First-principles study of potassium adsorption on TiO$_2$ surfaces

J. Muscat and N. M. Harrison

CCLRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom

G. Thornton

Surface Science Research Centre and Department of Chemistry, University of Manchester, Manchester M13 9PL, United Kingdom

We present an *ab initio* study of alkali metal adsorption on metal oxide surfaces. We have investigated the changes that occur to the structure and electronic properties of the rutile TiO$_2$ (100) surface when a $\frac{1}{2}$ monolayer of potassium atoms is adsorbed. The K atoms are reduced to K$^+$ ions as charge transfer occurs from the K$_{3s}$ orbital to localized Ti$_{3d}$ orbitals at the surface of the substrate. The occupied Ti$_{3d}$ states lie about 1 eV above the O$_{2p}$ valence band maximum in agreement with recent photoemission studies. The Ti$_{3d}$ states are spin polarized and are similar to those found at oxygen deficient TiO$_2$ surfaces. The geometric structure also undergoes significant relaxation as the lattice is polarized around the reduced Ti sites. The calculated surface structure is in excellent agreement with x-ray adsorption data. [S0163-1829(99)04224-1]

I. INTRODUCTION

Titanium dioxide and its surfaces have been extensively studied in recent years. This effort is motivated in part by the many important industrial applications of TiO$_2$. The material is a vital ingredient for the manufacture of pigments[1] and gas sensors.[2] The catalytic properties[3,4] are still being explored and new applications exploiting these properties are being investigated at the present time.[5] TiO$_2$ is also of interest as a model system for studying the physical and chemical properties of complex metal oxides. The simple, highly symmetric rutile structure is amenable to simulation using a variety of first principles (*ab initio*) techniques. The electronic structure is characterized by the ''empty'' *d* orbitals on the formally ''4+'' titanium ions. The role of the *d* states in the remarkable physical and chemical properties of stoichiometric TiO$_2$ is not yet fully understood.

TiO$_2$ is readily reduced with oxygen vacancies playing a crucial role in the formation of bulk defect phases[6] and the reconstructions of the (100) surface.[7–13] Studies of the reduced (100) (Ref. 7) and (110) (Ref. 14) surfaces have revealed that the excess electrons resulting from the formation of oxygen vacancies localize on the Ti *d* orbitals forming a state above the O$_{2p}$ band. The location of this state was determined, using band-mapping photoemission experiments, to be about 3 eV above the O$_{2p}$ band maximum.[15] Theoretical calculations on the reduced (110) surface have reported similar states at 1–2 eV above the O$_{2p}$ band[16,17] with the reduced Ti ions inducing local distortions of the lattice at the surface.[16]

A more controlled reduction of the surfaces can be achieved by adsorbing species which readily donate electrons to the substrate. Control of the exposure of the surface to the adsorbate and measurement of the coverage allows the degree of reduction to be varied and monitored. In this context the interaction of alkali metals with the surface is of particular interest. Various experimental studies of alkali metal adsorption on metal oxides have been reported, for example, potassium on NiO (Ref. 18) and ZnO,[19] cesium on

NiO,[20] and sodium on MgO.[21] The surface geometry of the adsorbed species is found to be strongly dependent on the nature of the substrate. The adsorption of potassium on ZnO (000$\bar{1}$) leads to an ordered *p*(2×2) overlayer[19] whereas potassium[18] or cesium[20] adsorption on NiO and sodium adsorption on MgO (Ref. 21) lead to the formation of islands around surface defects. On these metal oxides a strong interaction between the alkali metal and surface oxygen atoms can be inferred from charge transfer measurements. To our knowledge, no theoretical investigation of the nature of this interaction has been published.

A number of recent experimental investigations have probed the geometry and electronic structure of potassium and sodium adsorption on TiO$_2$ surfaces.[1,22–28] Low energy electron diffraction (LEED) data indicate that K adsorption on the (100) surface at half-monolayer coverage results in an ordered *c*(2×2) geometry.[22] This is confirmed by surface x-ray absorption fine structure (SEXAFS) studies which also probe the local geometry of the adsorption site.[26] The electronic structure of the surface has been studied using photoelectron spectroscopy[23] which revealed the existence of a K induced ''band gap'' state with Ti$_{3d}$ character about 3 eV above the valence band maximum (VBM). Similar states have been reported for K-adsorption on the TiO$_2$ (110) surface.[28] Such states are indicative of a reduced surface[7] and in this context are apparently populated by charge transferred from the K overlayer.

In recent years, the increasing sophistication of *ab initio* techniques has made it possible to simulate realistic processes at surfaces, often gaining valuable insights.[29–31] Most theoretical studies of solid state systems are based on either Hartree-Fock (HF) or density functional theory (DFT) which differ in their treatment of the electron exchange and correlation. HF theory treats electron exchange exactly but ignores correlation whereas DFT approximates both exchange and correlation effects. In the current work, we have carried out an investigation of alkali metal adsorption on a metal oxide surface using periodic *ab initio* simulations. We have used HF theory (which has been shown in recent work to

provide an accurate description of the ground state energetics and electronic structure of transition metal insulators[17,32]) to examine the K adsorption process in order to better understand the nature of the charge transfer state and its consequences for the geometry and electronic structure. Supplementary calculations were performed using DFT within the local density approximation (LDA) to facilitate comparisons with previous DFT studies[16,33] of reduced TiO_2 surfaces.

The paper is organized as follows. In Sec. II we describe how the system was modeled and give the computational parameters used. The results are presented in Sec. III and discussed in Sec. IV. Finally our conclusions are given in Sec. V.

II. COMPUTATIONAL DETAILS

All calculations in this study have been performed using the CRYSTAL95 program in which the crystalline orbitals describing the wave function of the system are built from a linear combination of atomic orbitals (LCAO).[34] Atom centered Gaussian functions with s, p, or d symmetry are used to describe the atomic orbitals. For comparison, electron exchange and correlation effects were treated using both HF and DFT-LDA (Refs. 35 and 36) approximations.

The approximation to the wave function introduced by using a finite basis set is critical to the cost and accuracy of the calculations. We have used titanium and oxygen basis sets optimized in recent studies of the bulk and surfaces of TiO_2 (Refs. 17, 37, and 38) which are presented elsewhere.[39,38] To calculate the optimal surface structure we have used a double valence (DV) basis set for Ti and O where the valence electrons are described by two independent radial basis functions. The potassium basis set is also a double valence basis set developed from that used in previous studies of KCl.[40] The core electrons are replaced with a small core pseudopotential (SC) which replaces the $1s$, $2s$, and $2p$ electrons in Ti and K (Ref. 41) and the $1s$ electrons in O.[42] The resultant DVSC basis set has been thoroughly tested in other bulk and surface investigations of TiO_2 and is found to yield structural parameters converged to within 0.02 Å of those extrapolated to the infinite basis set limit.[37] For the purpose of comparison, the calculation of small energy differences and for the calculation of the electronic structure we have used a more sophisticated triple valence all-electron (TVAE) basis set for Ti, O,[39,38] and K.[40,39]

The structural model for the (100) surface of TiO_2 is a two dimensional slab periodic in the [010] and [001] directions but finite in the [100] as illustrated in Figs. 1 and 2. This makes it unnecessary to converge the calculations with respect to the interslab vacuum distance inherent in the supercell approximation used in many plane wave (PW) studies of TiO_2 surface.[12,16] It has been shown in previous studies that a slab thickness of nine atomic layers (three TiO_2 formula units) is adequate to model the structure and energetics of this surface accurately.[37] The surface unit cell of the $c(2\times2)$ structure is shown in Fig. 2.

The k-space sampling was performed on a Pack-Monkhurst grid[34,43] of shrinking factor 4 yielding 18, 7, and 7 symmetry inequivalent points in the irreducible Brillouin zones of the bulk crystal and the (1×1), and $c(2\times2)$ (100) surface cells, respectively. This is sufficient to converge the
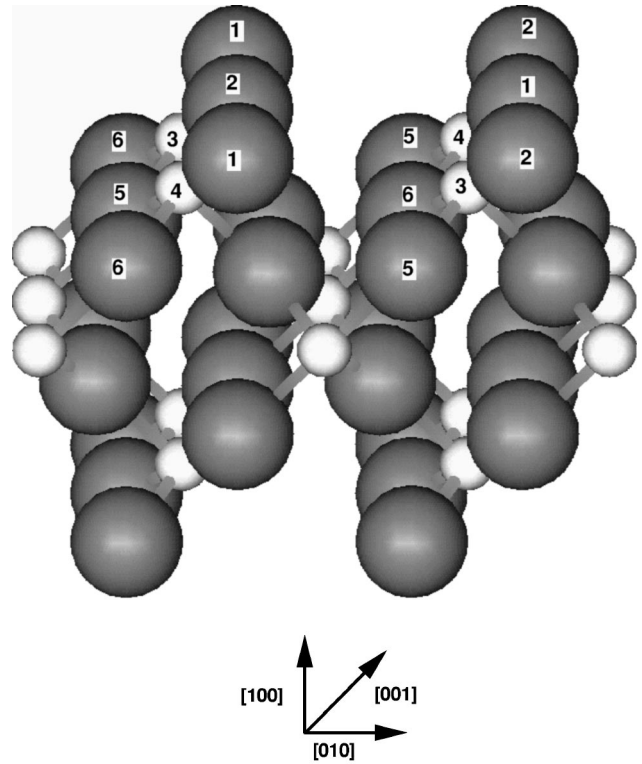

FIG. 1. A section through the nine layer slab model viewed in the [001] direction. All inequivalent atoms are labeled.

surface structure to within 0.01 Å.[37]

Other approximations are introduced as a consequence of the use of local basis functions. In CRYSTAL the convergence of the direct space summations of the Coulomb and exchange contributions to the Fock matrix are controlled by five overlap criteria. The control of these approximations is described elsewhere.[44] In this study, we have used values of 10^{-6}, 10^{-5}, 10^{-6}, 10^{-6}, and 10^{-12} which have been found to produce numerical errors in the relative energies of different structures in the order of 0.001 eV.[45,46,37]
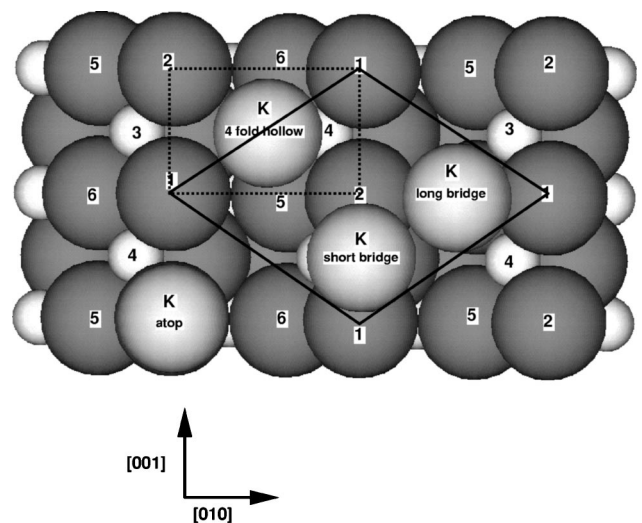

FIG. 2. Plan view of the unrelaxed (100) surface of the slab and the various adsorption sites investigated. The (1×1) unit cell is represented by the rectangular box and the diamond box marks the $c(2\times2)$ supercell used.

Analysis of charge and spin states was performed using the Mulliken scheme.[47] We emphasize that the partitioning of the charge density among individual atoms is arbitrary and, in the case of the Mulliken analysis, depends on the local basis functions used. However, in the current calculations the use of a consistent basis set approximation means that variations in the population analysis with structure do provide a useful guide to changes in the nature of the electronic state.

All surface structure optimizations were performed to a tolerance of 0.01 Å in the structural parameters or 10^{-4} eV in the energy. The adsorbate and the top three layers of the substrate were fully relaxed. To estimate the effect of this constraint on the relaxation, we performed tests on the clean (100) surface where we relaxed the surface with and without freezing the ionic positions below the third layer. We find that constraining the fourth layer has only a small effect (0.02 Å) on the calculated relaxation of the other ions at the surface.

III. RESULTS

We conducted a preliminary study to allow us to select a starting geometry for the optimization of the potassium adsorption site. We chose four possible sites on the surface as illustrated in Fig. 2. These were labeled the ''short bridge site'' (bridging $O_{(1)}$ and $O_{(2)}$) along the [001] direction), the ''long bridge'' site (bridging $O_{(1)}$ and $O_{(2)}$ along the [010] direction), the ''four-fold hollow'' site (equidistant from $O_{(1)}$ and $O_{(2)}$ along both the [001] and [010] directions) and the ''atop'' site (directly above an oxygen atom). The height of the potassium ion above the substrate oxygen layer was chosen to be equal to the sum of the O^{2-} and K^+ ionic radii.[48] Several distinctly different solutions of the self-consistent-field (SCF) procedure are stable for these surface geometries. Convergence of the solution at some geometries was unstable or slow but could be stabilized by the use of acceleration techniques such as ''level shifting.''[34] In all states, the K atom is fully ionized to K^+ and the charge is transferred to the substrate. The distinct types of electronic state obtained were as follows: First, with the donated electron delocalized over the surface to form a metallic system, secondly, with the electron localized on a particular surface or subsurface Ti site and, finally, states where charge was delocalized on more than one Ti ion. We find that the lowest energy configuration is where the potassium is adsorbed on the short bridge site with the electron localizing on a single Ti ion (the Ti ion nearest the K^+ ion). The resultant state is spin polarized; non-spin-polarized solutions were also investigated but were found to be much higher in energy (over 10 eV). We placed the K^+ ion in this site such that the ion labeled $Ti_{(3)}$ corresponds to the reduced Ti ion (3+) and $Ti_{(4)}$ is the Ti^{4+} ion (shown in Fig. 2). The position of the adsorbate and the top three layers of the substrate were relaxed. The resultant ionic displacements are presented in Table I and illustrated in Fig. 3 with the position of the K^+ ion given relative to the relaxed position of the $O_{(1)}$ ion.

The relaxed position for the K ion is similar to the ''four-fold hollow site'' but displaced towards $Ti_{(3)}$ by -0.43 Å (Fig. 2) and at 0.97 Å above the surface oxygen layer. The predicted $K-O_{(1/2)}$ bond length of 2.63 Å is in excellent

TABLE I. The relaxation of the surface layers (in Å) of the $c(2 \times 2)$ K TiO$_2$ (100) system computed within the HF approximation. Ionic displacements are relative to the bulk terminated coordinate system as defined in Figs. 1 and 2 with the location of the K^+ ion given relative to the relaxed $O_{(1)}$ position.

Label	$\delta[001]$	$\delta[010]$	$\delta[100]$
K	1.59	1.85	0.97
$O_{(1)}$	-0.08	-0.44	0.21
$O_{(2a)}$	0.08	-0.44	0.21
$Ti_{(3)}$	0.0	-0.09	-0.05
$Ti_{(4)}$	0.0	0.12	-0.02
$O_{(5)}$	0.08	-0.14	0.07
$O_{(6a)}$	-0.08	-0.14	0.07

agreement with the value of 2.62 Å found in recent SEXAFS experiments.[26] The angle of the inclination of the $O_{(1)}-K-O_{(2)}$ plane to the surface normal is calculated to be $62°$ compared to the range of $33°-50°$ measured by SEXAFS.[26] This represents a reasonable level of agreement particularly as bond angles are rather difficult to extract from SEXAFS studies.

The substrate geometry is strongly affected by potassium adsorption. The largest displacements at the clean surface are along the [010] direction with the surface O, Ti, and subsurface O ions moving by -0.3 Å, 0.1 Å, and -0.15 Å, respectively.[37] Displacements along [100] are no more than 0.05 Å. K adsorption induces larger displacements of the surface O ions along [010] and [100]. The adsorption also reduces the symmetry of the surface allowing the O ions to
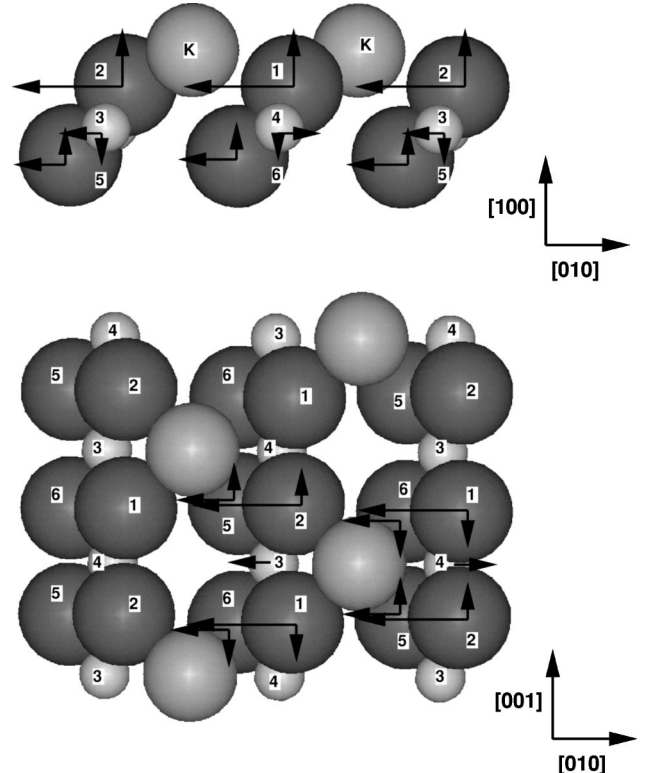

FIG. 3. Plan and side views of the top three layers of the relaxed K-TiO$_2$ (100) surface. The arrows indicate the direction of the ionic displacements and are approximately to scale.

TABLE II. The electron population $(Q|e|)$, charge difference with respect to the clean surface $(Q-Q_{clean}|e|)$, and spin density $(|e|)$ computed using the Mulliken scheme for the relaxed $c(2\times2)$ K TiO$_2$ (100) surface.

Atom	Q	$Q-Q_{clean}$	Spin
O$_{(1)}$	9.45	0.28	0.00
O$_{(2)}$	9.45	0.28	0.00
Ti$_{(3)}$	19.62	0.27	1.00
Ti$_{(4)}$	19.37	0.02	0.00
O$_{(5)}$	9.49	0.02	0.00
O$_{(6)}$	9.49	0.02	0.00
K	18.03		0.00

move along the [001] direction by 0.08 Å towards the Ti$_{(4)}$ ion, and thus away from the Ti$_{(3)}$ ion, as illustrated in Fig. 3. The two surface Ti ions have very different behavior with respect to displacements along the [010] direction. The Ti$_{(4)}$ ion moves by $+0.12$ Å, which is similar to Ti ion displacement at the clean surface, while the reduced Ti$_{(3)}$ ion moves by -0.09 Å.

There have been several theoretical studies of alkali metal adsorption on TiO$_2$ where the model of the TiO$_2$ surface is based on a (nonperiodic) cluster of Ti and O ions. Calculations of sodium adsorption on the (110) surface using HF theory[49] and combined molecular dynamics (MD) and cluster HF calculations of sodium[50] and potassium[51] adsorption on this surface have reported the formation of ordered overlayers of alkali metal ions. Recent calculations based on both cluster and fully periodic slab models (performed with the CRYSTAL95 package) using HF and DFT (Ref. 52) yield similar adsorption geometries. The adsorbed ions tend to occupy positions between either ''bridging'' or in ''plane'' oxygen ions with reported K-O distances similar to those in the current study.[52,51]

The electronic structure of the surface is also strongly influenced by potassium adsorption. The Mulliken charge populations are compared to that of the clean surface in Table II. As noted above, the K atom completely ionizes to form a K$^+$ ion. The donated electron is shared almost equally between the O$_{(1)}$, O$_{(2)}$, and Ti$_{(3)}$ ions. The degree of charge transfer to Ti$_{(3)}$ is in agreement with the experimental estimate of $0.25|e|$.[26] The charge on other ions differs from that of the clean surface by no more than $0.02|e|$. The Mulliken analysis of the spin density reveals that the induced spin polarization is localized on the Ti$_{(3)}$ ion which has a magnetic moment of $1.0\mu_b$.

Other theoretical studies of alkali metal adsorption on TiO$_2$ have also predicted charge transfer from the adsorbate to the substrate.[53,49,52,51] Bredow *et al.*[52] noted that it is energetically favorable for the donated spin density to localize on a particular fivefold coordinated Ti ion on the potassium-adsorbed (110) surface and reported similar Mulliken charge and spin populations to those presented in Table II.

The density of states (DOS) of the potassium adsorbed surface is compared to that of the clean surface in Fig. 4. The band gap of TiO$_2$ has been measured recently to be 4 eV,[15] which is somewhat larger than the value of 3 eV quoted previously.[54] Here the band gap is computed to be 12 eV. It
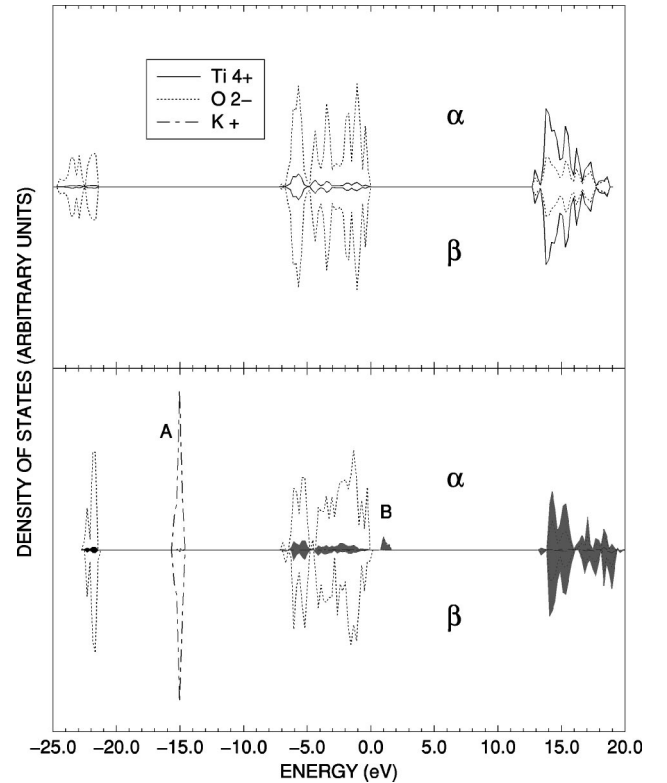

FIG. 4. Density of states projected onto surface titanium and oxygen sites for clean and $c(2\times2)$ K TiO$_2$ (100) surfaces calculated using HF theory. The valence band maximum has been aligned to 0 eV to facilitate comparisons. The shading represents states due to Ti^{3+} ions.

must be stressed that due to unscreened self-interaction in the exact exchange, HF theory always overestimates band gaps by factors of about 2–4. However, relative bandwidths and separations between occupied levels tend to be reasonably well reproduced.[32] The calculations indicate that the valence band is largely unaffected by potassium adsorption. It is predominantly composed of O$_{2p}$ orbitals which extend from 0 eV (fixed to be the VBM) to about -7 eV in good agreement with the experimental bandwidth of 6–6.5 eV.[22–25] The most striking changes to the DOS that occur upon adsorption of K are the appearance of two new peaks labeled A and B in Fig. 4. Feature A is due to the K$_{3p}$ state which lies about 8 eV below the valence band in excellent agreement with photoemission studies which reveal a peak at 8–9 eV below the valence band minimum.[24,25] Feature B is spin polarized and appears about 1 eV above the VBM and is due to d orbitals localized almost entirely on the reduced surface Ti$_{(3)}$ ion. Similar band gap states are observed experimentally at about 3 eV above the VBM.[22–25]

IV. DISCUSSION

A. Optimized geometry

The qualitative features of the surface relaxation can be understood in terms of a simple electrostatic model. For the clean surface the driving force for the relaxation is provided by the undercoordination (five-fold, rather than six-fold in the bulk crystal) of the surface Ti ions. The displacements of the surface O and Ti ions in the [010] direction (-0.3 Å

and $+0.15$ Å, respectively) serve to increase the effective coordination of the surface Ti ion.[37] After K adsorption, the relaxation of the surface O and unreduced Ti^{4+} ions is similar to that of the clean surface—moving along [010] by -0.44 Å and $+0.12$ Å, respectively. However, the behavior of the Ti^{3+} ion is quite different. It moves by -0.09 Å along [010]. The reduction of the ion has partially compensated for its undercoordination and thus it does not move under the $O_{(1)}$-$O_{(2)}$ pair—this is illustrated in Fig. 3. In addition the K adsorption reduces the symmetry of the surface, removing the mirror plane perpendicular to [001], and displacements along [001] now occur. These are of magnitude 0.08 Å and serve to increase the coordination of the Ti^{4+} ions at the expense of the Ti^{3+} ions (Fig. 3). Similar effects have been observed in calculations on oxygen deficient (110) surfaces of TiO_2.[16]

B. The nature of the electronic state

As noted above, the electron transferred to the substrate is localized at a particular surface Ti ion. The charge and spin populations indicate that a Ti d state is occupied and that it is spin polarized. This state is associated with a new peak in the electronic DOS about 1 eV above the VBM. States have been observed about 3 eV above the VBM in TiO_2 samples reduced by either adsorption of alkali metals[22–25,28,55] or by the creation of oxygen vacancies.[14,7,28] Spin-polarized states at a similar energy with respect to the VBM were found in recent theoretical investigations of potassium adsorption on the (110) surface[52] and on oxygen deficient (110) surfaces in which both DFT and HF approaches were used.[17,16,33] Although all of these approaches obtain a similar description of the occupied eigenvalue spectrum they give significantly different descriptions of the separation between the localized states and the conduction band minimum (CBM). The spectroscopy measurements in the literature do not determine accurately the size of this separation but there is some evidence that a small gap does exist.[56,14]

As noted in Sec. III, the HF approximation tends to overestimate the separation between occupied and unoccupied states and therefore it is not surprising that in the present calculation and in HF studies of the oxygen deficient surface[17] "gap states" well separated from the CBM are found. Recent all-electron DFT-LDA calculations for the oxygen deficient surface find Ti_{3d} states at the bottom of the conduction band and hence a conducting surface layer.[33] This is not unexpected as DFT tends to underestimate band gaps. In order to examine the effect of exchange and correlation approximations on the nature of the surface electronic structure of the K-adsorbed surface, we have relaxed the surface structure and computed the electronic structure using DFT-LDA. These calculations were performed with identical computational approximations to those used in the HF calculations described above, and were based on a fully relaxed bulk lattice. The relaxed geometry (Table III) is similar to that computed using the HF approximation (Table I). The DFT and HF results do show some differences in their description of the surface electronic structure. In both approximations the K atom is fully ionized with the donation of one electron to the substrate but the distribution of this charge is significantly different. Within DFT the majority of the

TABLE III. The relaxation of the surface layers (in Å) of the $c(2\times2)$ K TiO_2 (100) system computed within the LDA to DFT. Ionic displacements are relative to the bulk terminated coordinate system as defined in Figs. 1 and 2 with the location of the K^+ ion given relative to the relaxed $O_{(1)}$ position.

Label	$\delta[001]$	$\delta[010]$	$\delta[100]$
K	1.53	1.76	1.06
$O_{(1)}$	-0.05	-0.47	0.23
$O_{(2a)}$	0.05	-0.47	0.23
$Ti_{(3)}$	0.0	-0.04	-0.09
$Ti_{(4)}$	0.0	0.09	-0.02
$O_{(5)}$	0.05	-0.17	0.16
$O_{(6a)}$	-0.05	-0.17	0.16

charge is transferred to the surface oxygen ions ($0.34|e|$ per ion) with the remaining charge delocalized over the whole slab. In particular, the charge transferred to the surface Ti ions is very small (about $0.02|e|$) in contrast to the HF where we recall that $0.27|e|$ is transferred to $Ti_{(3)}$ (Table II). The DFT spin density is also rather delocalized with $0.42\mu_b$ on $Ti_{(3)}$ and $0.21\mu_b$ on $Ti_{(4)}$. The DOS computed within DFT is displayed in Fig. 5. The spin-polarized state due to the occupied Ti_{3d} orbital on the surface Ti sites appears about 2.5 eV above the VBM and overlaps strongly with the conduction band. This DOS is similar to that found in recent calculations on the reduced (110) surface.[33]

We find that the central results of this study do not depend strongly on the approximation of exchange and correlation.
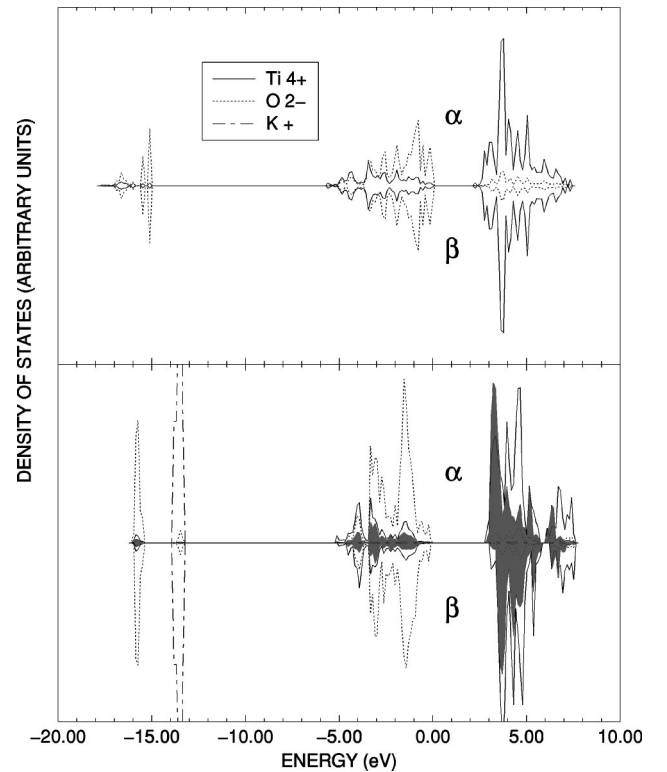

FIG. 5. Density of states projected onto surface titanium and oxygen sites for clean and $c(2\times2)$ K TiO_2 (100) surfaces calculated using DFT theory within the LDA. The valence band maximum has been aligned to 0 eV to facilitate comparisons. The shading represents states due to Ti^{3+} ions.

TABLE IV. Comparison of densities of states from experiment (Refs. 22–25) and present Hartree-Fock and density functional calculations. The position of the Ti_{3d} states is relative to the O_{2p} valence band maximum.

	O_{2p} bandwidth	Position of Ti_{3d} state	Width of Ti_{3d} state
Experiment	6 eV	3 eV	1 eV
HF	7 eV	1 eV	0.8 eV
LDA	5 eV	2.5 eV	0.3 eV

In both HF and DFT approaches K adsorption generates a spin-polarized state above the O_{2p} VBM. Experimental measurements have been made of the width and position of this state relative to the VBM; these are compared to the current calculations in Table IV. The results for the O_{2p} bandwidth are consistent with the usual trend for HF theory to overestimate, and DFT to underestimate, bandwidths. In a similar way the spin-polarized state is somewhat overlocalized and overstabilized in the HF approximation and perhaps too delocalized and understabilized in DFT. In the DFT approximation the spin-polarized state and the conduction band overlap. This is inevitable as DFT underestimates the bulk band gap by 50%.

The spin-polarized nature of the state has also been reported in studies of potassium adsorption on the TiO_2 (110) surface[52] but has yet to be observed experimentally. It may, however, be possible to use electron spin resonance (ESR) techniques, which have recently been applied to alumina surfaces,[57] to observe such states. In anticipation of such measurements we have calculated the hyperfine coupling constant and find it to be in the region of 20 G which appears to be within the resolution of current ESR techniques.[57]

If the surface spins were to form a magnetically ordered state then a number of techniques could be used to observe the spin density. We estimated the spin interactions by computing the energy of the ferromagnetically and antiferromagnetically ordered states of a double surface unit cell. In the HF approximation the energy difference between these states is about 0.1 meV, indicating that the magnetic interactions are too weak to yield magnetic ordering at the surface.

V. CONCLUSION

We have investigated the changes that occur to the geometric and electronic structure of the TiO_2 (100) surface upon adsorption of K. We find that the K ion donates one electron to the substrate, which results in the spin polarization of the surface Ti_{3d} orbitals. A rather localized ''band gap'' state results at about 1 eV above the O_{2p} valence band maximum as observed in recent photoemission studies. The state is similar to that observed in calculations of the reduced TiO_2 surfaces.

Although different treatments of exchange and correlation influence the distribution of the surface charge and spin density the physical picture of reduction of surface Ti ions resulting in a spin-polarized surface state is preserved and we conclude that spin polarization is essential for a correct description of the electronic structure of this system.

The predicted geometric structure is in excellent agreement with experimental observations of the K-O bond lengths. There is an intimate relationship between the electronic and geometrical structure with the localized electronic state giving rise to the surface relaxation. The qualitative features of the relaxation can be understood in terms of a simple electrostatic model which takes into account the relative screening of the surface Ti^{3+} and Ti^{4+} ions. The localization of the charge and the resultant distortion of the lattice are consistent with recent proposals concerning the existence of a self-trapped small polaron in this system.[26] We would expect to see similar polaronic behavior in other cases where Ti^{3+} ions are formed.

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