PHYSICAL REVIEW B **70**, 165405 (2004)

Density functional study of CO on Rh(111)

Lukas Köhler and Georg Kresse
Institut für Materialphysik and Center for Computational Materials Science, Universität Wien, A-1090 Wien, Austria

(Received 18 December 2003; revised manuscript received 7 April 2004; published 11 October 2004)

We present detailed density functional calculations for CO on Rh(111). At low coverage, the applied semilocal functionals clearly favor CO adsorption in the hollow site. This is in disagreement with experimental studies which all point towards atop adsorption at low coverage. The experimental assignment is confirmed by theoretical calculations of the vibrational frequencies and core level shifts at various coverages, ranging from $1/9$ to $3/4$ $[(2\times2)\text{-}3\text{CO}]$ monolayer CO. For atop adsorption the calculated vibrational frequencies and the Rh surface core level shifts are indeed found to agree very well with experiment. To understand these controversial results, a molecular GGA+U method is applied, which allows one to shift the CO $2\pi^*$ orbital towards the vacuum level. This reduces the binding energy in the hollow site and brings the theoretical site preference in agreement with experiment. It is investigated how this molecular GGA+U method influences the vibrational properties and the surface core level shifts. Furthermore, details on the molecular GGA+U method are presented.

DOI: 10.1103/PhysRevB.70.165405 PACS number(s): 68.43.Bc, 68.43.Fg

I. INTRODUCTION

Investigations about the adsorption of carbon monoxide on metal surfaces are prototypical in surface science, and the first studies on this subject date back at least 30 years. Insofar it is remarkable that only very recently the realization has emerged that state of the art density functional theory and experiments disagree on the stable adsorption site for CO on Pt(111).[1] Whereas experiments indicate that CO adsorbs on the top site at low coverage on the Pt(111) surface, theoretical studies show that the hollow site is preferred over the top site. Recent work explains this discrepancy by the observation that local and semilocal functionals overestimate the interaction of the lowest unoccupied molecular-orbital (LUMO) of CO with the metal substrate, in turn favoring the wrong site.[2,3]

A very similar situation is found for the adsorption of CO on the Rh(111) substrate. At high coverage theory and experiment seem to agree. A (2×2)-3CO structure is found at a coverage of 0.75 monolayer (ML) CO, with the experimental data pointing towards two CO molecules in hollow sites and one CO molecule at a top site.[4] But at low coverage, experimental and theoretical studies predict, as for Pt(111), different adsorption sites: the experimental studies indicate that CO adsorbs at the top site,[4] whereas the theoretical DFT studies show that the hollow site is *energetically* preferred.[5–7]

The preferred adsorption structures were and are subject of theoretical studies. Curulla *et al.* reported calculations on the vibrational frequencies of CO at a coverage of 0.75 ML using a *cluster* model for the Rh(111) substrate.[8] They calculated stretching frequencies of 2060, 1862, and 1795 cm^{-1}, which are indeed very close to the experimental ones at 2070, 1861, and 1795 cm^{-1} measured using high-resolution electron energy loss spectroscopy (HREELS).[9] This unequivocally proves the validity of the previously suggested high coverage structure.[4] The high frequency mode originates from the CO molecules adsorbed at the top sites, while the two lower frequencies were assigned to CO molecules in hcp and fcc hollow sites and correspond to the in-phase and out-of-phase normal modes. At low coverage the vibrational frequencies predicted from theory are in agreement with experiment only if CO is assumed to adsorb on top of Rh atoms (see below).

A density functional study on the Rh-3*d* and C-1*s* core-level shifts was performed by Birgersson *et al.* by means of pseudopotential density functional methods.[6] They found good agreement between the calculated and the experimental high-resolution core-level photoemission results,[10] again assuming on top adsorption at low coverage and the (2×2)-3CO structure at high coverage. For 0.25 ML and $1/3$ ML CO coverage and atop adsorption, two inequivalent Rh atoms exist in the surface layer and therefore two different binding energies are observed. One surface core-level shift (SCLS) is almost identical to that of the clean surface (-460 meV), whereas the SCLS for the Rh atom directly below the CO molecule (Rh_{OT}) was determined experimentally to be 270 meV and theoretically to be 290-240 meV (0.25 and $1/3$ ML). For high coverage $[(2\times2)\text{-}3\text{CO}]$, there are again two inequivalent Rh atoms in the first layer, one Rh atom located directly below the CO molecule (Rh_{OT}) and three Rh atoms coordinated to CO molecules in the threefold-hollow sites ($\text{Rh}_{3\text{F}}$). The experimental Rh_{OT} SCLS was determined as 240 meV, and is therefore slightly smaller than at low coverages, whereas the experimental $\text{Rh}_{3\text{F}}$ SCLS is -160 meV. The corresponding calculated values are 260 and -220 meV, in fair agreement with experiment.

The aim of the present study is twofold. First, we will report calculated vibrational frequencies and core-level shifts for different adsorption structures of CO on Rh(111). The core-level shifts of the present work have been obtained using the projector augmented-wave method with appropriate core exited potentials generated in the course of the *ab initio* calculations.[11] The present approach neglects the relaxation of other core electrons and requires some additional confirmation. To validate the new approach, we will therefore compare our present results with the previous theoretical calculations of Birgersson *et al.*[6] and with results obtained using "conventional" core excited PAW potentials (see Sec. II C).

Vibrational frequencies for CO on Rh(111) using the slab approach have not been presented before, and they serve as an additional confirmation that CO adsorbs at the top site at low coverage. We will show that the experimental core-level shifts and vibrational frequencies point unequivocally towards an adsorption of CO at the top site at low coverage, whereas the generalized gradient approximation (GGA) clearly favors the hollow site. In a final step, the molecular GGA+U method, suggested in previous work,[3] will be applied to CO on Rh(111). As for Pt(111), the proper low coverage adsorption site can be obtained, by shifting the CO $2\pi^*$ LUMO towards the vacuum level. We will also report the vibrational frequencies and surface core-level shifts within the GGA+U method.

The outline of this article is as follows. In Sec. II the theoretical and computational background of the present density functional study is described. Section II B briefly describes the calculation of the vibrational frequencies. A short definition of the core-level binding energy and the surface core-level shift is presented in Sec. II C. The molecular GGA+U method is presented in Sec. II D. Our results are detailed in Sec. III. The resolved geometries can be found in Sec. III A, the vibrational frequencies in Sec. III B, and the surface core-level shifts are discussed in Sec. III C.

II. THEORY

A. *Ab initio* calculations

The present first-principles calculations are based on density-functional theory (see, e.g., Refs. 12 and 13) and employ a plane wave basis set.[14,15] To determine the electronic ground state the Vienna ab-initio simulation package (VASP)[16,17] is used. In the present calculations, the interaction between the ions and valence electrons is described by the projector augmented wave (PAW)[18] method in the implementation of Kresse and Joubert.[19]

The surfaces are described by six layer thick slabs. The first three layers are fixed whereas the top three layers are allowed to relax (asymmetric setup). A plane wave cutoff of 400 eV was chosen for the present calculations. At this plane wave energy cutoff the relative energies are converged to a few meV. The generalized gradient approximation (GGA) according to Perdew and Wang[20] was used throughout this work. For all surface calculations grids corresponding to $12\times12\times1$ k points in the primitive surface cell were used. With the present setup the lattice constant of Rh is found to be 3.849 Å in good agreement with experiment and previous calculations.[5,6]

B. Vibrational spectrum

The vibrational spectra of the CO molecules were determined by displacing each C and O atom in six directions $\pm\Delta\hat{x}$, $\pm\Delta\hat{y}$, and $\pm\Delta\hat{z}$, where Δ was chosen to be 0.02 Å and $\hat{x}$, $\hat{y}$, and $\hat{z}$ are unit Cartesian vectors. From the induced forces the interatomic force constants can be deduced, and the resulting mass weighted force constant matrix was diagonalized. This yields the eigenmodes and eigenfrequencies of the adsorbed CO ad layer. The substrate was assumed to be frozen, which is an appropriate approximation, since the mass of the Rh atoms is about seven times larger than that of the C and O atoms. To estimate the error of this approximation we performed additional calculations were we allowed the first and second Rh layer to move as well. For atop adsorption we obtained metal-C frequencies that are about 50 cm^{-1} higher than in the frozen-substrate approximation. The changes in the metal-C frequencies for adsorption in bridge and hollow sites are below 13 cm^{-1}. The C-O stretching frequency is not changed significantly for all adsorption sites.

C. Core-level binding energy and surface core-level shifts

The energy which is necessary to remove a core electron from an atom is called core-level binding energy. Experimentally the electrons are excited by x-ray photons, and usually the binding energies are specified relative to the Fermi energy which is determined in the same experiment by exciting electrons at the Fermi edge.

In density functional theory, the binding energy of core electrons E_{CL} is calculated as the energy difference between two separate calculations.[21] The first calculation is a standard density functional calculation in which the number of core electrons corresponds to the unexcited ground state $[E(n_c)]$. In the second calculation one electron is removed from the core of one particular atom and added to the valence or conduction band $[E(n_c-1)]$. The energy difference is a measure for the experimentally determined core-level binding energy

$$E_{CL} = E(n_c - 1) - E(n_c). \tag{1}$$

This approximation assumes that the core hole remains entirely localized at the excited atom, which is usually a reasonable approximation. At the surface of a solid, atoms have a different local environment causing a shift of the core-level binding energy. The difference between these two core-level binding energies is called the surface core-level shift (SCLS)[21]

$$\begin{aligned} E_{\mathrm{SCLS}} = {} & [E_{\mathrm{surface}}(n_c - 1) - E_{\mathrm{surface}}(n_c)] \\ & - [E_{\mathrm{bulk}}(n_c - 1) - E_{\mathrm{bulk}}(n_c)]. \end{aligned} \tag{2}$$

Core electron binding energies can be calculated in the initial state approximation or the final state approximation. In the initial state approximation the core electron is removed but no change of the potential (e.g., by relaxing other electrons) is allowed. Electronic screening is therefore entirely neglected. The core electron binding energy in the initial state approximation can be calculated directly from the Kohn-Sham eigenvalues of the core state of interest ϵ_C and the Fermi level ϵ_F:[21]

$$E_{CL}^{\mathrm{initial}} = \epsilon_C - \epsilon_F. \tag{3}$$

In the final state approximation the electrons are allowed to relax after the core electron has been removed, so that the acquired localized hole is screened. Since the valence electrons screen the localized core hole rapidly in metals (sudden approximation), the core electron binding energy shifts between the bulk and the surface are expected to agree well with experiment in the final state approximation.

The core-level binding energies were calculated in the initial state and final state approximation using a modified projector-augmented wave method. For the initial state calculations, the Kohn-Sham equation is solved inside the PAW sphere for core electrons, after self-consistency with frozen core electrons has been attained. For the final state calculations, a single core electron is excited from the core to the valence, by generating the corresponding core excited ionic PAW potential in the course of the ab initio calculations. Screening by the core electrons is not taken into account (i.e., the other core electrons are kept frozen in the configuration for which the PAW potential was generated). Screening by the valence electrons is included, however. It is emphasized that this approach cannot yield absolute values for the core level binding energies, but our tests for a variety of systems indicate that the calculated core level binding energy *shifts* (differences in the binding energies) can be determined with an accuracy of about 20–50 meV. This correlates with the observation that core electron binding energies of one kind of atom in different environments are not sensitive to the precise configuration of the other core electrons, which is underlined by the success of the $Z+1$ approximation, in which the core hole is modeled by increasing the nuclear charge of the core ionized atom by one and adding an extra valence electron.[22] A detailed account of the present PAW method will be published at a later point.[11]

To validate the present approach, core level shifts are also determined using "conventional" core excited ionic PAW potentials. In this case, one electron is excited from the core to the valence during the generation of the PAW potential, and the selfconsistent calculations are performed with one surface or bulk atom replaced by this core excited ionic PAW potential. This is precisely the procedure adopted in Ref. 6 for the calculation of core-level binding energies for CO on Rh(111), and it includes (at least partially) core relaxation effects. The method is a routine practice for calculating core level shifts within the pseudopotential method (for an ample discussion of this method we refer to Ref. 6).

D. Molecular GGA+U method

The molecular GGA+U method has been applied in one previous work to obtain the proper adsorption site for CO on Pt(111).[3] It is an empirical approach that shifts the CO $2\pi^*$ single electron energies towards the vacuum level. The modified density functional is given by

$$E_{\mathrm{GGA+U}} = E_{\mathrm{GGA}} + \frac{\mathrm{U}}{2}\sum_{\sigma=1}^{2}\sum_{i=1}^{2}(\rho_i^\sigma - \rho_i^\sigma\rho_i^\sigma), \qquad (4)$$

where E_{GGA} and $E_{\mathrm{GGA+U}}$ are the conventional and modified density functionals, σ is an index for the spin, and ρ_i^σ are the occupancies of the two $2\pi^*$ orbitals for the up and down spin. They are determined by defining two projection operators, which are one for the two single electron LUMO orbitals of the free CO molecule and zero for all other CO one electron states. In the present work the projection operators are operating inside the carbon and oxygen PAW spheres only. The occupancies ρ_i^σ are determined by summing the quantity

$$\rho^i(\Psi) = \sum_{n,lm}\langle\Psi|\tilde{p}_{n,lm}\rangle\alpha^i_{n,lm}\alpha^i_{n,lm}\langle\tilde{p}_{n,lm}|\Psi\rangle$$

over all occupied single electron orbitals Ψ of the slab with spin σ. Here, $\tilde{p}_{n,lm}$ are the PAW projector functions for the atom n and the angular and magnetic quantum numbers lm as defined in Ref. 19, and $\alpha^i_{n,lm}$ are real coefficients which need to be chosen such that ρ^i is one for a single electron wave function corresponding to one particular free CO $2\pi^*$ orbital and zero for all other CO orbitals. In the present study, the CO molecule is always oriented exactly parallel to the $\hat{z}$ axis, which implies that we can distinguish between a $2\pi^*$ orbital oriented in the $\hat{x}$ direction $(i \rightarrow 2\pi_x^*)$ and a second $2\pi^*$ orbital oriented in the $\hat{y}$ direction. The coefficients α are additionally only nonzero for the carbon and oxygen atoms. This implies that we need to determine only two independent parameters $\alpha^{2\pi_x^*}_{\mathrm{carbon},p_x}$ and $\alpha^{2\pi_x^*}_{\mathrm{oxygen},p_x}$ to define the projection operator for the $2\pi_x^*$ orbital. These two coefficients are set, such that

$$\rho^{2\pi_x^*}(\Psi_{2\pi_x^*}) = 1,\ \rho^{2\pi_x^*}(\Psi_{1\pi_x}) = 0,$$

where $\Psi_{2\pi_x^*}$ and $\Psi_{1\pi_x}$ are the $2\pi_x^*$ and $1\pi_x$ one electron states of the free CO molecule. These are two equations for the two coefficients allowing to solve for $\alpha^{2\pi_x^*}_{\mathrm{carbon},p_x}$ and $\alpha^{2\pi_x^*}_{\mathrm{oxygen},p_x}$. The coefficients for the $2\pi_y^*$ orbital are identical. An additional complication arises from the fact, that we use oxygen and carbon potential with two projectors for each angular and magnetic quantum number lm. To solve this, a down-folding procedure as suggested in Ref. 18 is used.

As already mentioned in Ref. 3, the energies of the modified density functional and the original density functional are identical if the occupancies of the $2\pi^*$ orbital are one or zero, since the equality

$$\rho_i^\sigma - \rho_i^\sigma\rho_i^\sigma = 0$$

holds in this case. This implies that the vibrational properties of the free CO molecule and energies for exciting one electron from the HOMO to the LUMO are not modified by the additional term. We can regard the additional term as a penalty function, that forces the occupancy of the single electron eigenstates of CO to be either one or zero. This is in the spirit of the well known LDA+U method.[23] In the present case, a value of $U=0.75$ eV, as rationalized in our previous work,[3] was chose. It is admitted, that this is largely an empirical choice, although a physical incentive for this choice exists: The energy required for transferring *one* electron from the 5σ to the $2\pi^*$ orbital is 7.3 eV in GGA, if spin polarization is neglected (this excitation does not correspond to the triplet or the singlet transition[24] but is similar to the process on the surface). The one electron $5\sigma \rightarrow 2\pi^*$ gap is, however, only 6.9 eV. A correction of $U=0.75\ \mathrm{eV} \approx 2\ (7.3-6.9\ \mathrm{eV})$, yields a single particle gap in accordance with the calculated 5σ to $2\pi^*$ GGA transition energy.

III. RESULTS AND DISCUSSION

In this work we focus on five different systems: the clean Rh(111) surface, the (2×2) surface cell with a CO coverage of 0.25 monolayer (ML), the $(\sqrt{3}\times\sqrt{3})$ system corresponding to a CO coverage of 0.33 ML, and the (2×2)-3CO system with a coverage of 0.75 ML. These ordered structures were observed by LEED studies below a temperature of 120 K.[25–27] Additionally a (3×3) supercell ($\frac{1}{9}$ ML CO) was investigated as representative of the low coverage case.

A. Geometries and energetics

1. Clean surface

A small inward relaxation of the outermost plane was found. The distance between the first and the second layer is 2.18 compared to 2.22 Å in the bulk. This is a relative change of −1.9%.

2. CO covered surface

The geometries of the CO covered surface for $\frac{1}{9}$, $\frac{1}{4}$, and $\frac{1}{3}$ ML coverage were calculated for all possible adsorption sites: top, bridge, hcp hollow, and fcc hollow. For $\frac{3}{4}$ ML coverage, only the structure where one CO molecule adsorbs at a top site and two molecules adsorb in hollow sites was considered. The final relaxed geometries are summarized in Table I. To determine the most stable adsorption site within density functional theory, we inspected the adsorption energies, which are summarized in Table II. The calculated adsorption energies indicate that the hcp-hollow site is energetically preferred. At very low coverage, it is favored by 140 meV, and the energy difference decreases to 80 meV at 0.25 and 1/3 ML. This is in clear contradiction to the results of experimental studies which indicate an adsorption at the top site (see below). Our results, however, are in agreement with other GGA studies, which also show that the hollow site is preferred on Rh(111).[5,6]

Concerning the geometry relaxation, a few points are noted. First, it is clearly visible that adsorption of CO leads to an outward relaxation, which increases with coverage. The effect is most pronounced for the hollow site, but also clearly visible for atop adsorption. For atop adsorption, the Rh atom below the CO molecule is most strongly influenced and relaxes outward by about 0.2 Å with respect to the clean surface. The other CO uncovered Rh atoms are hardly influenced by the CO molecule. For the (2×2)-3CO structure, however, all four Rh surface atoms are almost coplanar and the buckling becomes negligible. In this case, all Rh surface atoms are coordinated to CO molecules.

Concerning the incorrect prediction of the adsorption site, it is noted that a similar situation was found for the adsorption of CO on Pt(111).[28] Clearly the calculated adsorption energies are not sufficiently accurate to predict the correct adsorption site and additional theoretical investigations are needed. The calculation of the vibrational frequencies and of the core-level shifts presented in the next two sections, however, do confirm the experimental assignment.

TABLE I. Structural parameters of CO on Rh(111). Δ_{12} is the mean change of the distance between the first and the second Rh layer in % relative to the distance in the bulk. Buckling b is the distance between the outermost and the innermost Rh atom in the first layer in Å. Rh-C is the vertical distance between Rh and C in Å. C-O is the vertical distance between C and O in Å. The theoretical bond length of the free CO molecule is 1.142 Å.

		(3×3)	(2×2)	$(\sqrt{3}\times\sqrt{3})$	(2×2)-3CO[a]
top	Δ_{12}	−1.3%	−0.9%	0.1%	2.9%
	b	0.220	0.194	0.247	0.006
	Rh-C	1.847	1.843	1.850	1.870
	C-O	1.164	1.163	1.163	1.153
bridge	Δ_{12}	−1.1%	−0.1%	0.6%	
	b	0.110	0.125	0.087	
	Rh-C	1.476	1.479	1.486	
	C-O	1.186	1.184	1.182	
hcp	Δ_{12}	−0.9%	−0.1%	1.0%	
	b	0.092	0.116	0.000	
	Rh-C	1.351	1.349	1.377	1.460
	C-O	1.197	1.195	1.192	1.184
fcc	Δ_{12}	−0.9%	0.3%	1.1%	
	b	0.094	0.075	0.000	
	Rh-C	1.376	1.385	1.401	1.423
	C-O	1.195	1.191	1.191	1.184

[a] For the (2×2)-3CO structure only a single model was calculated, and the result for the three individual CO adsorption sites are stated in the table (top layer relaxation and buckling are given in the top rows only).

To understand these controversial results the molecular GGA+U method is applied to the system. As explained in Sec. II D this method shifts the $2\pi^*$ orbital towards the vacuum level which weakens the interaction between the substrate and the $2\pi^*$ orbital and lowers the adsorption energy. In the hollow site the bonding interaction is dominated by the $2\pi^*$ orbital. Therefore, the hollow site is affected stronger than the top site, where bonding is dominated by the 5σ orbital. The resolved adsorption energies are summarized in Table III. It can be seen that the top site is now energetically preferred for all coverages. This is in agreement with the experiment and the results of the calculated surface core-level shifts and vibrational frequencies. The absolute binding energy is also significantly better described in the GGA+U approach. Experimentally a binding energy of 1.65 eV has been estimated from temperature programed reaction spectroscopy below 0.15 ML.[29] Compared to this experimental

TABLE II. Average adsorption energies in eV for CO on Rh(111) at various coverages using conventional GGA.

	Top	Bridge	hcp	fcc
(3×3)	−1.860	−1.867	−2.001	−1.930
(2×2)	−1.857	−1.808	−1.936	−1.825
$(\sqrt{3}\times\sqrt{3})$	−1.851	−1.823	−1.934	−1.882
(1×1)	−1.071	−1.142	−1.200	−1.194
(2×2)-3CO	−1.664			

TABLE III. Adsorption energies in eV calculated with the molecular GGA+U method for CO on Rh(111) at various coverages.

	Top	Bridge	hcp	fcc
(3×3)	−1.568		−1.520	−1.470
(2×2)	−1.562	−1.405	−1.471	−1.379
$(\sqrt{3}\times\sqrt{3})$	−1.562	−1.424	−1.478	−1.437
(2×2)-3CO	−1.302			

value, the GGA overestimates the binding energy by 0.35 eV (2 eV), whereas the GGA+U underestimates it slightly (1.57 eV). Using the Clausius-Clapeyron equation the heat of adsorption has been estimated to change from 1.55 eV at 0.18 ML coverage, to 1.40 eV at 0.25 ML coverage and 1.3 eV around 0.6 ML coverage.[30] These values are in very good agreement with the present GGA+U calculations.

B. Vibrational frequencies

Vibrational frequencies for CO on Rh(111) were experimentally determined by Dubois and Somorjai.[31] At low coverage (0.25 ML) they observed two frequencies at 480 and 1990 cm^{-1}. The first one was assigned to the Rh-C stretch frequency and the second one to the C-O bond stretching. The vibrational frequencies of the C-O bond are lower than those of the free CO molecule (2143 cm^{-1}), which is ascribed to the increased occupation of the antibonding $2\pi^*$ orbital, which also leads to an enlargement of the C-O bond length. The calculated vibrational frequencies for different adsorption sites can be found in Table IV. The calculated frequencies for adsorption in the top site are 2015 and 466 cm^{-1}, respectively, and agree very well with the experimental frequencies. Clearly the frequencies for adsorption in the bridge and hollow sites differ significantly from the experimental results, confirming the conclusion that CO adsorbs at low coverage atop Rh atoms. For high coverage, namely, the (2×2)-3CO structure, the experimentally observed picture changes. The Rh-C frequency decreases to 420 cm^{-1} which is explained by a weakening of the adsorbate-substrate bond at higher coverage. Furthermore an increase of the C-O stretching frequency to 2070 cm^{-1} is observed, again related to the weakening of the adsorbate-substrate bond, which leads to a stronger C-O bond. This picture is supported by the calculated Rh-C and C-O bond length which increases and decreases, respectively, when the coverage increases. However, other possible reasons for this effect are local field effects,[32,33] coupling of vibrations,[33] or dipole-dipole interactions,[34] which we believe to be rather small. Moreover, a third frequency at 1870 cm^{-1} is observed at high coverage. This frequency does not occur at lower coverage and was assigned to CO molecules in hollow sites. A more recent HREELS study on the (2×2)-3CO structure found two additional frequencies at 1785 and 1925 cm^{-1} both with very low intensity.[8]

TABLE IV. Calculated and experimental frequencies in cm^{-1} using conventional GGA.

	Exp.[a]	Exp.[b]	Top	Bridge	hcp hollow	fcc hollow
(2×2)	1990		2015	1833	1758	1777
	480		466	346	344	339
$(\sqrt{3}\times\sqrt{3})$			2016	1850	1777	1787
			440	349	324	338
(2×2)-3CO	2070	2070		2060		
		1925				
	1870	1861		1847		
		1785		1777		
	420	434		411		
				362		
				316		

[a] HREELS, Dubois and Somorjai, Ref. 31.
[b] HREELS, Curulla *et al.*, Ref. 8.

TABLE V. Calculated and experimental frequencies in cm^{-1} using the GGA+U method.

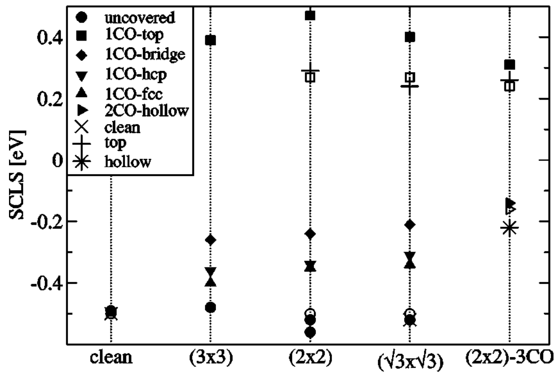
	Exp.[a]	Exp.[b]	Top	hcp-hollow
(2×2)	1990		2027	1785
	480		463	346
(2×2)-3CO	2070	2070		2082
		1928		
	1870	1861		1864
		1785		1789
	420	434		424
				354
				307

[a] HREELS, Dubois and Somorjai, Ref. 31.
[b] HREELS, Curulla *et al.*, Ref. 8.

Our present calculations compare very favorably with the experimental results (as does a previous density functional cluster calculation[8]). The calculated frequency at 2060 cm^{-1} arises from CO molecules adsorbed at the top site and can be assigned to the experimental value of 2070 cm^{-1}. For the two CO molecules adsorbed in hollow sites we obtain two different frequencies corresponding to the in-phase and out-of-phase vibration. The in-phase vibration yields a frequency of 1847 cm^{-1} which can be assigned to the high intensity peak at 1861, respectively, 1870 cm^{-1}. The out-of-phase vibration has a frequency of 1777 cm^{-1} which is related to the low-intensity peak of 1785 cm^{-1}. Since the two CO molecules in hollow sites are indeed not fully equivalent (one hcp and one fcc site) the out-of-phase vibration is not exactly antisymmetric, and possesses a small dipole intensity. The reported frequency at 1925 cm^{-1} cannot be reproduced with our calculations and might well correspond to CO molecules adsorbed at step edges.

The calculated vibrational frequencies within the GGA+U method are presented in Table V. For the (2×2) structure the C-O stretching frequencies are slightly larger then in the standard GGA. This can be explained by a decrease of the C-O bond length which is caused by the up-shifted antibonding $2\pi^*$ orbital. As expected, this effect is slightly larger for the hollow site ($27\ \mathrm{cm}^{-1}$) then for the top site ($12\ \mathrm{cm}^{-1}$). The Rh-C stretching frequencies are hardly affected by the GGA+U method. Likewise, for the (2×2)-3CO structure the C-O frequencies are slightly increased compared to the standard GGA calculations. For the CO molecules in the hollow site, the agreement with experiment is now almost perfect. The frequency for the CO molecules at the top site is slightly overestimated, whereas it was underestimated in the standard GGA calculations. In summary, the GGA+U method yields a reasonable description of the energetics and vibrational properties.

(a) Rh 3d final state SCLS



(b) Rh 3d initial state SCLS

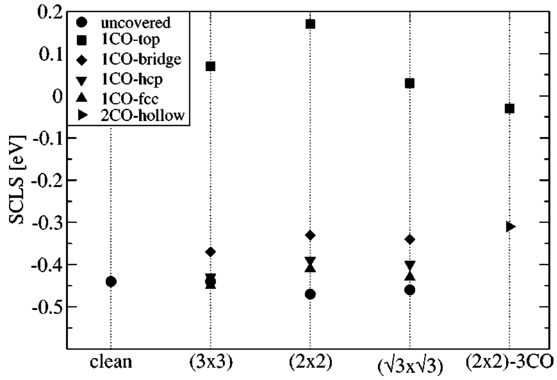


FIG. 1. Rh 3d surface core-level shifts in the final state approximation (top) and initial state approximation (bottom). Open symbols: experimental results from Ref. 10, filled symbols: calculated PAW results, crosses: calculated results from Ref. 6. For $(x\times x)$ the value "uncovered" corresponds to the surface core-level shift of a Rh surface atom not covered by CO for atop adsorption.

C. Surface core-level shifts

1. Rh 3d SCLS in the final state approximation

The Rh 3d surface core-level shifts were calculated according to Eq. (2), by replacing one of the surface atoms by a core excited ionized atom. The bulk reference values were obtained from a bulk calculation using a six layer hexagonal supercell with a similar periodicity in the basal plane as the corresponding surface supercell and replacing again a single bulk atom by a core excited atom. For the hexagonal $(\sqrt{3}\times\sqrt{3})$ and (2×2) supercell, the bulk reference values were identical within 76 meV, indicating that the lateral interaction between the core holes is rather small in both the $(\sqrt{3}\times\sqrt{3})$ and (2×2) supercell. The Rh 3d SCLS's were calculated for CO molecules in top, bridge, fcc hollow, and hcp hollow sites and for the clean surface. The calculated shifts are plotted in Fig. 1, where they are contrasted to the experimental shifts[4] and the theoretical shifts obtained from pseudopotential calculations.[6] First, the excellent agreement among theory and experiment for the surface core-level shifts of the CO uncovered surface atoms is noted. Experiment and the present theoretical calculations agree that the shift is about −0.45 eV. A number of previous theoretical all electron calculations are available. Using the linearized muffin tin orbital method and the local density approximation, Andersen *et al.*[35] obtained a shift of −0.42 eV, when surface relaxation was included, and Ganduglia-Pirovano *et al.* reported a value of −0.46 eV using the full-potential linearized-augmented plane-wave (FLAPW) method, GGA, and a (2×2) supercell.[36] The all electron values are in excellent agreement with our present PAW results. This substantiates our previous statement that core relaxation effects are not particular relevant for the relative change of core level binding energies with changing environment.

Turning now to the CO covered surface, it is noted, that for the (2×2)-1CO geometry, slightly different shifts are obtained for the three symmetry inequivalent CO uncovered Rh atoms. This is indicated by the two full circles in the graph. Remarkable is the fact that the surface core-level shift of the CO uncovered Rh atoms is practically independent of the CO coverage. This indicates that the CO induced shift is strongly localized, with little influence on the surrounding Rh atoms.

In the present study, it is, however, not possible to obtain a similar agreement with experiment for the SCLS's of CO covered Rh atoms. Initially, the experimental results were interpreted to give a coverage independent shift of 270 meV.[4] The experimental results were, however, refitted (Table 7 of Ref. 6) and a slightly different shift of 240 meV was determined for the (2×2)-3CO structure. Pseudopotential calculations found a coverage independent shift of about 270 meV for on-top adsorption.[6] Unfortunately the PAW calculations are not in full agreement with the previous calculations and give a coverage dependent shift. For the (2×2)-1CO top structure the calculated shift acquires a maximum of 470 meV, with a difference of 195 meV to the experimental results. The reason for this coverage dependency is partly found in the local geometries. Table VI shows the calculated Rh 3d SCLS's and the distance between the Rh atom directly below the CO adsorbate and the second layer. A close connection between the local geometry and the SCLS can be seen at low coverage. Elevated Rh atoms exhibit a smaller shift, whereas Rh atoms closer to the surface possess a larger shift [(2×2) structure]. When the structural parameters of the $(\sqrt{3}\times\sqrt{3})$ supercell are transfered to the (2×2) supercell, the shift is indeed found to be largely coverage independent. This is in accordance with the observation of Birgersson *et al.*[6] who observed that the CO induced core-level binding energy shift of the Rh-3d level depends

TABLE VI. Surface core-level shifts and layer distances for different structures. $Rh_{12,OT}$ is the distance between the first layer Rh atom directly below the adsorbate and the second Rh layer in Å, Rh_{OT} SCLS is the Rh3*d* SCLS of this Rh atom in eV.

	$Rh_{12,OT}$	Rh_{OT} SCLS
(3×3)	2.386	0.39
(2×2)	2.348	0.47
$(\sqrt{3}\times\sqrt{3})$	2.388	0.40
(2×2)-3CO	2.281	0.31

strongly on the buckling and can be determined to a very good approximation by the local geometry. In the high coverage limit, however, the picture is not that simple. Here the vertical distance $Rh_{12,OT}$ is much smaller than at low coverage. In fact, the other three Rh atoms are now located almost in the same plane as the CO covered Rh atom, which is a result of their two bonds to the CO molecules in the hollow sites. Here the local coordination and geometry has changed with concomitant effects on the positions of the core levels.

The discrepancy between the PAW results and the experimental results might be relativated. First it should be noted that both results show at least the same tendency (lower shifts at higher coverage). A close look at the experimental results furthermore reveals that the intensity of the top peak in the measured spectra (Fig. 8 of Ref. 4) is very low, except for the (2×2)-3CO structure. A shift of the binding energy of the CO covered Rh atoms to higher binding energies seems possible. It should be mentioned here that the fit in the experimental study (Ref. 4) seems to be done under the condition that the shift is coverage independent.

The results of the pseudopotential study, however, cannot be explained at present, but the most likely reason is that the optimized geometries in Ref. 6 differ somewhat from the present result, in particular for the buckling. As discussed before this has a pronounced influence on the core-level shifts. To double check our results we have also recalculated the core-level binding energy shifts using PAW potentials, in which one core electron was excited from the core to the valence during the generation of the potential. This is precisely the procedure adopted in Ref. 6 for the calculation of core-level binding energies, and it includes (at least partially) relaxation effects of core electrons. The calculated binding energy shifts for Rh atoms with CO adsorbed on top are 0.415 eV (0.465 eV) for the (2×2) structure, 0.348 eV (0.401 eV) for the $(\sqrt{3}\times\sqrt{3})$ structure, and 0.289 eV (0.306 eV) for the (2×2)-3CO structure. For the Rh atoms coordinated to 2 CO molecules in the hollow site we obtained a shift of −0.095 eV (−0.139 eV). The values in brackets are those obtained with the PAW method without core relaxation (as reported in Fig. 1). Clearly the shifts are about 50 meV smaller for the core excited PAW potential, but the trends are not affected by this constant shift.

2. Rh3d SCLS in the initial state approximation

In Fig. 1 the Rh3*d* surface core-level shifts in the initial state approximation are presented. These shifts are quite well understood for uncovered transition metal atoms.[37,38] Since the atoms in the surface layer have fewer neighbors than in the bulk, the density of states narrows at the surface. This leads to an energy shift of the band. The center of the *d* band shifts to lower (higher) binding energies if it is filled more (less) than half. Concomitant this yields to a repulsive (an attractive) contribution to the Kohn-Sham potential. This potential also affects the core electrons resulting in a positive initial state SCLS for early and a negative initial state SCLS for late transition metals. The initial state shift of −0.44 eV for CO uncovered surface atoms found here agrees with this concept. For CO covered atoms, on the other hand the *d* band becomes broader than in the bulk, and an opposite initial state shift is therefore expected and in fact found in the calculations.

It is an interesting question, whether the coverage dependency found in the final state SCLS's is caused by initial state or by screening effects. The results clearly indicate that both, the coverage dependent shift for Rh atoms with CO adsorbed atop and the coverage independent shift of the uncovered Rh atoms, are dominated by initial state effects. The screening contribution is nearly constant in both cases. However, it is notable that screening at the uncovered Rh atoms is very small and negative, while it is positive and much larger at Rh atoms below a CO molecule. This implies that screening at the clean surface atoms is more effective than in the bulk, while at Rh atoms below CO adsorbates it is less effective than in the bulk.

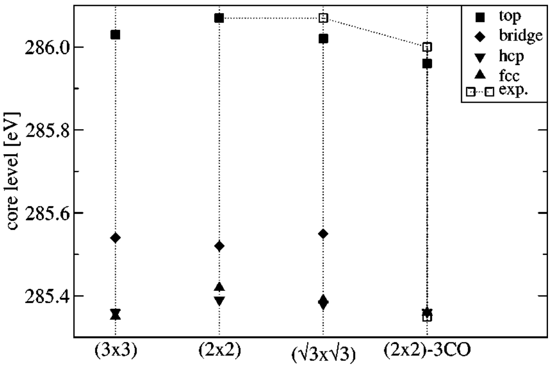
3. C-1s and O-1s binding energies

A difficulty for the comparison of core-level binding energies with experiment is that density functional theory is not sufficiently accurate to determine absolute values for the C-1*s* and O-1*s* binding energies. In the present implementation the errors are even larger than usual, since core relaxation is not included in our calculations. The situation is, however, similar when core excited pseudopotentials are applied: only relative shifts can be determined.

The calculated and experimental C-1*s* core-level binding energies are shown in Fig. 2. In the final state approximation, the energies of the calculated core levels have been shifted such that the calculated and experimental values for the (2×2) structure coincide for atop adsorption. The energies of the core levels in the initial state approximation are specified with respect to the Fermi energy of the bulk and correspond to the calculated Kohn-Sham eigenvalues of the core electrons. The calculated O-1*s* core levels are shown in Fig. 3. In the absence of experimental data, the final state O-1*s* energies have been shifted such that atop adsorption corresponds to the energy zero.

A number of earlier studies on C-1*s* core levels on various surfaces [Ni(100),[39] Pd(100),[40] and Cu(100) (Ref. 41)] came to the conclusion that the C-1*s* binding energy depends mainly on the adsorption site. Changes caused by the interaction between the CO molecules through different coverages influence the binding energies only slightly (100 meV). We find this conclusion confirmed in the present case. For both, the C-1*s* and the O-1*s* states, the changes in the binding energy are small, when the coverage changes.

(a) C 1s final state core levels



(b) C 1s initial state core levels

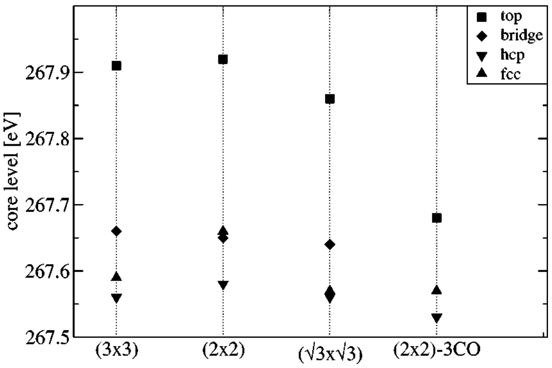
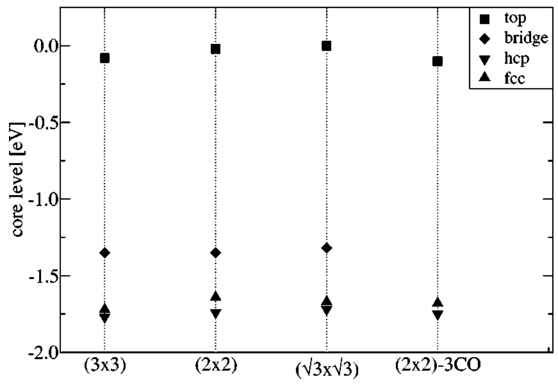


FIG. 2. Top: calculated and experimental final state C-1*s* binding energies, experimental results from Ref. 10. Bottom: calculated initial state C-1*s* binding energies. The final state C-1*s* energies have been shifted such that they coincide with experiment for atop adsorption.

(a) O 1s final state core levels



(b) O 1s initial state core levels

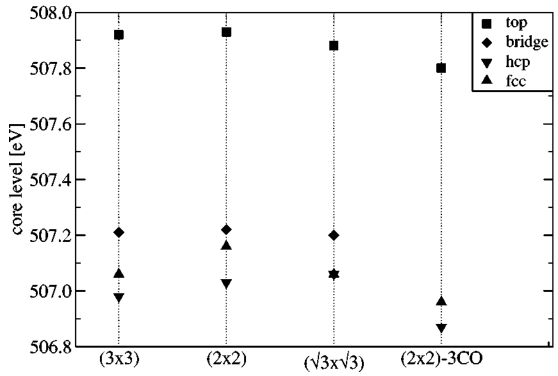


FIG. 3. Top: calculated final state O-1*s* binding energies. Bottom: calculated initial state O-1*s* binding energies. The final state O-1*s* energies have been shifted such that atop adsorption corresponds to the energy zero.

The experimental difference of 650 meV between the C-1*s* binding energy in the top and the hollow site for the (2×2)-3CO structure is reproduced nicely by theory. It is interesting that the C-1*s* and the O-1*s* binding energies for top site adsorption show a coverage dependency very similar to the $\mathrm{Rh_{OT}}$ surface core-level shifts. Here the experimental data confirms the coverage dependency.

4. Surface core-level shifts within the GGA+U method

The Rh 3*d* surface core-level shifts within the GGA+U method are presented in Table VII. They are generally smaller (50–70 meV) than the shifts calculated with the standard GGA approach, but otherwise, they show the same coverage dependency. As a result of the reduction of the shift, the agreement with the experiment is slightly better.

IV. CONCLUSION

We have presented a careful theoretical investigation of CO adsorption on Rh(111). One main objective of this work was to show beyond doubt that the experimental results can be understood only assuming that CO adsorbs atop of Rh surface atoms at low coverage. This aim has been achieved by studying the vibrational frequencies of CO at various coverages and for various adsorption sites. As expected, the experimentally observed CO stretch mode of 1990 $\mathrm{cm^{-1}}$ is certainly only compatible with CO adsorption on top of Rh atoms, for which the theoretical calculations yield a CO stretch frequency of 2015 $\mathrm{cm^{-1}}$. The adsorption in the bridge or hollow site results in significantly lower frequencies of 1850 and 1770 $\mathrm{cm^{-1}}$, respectively, which are certainly not compatible with the experiment.

A similar conclusion can be drawn from the Rh surface core level shifts which are only in agreement with experiment, if CO is assumed to adsorb on top of Rh surface atoms. For the 3*d* binding energy of Rh atoms below the CO molecule, we determined the shift to be coverage dependent with values between 300 and 450 meV. Experiments yield a smaller binding energy shift of roughly 270 meV. The reason for the discrepancy is presently not understood, in particular,

TABLE VII. Rh 3*d* surface core-level shifts in eV for atop adsorption within the GGA+U method compared to standard GGA.

	Initial state		Final state	
	standard	GGA+U	standard	GGA+U
(2×2)	0.17	0.13	0.47	0.40
$(\sqrt{3}\times\sqrt{3})$	0.04	0.01	0.40	0.34
(2×2)-3CO	0.03	−0.01	0.31	0.27

since a previous pseudopotential density functional study found much better agreement with experiment.[6] But even with this large error, the surface core level shifts are certainly only compatible with CO adsorption on top of Rh atoms, since the surface core level shifts for adsorption in the bridge or hollow sites are -200 to -300 meV.

The calculated energetics determined by the semilocal density functionals, however, clearly convey the opposite result: CO prefers the hollow site. At low coverage the hollow site is preferred by 140 meV. To understand these controversial results, the molecular GGA+U method was applied to CO on Rh(111). The objective of this method is a shift of the $2\pi^*$ orbital towards the vacuum level which reduces the back donation from the surface to the CO molecule. Since π bonding is particularly strong in the hollow site, a reduction of the strength of this binding mechanism reduces the adsorption energy in the hollow site. The top site is also affected, but changes are much smaller than for the hollow site. Hence the GGA+U method leads, as for CO on Pt(111), to the proper site ordering.[3]

We emphasize that our observations are consistent with those of Grinberg *et al.*,[42] who argued that present density functionals underestimate the cost for breaking one CO bond. An upshift of the one electron $2\pi^*$ orbital makes a partial charge transfer from the 5σ to the $2\pi^*$ orbital more difficult and therefore stabilizes the CO bond.

We have also presented results for the vibrational properties and the core level shifts in the GGA+U method. For the core levels the GGA+U method yields slightly smaller core level shifts for the Rh atom below the CO molecule, leading to a better agreement with experiment. The vibrational frequencies within the GGA+U method also show a slightly better agreement with experiment, but the changes from standard GGA to GGA+U are so small that they are hardly significant compared to the numerical errors introduced by the finite difference method.

---

[1] P. Feibelmann, B. Hammer, J. K. Nørskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe, and J. Dumesic, J. Phys. Chem. B **105**, 4018 (2001).

[2] A. Gil, A. Clotet, J. M. Ricart, G. Kresse, M. García-Hernández, N. Rösch, and P. Sautet, Surf. Sci. **530**, 71 (2003).

[3] G. Kresse, A. Gil, and P. Sautet, Phys. Rev. B **68**, 073401 (2003).

[4] A. Beutler, E. Lundgren, R. Nyholm, J. N. Andersen, B. J. Setlik, and D. Heskett, Surf. Sci. **396**, 117 (1998).

[5] A. Eichler and J. Hafner, J. Chem. Phys. **109**, 5585 (1998).

[6] M. Birgersson, C.-O. Almbladh, M. Borg, and J. N. Andersen, Phys. Rev. B **67**, 045402 (2003).

[7] M. Gajdos, A. Eichler, and J. Hafner, J. Phys.: Condens. Matter **16**, 1141 (2004).

[8] D. Curulla, R. Linke, A. Clotet, J. M. Ricart, and J. W. Niemantsverdriet, Chem. Phys. Lett. **354**, 503 (2002).

[9] M. J. P. Hopstaken and J. W. Niemantsverdriet, J. Chem. Phys. **115**, 8209 (2001).

[10] A. Beutler, E. Lundgren, R. Nyholm, J. N. Andersen, B. J. Setlik, and D. Heskett, Surf. Sci. **396**, 117 (1998).

[11] L. Köhler and G. Kresse (unpublished).

[12] W. Kohn and L. Sham, Phys. Rev. **140** A1133 (1965).

[13] R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

[14] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[15] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

[16] G. Kresse and J. Hafner, Phys. Rev. B **48**, 13 115 (1993).

[17] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); Phys. Rev. B **54**, 11 169 (1996).

[18] P. E. Blöchl, Phys. Rev. B **50**, 17 953 (1994).

[19] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[20] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).

[21] S. Lizzit, A. Baraldi, A. Groso, K. Reuter, M. V. Ganduglia-Pirovano, C. Stampfl, M. Scheffler, M. Stichler, C. Keller, W. Wurth, and D. Menzel, Phys. Rev. B **63**, 205419 (2001).

[22] B. Johansson and N. Mårtensson, Phys. Rev. B **21**, 4427 (1980).

[23] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B **57**, 1505 (1998).

[24] T. Zeigler, Chem. Rev. (Washington, D.C.) **91**, 651 (1991).

[25] P. A. Thiel, E. D. Williams, J. T. Yates, and W. H. Weinberg, Surf. Sci. **84**, 54 (1979).

[26] A. Beutler, E. Lundgren, R. Nyholm, J. N. Andersen, B. Setlik, and D. Heskett, Surf. Sci. **396**, 117 (1998).

[27] A. Beutler, E. Lundgren, R. Nyholm, J. N. Andersen, B. Setlik, and D. Heskett, Surf. Sci. **371**, 381 (1997).

[28] P. J. Feibelman, B. Hammer, J. K. Norskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe, and J. Dumesic, J. Phys. Chem. B **105**, 4018 (2001).

[29] M. J. P. Hopstaken, W. J. H. van Gennip, and J. W. Niemantsverdriet, Surf. Sci. **433-435**, 66 (1999).

[30] M. Smedh, A. Beutler, M. Borg, R. Nyholm, and J. N. Andersen, Surf. Sci. **491**, 115 (2001).

[31] L. H. Dubois and G. A. Somorjai, Surf. Sci. **91**, 514 (1980).

[32] J. G. Roth and M. J. Dignam, Can. J. Chem. **54**, 1388 (1976).

[33] M. Moskovits and J. W. Hulse, Surf. Sci. **78**, 397 (1978).

[34] M. Scheffler, Surf. Sci. **81**, 562 (1979).

[35] J. N. Andersen, D. Hennig, E. Lundgren, M. Methfessel, R. Nyholm, and M. Scheffler, Phys. Rev. B **50**, 17 525 (1994).

[36] M. V. Ganduglia-Pirovano, M. Scheffler, A. Baraldi, S. Lizzit, G. Comelli, G. Paolucci, and R. Rosei, Phys. Rev. B **63**, 205415 (2001).

[37] D. Spanjaard, C. Guillot, M. C. Desjonqueres, G. Treglia, and J. Lecante, Surf. Sci. Rep. **5**, 1 (1985).

[38] W. F. Egelhoff, Surf. Sci. Rep. **6**, 253 (1987).

[39] H. Antonsson, A. Nilsson, N. Mårtensson, I. Panas, and P. E. M. Siegbahn, J. Electron Spectrosc. Relat. Phenom. **54/55**, 601 (1990).

[40] J. N. Andersen, M. Qvarford, R. Nyholm, S. L. Sörensen, and C. Wigren, Phys. Rev. Lett. **67**, 2822 (1991).

[41] O. Björneholm, A. Nilsson, E. O. F. Zdansky, A. Sandell, B. Hernnäs, H. Tillborg, J. N. Andersen, and N. Mårtensson, Phys. Rev. B **46**, 10 353 (1992).

[42] I. Grinberg, Y. Yourdshahyan, A. M. Rappe, J. Chem. Phys. **117**, 2264 (2002).