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# Controlling the spin of metal atoms adsorbed on oxide surfaces: Ni on regular and defective sites of the MgO(001) surface

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We have analyzed the relative energy of nonmagnetic and magnetic low-lying electronic states of Ni atoms adsorbed on regular and defective sites of the MgO(001) surface. To this end cluster and periodic surface models are used within density functional theory. For Ni atoms adsorbed on oxygen vacancies at low coverage, the interaction energy between the metal and the support is much larger than on regular sites. Strong bonding results in a diamagnetic adsorbed species and the energy required to reach the high-spin state increases. Moreover, a correlation appears between the low-spin to high-spin energy difference and the interaction energy hypothesizing that it is possible to prepare the surface to tune the high-spin to low-spin energy difference. Magnetic properties of adsorbed thin films obtained upon increasing coverage are more difficult to interpret. This is because the metallic bond is readily formed and dominates over the effect of the atoms directly bound to the vacancy.

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## I. INTRODUCTION

The interaction of metals with oxide surfaces is important for different technical reasons, electronic devices, and data storage among them. Electronic storing devices are commonly based on the magnetic properties of supported metallic particles and films.<sup>1,2</sup> However, depending on the preparation method different kinds of defects can be present in a fairly large amount at the surface. This is especially the case when oxide surfaces are prepared by growing thin films on a metal substrate.<sup>3–5</sup> The presence of these defects can substantially affect the properties of the oxide surface. For instance, there is evidence that point defects have a crucial function in the reactivity of supported particles.<sup>6,7</sup> Therefore, it is well possible that the presence of defects, believed to be to a large extent responsible for the initial steps of metal adhesion, can modify the properties of the adsorbed particle.<sup>8–11</sup> From the experimental point of view, the study of the metal–oxide interaction focuses mainly on the size, shape, and reactivity of adsorbed metal particles<sup>12,13</sup> and there is almost no direct information about the interaction of metal particles on point defects of these substrates.<sup>14</sup> This is due to the experimental difficulties arising from the low concentration of point defects, especially when compared to the surface metal loading. A complementary way to gain understanding of the interaction of metal particles with oxides and other related substrate is to use theoretical models coupled to first principle electronic structure calculations. In the past few years a rather large number of articles have appeared in the literature dealing with the interaction of several metal atoms, cluster, and films on different oxide surfaces. Since this field has been recently reviewed<sup>15</sup> we just quote some recent work on complex surfaces such as  $\alpha$ -alumina<sup>16–21</sup> or TiO<sub>2</sub>.<sup>22,23</sup> However, most of these papers are devoted to the interaction of metal atoms and clusters with regular surface sites and, in particular, to the prediction of the active site, the

interaction energy and the adsorbate geometry. Nevertheless, the interaction of metals with point defects sites has also attracted the attention of researchers, and several studies on the interaction of metal atoms and cluster on oxygen vacancies of MgO,<sup>4,24,25</sup> TiO<sub>2</sub>,<sup>26,27</sup> and several point defects of SiO<sub>2</sub> (Refs. 28, 29) are available. Again the main focus of these works lies in the proper description of the interaction and in the prediction of the structure and energetic.

Other properties of interest related to the low-lying spectra of the adsorbed metal atom have been less studied. This is the case of the energy difference between the closed, diamagnetic, and open-shell, paramagnetic states of transition metal atoms adsorbed on oxides. This is a very important property with potential technological implications because it is related to the possibility of obtaining and handling magnetic centers at the surface at the molecular level. Yudanov *et al.*<sup>30</sup> reported a systematic study of the interaction of transition metals on regular centers of MgO and concluded that whenever possible the formation of a new chemical bond leads to a reduction of the spin multiplicity with respect to that of the isolated atom. A similar behavior has been found for Ni and Co atoms on MgO(001) although small metal Co<sub>4</sub>, Ni<sub>4</sub>, and Ni<sub>8</sub> clusters tend to almost preserve the number of unpaired electrons of the gas-phase metal cluster.<sup>31,32</sup> However, it has been recently shown that even the interaction of isolated Ni atoms with regular sites on the MgO(001) is more complex than initially imagined. In particular, a near degeneracy between the two possible spin states of adsorbed Ni exists with a significant geometric difference depending on the final electronic state.<sup>33</sup> Based on the performance of different density functionals, our previous study suggested that the larger the interaction the stronger the spin quenching. Pacchioni *et al.*<sup>4</sup> have shown that while the interaction of metal atoms with regular sites of oxide surfaces is generally

weak, a significant enhancement of the metal-support interaction is found when the adatom interacts with surface oxygen vacancies. These are precisely the most common bulk and surface point defects on a simple oxide like MgO.

The above discussion suggests that the final spin state of an adsorbed metal atom can be different depending on whether it interacts with a regular or a point defect site. The aim of the present work is precisely to discuss the magnetic properties of Ni atoms and adlayers adsorbed on oxygen vacancies at the MgO(001) surface. Even if MgO is a nonreducible oxide, oxygen vacancies can be generated through various preparation processes, e.g., annealing of the hydroxide or by thin film grown on excess of Mg; charged vacancies can be created by Ar<sup>+</sup> sputtering or gamma-ray irradiation. The presence of these point defects at the MgO(001) surface is well characterized by recent spectroscopic measurements<sup>5</sup> and confirmed by theoretical analysis.<sup>34</sup> Three types of oxygen vacancies present on the MgO(001) surface have been considered. First, a neutral oxygen vacancy, denoted by  $F_s$ , where an O atom is removed from the surface. For this defect, two electrons remain trapped in the vacancy, generating an impurity level on the band gap of the substrate. The neutral vacancy shows a reduced ionization potential when compared to the regular surface although the topography of the electronic density is similar to that of the regular surface.<sup>3,35</sup> In fact, electrons are trapped in the vacancy because of the very large band gap of this material. Processes generating oxygen vacancies can also produce the removal of an O<sup>-</sup> anion from the surface, the corresponding generated point defect is charged and paramagnetic, i.e., EPR active; it is often denoted as  $F_s^+$ . Such a point defect presents a singly-occupied defect state in the band gap, and shows a smaller ionization potential (IP) and larger electronic affinity (EA) than for the perfect surface. Finally, if O<sup>2-</sup> is removed from the surface, the resulting defect is described as  $F_s^{++}$  and the system does not present any occupied level on the band gap. In this case EA is largely favorable while the IP is similar to that of the perfect surface.<sup>3</sup> Relaxation processes and polarization effects have demonstrated to play an important role in the EA and IP values for charged defects.<sup>36,37</sup>

## II. SURFACE MODELS AND COMPUTATIONAL APPROACH

The computational approach is based on the use of density functional theory (DFT) and both cluster and periodic models. Cluster models with DFT have demonstrated to be very powerful in the description of the interaction of a single metal atom with a nondefective nonpolar oxide surface.<sup>15,38-40</sup> On the other hand, the combined use of cluster and periodic models gives us a complete picture for low and high coverage properties.<sup>18</sup>

For the planar surface, an embedded stoichiometric cluster model containing 13 O and 13 Mg atoms has been used; the central O atom has been removed when representing a vacancy. In both cases the cluster is surrounded by total ion potentials (TIPs), that represent Mg cations in direct contact to the O atoms in the edges of the cluster and by an appropriate array of point charges (PC) with formal absolute val-

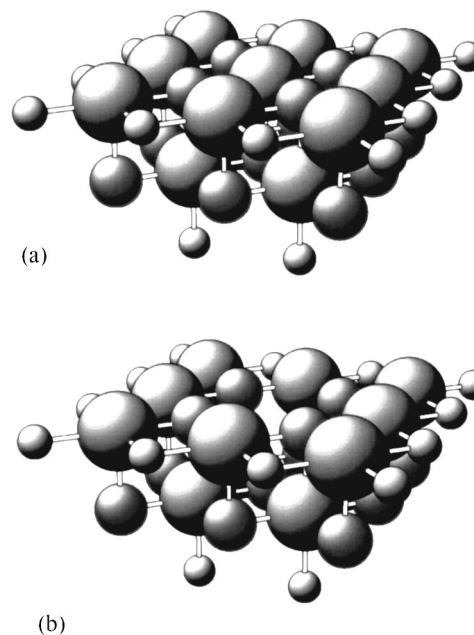


FIG. 1. Cluster model describing the regular surface and the oxygen vacancy. (a)  $[O_{13}Mg_{13}] + \text{TIPs}$  and (b)  $[O_{12}Mg_{13}] + \text{TIPs}$ . Small spheres represent TIPs, medium spheres Mg cations, and large spheres O anions.

ues of 2. The use of TIPs avoids spurious polarizations of the electronic density while the array of PCs mimics the long range electrostatic effects due to the rest of the crystal. In particular we have PCs so that the total model, atoms plus TIPs plus PCs, add up to a  $16 \times 16 \times 4$  crystal network. The resulting set of point charges is large enough to ensure that the Madelung potential in the chemisorption region is reproduced with reasonable accuracy.<sup>41</sup> The entire system, cluster plus TIPs plus PCs, is neutral for the regular surface. Cluster models, atoms plus TIPs, are shown in Fig. 1.

For each adsorption site, the interaction of the Ni atom with the surface is studied by allowing the Ni atom to move in the direction perpendicular to the surface and, except for the regular surface, the four Mg cations surrounding the vacancy have been relaxed. This approach has proved to provide a reasonable description of the geometrical rearrangement induced by the point defect.<sup>4,36</sup> The B3LYP hybrid functional<sup>42</sup> has been chosen since it has been shown to provide a rather accurate description of the metal/oxide interaction.<sup>40</sup> Moreover, for the magnetic systems it provides a reasonable albeit not perfect picture which lies midway between the HF and pure GGA descriptions.<sup>43,44</sup> Even if the DFT has well-known problems with the description of magnetic properties, hybrid functionals such as B3LYP provide a fair indication of the relative energies; in some cases the resulting differences between the experimental values and the calculated ones can be considered a systematic error.<sup>45</sup>

For cluster calculations we have considered two electronic states. One is a low-spin state (i.e., a closed-shell except for cluster representing  $F_s^+$ ) and hence involves Ni in a  $3d^{10}$ -like configuration. The second electronic state is the lowest triplet state involving an intra-atomic single excitation from the  $3d$  to the  $4s$  orbital. In these calculations a contracted Gaussian basis set is used to represent the elec-



tronic density. The Gaussian basis set employed in this work are the same previously used by Markovits *et al.*<sup>33</sup> Hence, a  $[13s8p/6s3p]$  set is used for the Mg atoms close to the vacancy and  $[12s7p/5s2p]$  for the rest. A  $[8s4p/4s2p]$  set optimized for  $O^-$  has been used for the cluster O atoms although in the case of the regular surface an extra polarization  $d$  function has been added to the central O atom basis set. Finally, for Ni a relativistic pseudopotential is used to take into account the effect of the inner shell electrons, whereas the valence  $3s$ ,  $3p$ ,  $3d$ , and  $4s$  electrons are described by an uncontracted  $4s$ ,  $4p$ , and  $4d$  Gaussian set. Pseudopotentials and basis sets for Ni have been taken from Hay and Wadt.<sup>46</sup> All cluster calculations have been carried out using the GAUSSIAN 98 package.<sup>47</sup>

Periodic calculations have been carried out for the two spin orders that can be related to the spin states described above for the cluster calculations. This is achieved by fixing the number of unpaired electrons per unit cell either to 0 or 2. The periodic calculations have been carried out using the DACAPO code<sup>48</sup> employing ultrasoft pseudopotentials<sup>49</sup> and a plane wave basis set with a cutoff energy of 25 Rydberg. Both the regular surface and the neutral oxygen vacancy (coverage 0.25 ML) have been studied for the adsorption of a single atom (also 0.25 ML coverage) and for a full monolayer; for the vacancy a  $p(2 \times 2)$  unit cell was used. Only the neutral oxygen vacancy has been studied within the periodic approach. This is because of the inherent difficulty to deal with charged point defects which require charge compensation through a rather artificial background charge. For the periodic models a Monkhorst–Pack  $[4 \times 4 \times 1]$  mesh has been employed (and changed accordingly for smaller unit cell calculations). The slab representing MgO(001) contains 3 atomic layers and the unit cell parameters are those employed for the cluster calculations with a vacuum width of more than 10 Å between slabs. A correction for the electric field in the vacuum region has been used. The atoms in the slab first layer have been relaxed and, in all cases, the  $z$  component of the adsorbate has been optimized. In the periodic calculations both self-consistent PW91<sup>50</sup> and RPBE<sup>51</sup> (energy evaluation on the PW91 density) exchange-correlation functionals have been used.

### III. RESULTS AND DISCUSSION

To facilitate the discussion of the rather large set of results we have chosen to present separately the description of the interaction energy and equilibrium geometry of Ni atoms and films above the different surface sites and the discussion about the relative stability of the nonmagnetic and magnetic states.

#### A. Interaction energies and equilibrium geometries

The bare nondefective MgO(001) surface exhibits very small relaxation only and therefore it has been kept fixed when studying adsorption metal atoms. However, surface relaxation effects are much larger if discontinuities, like steps or point defects, are present.<sup>3,4</sup> Table I summarizes the results obtained for the structure of the surface containing oxygen vacancies before and after metal adsorption. Geometries of the different oxygen vacancies predicted in this work are

TABLE I. Relaxation of the first layer of Mg cations surrounding an oxygen vacancy;  $d_{V-Mg}$  stands for the distance from the cation to the center of the vacancy and  $z_{Mg}$  stands for the vertical distance to the surface plane. For the regular surface  $d_{V-Mg}=2.104$  and  $z_{Mg}=0.0$ . All distances are in Å.

Surface site	Model/method	Ni spin state	$d_{V-Mg}$	$z_{Mg}$
$F_s$	Cluster/B3LYP	...	2.11	0.07
	Slab/PW91	...	2.14	0.10
$F_s^+$	Cluster/B3LYP	...	2.26	0.06
$F_s^{++}$	Cluster/B3LYP	...	2.32	0.05
Ni: $F_s$	Cluster/B3LYP	Low	2.17	0.10
	Cluster/B3LYP	High	2.16	0.08
	Slab/PW91	Low	2.17	0.12
Ni: $F_s^+$	Slab/PW91	High	2.16	0.10
	Cluster/B3LYP	Low	2.26	0.06
Ni: $F_s^{++}$	Cluster/B3LYP	High	2.24	0.04
	Cluster/B3LYP	Low	2.30	0.01
	Cluster/B3LYP	High	2.31	0.02

very similar to the Hartree–Fock values reported earlier by Ferrari and Pacchioni.<sup>4</sup> For a surface containing oxygen vacancies the surrounding Mg atoms relax outwards the cavity, i.e., towards the nearest neighbor ions and up to the vacuum. The degree of relaxation depends on the nature of the vacancy, i.e., the first distortion (distance to the missing O center) increases with the charge of the defect, while the second shows a slightly decreasing behavior. It should be pointed out that the relaxation of charged species is more difficult to simulate because of the long-range polarization of the substrate in response to the presence of the charge. Upon metal adsorption, further rearrangement of the vacancy region takes place. For charged vacancies, the Mg atoms surrounding the missing oxygen get closer to the adsorbate, reducing the vacancy space.

Metal-related parameters upon adsorption are summarized in Table II. For the low-spin state and all O vacancies Ni atoms get closer to the surface than for the nondefective surface, due to the smaller Pauli repulsion in the former case.<sup>35</sup> On the other hand, the distance to the surface differences between low- and high-spin states encountered for the regular surface<sup>33</sup> are still significant when Ni interacts with

TABLE II. Distances from Ni to the surface plane for the low- and high-spin states,  $r_e^L$  and  $r_e^H$ , and their difference  $\Delta r_e^{L-H}$ . All the distance are in Å. For the high coverage only the ground state is considered, see text.

Surface site	Model/method	$r_e^L$ (Å)	$r_e^H$ (Å)	$\Delta r_e^{L-H}$ (Å)
Low coverage				
MgO(001)	Cluster/B3LYP	1.82	2.12	-0.30
	Cluster/PW91 <sup>a</sup>	1.81	2.03	-0.22
	Slab/PW91	1.82	1.98	-0.16
$F_s$	Cluster/B3LYP	1.44	1.94	-0.50
	Slab/PW91	1.46	1.85	-0.39
$F_s^+$	Cluster/B3LYP	1.60	2.72	-1.12
$F_s^{++}$	Cluster/B3LYP	1.74	1.84	-0.10
CaO(001)	Cluster/B3LYP	1.84	2.13	-0.29
High coverage				
MgO(001)	Slab/PW91	1.99		
$F_s$	Slab/PW91	1.77–2.07 <sup>b</sup>		

<sup>a</sup>Reference 33.

<sup>b</sup>Highest and lowest point of the adsorbed film.

TABLE III. Binding energy for the low-spin state:  $BE^L$ ; and energy of the high-spin state relative to the low-spin state,  $\Delta BE^{L-H}$ . Free ( $d^{8s^2} \rightarrow d^{10}$ ) at the B3LYP level is 3.00 eV.  $q^L$  and  $q^H$  stand for the Mulliken charges for the low- and high-spin states on Ni. The last column represents the magnetic moment per atom in bohr magnetons for a monolayer. For the low coverage situation the magnetic moment on the Ni atom is forced by the choice of the number of unpaired electrons and hence it is not reported in the table.

Surface site	Model/method	$BE^L$ (eV)	$\Delta BE^{L-H}$ (eV)	$q^L$	$q^H$	Magnetic moment/ atom $\mu_B$
Low coverages						
MgO(001)	Cluster/B3LYP	0.97	-0.03	-0.08	-0.04	
	Cluster/PW91 <sup>a</sup>	1.85 <sup>b</sup>	0.30			
	Slab/PW91 (RPBE)	...	0.46 (0.43)			
CaO(001)	Cluster/B3LYP	1.24	0.13	-0.28	-0.16	
	$F_s$ Cluster/B3LYP	2.16	0.38	-1.22	-0.65	
	Slab/PW91 (RPBE)	...	1.22 (1.05)			
$F_s^+$ Cluster/B3LYP	2.50	2.20	-0.59	0.07		
$F_s^{++}$ Cluster/B3LYP	-0.32 <sup>c</sup>	-1.24	0.12	0.12		
High coverages						
MgO(001)	Slab/PW91					0.88
$F_s$	Slab/PW91					0.76

<sup>a</sup>Reference 33.

<sup>b</sup>Calculated with respect to the PW91 atomic Ni lowest state, 5.60 with respect to the experimental Ni ground state, see discussion in Ref. 33.

<sup>c</sup>In this case the BE is computed with respect to  $F_s^+ + Ni^+$ .

O vacancies. For low coverages, periodic and cluster models predict similar equilibrium distances. For a Ni adlayer, a significant corrugation of the metal film is observed when supported by a defective surface. For instance, for a reduced MgO containing a 0.25 ML of vacancies the distances from the Ni to the surface range from 1.767 to 2.074 Å while the value for a regular surface is 1.993 Å. This leads to a difference of about 0.3 Å between the highest and lowest points similar to the high-spin value. Notice, that in this case the point defect concentration is still 0.25 ML, whereas the Ni coverage is 1 ML. Hence, the relative concentration of Ni atoms above F centers is also 0.25 ML. The corrugation of the reduced MgO substrate is transferred to the supported metallic film. In fact, average Ni–surface distances are similar to those predicted for a regular surface but low and high points of the adsorbed film, depending on the distribution of vacancies, are present. Therefore, it can be safely concluded that corrugation can be considered as a fingerprint of the presence of oxygen vacancies in the MgO(001) surface.

Binding energies are reported in Table III. The binding energy of the metal atom to the oxide surface for the  $F_s$  and  $F_s^+$  point defects is larger than for the regular sites.<sup>4</sup> For  $F_s^+$ , where a covalent bond can be formed by coupling unpaired electrons from the substrate and the adsorbate, the interaction is particularly strong. The energy difference corresponding to adsorption above the regular surface and above the  $F_s$  may be understood from the Pauli repulsion reduction in the latter with respect to the former and the larger structure reorganization in the latter. For Ni above an  $F_s^{++}$  center, the binding energy is smaller than for the regular site since disproportionation according to



takes place.<sup>4</sup> This is supported by the positive charge on Ni (+0.12e) obtained in the Mulliken population analysis.

In the periodic approach, binding energies for isolated metals have not been calculated due to the reported problems in the description of single Ni atoms by DFT.<sup>33</sup>

## B. Electronic and magnetic properties

The bonding mechanisms described above are fully consistent with the Mulliken population analysis data reported in Table III. For the high-spin state the net charge on the Ni atom is always smaller than for the low-spin case as expected from the larger distance to the surface. Similarly, the net charge of the Ni adatom in the low-spin state is larger when the interaction occurs above the  $F_s$  and  $F_s^+$  oxygen vacancies in agreement with the stronger chemical bond and with the larger interaction energy. For the  $F_s^{++}$  the Ni atom remains slightly positively charged in both spin states, and is a result of the large positive charge of this point defect.

The relative energy of the singlet and triplet electronic states of Ni adsorbed on the anionic site of the regular MgO(001) surface have been analyzed in a recent paper.<sup>33</sup> Nevertheless, it has been shown that the strength of the interaction is largely dependent on the exchange-correlation functional. For the methods predicting a larger interaction, the magnetic moment is quenched and the low-spin structures appear as the most stable one. These previous results suggest that by extending this type of study to different adsorption sites on this substrate, a nonmagnetic or a magnetic ground state can be obtained depending on the characteristics of the site. Results in Table III show that this is indeed the case, the transition from the low-spin to the high-spin state shifts to higher energies for stronger metal-support interactions. For the case of a single Ni atom adsorbed on the regular MgO(001) the behavior is the result of the competition between Hund's rule for the adsorbed atom and the formation of a chemical bond at the interface. The first mechanism

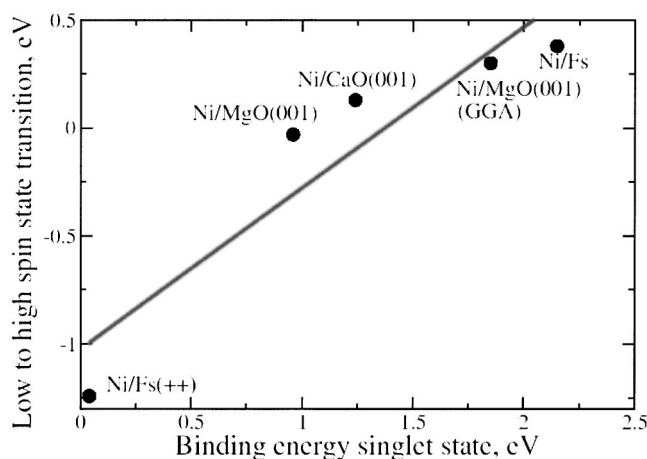


FIG. 2. Singlet to triplet transition energy of Ni vs the binding energy for the adatom singlet state. Energies are in eV.

favors the highest multiplicity within the near-degenerate  $d$ -manifold, while the second favors the largest possible coupling between electrons.<sup>33</sup> Results in Table III confirm that this competition between magnetism and chemical bonding holds also for the interaction with surface point defects. However, it is important to notice that for the  $F_s^+$  paramagnetic defect the interaction is dominated by the covalent bonding contributions due to the coupling of one electron from the substrate and a second electron from the metal. Consequently, the magnitude of the energy difference between the low- and the high-spin states includes also the energy needed to break this localized chemical bond. Therefore, the energy difference between the two considered states is significantly larger than for the other cases.

The relationship between the low-spin to high-spin energy difference and the interaction energy is clearly seen in Fig. 2 where the former quantity is plotted versus the latter. The existence of this correlation validates the interpretation in terms of the competition between Hund's rule and chemical bonding. To give further support to this interpretation we have also considered the interaction of Ni with CaO. The choice of this support is justified by the results of a recent systematic study of the interaction of Pd and Pt on the (001) surface of the alkaline-earth oxide series which suggest a moderate enhancement of the metal-support interaction in going from MgO to BaO.<sup>52</sup> For these additional calculations we have employed the basis same basis set for Ni and O, whereas the Ca basis is the one previously used in Ref. 53. The values obtained for Ni on CaO(001) lie clearly on the linear relationship represented in Fig. 2. Hence, we can conclude that, except for the  $F_s^+$  paramagnetic state, the low- to high-spin energy transition is mainly determined by the strength of the bond.

This result can be rationalized through a rather naïve picture where the interaction between the metal and the support relies on the mixing of the metal  $d_{z^2}$  and the  $s$  orbitals of the Ni atom plus the lone pair coming from O or the equivalent orbital representing the electronic density centered on the vacancy. The interaction between these three orbitals generates three molecular orbitals; the most stable one belongs mostly to the surface (surface orbital with small con-

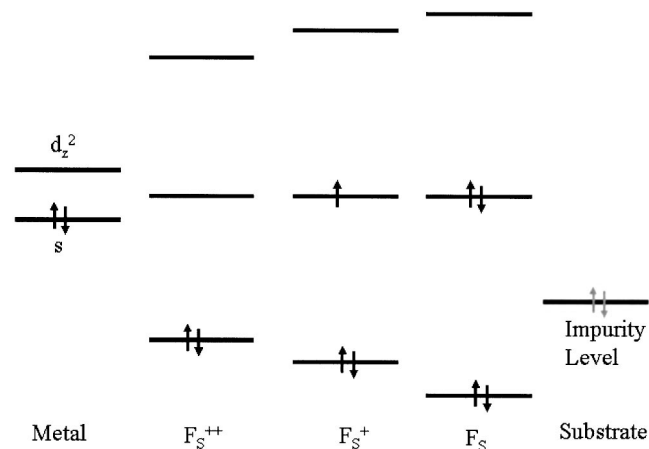


FIG. 3. Schematic representation of the molecular orbitals involved in the interaction between the metal and the support. Gray arrows stand for the electrons in the vacancy: two for  $F_s$ , one for  $F_s^+$ , and zero for  $F_s^{++}$ . Occupancy of the Ni atom levels in the figure correspond to a singlet coupling of the  $d^8$  configuration leaving the  $d_{z^2}$  orbital empty.

tributions from  $d_{z^2}+s$ ) while the other two belong to the metal (one mostly nonbonding  $d_{z^2}-s$  and a second antibonding  $d_{z^2}+s$  plus a small contribution from the surface). This is parallel to the ligand effect occurring in bulk transition metal oxides. A schematic representation of the orbital diagram can be found in Fig. 3.

When regular sites or neutral vacancies are considered, both the level from the surface and the  $d_{z^2}-s$  are doubly occupied, and the singlet to triplet transition depends mainly on the antibonding character of the  $d_{z^2}+s$  hybrid. This in turn, depends on the strength of the interaction which explains the relationship between the energy of that transition and the binding energy from the singlet state. For  $F_s^{++}$  only two electrons are involved in the bond which are mainly located in the most stable orbital of this set (mainly a substrate orbital) and are at least partially transferred to the surface as shown by the Mulliken population analysis, Table III. The low- to high-spin transition involves a electron jump from an orbital, mainly centered on the surface, to one concentrated on the metal. The stronger the bond the larger is the stabilization of the orbitals and the higher the energy for the singlet to triplet spin transition. For  $F_s^+$ , the high-spin state implies an excitation from the lowest to the highest orbital in Fig. 3 thus explaining that the low to high transition takes place at much higher energies.

This result implies that in case the bonding mechanism could be controlled, i.e., production of a surface with a low concentration of  $F_s^+$  centers, it would be possible to tune the low to high spin transition within a 1 eV interval. In fact, even restricting ourselves to the case of regular sites and neutral vacancies it is quite clear that modifying the nature of the support (MgO to CaO) or its quality (regular versus  $F_s$ ) one should be able to select a window of excitation energies for adsorbed atoms. This opens the possibility of switching from magnetic to nonmagnetic surface species in a controlled way. Here, it is possible to argue that the overall discussion, in particular the transition from nonmagnetic to magnetic surface species, is too dependent on the choice of

the exchange-correlation method. The straight line in Fig. 2 can shift up or down depending on the DFT method used, but it is unlikely that the qualitative trend will change. In fact, the GGA value for Ni on the regular MgO does not deviate substantially from the straight line reported in Fig. 2, provided the adsorption energy is computed with respect to the lowest GGA atomic state.<sup>33</sup>

To end this discussion we will consider a full monolayer adsorbed on the regular and reduced surface. In that case the description of low and high energy states is not straightforward since due to the formation of the metallic bond a continuum of electronic states is available. Therefore, it seems more appropriate to perform an analysis of the ground state properties by determining the presence and magnitude of localized magnetic moments on the adsorbed film. In fact, when a full Ni monolayer is considered, the magnetic moment is smaller when neutral vacancies are present, 0.88 versus  $0.76 \mu_B/\text{atom}$ , see Table III. This decrease in the magnetic moment indicates that vacancies are more effective than regular oxygen anions on the surface in quenching the magnetic moment. However, the low-dimensionality of the film results in a clear enhancement of the magnetic structure since the magnetic moment for the bulk Ni is only  $0.58 \mu_B$ . Due to the properties of isolated metal atoms interacting with the vacancy and the regular surface it is likely that the largest quenching with respect to the isolated atom corresponds to the atom adsorbed in the vacancy, whereas the largest spin density is likely to be found for metal adsorbed on regular sites.

#### IV. CONCLUSIONS

Previous works regarding the interaction of a single metal atom with a simple oxide surface have indicated that the determining contributions to the adhesion energy can be described in terms of charge transfer and covalent variations along a series of materials.<sup>24,52</sup> In the present work, we have explored the applicability of these rules to the two lowest electronic, nonmagnetic and magnetic, states of Ni adsorbed in regular anions and neutral or charged oxygen vacancies, of MgO. It has been shown that, at low coverage, the energy difference between the nonmagnetic and magnetic states is directly related to the strength of the interaction which in turn is determined by related with the physical nature of the adsorption site. The same physical mechanism applies when a full Ni adlayer is considered, although, in this case, this is only a second order effect since spin quenching is mainly driven by the direct metal-metal interaction.

According to the present findings it should be possible to prepare oxide surfaces where adsorbed Ni atoms exhibit a selected nonmagnetic or magnetic ground state. Moreover, the low- to high-spin state energetic difference could be controlled within 1 eV approximately. The present results have been obtained for Ni on MgO but it is likely that other metal atoms will exhibit the same behavior. Nevertheless, the possibility to prepare oxide surfaces with magnetic adatoms is not so straightforward because the sites which are less effective sites in magnetic quenching,  $F_s^{++}$ , are precisely those with the lowest adsorption energy and hence where adsorp-

tion is less likely to occur. In conclusion, the preparation of magnetic atoms adsorbed on oxide surfaces is strongly correlated with defect engineering.

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