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Magnetism in Rh monolayers

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We have studied the magnetic behavior of a $4d$ transition metal Rh monolayer (ML) on different substrates (Ag, Au, Cu) and orientations. We find the Rh monolayer to be magnetic in the (001) orientation on all the substrates, in the (111) direction for Au and Ag alone ($\mu \approx 0.6\ \mu_B$) for both, in the (110) one we do not find any magnetic activity. We analyze the parameters that have been suggested as general criteria for magnetism in the monolayer-substrate system. In particular, we study several possible geometric parameters and the bandwidth as possible clues to predict the magnetic behavior. A detailed analysis shows that the physics underlying the switching on of magnetism in a Rh-ML on noble metal substrates, is determined by an intraband transfer of d-electronic states (as compared to the Rh surface), from lower and higher energies to the Fermi level. This effect enhances the density of states at that energy, in an important way and shrinks the d-bandwidth. It seems to depend strongly on specificities of the interaction between the ML and the substrate that are hardly taken into account by a single parameter, in a general way. We impose charge neutrality in our calculations but deal explicitly with the changes to be expected if charge transfer would actually occur.

Keywords: Magnetic properties; monolayers; thin films; density of states.

Presentamos el estudio de la actividad magnética de una monocapa de Rh sobre sustratos de (Ag, Au, Cu), en las tres direcciones principales (001), (111) y (110). Comparamos nuestros resultados con trabajos anteriores. Encontramos actividad magnética de la monocapa de Rh sobre Au(111) y Ag(111) ($\mu \approx 0.6\ \mu_B$) en ambos. Encontramos también que sobre Cu, sólo en la dirección (001), la monocapa tiene alguna actividad magnética. Este hecho lo inclina a uno a pensar que la constante de red del sustrato, es la que gobierna la aparición del momento magnético. Sin embargo, sucede que en la dirección (110) no aparece momento magnético ni sobre Ag ni sobre Au. Por esta razón intentamos buscar otro parámetro geométrico como criterio fundamental para la aparición del magnetismo. Ensayamos varios y sólo encontramos correlación con el volumen por átomo en la región de la interface monocapa-sustrato, Ω_0. Este parámetro, sin embargo, no parece seguir la tendencia que uno esperaría intuitivamente y, por lo tanto, no debe ser de validez general. Esto, efectivamente, fue lo que comprobamos, estudiando otro tipo de sustratos. Concluimos que la actividad magnética depende de detalles específicos que no pueden caracterizarse sólo por un parámetro geométrico. En nuestros cálculos usamos neutralidad de carga, pero tratamos el problema de lo que ocurriría si hay transferencia de carga.

Descriptores: Propiedades magnéticas; monocapas; películas delgadas; densidad de estados.

PACS: 75.10-b; 75.30-m; 75.70.Ak; 73.20.At

1. Introduction

One of the most interesting results in the field of magnetism of low dimensional systems is the discovery that magnetic entities can be built out of materials such as transition metals from the end of $4d$ and $5d$ series that are not magnetic in the bulk state [1]. For these metals, magnetism with a sizeable magnetic moment per atom has been predicted by several theoretical studies. For the $4d$ transition metals, monolayer magnetism has been predicted for Tc, Ru, and Rh [2–7]. Within the $5d$ series Os and Ir [2,3] were found magnetic. Magnetic behavior has also been predicted, either for isolated clusters [8–12], for deposited small clusters on silver [13], and in epitaxial ultrathin layers deposited on Rh(001) and Pd(001) surfaces [14,15]. These calculations either use *ab initio* approaches based on the local spin density approximation (LSDA) or other methods of electronic structure calculations as, for example, the self-consistent tight-binding methods. Molecular beam experiments on free clusters by Cox, Louderbaek, and Bloomfield [16], showed that small Rh clusters consisting of a few tens of atoms present magnetic ordering of the $4d$ electrons. From weak localization and anomalous Hall effect measurements [17], it is anticipated that very small Rh clusters (atom pairs) on Au, corresponding to a coverage of only a few percents of a monolayer, might bear a finite magnetic moment (about 0.1 μ_B). Recently, magnetic dichroism has been measured at the Rh(100) surface [18], while Rh clusters on graphite have been found nonmagnetic [19]. R. Pfandzelter, G. Steierl, and C. Rau [20] using Auger electron spectroscopy, found that a Ru monolayer film grown on a C(0001) substrate is ferromagnetic below a surface Curie temperature $T_c^{sce} \approx 250\ K$.

A good candidate to investigate low dimension magnetic effects is the $4d$ element Rhodium. Rh is particularly interesting because, although it is paramagnetic in the bulk, it exhibits ferromagnetic properties when prepared in low dimensional forms. In fact, bulk Rh is already very close to satisfying the Stoner criterion of ferromagnetism [14, 21], and, because of the lower number of nearest-neighbor atoms, the d-derived band width in low dimensional Rh systems is considerably narrower than in the bulk. The increased density of states at the surface or in small clusters, therefore, is likely to stabilize the magnetic state in these low dimensional structures. Indeed, experimental results [16] confirm that free standing clusters of Rh formed by 9-36 atoms exhibit a magnetic moment reaching a maximum value of 1.1 μ_B. These clusters, which were at equilibrium and at temperatures around 100 K, are superparamagnetic, that is, their magnetic moment orients itself freely along the applied magnetic field and completely ignores the atomic (crystalline) arrangement of the building atoms. These experimental observations have found correspondence in many theoretical approaches [8]. According to $abinitio$ [2, 4–7] and semiempirical calculations [22] pseudomorphically grown Rh monolayers on Ag(001) could be ferromagnetically ordered with a magnetic moment of 1.0 μ_B. By using a scalar-relativistic norm-conserving pseudopotential and a Gaussian-orbital expansion, Zhu, Bylander, and Kleinman [5] 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.*, [6] predicted a ferromagnetic ground state for Rh on Ag(001). The ferromagnetism for Rh on Ag(001) has been confirmed by Wu and Freeman [7] who found a magnetic moment of 0.96 μ_B using a full-potential linearized augmented-plane-wave method (FLAPW). General trends for magnetism of transition metal overlayers on noble metal (001) substrates were established and discussed by Blügel [2] who also using the FLAPW method found $\mu = 1.02$ μ_B for a Rh/Ag(001) monolayer and $\mu = 1.1$ μ_B for a Rh/Au(001) monolayer. Redinger, Blügel, and Podloucky [3] discussed the dependence of magnetism of monolayers on substrate orientation and the local atomic coordination. They reported for a Rh monolayer on Ag(111) a reduction on the magnetic moment (0.67 Bohr magnetons) about 70% of its value as compared with the corresponding to the (001) orientated Ag substrate. They argue that the increase of the in plane hybridization with the increase of the coordination number in the monolayer film leads to smaller exchange splitting and therefore a smaller magnetic moment is obtained. E. García, V. González-Robles, and R. Baquero [23] studied the ferromagnetic activity of $4d$ and $5d$ transition metal monolayers on a Cu(001) substrate. Using the surface Green's function matching (SGFM) method together with tight-binding Hamiltonians and the Stoner model, they reported a magnetic moment of 0.52 μ_B for a Rh monolayer on this substrate. Despite many efforts, ferromagnetic order was never observed experimentally on a Rh monolayer [17, 24, 25]. While the former experimental results using the surface magneto-optic Kerr effect (SMOKE) [24, 25] did not report on any ferromagnetism for the Rh/Ag(001) monolayer, a somewhat different approach was proposed later. Li *et al.*, [26] found a splitting of the $4s$ level in their photoemission experiment (UPS). Although this splitting can have many nonmagnetic origins, they favored the explanation that the Rh atoms possess a magnetic moment. The discrepancy between theory and experiment might likely be related to the experimental difficulties of growing the ideal monolayer configuration. The growth process depends dramatically on the experimental conditions, such as the substrate temperature and cleanliness, the deposition rate, etc. In addition, most transition metal monolayer systems on noble metal substrates are not in thermodynamic equilibrium and diffusion of transition metal adatoms into the substrate represents a serious problem [27]. Schmitz *et al.*, [28] propose that the equilibrium structure of Rh on Ag(001) is actually that of a sandwich with a Ag monolayer atop. To overcome some of the experimental problems, graphite has been suggested as an alternative substrate since transition metal atoms diffuse much less into it. The graphite (0001) surface is furthermore known to be very flat and, as in the case of noble metals, the overlap with the transition metal $d - band$ is expected to be small. Moreover, spin-polarized secondary-electron emission spectroscopy [20] applied to a monolayer of Ru on highly oriented pyrolytic graphite (HOPG) seems to confirm the presence of bidimensional ferromagnetism in this system. This evidence of magnetism in a $4d$ monolayer is very encouraging and prompts verification with other experimental techniques and other $4d$ materials like Rh. More recently, Chado, Scheurer, and Bucher [29] investigated the growth and magnetism of Rh films in the thickness range between 0 and 6 monolayers on Au(111) over a wide range of coverages and deposition temperatures by means of variable temperature UHV-STM, Auger spectroscopy, and $in\ situ$ Kerr effect measurements. Contrary to theoretical predictions, no ferromagnetism was detected irrespective of the film thickness and growth conditions. They suggest that the Rh-Au intermixing in the first stage of growth is at the origin of the lack of the ferromagnetism of Rh films.

In this paper we investigate the electronic structure and magnetic moment of a Rh monolayer grown on a (001), (110), and (111) oriented Ag, Au, and Cu substrates. Copper substrate has been used in recent experiments with monolayers of Fe and good agreement with the theory was found [30]. The lattice mismatch between bulk Rh and Ag and Au substrates is smaller than 7% and it should be possible to grow these systems. The lattice constant for the copper substrate is smaller than the corresponding for bulk Rh and the lattice mismatch is about 6%. Since the monolayer usually adopts the substrate lattice parameter value, the Rh atoms are split off on the Ag and Au substrate and are brought together on the Cu substrate as compared to the Rh bulk.

In this work we use the known surface Green's function matching (SGFM) method [31] to calculate the local density of states (LDOS) for the monolayer. We use this method in the form specifically adapted to the use of bulk tight-binding Hamiltonians as input. To calculate the magnetic moment, we use the Stoner method [32]. SGFM has been used extensively for this kind of calculations [33–40]. We omit here the details of the calculation and rather remit the interested reader to Ref. 23. The rest of the paper is organized as follows. In Sec. 2, we present our results. We reproduce the other existing calculations to show that our method is accurate enough for our purposes here. Finally, we devote Sec. 3, to our conclusions.

2. Results

We have considered three different fcc substrates (Ag, Au, Cu) on top of which a monolayer of the $4d$-transition metal Rh, is grown. We consider the substrate to be grown in three possible orientations, *i.e*., (001), (110) and (111). In the (001) orientation, a Rh monolayer grown on silver and gold has been considered previously by Blügel, [2] and by García *et al*. [23], on a Cu substrate. The Rh/Ag(111) system has been considered by Redinger *et al.* [3] There is no work on Au and on Cu for that orientation as there is no work at all in the (110) direction, known to us. For purposes of comparing, we have studied the Rh surfaces as well. We will refer to it, sometimes, as a Rh monolayer on a Rh substrate, in the rest of this paper.

2.1. The density of states

First, we have calculated the total paramagnetic density of states (DOS), $N(\varepsilon)$, on the Rh monolayer, for each system and each orientation considered. Its value at the Fermi level does depend on whether charge transfer is considered or not. Some multiconfigurational molecular results using the *Gaussian-98 ab initio* code, seem to indicate that some small transfer of charge might occur. We have chosen to consider three different situations. First, we consider charge neutrality on every layer and therefore, no charge transfer. Our results for the density of states are presented in Fig. 1. Changes due to charge transfer to the monolayer and from the monolayer will be considered below.

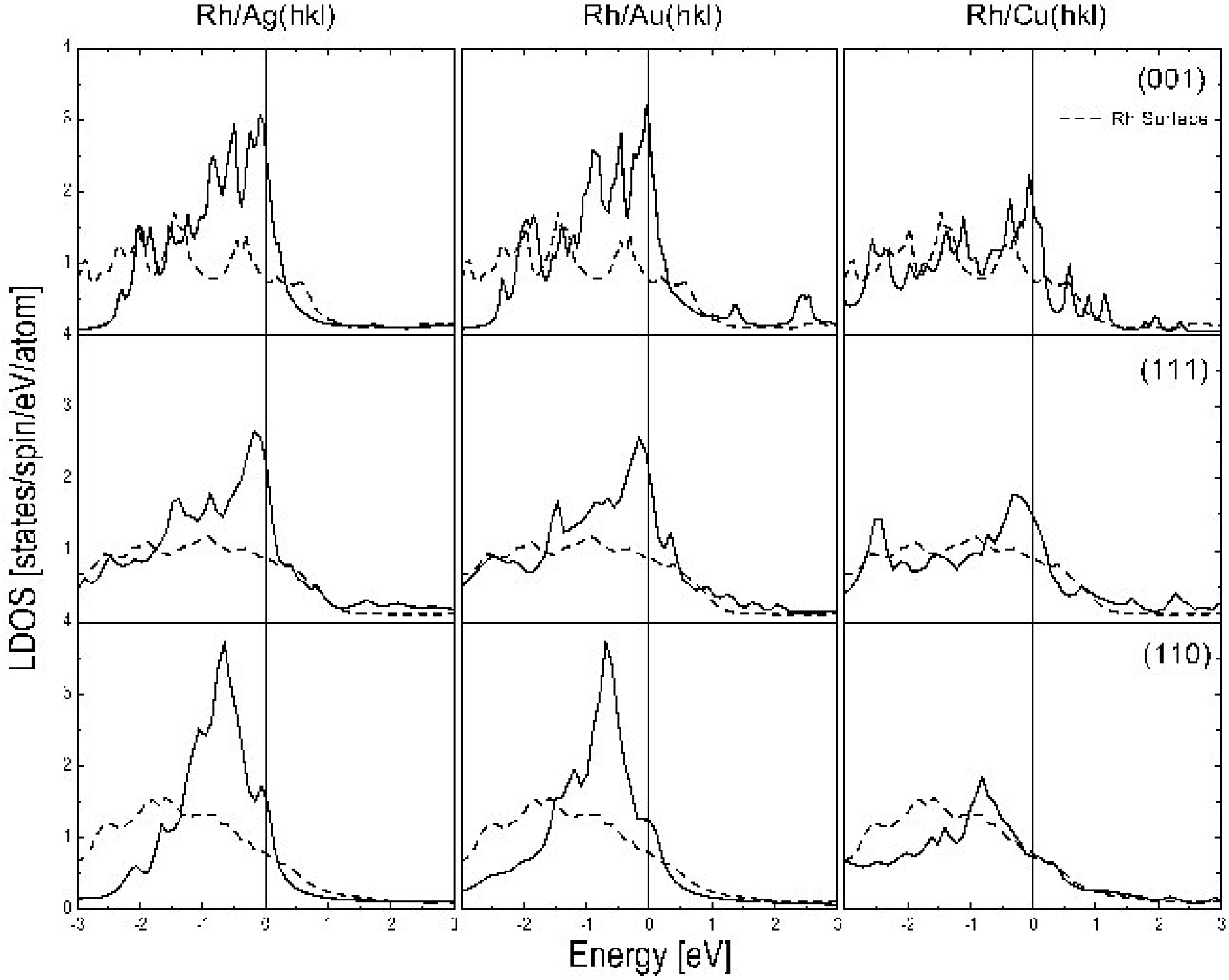

FIGURE 1. Our results for the Rh monolayer paramagnetic density of states (continuous lines) on the three substrates and in the three different orientations studied. We draw on each graph the Rh-surface (dashed lines) in the corresponding direction, for comparison. The origin is at the Fermi energy (See also Table I).

In Table I, we give the Rhodium paramagnetic total density of states at the Fermi level, $N(\varepsilon_F)$. Magnetism is attributable to the behavior of the d-electrons, and, therefore, their contribution to $N(\varepsilon_F)$, should be, in principle, more significant. We quote this value (d) in Table I, as well.

The first thing to notice is that the total $N(\varepsilon_F)$ and the d-contribution to it, d, align with each other. As it is shown in Table I, the highest $N(\varepsilon_F)$ value appears in the (001) orientation and the smallest one in the (110). So, there is, at first sight, a general trend in the Rh-$N(\varepsilon_F)$ which is attributable solely to the orientation. Nevertheless, we have to notice that the Rh surface does not follow it.

From the point of view of the substrate, the Rh/Au system presents the highest value of $N(\varepsilon_F)$ and of the d-contribution to it in the (001) orientation as we can see from Table I. But in the (111) and (110) orientations, it is the Rh/Ag system the one that has the highest density of states and Rh/Cu the smallest ones. So there is no clear trend attributable to the specific substrate below the Rh monolayer. It is interesting to notice that the Rh surface follows a trend in $N(\varepsilon_F)$ with respect to the orientation, that is not followed by any of the substrates considered.

In conclusion, in spite of the fact that the values for $N(\varepsilon_F)$ and (d) align well with each other for all the cases considered, there is no clear trend that relates these quantities neither to the substrate nor to the direction, in a real general way.

2.2. The Stoner criterium

We can use Table I to predict the magnetic activity to be expected from the Stoner criterium [41] for magnetism, $N(\varepsilon_F)\,J > 1,$ if we assume that the Stoner parameter for bulk Rh [42] can be used to describe a Rh monolayer or a Rh-surface [43]. Accordingly, magnetism can be expected if $N(\varepsilon_F) > 1.6$ states eV^{-1}atom^{-1} spin^{-1} on the Rh monolayer. We will use the total density of states in the criterium and remark that there is no difference in the conclusions whether we used the d-contribution instead.

First, let us remark that according to our results and the Stoner criterium, magnetism should appear in the (001) orientation for all the substrates considered. Nevertheless, no Rh-surface should be magnetic in any orientation whatsoever.

Further, no magnetism at all should appear on the Rh monolayer in the (110) direction for any of the substrates considered. Notice, nevertheless, that the $N(\varepsilon_F)$ for the Rh/Ag(110) system is not far away from fulfilling the Stoner criterium. In addition, no magnetic activity is to be expected in the (111) orientation on the Cu-substrate. At this point it is interesting to ask the following question. Could this situation be changed by any physical factor? Can magnetism be *turned on*? By pressure (or expansion) on the Rh monolayer, so that the distance between the monolayer and the substrate changes? Or by effect of an internal charge transfer? (we have impose charge neutrality in our calculations so far). We turn back to Fig. 1 to try to answer this question. The situation is slightly different for the Rh (111)-surface and the Cu(111) substrate, for example. Even if for the Rh(111) surface, $N(\varepsilon_F)$ is not at a maximum , the nearby maxima are too low to satisfy the Stoner criterium and therefore any external or internal factor that can be described within the rigid band approximation could introduce changes in the value of $N(\varepsilon_F)$ but these will not be enough for magnetism to appear. In the case of the Cu(111) substrate, if a certain amount of charge is transferred to the substrate from the monolayer, the highest occupied level would have an increased the number of states at that energy, higher than 1.6 states eV^{-1}atom^{-1} spin^{-1} (see Fig. 1) and the Stoner criterium can be fulfilled. We will come back to this point below.

TABLE I. We present here our results for the Rh monolayer paramagnetic density of states at the Fermi level, $N(\varepsilon_F)$, for all the substrates and directions considered. d refers to the contribution to the *total* density of states from electronic states of d-symmetry. Column labelled "Rh", refers to the Rh-surfaces data. Ag, Au, and Cu identifies the substrate on top of which the monolayer lies.

Orientation	$N(\varepsilon_F)$ [states/spin/eV/atom]							
	Ag		Au		Cu		Rh	
	total	d	total	d	total	d	total	d
001	2.59	2.54	2.94	2.83	1.85	1.80	0.783	0.738
111	2.26	2.17	2.08	1.96	1.47	1.38	0.894	0.850
110	1.56	1.54	1.24	1.22	0.72	0.69	0.785	0.742

Also, in the (111) direction, magnetism could be expected for Rh/Ag and for Rh/Au, since $N(\varepsilon_F)$ is higher that the limit value to fulfill the Stoner criterium (see Table I).

We proceed now to present our calculation of the magnetic moment.

2.3. The magnetic moment: our calculation

For the ferromagnetic case, a Hubbard tight-binding Hamiltonian and the Stoner model gave us essentially the same result. In the Stoner model, the magnetic moment, in units of Bohr magnetons, μ_B, is given by

$$\mu(\Delta) = \int_{-\infty}^{\varepsilon_F} \left[n_d^{+}(\varepsilon) - n_d^{-}(\varepsilon) \right] d\varepsilon = \int_{\varepsilon_F - \frac{\Delta}{2}}^{\varepsilon_F + \frac{\Delta}{2}} \left[n_d(\varepsilon) \right] d\varepsilon, \quad (1)$$

where Δ is the magnetic band splitting, $n_d^{\pm}(\varepsilon)$ indicates $n_d(\varepsilon \pm \Delta/2)$ and, $n_d(\varepsilon)$ is d-band contribution to the paramagnetic density of states per spin, per eV, per atom.

We conserve the total d-band electronic occupation, N_d, at each step,

$$N_d = \int_{-\infty}^{\epsilon_F} \left[n_d^{+}(\varepsilon) + n_d^{-}(\varepsilon) \right] d\varepsilon, \quad (2)$$

so that charge transfer to or from the $p-$ or $s-$ bands is neglected.

The total energy, E, of the system, in this approximation, is calculated from

$$E(\Delta) = \int_{-\infty}^{\varepsilon_F} \left[n^{+}(\varepsilon) + n^{-}(\varepsilon)\right] \, \varepsilon \, d\varepsilon + \frac{J\mu^2}{4}, \qquad (3)$$

where $n^{\pm}(\varepsilon) = n_s(\varepsilon) + n_p(\varepsilon) + n_d^{\pm}(\varepsilon)$, where $n_s(\varepsilon)$ and $n_p(\varepsilon)$ are the contributions to the LDOS from the s and p states, respectively, and J is the Stoner parameter. In these equations the only independent variable is Δ. We get the magnetic moment from the value of the magnetic band splitting, Δ_0, that minimizes $E(\Delta)$ in Eq. (3) with $\mu(\Delta)$ defined in Eq. (1).

The Rh-ML spin discriminated local density of states (SLDOS) appears in Figs. 2 and 3 for all the cases where we find the magnetic band splitting, Δ_0, different from zero. We have calculated the magnetic moment, μ, from the value of the magnetic band splitting, Δ_0, that minimizes $E(\Delta)$ in Eq. (3), as we stated above. We use for the Rh-ML the Stoner parameter calculated by Sigalas and Papaconstantopoulus [42], $J = 0.617$ eV. Our results appear in Table II. All these results are in agreement with the analysis that we made above using the Stoner criterium. Notice that the magnetic band splitting, Δ_0, correlates directly with μ.

From Table II, we see that the trend that the Rh-ML magnetic moment, μ, has, does correlate with the direction of growth. It is highest in the (001) direction and smallest in the (110). But, on the contrary, the correlation does not hold true from the point of view of the substrate. On Au, Rh presents the highest μ in the (001) direction but not in the (111). Since Au and Ag have approximately the same lattice constant, this points to the fact that the inter-monolayer atomic interactions are not the only factor that determines the magnetic moment but that the monolayer-substrate interactions play an important role as well. Finally, we point that we get a zero magnetic moment for all the Rh-surfaces, according to the prediction using the Stoner criterium.

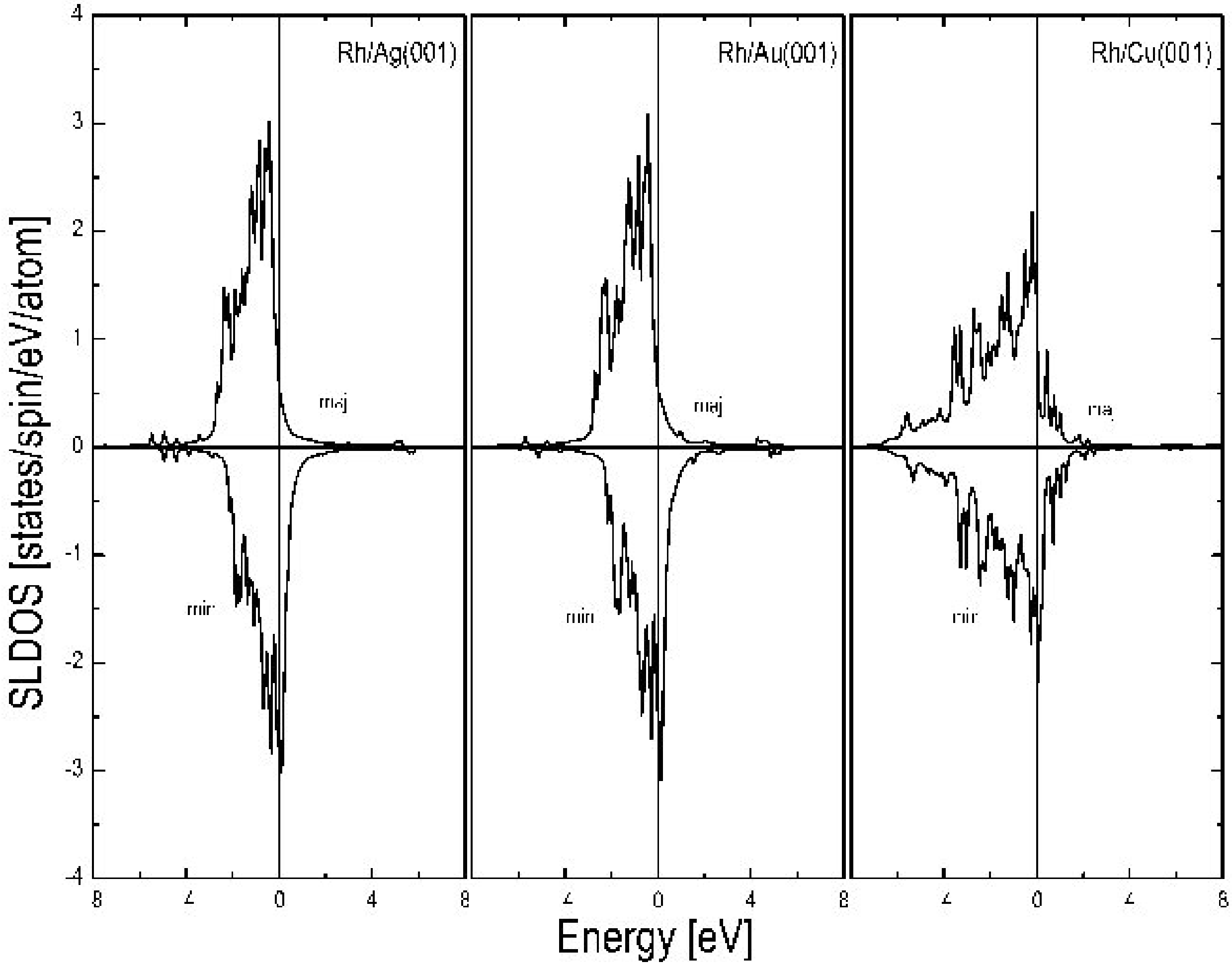

FIGURE 2. We show here the spin-discriminated density of sates for the cases for which we found the magnetic band spliting, $\Delta_0 \neq 0$ and therefore a magnetic moment, $\mu \neq 0$, for Rh-ML in the (001) orientation.

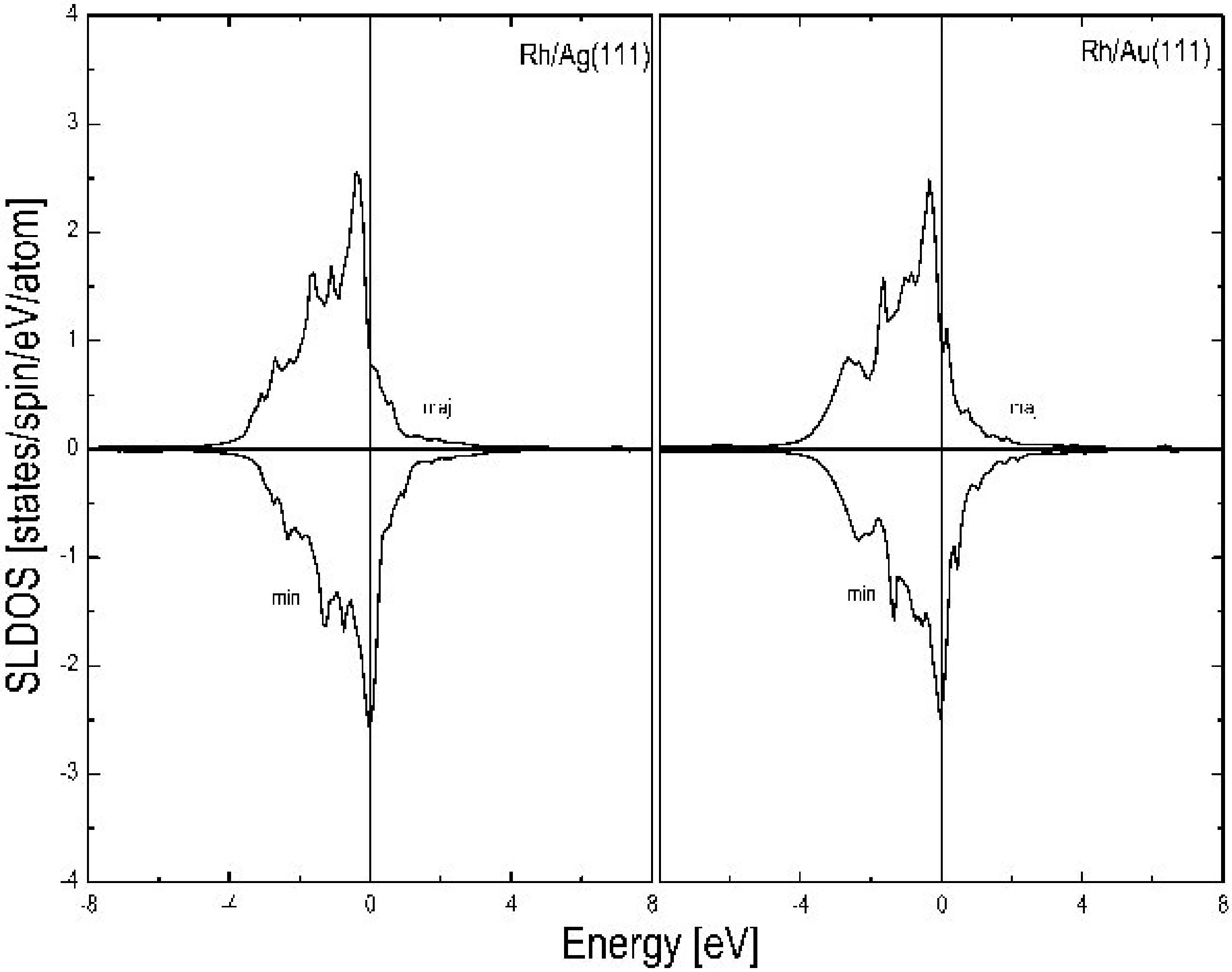

FIGURE 3. We show here the spin-discriminated density of sates for the cases for which we found the magnetic band spliting, $\Delta_0 \neq 0$ and therefore a magnetic moment, $\mu \neq 0$, for Rh-ML in the (111) orientation.

TABLE II. We present here our calculated magnetic moment, μ, and the corresponding magnetic band splitting, Δ_0, for the substrates studied and for the Rh surfaces. μ is in units of Bohr magnetons (μ_B), and Δ_0 in electronvolts (eV).

	The Magnetic Moment and the Magnetic Band Splitting			
Orientation	μ $[\mu_B]$,$\Delta_0[eV]$			
substrate	Ag	Au	Cu	Rh
001	1.00 , 0.58	1.05 , 0.62	0.50 , 0.30	0.00 , 0.00
111	0.70 , 0.43	0.60 , 0.37	0.00 , 0.00	0.00 , 0.00
110	0.00 , 0.00	0.00 , 0.00	0.00 , 0.00	0.00 , 0.00

For the (001)-orientation, we find μ = 1.0 μ_B for Rh/Ag and μ = 1.05 μ_B for Rh/Au, reproducing, essentially, the results by Blügel [2], we find μ = 0.5 μ_B for Rh/Cu, in agreement with the results by García *et al.*, [23]. For the (111) direction, the magnetic moments are $\mu = 0.7$ μ_B for Rh/Ag, and for Rh/Au we get $\mu = 0.6$ μ_B. J. Redinger *et al.*, [3] reported systematic spin-polarized *ab initio* calculations on ferromagnetism of $4d$ and $5d$ transition metal monolayers on Ag(111). They get for Rh $\mu = 0.67$ μ_B which is close to our value. This confirms that our method of calculation is accurate enough for our purpose here.

Since the magnetic moment, μ, correlates with the direction of growth, it is natural to try to associate it to a geometrical parameter. The magnetic activity in a Rh-ML on Au and on Ag could be expected on the grounds of the lattice constant value that each of these isoelectronic noble transition metal substrates has. The lattice constant for Ag and Au is approximately equal, *i.e.*, 4.08 Å. Cu has a lattice constant equal to 3.61 Å and the Rh-lattice constant is 3.80 Å. Therefore the Cu-substrate, in general, in any orientation, shrinks the space between the Rh-atoms in the ML atomic layer, as compared to the ideal Rh surface, an effect that enhances the in-plane interatomic interaction which seems to be against the magnetic activity as it is discussed elsewhere [23]. The Rh-atoms on Cu have an interatomic distance which is even shorter than the one on the corresponding Rh surface which is not magnetic in any orientation, according to our calculation. For the Au and the Ag substrates, the situation is opposite since the interatomic distance within the Rh ideal monolayer will be larger than in the Rh-surface or the bulk. So from this point of view, no magnetic activity is expected in a Rh-ML on Cu and a magnetic activity which is approximately the same for both, is to be expected on Au and Ag.

Nevertheless, the fact that for the (110) direction we get a null magnetic moment in Rh/Au and Rh/Ag, and that we do get a non-zero magnetic moment for Rh/Cu in the (001) orientation, has called our attention since the lattice constant argument does not seem to hold true for any of these cases. We deal with these cases in more detail in what follows.

2.4. Magnetism and geometric properties

Within each system, μ is always highest on the (001) orientation and lowest in the (110) one. This fact seems, at first sight, to be easily related to a geometric property as we have just mentioned. But the parameter that governs the switching on of magnetism on the Rh-ML is not so obvious as we shall see in the following.

Let us try to find a simple geometrical parameter that agrees with the result that μ is zero in the (110)-orientation and smaller in the (111)-orientation than in the (001) one. In an fcc-lattice the first-nearest neighbors (FNN) distance is $a/\sqrt{2}$, with a the lattice constant. When a monolayer is grown on top of a substrate, the number of FNN that an atom on the ML has (the coordination number) varies with the crystallographic orientation. Some of these neighbors are on the ML-atomic layer and others belong to the substrate. If one restricts the analysis to the monolayers with magnetic moment different from zero, the coordination number (FNN) appears to be a good geometrical parameter that governs this phenomenon. But if we also take into account in the analysis the monolayers and the directions where the magnetic moment is zero, this parameter fails, as we shall show below. It is interesting to include these cases since it allows a closer look at the mechanism that switches on magnetism.

Table III summarizes these observations. The rows are presented following the trend that we got for the magnetic moment value. Since the correlation number has been proposed [3] as the proper parameter, we notice that a monolayer atom in the Rh/Ag(110) system has a coordination number that is less than the one for the same system in the (001) direction. Thus, in this case, the criterium that the smaller coordination number gives rise to a higher magnetic moment, fails. We see from this Table that neither the total number of FNN, nor the number of them on the ML-atomic layer or in the substrate, correlate with the magnetic moment. The third column in Table III is the distance between the ML-atomic plane and the first substrate atomic plane. This parameter does not correlate with μ, as well. Let us try now the surface available per atom on the monolayer. Column four, shows these numbers. They do not correlate.

Finally, since hybridization plays a role, the volume per atom within the monolayer-substrate interface space, is another parameter to try. We have defined the quantity, Ω_0, that we construct in the following way. Consider the family of the planes perpendicular to the particular direction. Take a monolayer atom on the first of these planes. Build up the surface defined by its nearest neighbors on that monolayer plane. Repeat this procedure with an atom in the first atomic layer belonging to the substrate below. Construct the minimum volume, V_m, that we can form with this two surfaces. We define $\Omega_0 = V_m/N_m$, where N_m is the number of atoms contained within V_m . Ω_0 represents the volume per atom at the interface monolayer-substrate region. We see in Table III, column 5, that this parameter aligns with the magnetic moment. It seems that the only parameter that correlates for all the cases dealt with in this paper, with the magnetic moment, μ, is Ω_0. We remark that it emphasizes the hybridization, at the substrate-monolayer region, of the states that are responsible for magnetism. The higher the Ω_0, the lower the μ. The smaller the Ω_0, the higher the interaction between the substrate and the atoms on the monolayer. But this seems to contradict, at first sight, the idea that a higher lattice parameter of the substrate (Au, Ag) enhances the space between the atoms on the monolayer and produces magnetism. It is convenient at this point to summarize our ideas so that we can analyze them more deeply.

TABLE III. Rows are ordered following the magnitude of the magnetic moment, μ. *ML* in this Table, means the number of first nearest neighbors of an atom in the monolayer that lie in the monolayer atomic layer in each orientation. *Substrate* means the same but in the substrate. The third column shows the monolayer-substrate distance in each orientation. The next column shows the area at disposal per atom on the monolayer atomic layer. None of these parameters correlates with the magnetic moment as can be seen directly from the Table. The last column is the volume per atom, Ω_0, in the substrate-monolayer interface region. This is the only parameter that correlates: the smaller Ω_0, the bigger μ. But the trend seems against intuition (See the discussion in the text).

Orientation	ML	Substrate	ML-substrate distance	$\frac{\text{Sce.}}{\text{atom}}$	$\frac{\text{Vol}}{\text{atom}}$
001	4	4	0.50 a	0.50 a^2	0.17 a^3
111	6	3	0.58 a	1.04 a^2	0.25 a^3
110	2	5	0.35 a	0.71 a^2	0.29 a^3

Summarizing, the magnitude of the magnetic moment on a Rh-ML grown on a noble metal correlates with the direction of growth for a specific substrate. Within each system the magnitude of μ is higher in the (001) orientation and smallest on the (110). It depends strongly on the lattice constant. It is about the same on Ag and Au and for Cu(001) it is almost the half of the value obtained for Ag and Au in the same orientation.

The trend of the ML-total-paramagnetic density of states at the Fermi-level, $N(\varepsilon_F)$, correlates with the corresponding $d-$band contribution to it, but this correlation can not be related neither to the orientation nor to the substrate in a universal way.

When we look for a possible geometrical parameter to apply to the switching on of the magnetic activity of a Rh monolayer in different substrates and directions, we discarded some obvious parameters. We have defined above a parameter, Ω_0, that seems to be the proper one. This parameter points to the importance of hybridization of the electronic states at the interface monolayer-substrate region.

In spite of the fact that Ω_0 correlates well with the magnetic moment that we have calculated, its trend is against intuition, at first sight. One expects that a smaller space available for a Rh-ML atom would spoil magnetism instead of improving it. That is how magnetism is lost or weakened in a solid as compared to a single atom. The conclusion is that the hybridization of the electronic states at the interface region between the ML and the substrate is very specific and plays, very probably, the most important role. Being specific to each system, this factor might inhibits the possibility to relate the magnetic moment magnitude to a property that is general and merely geometric. Therefore, the criterium just mentioned (the Ω_0 parameter) could be valid only for Rh on noble metal substrates and does not actually reflects the whole complexity of the problem. If we looked at the bcc lattice instead, we would conclude that the trend of Ω_0 does not turn out to be the same. We will look now closer at the influence of the substrate in our problem here.

2.5. The influence of the substrate

An interesting point to look at, before we consider charge transfer, is the influence of the substrate on a Rh monolayer. To this purpose we study the artificial system Rh/Rh which amounts to a Rh-surface. This is presented in Fig. 1 above. There we draw the Rh-ML-total-paramagnetic density of states for the three directions and substrates considered and compare them to the corresponding surface density of states (SDOS).

In the (001) direction, for example, we can see that the SDOS is more intense at lower energies that the Rh-ML total paramagnetic density of states. What the substrate does is to shift these states to higher frequencies nearer to the Fermi energy. The same effect occurs above the Fermi level specially in the Au and Ag cases. This extra spectral weight is also transferred to the Fermi energy region. The result is an important enhancement of the intensity of $N(\varepsilon_F)$, *i.e.*, charge of d-band symmetry is transferred from lower and higher energies towards the Fermi level. This is what really influences the resultant magnetic moment and determines its value. While the highest peak in the Rh-ML DOS, $N(\varepsilon)$, around ε_F is, in the surface case, about 1.5 states eV^{-1}atom^{-1}spin^{-1}, it is on the Au or Ag substrates about 3.0. It is twice the corresponding surface value. We reproduce the d-band paramagnetic density of states for Rh on Ag at a broader range of energy in Fig. 4 so that the phenomenon is fully appreciated. We see that the effect is very noticeable at low energies.

It is interesting to notice that the d-bandwidth is higher in the (111) direction by about 0.6 eV as compared to the (001) orientation. This result is in agreement with the calculation of Redinger *et al.* [3] Also notice that the d-bandwidth in the (110) direction is even narrower in spite of the fact that the magnetic moment in that direction is zero. So the criterium that to a narrower d-bandwidth corresponds a higher magnetic moment fails in this case. The d-band charge transfer to energies closer to the Fermi level is the result of details in the interaction between the substrate and the monolayer and occurs in the three directions. In the (110) orientation, in the case of Ag and Au, a peak forms below the Fermi level and another (small one) above it as we can appreciate from Figs. 1 and 4. The Fermi level turns out to lie at a local minimum. This fact determines that there is no magnetic activity on the Rh-ML for these substrates in the (110) orientation according to our calculations. The formation of a big peak just below it, makes it particularly interesting to study since some charge transfer from the monolayer to the substrate might bring the highest occupied level near the peak and a non-zero magnetic moment could appear. We deal now with this point. For Rh/Cu(110) the effect is essentially the same and a peak is formed in $N(\varepsilon)$ below ε_F, with maximum intensity big enough to satisfy the Stoner criterium. It is nevertheless too far away from ε_F so that the amount of charge transfer needed to bring the highest occupied level to the maximum might, actually, be too large to be realistic. Notice that the narrowing of the d-band is a consequence of this transfer of electronic states towards the ε_F . But since pressure or expansion could switch on magnetism without changing the bandwidth, in some cases, this parameter turns out to be indicative but does not contain enough information to characterize the whole complexity of the phenomenon by itself as we have already commented above. Actually, the narrowest d-band occurs in the direction where the magnetic moment is zero, as we have already stated.

We, then, conclude that the effect of switching on magnetism depends on details of the interaction between the monolayer and the substrate to such an extension that inhibits a true general criterium based on a single geometric parameter or on the bandwidth. The switching on of the magnetic activity is due to a transfer of d-electron states from lower and higher energies to energies close to the Fermi level. This, we find, is the essential physics underlying the magnetic activity of a Rh-ML on noble metal substrates. The Stoner criterium has shown to be powerful enough to predict qualitatively all the result of our calculations.

2.6. Charge transfer

We have performed few multiconfigurational molecular calculations using the *Gaussian-98 ab initio* code, to seek for indications whether some transfer of charge could occur, in the ground state, for the ideal Rh/Substrate system. Our results seem to indicate that a small transfer of charge might occur. Even if there is no charge transfer in the ground state, it can be induced by pressure, for example. We have chosen to study some hypothetical cases of interest.

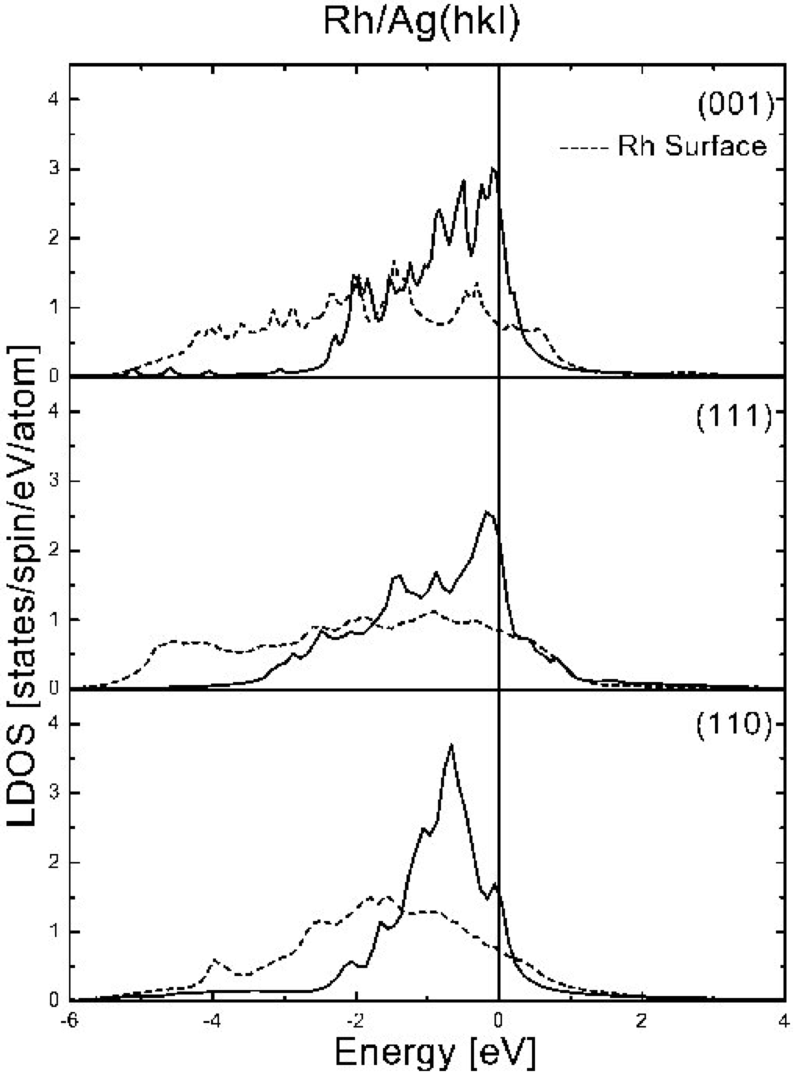

FIGURE 4. We present here the Rh-ML d-band paramagnetic density of states on the Ag substrate (continuous lines). We also draw the Rh surface d-band paramagnetic density of states (dashed lines) so that the influence of the substrate can be fully appreciated. The substrate causes a transfer of charge of d-symmetry from lower and higher energies to the Fermi energy region. This effect causes the density of states at the Fermi level to increase in a very important way and shrinks the d-band (See text for details and analysis).

Our point is best illustrated in the (110) direction example. We have a zero magnetic moment in this direction in all the cases considered. We have addressed the question whether some charge transfer could activate magnetism or not on the Rh-ML for some of the substrates under study. We assume that we can use a rigid band approximation to describe a small transfer of charge. We have presented in Fig. 1 the Rh-ML DOS, $N(\varepsilon)$, with charge neutrality imposed. There is no important maximum above the Fermi level, in the case we want to deal with, here, *i.e.*, the (110) direction. So, if some transfer charge occurs to the monolayer, the density of states at the highest occupied energy level on the Rh-ML will not be enhanced in an important way and therefore no magnetic moment is expected. A different situation occurs when charge is transferred to the substrate from the Rh-ML, instead. Below ε_F, there is a high peak in $N(\varepsilon)$ (see Fig. 1). So, if enough charge is transferred as to bring the highest occupied energy level in the local density of states of the Rh-ML down in energy, closer to the peak just mentioned, from a certain amount on, a magnetic moment appears. This is illustrated, in detail, in Fig. 5.

For Rh/Ag(110), 0.08 electrons atom^{-1} spin^{-1} give rise to $\mu = 0.1\,\mu_B$. For Rh/Au(110), 0.38 electrons atom^{-1} spin^{-1} transferred from the Rh-ML switches on magnetism. Notice that the influence on the Rh-ML from the two substrates, Au and Ag, is different. We also get, in this way, a magnetic moment for Rh/Cu(110). In this case, the amount of charge transferred necessary to produce a magnetic moment is about 0.84 electrons atom^{-1} spin^{-1} which is quite larger (see Fig. 5). Finally, for the Rh/Cu(111) system, 0.42 electrons atom^{-1} spin^{-1} give rise to $\mu = 0.2\,\mu_B$.

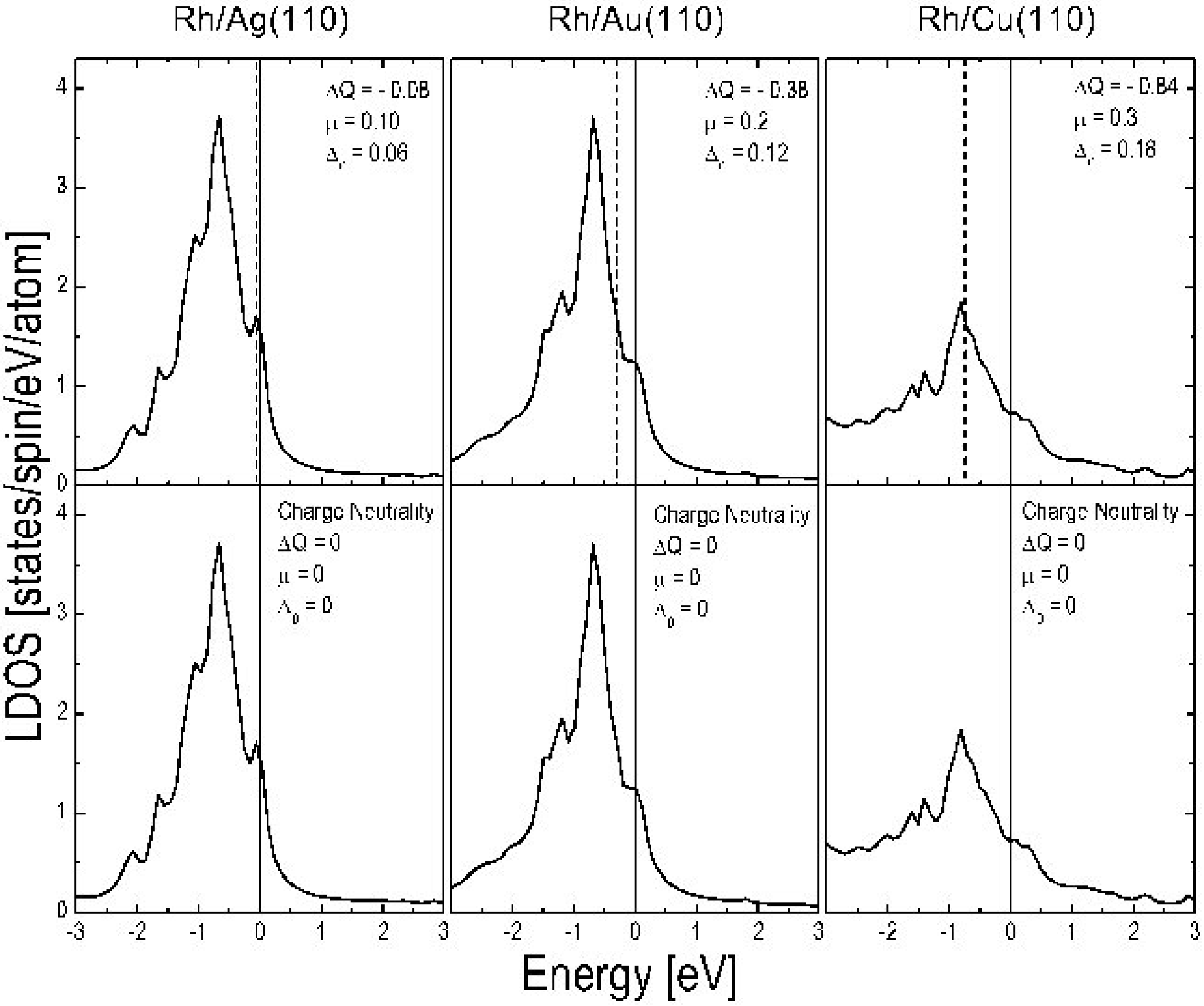

FIGURE 5. We study here the (110) direction. Charge transfer could switch on magnetism in cases where charge neutrality gives a zero magnetic moment. The highest occupied electronic state (dashed lines) can be moved by the influence of pressure, for example. The Fermi level is at the origin. We have assumed that charge can be transferred from the monolayer to the substrate without altering the band structure. For small charge transfer this hypothesis might hold true. ΔQ is the amount of charge transfer. The minus sign means that charge is transferred from the monolayer to the substrate.

3. Conclusions

We have studied the magnetic activity of a Rh-ML grown on three different substrates, *i.e.*, Ag, Au and Cu in three crystallographic orientations, (001), (111), and (110). We have first calculated the Rh-ML paramagnetic density of states (see Fig. 1 and Table I) and used the Stoner criterium to predict the magnetic activity. We assumed that the bulk Stoner parameter for Rh can also be used for a monolayer and for a Rh-surface [43] in all the cases considered here. The qualitative predictions agree with the results of the calculation. In the (001) orientation, we reproduced the results already obtained by Blügel [2] and by García *et al.* [23] In the (111) orientation, we reproduce the spin-polarized *ab initio* calculations for Rh/Ag by Redinger *et al.* [3] This shows that our method is accurate enough for our purposes here. The rest of the results are new.

We get a magnetic moment, μ, different from zero for Rh/Ag and Rh/Au in the (001) and the (111) orientations. Rh/Cu is not magnetic neither in the (111) nor in the (110) orientation. Within each system, μ is highest on the (001) orientation and lowest on the (110)-one. For Rh/Ag, $\mu = 1.0\,\mu_B$ in the (001), $\mu = 0.7\,\mu_B$ in the (111), and $\mu = 0$ in the (110). For the Rh/Au, $\mu = 1.05\,\mu_B$ in the (001), $\mu = 0.6\,\mu_B$ in the (111), and $\mu = 0$ in the (110). For Rh/Cu, $\mu = 0.5\,\mu_B$ in the (001), $\mu = 0$ in the (111) and in the (110) orientation. See Table III and Figs. 2 and 3.

At first sight, it looks like the lattice parameter is the clue to switch on magnetism at a Rh-ML on a noble metal substrate. This is because it becomes magnetic on Ag and Au (with a lattice constant higher than Rh) and does not become magnetic on Cu (with lattice constant smaller than Rh) in the (001) and (111) orientations. The Rh surface is not magnetic in any direction according to our calculations. But since we found Rh/Au and Rh/Ag non magnetic in the (110) orientation, and Rh/Cu magnetic in the (001) direction, we have tried to look for a clue parameter in more detail.

We have next try to find a geometrical parameter that governs the switching on of the magnetic activity. We have tried several. We have found that neither the total number of first nearest neighbors (coordination number), nor the number of them on the ML-atomic layer or in the substrate correlate with the magnetic moment. The distance between the ML-atomic plane and the first substrate atomic plane for each orientation, does not correlate with μ, as well. Also the surface at disposal per atom at the monolayer, fails to be the parameter. Finally, we found a parameter, Ω_0, which is defined, in detail, above in the text and roughly represents the volume per unit atom in the monolayer-substrate interface region, that does correlate well, in the sense that the smaller Ω_0, the higher μ. This trend seems against intuition and therefore this geometric parameter, very probably, does not represent a general property of a Rh-ML, essential to magnetism. It fails if the substrate is bcc instead of fcc as we have considered here. It is therefore not appropriate for the purpose we are seeking. We have actually shown that this is, indeed, the case. When compared to the Rh-surface, we see that the Rh-ML paramagnetic density of states presents characteristics that can be only attributable to details in the interaction between the monolayer and the specific substrate. The physics underlying the switching on of magnetism in the Rh-ML on noble metal substrates, is a d-band transfer of electronic states from lower and higher energies to the Fermi energy region. This enhances the paramagnetic density of states at the Fermi level in a very important way and diminishes the d-bandwidth. This is a general phenomenon for the problem we are dealing with here. But the resulting paramagnetic density of states at the Fermi level is very specific to each substrate and determines the switching on or not of magnetism at the Rh-ML. This phenomenon cannot be accounted for by the d-band bandwidth alone (see Fig. 4 and the text above).

Finally, we have consider charge transfer and its possible effect on the magnetism of the Rh-ML. In the (110) orientation, we find that if charge is transferred from the monolayer to the substrate (by pressure, for example), magnetism could be switched on for Rh on Au and Ag. A higher transfer of charge is needed to produce magnetism on Rh/Cu (see Fig. 5). Further we observe that to transfer charge from the monolayer to the substrate could produce magnetism also on Rh/Cu(111) but the amount of charge is higher.

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