63. We reproduce the results of Refs. 2,3 with these values. In Ref. 5 different J values are given. The magnetic moment would change accordingly.

Table III summarizes the data for the 5*d* transition metals considered. The conventions are the same as in Table II. The data for the magnetic moment on a Ag(001) and a Au(001) substrate are taken from the Refs. 2,3. Our calculated values agree very well with these results.

V. CONCLUSIONS

The goal of this paper was twofold. First, to show that the surface Green's function matching method (SGFM) can be successfully used to calculate the local density of states for a monolayer on a particular substrate. This method has been developed specifically to calculate the Green's function of discrete media with a surface or interface in different configurations. The input for the method are the bulk Slater-Koster tight-binding parameters which are accessible for a wide series of materials. On these bases using either the Stoner model or a Hubbard tight-binding Hamiltonian, for ferromagnetism, we can predict whether or not a monolayer will be ferromagnetic. We have reproduced the known results of Blügel for several 4*d* and 5*d* monolayers on Ag(001) and Au(001) substrates and found very good agreement.

Second, we have studied the ferromagnetic activity of 4*d* and 5*d* transition metal monolayers on a Cu(001) substrate and calculated the expected magnetic moment. The method has been also implemented for antiferromagnetic situations by using a Hubbard tight-binding Hamiltonian. A Hubbard Hamiltonian can be used for ferromagnetic situations as well. It gave us the same results as the Stoner model for the cases considered here.

Summarizing, we have calculated the paramagnetic local projected density of states (LDOS) for monolayers of Tc, Ru, Rh, Pd among the 4*d* series and Ir and Pt among the 5*d* series on a Cu(001) substrate. The magnetic moment is calculated from the minimum of the total energy $E(\Delta)$ as a function of the magnetic band splitting Δ. We use the Stoner

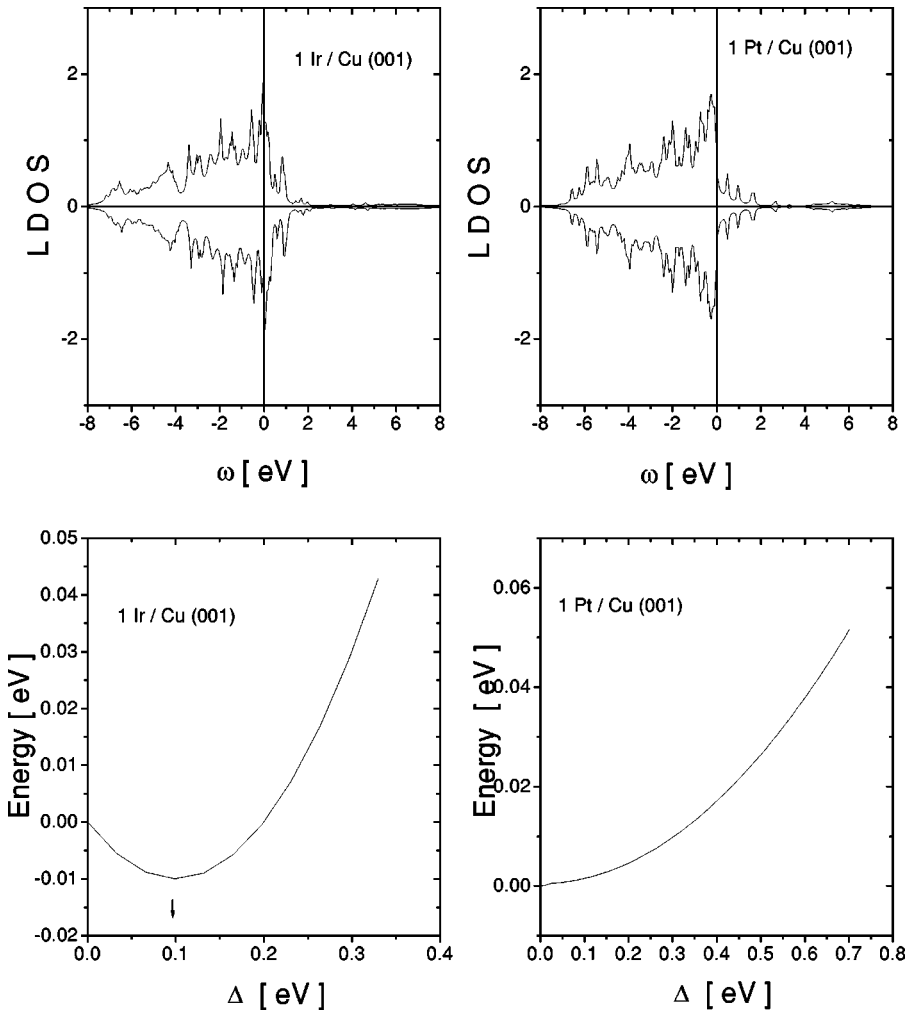

FIG. 8. Our results for the $5d$ series monolayers are presented. The conventions are the same as in Fig. 6. We find the Ir-Cu(001) system (left side) magnetic. Also Pt-Cu(001) is shown (right). We find it nonmagnetic.

parameter J given in Ref. 63 to calculate the magnetic moment. We find Rh and Ir to be ferromagnetic with magnetic moments equal to 0.525 and $0.173\mu_B$, respectively. The rest of the monolayers are nonmagnetic according to our calculations.

The case of Ru is interesting since it is the monolayer with the highest magnetic moment on Ag(001) and Au(001) among the $4d$ and $5d$ transition metals. We have found that the small lattice constant of Cu (3.61 Å) is the most important factor responsible for the loss of the magnetic activity. When this lattice constant is artificially enhanced up to the Ag (4.09 Å) value, we recover a magnetic moment that increases with the interatomic distance and reaches $\mu = 1.9\mu_B$ at the Ag value. The Ru bulk lattice constant lies in between the Cu and the Ag one (see Table I). If the interatomic distance in the monolayer were the only important factor, the Ru(001) surface would be magnetic with a small magnetic moment (see Fig. 6). We found it nonmagnetic. This leads us to conclude that the monolayer-substrate interaction can play a non-negligible role in certain systems for magnetism to occur. When the monolayer-substrate distance is varied, expansion does not lead to a magnetic behavior but contraction does (see Fig. 7). The system appears to behave as if normal pressure would render a monolayer of Ru atoms on a Cu(001) substrate magnetic, an effect that might turn out to be of technological interest if it is confirmed experimentally.

This paper was a study of these monolayers on a Cu(001) substrate and an application of the SGFM method to adlayer magnetism. Our method is simple, well defined at each step, needs no fitting parameters, and is not computationally demanding. It can be applied to a variety of systems (monolayers, surfaces, quantum wells, interfaces, superlattices, etc.) and to different situations (such as relaxation, for example) to study trends and to find meaningful results and predictions that constitute a complementary tool to guide more elaborated *ab initio* calculations, or to limit the experimental conditions under which 2D magnetism can be observed.

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