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Fe phthalocyanine on Co(001): Influence of surface oxidation on structural and electronic properties

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The adsorption of FePc on Co(001) and $c(2 \times 2)$O/Co(001) was studied by means of density functional theory calculations, taking into account the long range van der Waals dispersion forces. Several high symmetry adsorption sites were analyzed, together with two possible orientations of the molecules. For the adsorption of FePc on the bare surface the on-top-of Co position, rotated by 45° relative to the substrate orientation, is most stable, whereas on the surface covered by an O adlayer the on-top-of O position is preferred. This has strong impact on the magnetic coupling but leaves the spin state of $S = 1$ unaltered. The total energies of the studied adsorption sites on the bare metal differ by at least 0.75 eV and are characterized by a strong hybridization of the carbon atoms in the peripheral benzenic rings with the Co atoms beneath. In the presence of the O adlayer the various sites are closer in energy, which turns out to be related to the screening of the ferromagnetic film by the oxygen atoms.

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I. INTRODUCTION

Paramagnetic molecules such as metal phthalocyanine (Pc) (see Fig. 1) and porphyrin are intensively discussed in view of their tunable magnetic properties in combination with metallic substrates and/or ligands [1–8]. For example NO ligands could be used to manipulate the coupling between Fe porphyrin molecules and an oxidized Co substrate [5] or it is proposed that for Fe porphyrin on graphene the spin state can be switched by stretching the graphene sheet [3]. Though magnetic measurement techniques such as x-ray absorption spectroscopy (XAS) reveal (element-specific) information of the magnetic properties of the system, they do not give much information about possible adsorption positions, about the electronic structure or the coupling mechanism [9,10]. Only very few studies offer simultaneously structural and magnetic data for these systems [11–15]. It has been shown that the coupling to the surface, i.e., the strength and the mechanism, can be tailored by ligands [5] and adlayers such as oxygen or graphene [9,16]. In this paper we focus on phthalocyanine molecules with an Fe center (FePc). These molecules have been studied in combination with a variety of substrates including investigations of charge transfer, orientation of the molecule on the substrate, and influence on magnetic properties. Furthermore the influence of the molecule on the reconstruction of the substrate has been investigated [17]. On simple metal surfaces such as fcc Ni(001) one adsorption site is far lower in energy than the others [1]. With increasing complexity of the surface structure, e.g., in the case of hexagonal metal surfaces, the energy landscape seems to become more complex but with smaller energy differences between minima and maxima [18]. Scanning tunneling microscopy (STM) measurements by Cheng *et al.* for FePc/Ag(111) show indications for different adsorption positions [19] which correspond to theoretical findings by Zhang *et al.* for the same molecule on Au(111) [18]. Different orientations of the molecule on the same adsorption site have been observed for FePc on (2×1)O/Cu(110) [20]. Although in many cases the spin state of FePc on metal substrates is reported to be $S = 1$ [21,22], it can be turned to $S = 0$ depending on the electronic coupling between molecule and substrate [20]. Phthalocyanine molecules with Fe center, which are studied in the present paper, couple ferromagnetically to Co(001), but the coupling turns into an antiferromagnetic one in the presence of an oxygen layer on the surface [9]. Previous density functional theory (DFT) calculations have shown that the change of the magnetic coupling is related to a change of the adsorption position from an on-top-of Co to an on-top-of O site if an O adlayer is included [9]. The present paper represents a full theoretical account of structural aspects, magnetism, and the electronic structure of this system.

Though there exist a number of theoretical investigations of the adsorption of FePc on metal substrates, they do not give a unique picture. The electronic structure and distance between molecule and substrate are very sensitive to the exchange correlation functional. The local density approximation (LDA) tends to overbind the molecule whereas the bonding is underestimated by gradient corrections (GGA) [18]. This underestimation can be compensated by the inclusion of van der Waals corrections. In this paper van der Waals corrections are taken into account by employing the semiempirical formulation of Grimme in combination with the GGA of Perdew, Burke, and Ernzerhof (PBE) [23,24].

Another issue is the description of the d electrons of the transition metal center. Using GGA or LDA only leads in the case of FePc to unphysical Fe d states close to the Fermi level, which contradicts experimental studies with photoemission spectroscopy [25]. To overcome this problem a Hubbard U term has been added to the Fe d states throughout this paper.

The focus of the paper is a detailed analysis of the structural and electronic properties of FePc molecules on Co(001) and $c(2 \times 2)$O/Co(001) taking into account different adsorption sites and moreover to investigate the energy barriers between the most stable adsorption sites which gives evidence whether the molecule is likely to stay in a local minimum or drops to the ground state. However, the adsorption position in experiment may also depend on growth conditions (temperature and flux rate), the coverage of the surface, and not least on the synthesis of the molecules [11]. For low growth temperatures or larger amounts of molecules not all molecules may reach the ground

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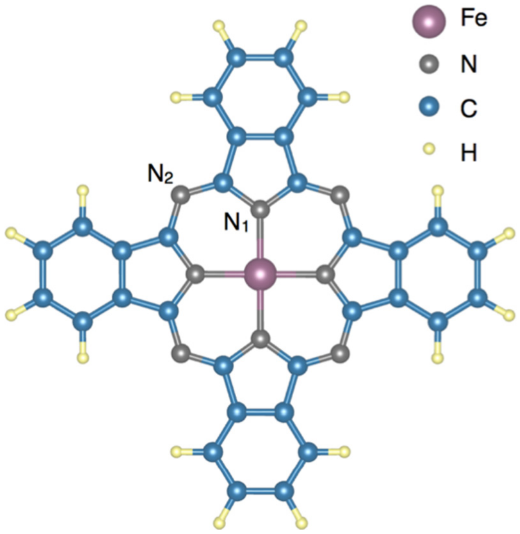

FIG. 1. (Color online) Sketch of an FePc molecule. The molecule contains two types of nitrogen atoms denoted N_1 and N_2, whereby the latter one has no direct bond to the Fe center.

state configuration, which is assumed to lead to changes in molecule surface interaction. The investigation of the same molecule on bare and oxidized Co(001) provides the opportunity to study the influence of the surface structure on the energy surface as well as on the electronic and magnetic structure.

The structural properties of FePc on different adsorption sites will be presented in Sec. III after a short overview of the computational methods (Sec. II). Related magnetic properties will be discussed in Sec. IV. A summary is given in Sec. V.

II. COMPUTATIONAL METHODS

The VASP [26] code and the projector augmented wave method [27] have been used to calculate the structural and electronic properties of an FePc molecule adsorbed on fcc Co(001). Investigations have been performed on the bare Co surface [Fig. 2 (a)] and in presence of 0.5 monolayer (ML) oxygen. In case of oxygen coverage in agreement with the experiment a $c(2\times2)$ reconstruction of the Co(001) surface was achieved, see Fig. 2(b) [28,29]. The PBE approach has been adopted for the exchange correlation functional. An effective Hubbard term (Dudarev's method [30]) of $U_{\text{eff}} = U - J = 3$ eV has been included for the 3d orbitals of the Fe center to open the gap between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital in the minority spin channel. No U value has been added to the Co 3d states because the substrate has in both cases metallic character, and the changes due to a Hubbard term are expected to have minor influence on the results. In order to incorporate the long-ranged dispersion forces in the molecular system, Grimme's 2nd method (D2) has been used [23].

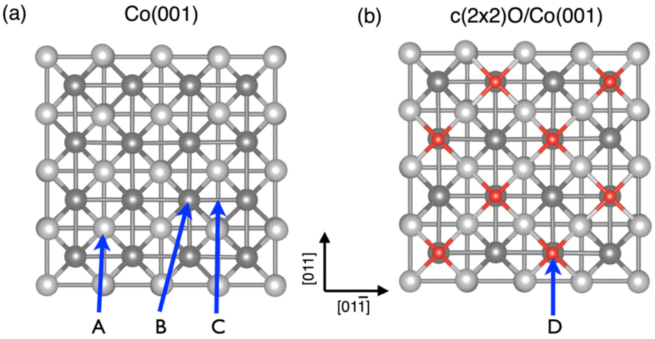

FIG. 2. (Color online) (a) Cleavage of the fcc Co surface (a) and the $c(2\times2)$ reconstructed oxidized surface (b). Capital letters denote centers of the investigated adsorption positions of the FePc molecule: Top of Co (A), hollow site (B), bridge (C), and top of O position (D). Adsorption positions A–C have also been studied in the case of the oxidized surface.

Co films with fcc structure are commonly grown on Cu(001) especially in the case of surface oxidation [31], therefore the Cu lattice constant (3.61 Å) has been used for the Co film in our calculations. The size of the super cell amounts to $(25.527\ \text{Å})^3$ and contains a 3 ML thick Co film and one FePc on top of the film. Except the bottom Co layer all atomic positions were relaxed until the forces are smaller than 0.02 eV/Å. The plane wave cutoff was 400 eV and a Γ-point-only k mesh has been used. For particular configurations calculations with a $3 \times 3 \times 3$ k-point mesh have been performed which give in principle the same results. The initial magnetic orientation between the Fe atom and the Co substrate has been chosen ferromagnetic in the case of the plain Co substrate and antiferromagnetic in the presence of the O layer, which is in line with previous findings for the magnetic exchange coupling in these systems [9].

III. STRUCTURAL PROPERTIES

To determine the adsorption geometry of FePc on Co(001) we have considered three different sites on the bare Co(001) surface: on-top-of Co (named A in Fig. 2), hollow (B), and the bridge (C) position, identified by the adsorption position of the Fe atom. In the on-top configuration, the Fe atom is located above an atom of the upper surface layer, in the bridge configuration, the Fe atom is directly bonded to two Co atoms, and in the hollow configuration, the Fe atom lies above a hollow site on the Co surface, which means that it is above a Co atom in the second surface layer. In case of the $c(2\times2)$ reconstructed oxygen covered surface, the on-top-of O position (D) was studied additionally. For each configuration, we have chosen two possible orientations of the molecule. Either the molecular axes that cross the atoms N_1-Fe-N_1 were oriented parallel to the $[01\bar{1}]$ and [011] azimuthal surface directions (Figs. 1 and 2) or, after an azimuthal rotation by 45°, the N_1-Fe-N_1 axes were oriented parallel to the [001] azimuthal surface directions (indicated as 45°). Note that these two orientations were the two considered starting configurations. The subsequent geometry relaxation gave several other orientations, as described below. The results obtained for the five lowest energy configurations are summarized in Table I.

A. FePc/Co(001)

In all investigated cases the molecule resulted to be chemisorbed on the surface, in agreement with a previous work considering metal-Pc molecules adsorbed on magnetic surfaces [21]. The total energies in the five cases vary by more

TABLE I. Energy difference (ΔE) and difference van der Waals contribution to the total energy (ΔE_{vdW}) for different adsorption sites on the plain and on the oxygen covered $c(2\times2)$ Co(001) surface. The total van der Waals energy for the ground state configurations amounts to -87.874 eV and -91.644 eV in the case of Co and O/Co, respectively. The vertical distances between the Fe atom and the closest Co($d_{\mathrm{Fe\text{-}Co}}$) or O($d_{\mathrm{Fe\text{-}O}}$) atoms from the substrate layer are provided together with the average vertical distance of the Fe atom from the surface.

	Without O					With O				
Position of Fe center	top of Co 45°	top of Co 10°	bridge site 10°	hollow site 0°	bridge site 45°	top of O 0°	top of O 35°	top of O 45°	top of Co 45°	top of Co 0°
Δ E (eV)	0.0	0.775	1.425	1.475	2.245	0.0	0.297	0.313	0.293	0.660
Δ E_{vdW} (eV)	0.0	0.101	0.103	0.239	0.213	0.0	0.057	0.241	0.224	0.440
$d_{Fe\text{-}Co}$ (Å)[a]	2.39	2.33	2.18	2.52	2.38	3.17	3.06	3.12	3.40	3.17
$d_{Fe\text{-}O}$ (Å)[a]						2.19	1.96	2.21	2.63	2.56
$d_{Fe\text{-}S}$ (Å)[b]	2.25	1.94	2.08	2.41	2.33	2.48	2.34	2.44	2.69	2.48

[a] Vertical distance of Fe from the closest Co or O atoms underneath.

[b] Average vertical distance of Fe from the Co (for FePc/Co) or O (for FePc/O/Co) film.

than 2 eV from the ground state to the bridge position with a rotation of 45°. The most energy favorable position is the top site rotated by 45°, with a distance of 2.39 Å between the Fe atom and the Co atom beneath. The structure is shown in Fig. 3(a). In this molecular orientation, the inner N atoms, or N_1, are above hollow positions on the Co substrate, while the outer N atoms, or N_2, are almost on top of Co atoms, at a distance of 2.10 Å. The distance between the Fe atom and the atoms of type N_1 is 1.97 Å, which differs by 0.04 Å from the value of 1.93 Å determined experimentally [32]. A slight vertical distortion affects the central part of the molecule: the Fe atom is lifted by about 0.28 Å and the N_1 atoms are lifted by about 0.35 Å with respect to the benzene rings of the molecule. This implies that it is mostly the N_2 atoms and the C atoms in the benzene rings that are responsible for the hybridization with the surface states. The role of the latter C and N atoms in the hybridization is also evident from the geometry relaxations initiated from the on-top position at 0°, which is the second lowest energy configuration and is shown in Fig. 3(b). In the resulting structure, the molecule has undergone a rotation of about 10°, and has a total energy 0.775 eV above the ground state. In the initial position at 0° the C atoms in the benzene rings are not located in any symmetric site above the substrate, while after the 10° rotation, some of these C atoms are now placed on top of Co atoms of the surface layer, at a distance of 2.06 Å. In the relaxed geometry, both types of N atoms lie almost on top of Co atoms, with average distances of 2.17 Å for the N_1 atoms and of 2.09 Å for the N_2 atoms. The upper Co layer undergoes a significant buckling. The Co atom right beneath the Fe atom is most affected and sinks 0.4 Å into the surface with respect to the average vertical position of the upper metal layer, as can be seen in the side view of Fig. 3(b). Due to the described surface deformation, the Fe-Co distance evaluated for the direct Fe-Co bonding is 2.33 Å, while the distance between the Fe atom and the average vertical position of the Co upper layer is only 1.94 Å. In previous works on Fe porphyrins, which have only one kind of N atom corresponding to the N_1 type, it had been observed that the N atoms play a major role in the molecule/surface hybridization in the case of magnetic surfaces like Co and Ni [1] as well as on nonmagnetic surfaces such as Cu [11]. Our analysis of the FePc chemisorption on Co(001) suggests a different mechanism of adsorption for phthalocyanines, in which it is mostly the outer N atoms (N_2), and the outer C atoms, that hybridize with the surface. The other sites reported in Table I, e.g., the relaxed bridge 10°, the hollow, and the bridge 45°, have significantly higher energies above the ground state, amounting to 1.425 eV, 1.475 eV, and 2.245 eV, respectively, and even higher energies were found for the other adsorption positions. In the bridge position with a rotation of 10° the molecule is closer to the neighboring surface atoms, as can be seen in Table I. Although the total energy largely varies depending on the adsorption position and orientation of the FePc molecule, the van der Waals contribution obtained from Grimme's second method changes only by 0.24 eV and plays a minor role for the bonding. Since previous works on metal phthalocyanine molecules on Co surfaces had focused on the bridge site [21,33,34], we have analyzed the local potential energy by moving the FePc along a straight line between the top 45° and the bridge 45° adsorption sites by steps of 0.2 Å in the $[01\bar{1}]$ direction. At each step, the in-plane position of the Fe atom was kept fixed, allowing all the other atoms of the

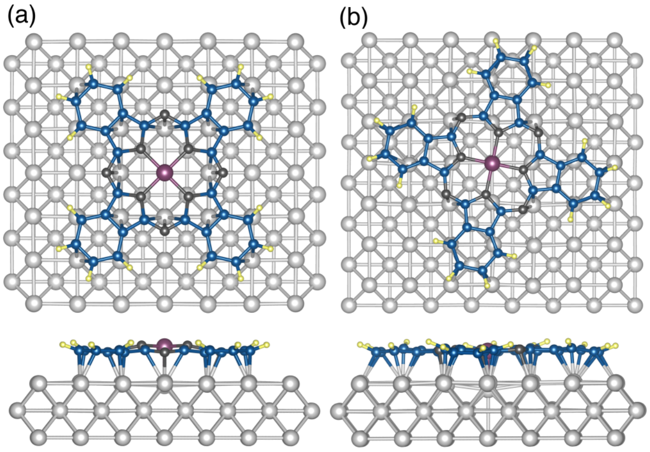

FIG. 3. (Color online) (a) FePc on Co(001) adsorbed on top of a Co surface atom at $\phi = 45°$. The Co atoms are given in light gray, C atoms are blue, N in dark gray, hydrogen in yellow, and Fe is marked by the purple sphere. In the lower panel a side view of the same configuration is shown. (b) FePc molecule on top position rotated by $\phi = 10°$ relative to the surface axes. Side view of the same configuration.

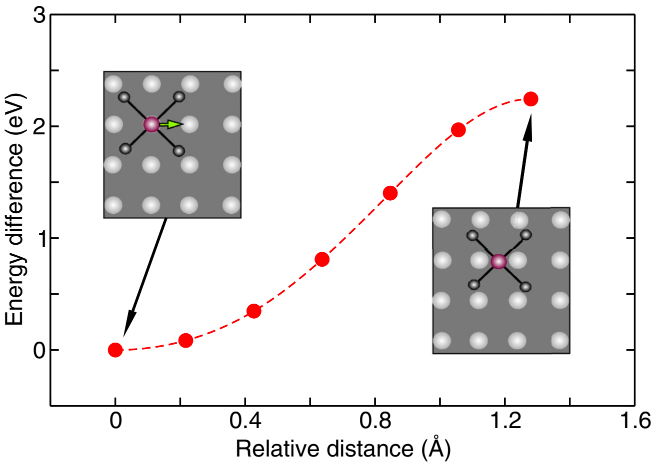

FIG. 4. (Color online) Energy difference curve of FePc/Co(001) for FePc moving from the bridge 45° to the top 45° configuration, by steps of 0.2 Å. The configuration in each of the intermediate steps was relaxed to give the lowest energy, and the relative energies are given as the difference with respect to the ground state energy (0.0 eV). The Fe atom position in each step is given as the relative distance with respect to the position of the Fe atom in the top 45° site. Energy equal to 0.0 eV and relative position equal to 0.0 Å correspond to the ground state. The insets mark the position of the molecule relative to the surface whereby only the Fe-N$_1$ core of the molecule is plotted.

molecule to relax. As in the previous calculations, also the two outer Co layers were relaxed. The total energy curve obtained is shown in Fig. 4, where the difference between the total energy of each relaxed step with respect to the ground state energy is shown. The graph shows that the total energy increases monotonically by moving from the ground state towards the bridge position (45°), and it gives no hints of a considerable energy barrier along this surface direction.

B. FePc/O/Co(001)

In the presence of O on the surface, the on-top-of-Co position is no longer the ground state of the FePc molecule. Instead the on-top-of-O position is lowest in energy, see Table I. This agrees with previous investigations of Fe porphyrin on $c(2 \times 2)$O/Co(001) [2]. The vertical distance between the Fe atom and the O atom beneath is 2.19 Å, which means the molecule is strongly chemically bonded to the surface. The average vertical distance between the Fe atom and the O adlayer on the Co(001) surface is slightly larger being 2.48 Å, because the distance of the O atoms on the surface is strongly modulated due to the presence of the molecule. The vertical position between O and Co atoms of the surface differs up to 0.5 Å. However, the Fe-O distances are slightly larger than the calculated value of 1.92 Å given in Ref. [2] for Fe porphyrin molecules on the same substrate. On the other hand the authors of Ref. [2] obtained a much larger O-Co distance (1.74 Å) compared to the present value of 0.62 Å which corresponds to the average vertical distance between all O and Co atoms of the surface layer. This may be related to the fact that the authors of Ref. [2] used a simplified model to describe the oxygen coverage of the surface and to the fact that the bonding between FePc and the Co substrate is somewhat weaker compared to Fe porphyrin. Due to the presence of the oxygen layer, the distance between the magnetic ions of the substrate and the Fe atom is larger compared to the previous case discussed in Sec. III A. For the ground state configuration we obtain an Fe-Co distance of 3.17 Å, which is about 0.5 Å larger than for FePc on Co(001), see Table I. Therefore, the bonding between molecule and substrate is expected to be weaker than without the O layer.

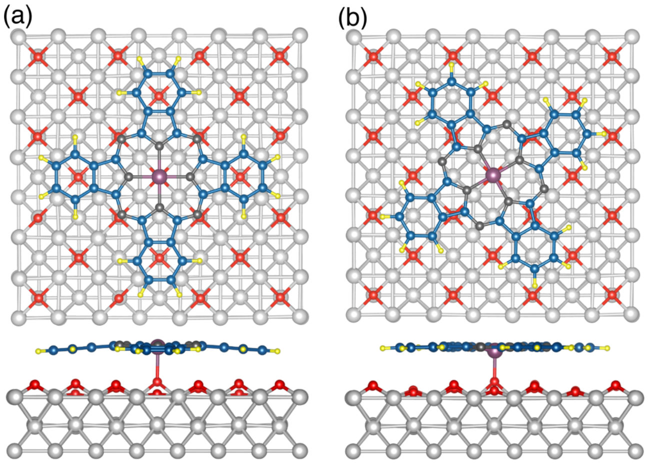

FIG. 5. (Color online) (a) FePc on $c(2\times2)$O/Co(001) adsorbed on the on-top-of-O position with $\phi = 0°$. Co atoms are given in light gray, small red spheres denote O atoms, C atoms are painted in blue, N in dark gray, hydrogen in yellow, and Fe is marked by the purple sphere. A side view of the same configuration is shown in the lower panel. (b) FePc molecule on top of O position rotated by $\phi = 35°$ relative to the substrate axis. Side view of the same configuration. Due to a strong Fe-O interaction the Fe atom moves slightly out of the molecular plane and the O atom under the Fe atom sticks out of the surface, which is obvious from the side view of the structure in the lower panel of (b).

In the ground state the outer benzene rings are almost centered around an O atom, see Fig. 5(a), whereby the O atom under the benzene ring has moved into the Co surface. The Fe-N$_1$ bonds point along the [001] and [010] direction, respectively, with the N$_1$ atoms sitting almost on top of hollow site positions. The distance between the transition metal center and the N$_1$ atoms amounts to 1.95 Å, which is slightly smaller than the value obtained for the molecule on the plain Co(001) substrate, cf. Sec. III A. However, this matches with the value obtained from calculations of the free FePc molecule [35], which indicates that the influence of the Co surface is smaller due to the screening of the O adlayer. Nitrogen atoms of type 2 are located on top of O atoms with a vertical distance of about 2.69 Å. This scenario is quite different from the observations on the bare Co(001) surface and from previous investigations of Fe porphyrin on O/Cu(001) [11], where the N atoms sit preferably on top of the transition metal atoms of the substrate. Another striking difference to the observations on the bare Co(001) substrate is that the binding energy surface is much flatter in the presence of an oxygen adlayer, i.e., the energy difference between different adsorption positions is smaller. The adsorption of the molecule on the on-top-of-O position with a 45° rotation where the Fe-N$_1$ bonds are oriented along the [011] and [01$\bar{1}$] direction is only 0.31 eV higher in energy than the ground state and the Fe-O distance remains mainly unchanged, see Table I. The same holds for the adsorption on top of Co (45°), see Table I, except that the Fe-O distance is about 8% larger compared to the ground state configuration. All other investigated adsorption positions have higher energies, e.g., on-top-of Co has 0.66 eV higher energy. The hollow site positions are even less favorable being more than 0.7 eV higher in energy than the ground state configuration. However, in contrast to the energy differences obtained for the molecule on the plain Co(001) substrate the energy surface is considerably flatter. This means that other than the on-top-of-O configuration may be partially occupied in experiment especially at higher temperatures and in the case when the oxidized surface is oversaturated with molecules.

In the experiment the molecules may land on other sites than the ground state adsorption site or on the proper site but with a rotation by some angle [19]. Depending on the growth conditions such as substrate temperature, flux rate, and pressure they may be trapped in local minima or be able to relax to the ground state. Here we discuss two scenarios between lowest energy configurations (see Table I): A rotation of the molecule on top of O (ground state) and a lateral movement between the top of O position (45°) and the top of Co position (45°), which are close in energy, cf. Table I. No significant energy barrier exists between the two 45° rotated positions, see Fig. 6. The energy of the bridgelike position ($d = 0.9$ Å) is between those of the two on-top adsorption sites (with 45° rotation) such that the molecule can easily move from the top of O position (45°) to the top of Co (45°) position. However, these adsorption positions are well above the ground state configuration. Since the hollow site position and the top of Co position with $\phi = 0°$ are even higher in energy, a movement of the molecule towards these sites is very unlikely. Another option to reach the ground state position would be a rotation on the on-top-of-O site. This rotation has been investigated in steps of 5°. In order to prevent the molecule from rotating back to $\phi = 0°$ the in-plane positions have been kept fixed for the calculations of structures with $0° < \phi < 45°$. The energy landscape of this rotation is depicted in Fig. 6. For small deviations from the 45° position the energy landscape is flat. However, a shallow minimum appears around $\phi = 35°$, see Fig. 6, which is only about 13 meV lower in energy than the top of O position (45°). Although the adsorption site is the same as in the ground state configuration, significant structural changes occur [see Fig. 5(b)] which entail changes in the magnetic structure, see also Sec. IV B. In contrast to the ground state configuration the distance between the Fe center and the O atom underneath is reduced to 1.96 Å whereby the O atom moves out of the surface causing a stretching of the O-Co bonds by up to 6%. The Fe atom moves slightly out of the molecular plane such that the average Fe-surface distance decreases to 2.34 Å, see Fig. 5(b). The typical umbrellalike shape of the molecule (see Fig. 5) with the slightly bended periphery disappears if the molecule is rotated to the $\phi = 35°$ position, cf. Fig. 5. Similar structural changes occur also for other angles, but only in the range of ϕ between 30° and 40° are these structural changes sufficiently significant to also have an impact on the magnetic properties. The remaining question is: What is the driving force which leads to the energy barrier depicted in Fig. 6? For smaller angles ϕ up to 25° the changes in the total energy are almost identical to the changes in the van der Waals contribution, whereas for larger angles the changes in the total energy cannot be explained by changes in the dipole-dipole interaction, because the variation in the total energy is smaller than the changes due to the van der Waals interaction. Without van der Waals forces the minimum would occur at $\phi = 30°$ instead of 0°, see Fig. 6. Here the driving force is the magnetic interaction which is in large part compensated by the van der Waals forces. In this region the Fe-Co and Fe-O distances are decreased to 3.06 and 2.19 Å, respectively. This leads to an increase of the magnetic moment of the Fe atom by about 0.57 μ_B for $30° < \phi < 40°$ (see next section), cf. Fig. 6.

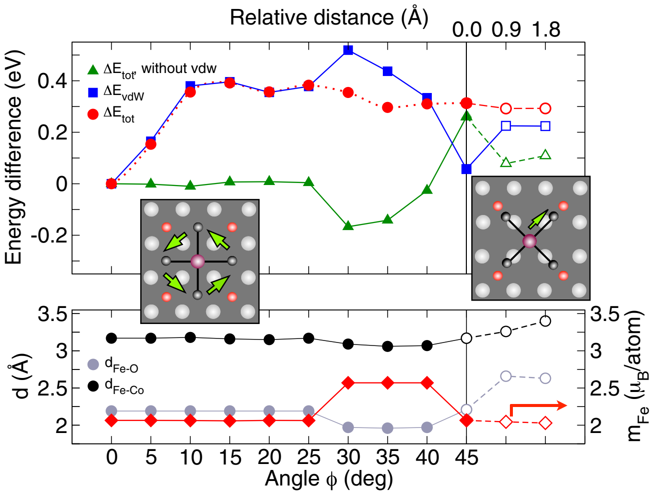

FIG. 6. (Color online) (a) Energy differences of FePc on O/Co(001) adsorbed on the top of O position (filled symbols) depending on the relative orientation to the substrate denoted by the angle ϕ. Zero energy refers to the ground state configuration with $\phi = 0°$. Open symbols mark the energy differences which occur if the molecule moves from the top of O (45°) to the on-top-of-Co (45°) position as sketched by the inset on the right side. Circles (triangles) denote the difference in total energy with (without) the van der Waals correction. The variation of the van der Waals contribution relative to the one of the ground state is marked by squares. The lines are given as a guide to the eyes. Except for $\phi = 0°$ and 45° the in-plane coordinates of the molecule have not been relaxed, see text. (b) The nearest Fe-Co (gray) and Fe-O (black) distances for different angles (filled symbols) and on the path from the top of O 45° to the top of Co 45° position (open symbols). The diamonds mark the corresponding magnetic moment of the Fe atom.

IV. ELECTRONIC PROPERTIES AND SPIN MOMENT

In this section the focus is on the magnetic and electronic structure of the transition metal atom at the center of the Pc molecule. The magnetic properties of the ring and the surface are discussed in Ref. [9]. Only some moments which are related to the present discussion will be given in this paper.

The orbital projected density of states provided by the VASP code is related to the global coordinate system. To obtain

TABLE II. Magnetic moments of the FePc molecule on Co(001) and $c(2 \times 2)$O/Co(001) for the different adsorption sites. Here $m_{\rm Fe}$ denotes the projected magnetic moment on the Fe center, $m_{\rm ring}$ is the magnetic moment of the metal free molecular ring, and $m_{\rm tot}$ corresponds to the resulting moment on the FePc molecule.

Position	$m_{\rm Fe}$ ($\mu_{\rm B}$)	$m_{\rm ring}$ ($\mu_{\rm B}$)	$m_{\rm tot}$ ($\mu_{\rm B}$)
		Co(001)	
top of Co 45°	2.01	−0.37	1.64
top of Co 0°	1.98	−0.24	1.74
bridge 10°	1.95	−0.20	1.75
hollow 0°	2.03	−0.42	1.61
bridge 45°	2.02	−0.20	1.82
		O/Co(001)	
top of O 0°	−2.06	0.22	−1.84
top of O 35°	−2.57	0.11	−2.46
top of O 45°	−2.06	0.18	−1.89
top of Co 45°	−2.03	0.18	−1.84
top of Co 0°	−2.03	0.16	−1.87

the proper projection for $\phi \neq 0°$ the density of states of the molecule has been lined up to the local Cartesian coordinate system following Refs. [36] and [37].

A. FePc/Co(001)

The projected magnetic moment of the ground state of FePc on Co(001) is about $2\mu_B$, and the molecule is in an intermediate spin configuration with $S = 1$. Table II reports the computed magnetic moments of the Fe atom and in the rest of the molecule, denoted here as *ring*, for the different adsorption sites discussed. As can be seen in Table II, in the top position 45°, part of the magnetic moment is distributed in the C and N atoms, resulting in a total moment of the ring of $-0.37\mu_B$. This corresponds to about 20% of the moment of the Fe atom (with opposite sign), and the total moment on the molecule is 1.64 μ_B. Similar results are obtained also for the other adsorption sites studied with C and N moments between 20% (hollow site) to about 10% of the Fe atom, all with opposite sign to the Fe moment. The magnetic moment in the central Fe atom was about 2 μ_B also in the other four configurations considered (see Table II). Although in the ground state and in the other adsorption sites the total moment of the adsorbed molecule is lower than 2 μ_B as shown in Table II, we do not observe the strong decrease reported by Mugarza *et al.* for the adsorption of FePc on Ag(100), where they obtained a total magnetic moment of 1 μ_B for the molecule [38]. In their case about 50% of the moment was distributed among the C and N atoms in the ring when FePc was adsorbed on Ag(100). The projected d density of states (DOS) for the five lower energy structures are illustrated in Figs. 7 and 8. In the ground state as well as in the hollow and in the bridge (45°) sites, we have obtained a $(\mathrm{d}_{xy})^2$ $(\mathrm{d}_{z^2})^2$ $(\mathrm{d}_\pi)^2$ electronic configuration, which has also been proposed for the ground state of the molecule in the gas phase. In the top position rotated by 10° and in the bridge with the same rotation, instead, the d_{xy} are not fully occupied and small d_{xy} density is visible in the unoccupied part of the DOS at the same energy as the $\mathrm{d}_{x^2-y^2}$. It is also evident that a strong hybridization with the substrate affects both the d_{z^2} and the d_π electronic states especially in the top position (10°) and in

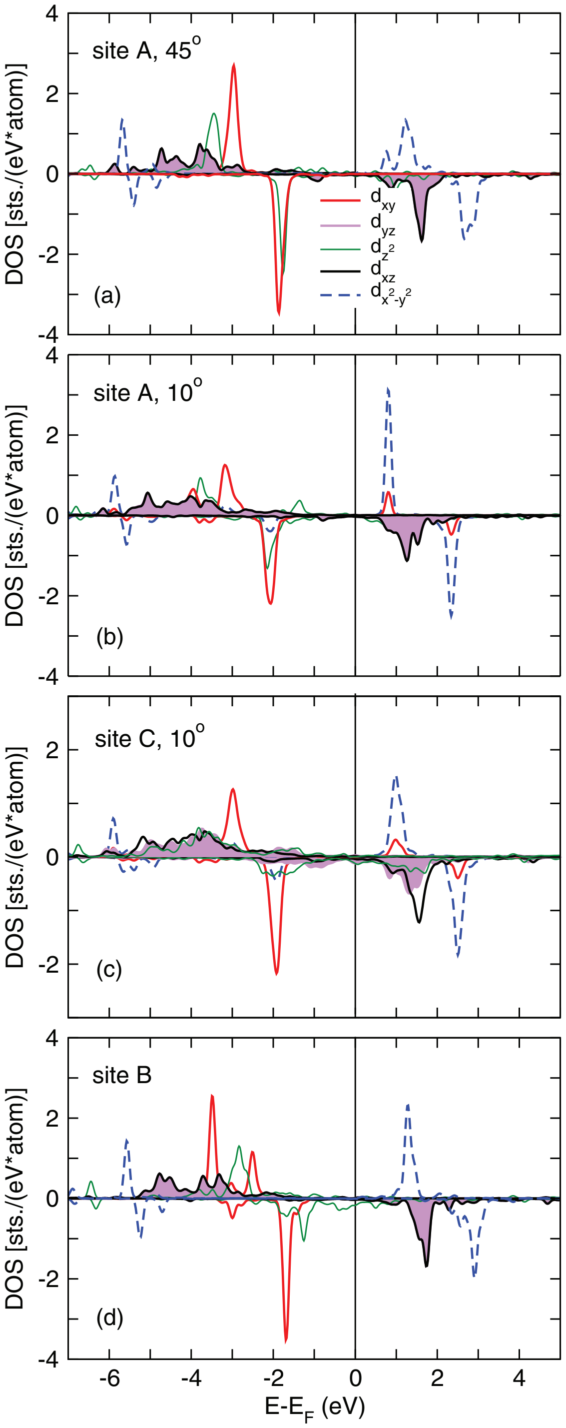

FIG. 7. (Color online) Projected density of states (DOS) of the Fe d orbitals in the FePc/Co(001) for different adsorption sites. The ground state configuration with the Fe atom sitting on top of Co (45°) (site A) is given in (a). Furthermore, the DOS for metastable solutions with Fe on top of Co rotated by 10° (b), on the hollow site (c), and the bridge site with $\phi = 45°$Fe (d) are shown. The filled areas denote d_{yz} states which are degenerated with the d_{xz} states (black lines) as long as the molecule has D_{4h} symmetry.

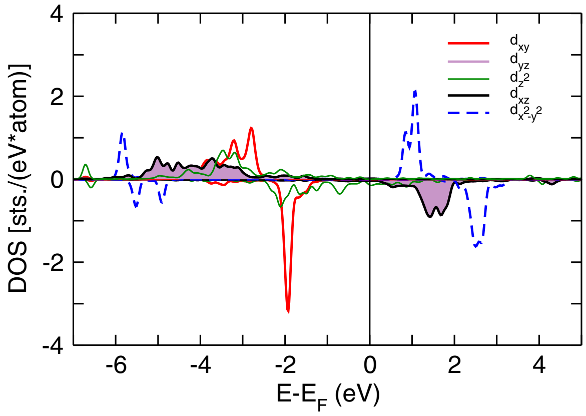

FIG. 8. (Color online) Projected density of states (DOS) of the Fe d orbitals in the FePc/Co(001) for the Fe atom sitting on the bridge adsorption site rotated by 45° (site C 45°, cf. Fig. 2). The filled areas denote d_{yz} states which are degenerated with the d_{xz} states (black lines) as long as the molecule has D_{4h} symmetry.

the bridge position (10°), where these levels are widely spread in energy. A reason could be the reduced symmetry of the system in these configurations. In the case of bridge position with a rotation of 10° the d_π orbitals are also split apart, due to reduced symmetry.

B. FePc/O/Co(001)

The spin state remains unchanged, $S = 1$, in the presence of O on the Co surface. Only the coupling to the Co substrate changes, because of the different texture of the surface. The projected magnetic moment on the Fe atom is $-2.06\mu_B$, see Table II. This means the FePc couples antiferromagnetically to the Co film and the coupling strength is reduced compared to that of the molecule on the plain Co(001) substrate. This antiferromagnetic coupling is caused by the super exchange between the Fe and Co atom via the oxygen; for details we refer to Ref. [9]. Not only does the Fe atom at the center carry a magnetic moment, but the C and N atoms of the ring also contribute. Since the magnetic moments of the atoms in the ring are antiparallel oriented to the Fe moment, the actual magnetic moment of the molecule is about 1.84 μ_B (top of O), see Table II. The reduction of the total magnetic moment of the molecule by the atoms of the periphery is comparably small.

As in the previous case on the bare Co substrate, small spin moments of about 0.02 μ_B occur at the N_1 atoms. On the $c(2 \times 2)$ reconstructed O/Co(001) surface the O atoms also carry a magnetic moment. The average magnetic moment of the O atoms for the ground state configuration is about 0.18 μ_B. However, the size varies with the positions relative to the molecule on top.

For adsorption sites with $\phi = 0°$ or 45° on the $c(2 \times 2)$ reconstructed O/Co(001) substrate the electronic structure corresponds to $(d_{xy})^2$ $(d_{z^2})^1$ $(d_\pi)^3$, see Fig. 9, which is, according to XAS experiments by Kroll *et al.*, one possible configuration for FePc [22]. Although the electronic configuration does not depend on the adsorption site, significant changes in the Fe d density of states occur if the molecule is adsorbed at the local

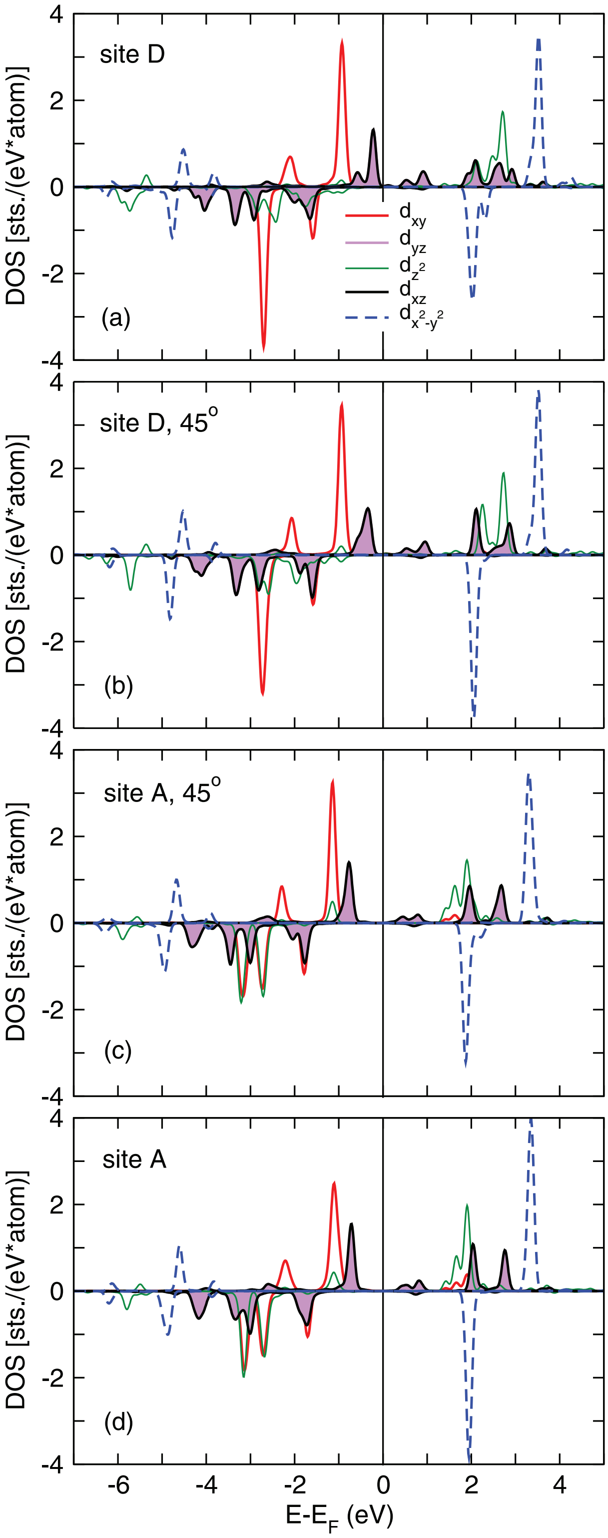

FIG. 9. (Color online) Projected density of states (DOS) of the Fe d orbitals in the FePc/O/Co(001) for different adsorption sites. The ground state configuration with the Fe atom sitting on top of the O (site D) is given in (a). Furthermore, the DOS for metastable solutions with Fe on top of O rotated by 45° [(b)] and Fe on top of Co [(c) and (d)] are shown. The filled areas denote d_{yz} states which are degenerated with the d_{xz} states (black lines) as long as the molecule has D_{4h} symmetry.

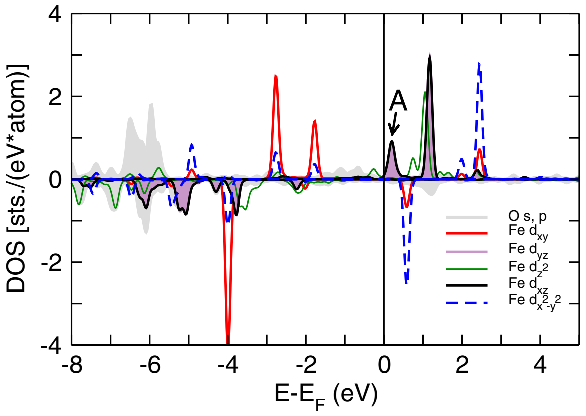

FIG. 10. (Color online) Projected density of states (DOS) of the Fe d orbitals of FePc on O/Co(001) for the molecule adsorbed on the top of O site rotated by $\phi = 35^\circ$. The gray shaded areas denote the DOS of the O atom directly under the Fe atom. The d_π states marked by A were occupied in the ground state and crossed the Fermi level due to strong Fe-O bonding. The d_π states (filled area and black line) remain degenerated.

minimum position (top of O with $\phi = 35^\circ$). The shortening of the distance between the Fe atom and the O atom beneath compared to the ground state configuration is accompanied by a small charge transfer from Fe to O which leads to an increase of the magnetic moment of the Fe atom by 0.5 μ_B, whereas the O moment is almost quenched (0.07μ_B), see Table II. This manifests itself in a shift of the previously occupied d_π peak (named A in Fig. 10) across the Fermi level to the unoccupied part of the density of states. A similar enhancement has been observed by Hu and Wu for FePc on O/Cu(110) [39]. They also report an increase of the Fe moment by about 0.4 μ_B and a short Fe-O bond length of 1.95 Å.

The magnetic moment of the Fe atom is increased on the $\phi = 35^\circ$ position and the magnetic moment of the C and N atoms is smaller compared to all other cases, although the magnetic moments of the N_1 which are directly bonded to the Fe atom are increased to 0.025 μ_B (0.019 μ_B for the ground state). However, the increase of the total magnetic moment for the FePc molecule adsorbed on-top-of O position with an angle ϕ between 30° and 40° is not tantamount with the high-spin state and leads only to small changes in the electronic structure. The situation is similar to the scenario observed for Fe porphyrin on O/Cu(001) when a Cl ligand is attached to the Fe center [11]. Here the O atom which sticks out of the surface acts like a ligand. Furthermore, the occupied Fe d states with out-of-plane components are broadened and shifted to lower energies due to strong hybridization with the *s* and *p* states of the oxygen atom underneath shown as the gray shaded area in Fig. 10. A significant amount of d_{z^2} and d_π DOS appears between −6 and −8 eV below the Fermi level and not between −2 and −4 eV as in the ground state, cf. Figs. 9(a) and 10. However, in contrast to the observations on the plain Co(001) substrate deviations from high symmetry positions or rotations do not break the symmetry of the molecule. This is related to the larger adsorption distance and the weaker bonding to the surface in the presence of the O layer.

V. CONCLUSIONS

FePc and other phthalocyanine molecules with transition metal center have been studied in the literature on a variety of different substrates. However, in most studies only one type of substrate was taken into account, i.e., ferromagnetic, nonmagnetic, oxidized, etc. In order to reveal the influence of the nature of the substrate on the magnetic, electronic, and structural properties of phthalocyanine molecules in more detail we have investigated FePc on Co(001) with and without an oxygen adlayer as an example. We have performed extensive DFT calculations including van der Waals interactions and a Hubbard-U term for the localized d electrons of Fe. The investigations have shown that the FePc molecule behaves quite differently on the two surfaces. In the case of Co(001) the interaction with the ferromagnetic substrate is strong and the benzenic rings are important for the bonding of the molecule. The $c(2\times2)$ reconstructed O layer screens the surface, and the coupling between Co and FePc becomes significantly smaller in this case. This leads to a larger bonding distance between molecule and substrate. The ground state position changes from the on-top-of-Co to on-top-of-O site, and the coupling to the Co surface is mainly via the O atom beneath the Fe center of the molecule. The preference of the O adsorption site has also been observed on other substrates such as O/Cu(110).

The present calculations show that the O adlayer not only has influence on the ground state position but changes the whole energy surface. On the bare ferromagnet one adsorption site is clearly preferred, being several eV lower in energy than the others which agrees with previous findings on Ni substrates. In contrast to that the energy differences become significantly smaller on the O covered film, lying within 0.3 eV for most adsorption sites. This is in line with results from the literature for nonmagnetic and oxidized substrates. Without van der Waals interaction the energy differences are even smaller.

Furthermore, it turned out that van der Waals interactions play an important role for the determination of energy barriers. The ground state top-of-O configuration with $\phi = 0^\circ$ is stabilized by van der Waals forces. Without the van der Waals corrections the ground state configuration would be close to $\phi = 30^\circ$ due to magnetic interaction. Even though Grimme's second method may slightly overestimate the effect, it reveals a clear trend.

Though adsorption positions as well as the coupling strength and mechanism strongly depend on the structure of the surface, the spin state of the molecule does not. In all cases it remained $S = 1$. However, on the oxidized substrate the molecule could be trapped in a local minimum position, i.e., rotated on the ground state adsorption site, the Fe moment increases by approximately 0.5 μ_B, and the bond between the Fe atom and the O beneath shrinks to 1.95 Å. A similar effect is known from FePc on O/Cu(110).

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