

Electronic structure of reduced titanium dioxide

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We use the local spin-density approximation in density-functional theory to study the electronic structure of TiO_2 and its (110) stoichiometric surface, as well as Ti_2O_3 and the reduced (110) surface, which are examples of reduced TiO_2 , in order to address the question of how donated electrons are distributed among the previously unoccupied Ti 3*d* states. We conclude that, whereas a split-off band in Ti_2O_3 probably leads to Mott-Hubbard insulating behavior, a picture of itinerant electrons in approximately one-electron states with Stoner exchange splitting is an appropriate description in the case of the reduced surface. Our calculations will be useful in interpreting photoemission experiments as well as measurements of core-level shifts at surfaces. [S0163-1829(98)08803-1]

I. INTRODUCTION

Transition-metal oxides have been for many years the subject of much experimental and theoretical study. Not only is the electronic structure of great interest, oxides have technological relevance—in particular, as supports of metal catalysts.^{1–3} As a preliminary to reporting upon the calculated electronic structure of transition-metal overlayers on rutile TiO_2 surfaces,⁴ we report here our electronic-structure calculations on pure Ti-O systems. We address two questions. First can we find an appropriate solution within the context of modern band-structure methods? Second, what is the electronic structure of *reduced* TiO_2 ? This question is of interest in the light of photoelectron spectroscopy experiments at stoichiometric and reduced surfaces of TiO_2 and Ti_2O_3 .⁵ When the Ti-derived conduction-band states become occupied upon reduction there arises the possibility of magnetic ordering and of states appearing in the band gap that have “split off” from the conduction band. The question of interest is this: When oxygen atoms are removed from stoichiometric TiO_2 how are the remaining electrons redistributed among the unoccupied Ti 3*d* orbitals? If the physical picture is one of electron correlation among rather localized Ti 3*d* states, then it is likely that the local spin-density functional approximation (LSDA) will fail to provide a correct description and an extension such as $\text{LDA}+U$ will need to be invoked.⁶ On the other hand, if the electrons can be thought of as occupying approximately one-electron levels in the conduction band of the oxide, then LSDA will be appropriate.

The local spin-density functional approximation has recently found application in studies of the electronic structure of transition-metal oxides, their surfaces and defects.^{7–11} This provides a new challenge to density-functional theory since it is not clear how appropriate the pseudopotential approximation is when dealing with transition metals or first row elements like oxygen. On the other hand, the all-electron methods that involve augmentation in muffin-tin or Wigner-Seitz spheres suffer from problems associated with poor packing of open crystal structures and, in the atomic spheres approximation at least, the results may depend too strongly on the choice of atomic sphere radii.¹² In this paper we use

the full-potential linear muffin-tin orbital (FP-LMTO) method¹³ to study the question of the electronic structure of reduced titanium oxides. We show first the electronic structure of bulk rutile TiO_2 . We also show calculations of the corundum sesquioxide Ti_2O_3 , which exposes a number of the questions that arise when the transition-metal states are occupied. We then describe our results on the electronic structure of the stoichiometric and fully reduced (1×1) (110) surfaces in TiO_2 .

II. METHOD

We employ the FP-LMTO method.¹³ Hankel functions of three kinetic energies, -0.4 , -5 , and -8 Ry, are augmented within almost touching muffin-tin spheres by numerical solutions of the radial Schrödinger equation. Sphere radii are typically 1.74 a.u. for Ti and 1.84 a.u. for oxygen. The basis set on oxygen atoms comprises $2s2p3d$ functions at the first energy, $2s2p$ at the second, and $2s$ on the third. The basis on the Ti atoms is $4s3p3d$ in the first two energies and $4s$ only in the third. We have chosen to include the $3p$ rather than the $4p$ Ti states in the basis, since the latter are so high in energy that tests have shown their inclusion to be unnecessary. On the other hand, as will be shown below, the Ti $3p$ show significant dispersion and it would be inappropriate to treat these as core states as is done in the so called “large core” pseudopotentials. Space is filled where appropriate by “empty spheres,” which carry no basis functions but which are used in the one-center expansions of the charge density, which is accomplished by expansion in two sets of Hankel functions with fit energies¹³ -3 and -5 Ry. We furthermore make another diagonalization of the Hamiltonian in a “second panel” so that the Ti $3s$ electron dispersion and charge density is accounted for. In this panel, the Hankel function kinetic energies are -0.6 , -10 , and -20 Ry with the same basis functions as in the main panel. The core is allowed to relax, but is treated as spherically symmetric. All relativistic effects except spin orbit coupling are included. Exchange and correlation are treated within the LSDA using the functional of von Barth and Hedin modified by Moruzzi Janak and Williams.¹⁴ We have also used an exchange correlation functional including gradient corrections (GC's).¹⁵

TABLE I. Structural parameters and oxidation states in TiO_2 and Ti_2O_3 (in the hexagonal setting of the corundum structure).

	Ref.	$a(\text{\AA})$	c/a	u	$z(\text{Ti})$	$x(\text{O})$	Oxidation state			
							Formal	Mulliken	Formal	Mulliken
TiO_2	Ref. 14 ^a	4.562	0.643	0.305			4 ⁺	1.24 ⁺	2 ⁻	0.62 ⁻
	Ref. 15 ^b	4.562	0.653	0.305						
	Ref. 9 ^c	4.567	0.642	0.307						
	Ref. 10 ^d	4.625	0.629	0.305						
	Ref. 10 ^e	4.781	0.643	0.305						
	expt.	4.594	0.644	0.305						
Ti_2O_3	Ref. 14 ^a	5.072	2.778		0.3421	0.3128	3 ⁺	1.05 ⁺	2 ⁻	0.7 ⁻
	Ref. 15 ^b	5.101	2.748		0.3416	0.3150				
	expt.	5.158	2.639		0.3447	0.3106				

^aPresent work: LSDA.^bPresent work: LSDA+GC.^cLDA pseudopotential including Ti 3*p*.^dLDA pseudopotential neglecting Ti 3*p*.^eLDA+GC pseudopotential neglecting Ti 3*p*.

In order to interpret the electronic structure in terms of local orbitals we use a Mulliken decomposition of the density of states, which is projected onto a minimal basis set of functions localized with a kinetic energy of about -1 Ry. The decomposition is not unique, but we find little change in the local densities of states if we vary the localization around this value. We use the Mulliken analysis to determine the approximate charge states of the oxygen and Ti atoms.

III. PERFECT CRYSTAL CALCULATIONS

It is very instructive to look briefly at the electronic structure of bulk TiO_2 and Ti_2O_3 , although calculations of this sort using the local-density approximation (LDA) or tight-binding approximation have been presented previously.^{7,8,16} In both crystals we have minimized the total energy with respect to the lattice parameters and internal coordinates. These are reported in Table I and compared to experiment and previous first-principles calculations. It is clear that the LDA very adequately predicts the structural parameters except for the axial c/a ratio in Ti_2O_3 , which is overestimated. There is also the usual about 1% underestimation of the lattice constant. The pseudopotential calculation that neglects Ti 3*p* overestimates the lattice constant of TiO_2 rather than underestimating it. Gradient corrections to the local-density approximation do not significantly affect the structural properties or density of states of TiO_2 or Ti_2O_3 . Note how greatly the Mulliken charges differ from the formal charges. This is an indication of covalency in the bonding. Equivalently, this is viewed as hybridization between the Ti 3*d* and oxygen 2*p* states, which can be seen in the local densities of states shown in Fig. 1. This figure also illustrates the point we wish to make about reduction. In stoichiometric TiO_2 the valence band comprising mostly oxygen 2*p* states is filled and the mostly Ti 3*d* conduction band is empty. TiO_2 is an insulator; and the LDA band gap is 1.8 eV compared to the experimental value of 3 eV—this is the familiar “gap problem” in LDA. However, the stoichiometry of Ti_2O_3 is such that after filling the oxygen 2*p* band there is one electron per Ti atom

that has to be accommodated in the conduction band. The LDA densities of states in Fig. 1 show how, whereas in TiO_2 the Ti-derived 3*d* bands are split approximately into t_{2g} and e_g subbands by the octahedral crystal field, in Ti_2O_3 the distortion of the octahedra further splits the t_{2g} states into bonding and antibonding a_{1g} subbands that appear above and below an e_g^π subband.⁸ At low temperature a semiconducting

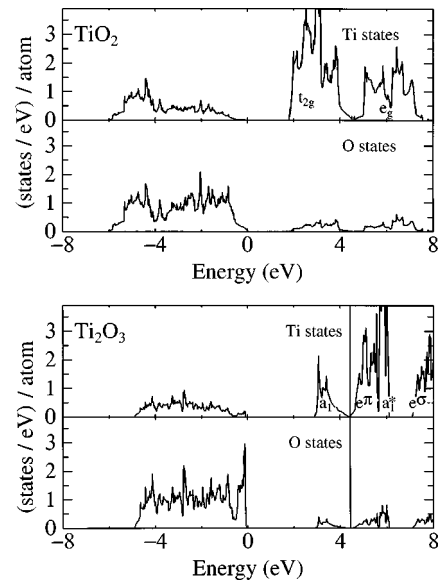


FIG. 1. Mulliken projected density of states in TiO_2 and Ti_2O_3 . Upper and lower panels show Ti and oxygen derived states, respectively. The lowest band shown is the valence band of principally oxygen 2*p* states and the upper bands are the Ti 3*d* states separated into subbands as indicated by the crystal-field splitting. The vertical line shows the Fermi level in Ti_2O_3 , which is predicted in the local-density approximation to be metallic: the density of states at the Fermi level is 0.06 states per eV per Ti_2O_3 formula unit. This is a case of the LDA “gap problem:” at low temperature Ti_2O_3 is observed to be a semiconductor with a 0.1-eV gap between the a_{1g} and e_g^π manifolds.

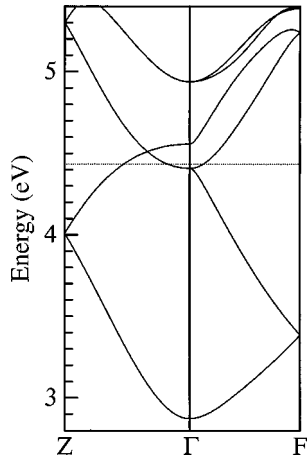


FIG. 2. Energy bands in Ti_2O_3 (in the trigonal setting) around the Fermi level showing the two spin degenerate bands in the a_{1g} manifold (containing one electron per Ti atom below the Fermi level) and the four spin-degenerate bands in the e_g^π manifold above the Fermi level (horizontal dotted line).

gap appears, possibly between the a_{1g} and e_g^π bands, the former containing just one electron per Ti atom (or two spin degenerate bands per Ti_4O_6 trigonal unit cell, as shown in Fig. 2). Although the LDA predicts Ti_2O_3 to be metallic with a small density of states at the Fermi level, at first sight this could be regarded as the usual gap problem at work—especially since, if strong correlations were operating, one would expect Ti_2O_3 to be a magnetic insulator, rather than a semiconductor.¹⁷ However, Fig. 2 showing the bands around the Fermi level makes it clear that there can be no gap between the a_{1g} and e_g^π bands unless there is splitting by an added term in the Hamiltonian such as a Hubbard U ,⁶ an antiferromagnetic field, or a crystal distortion. One would expect the screened U to be on the order of just a few eV in Ti, but because of the narrowness of the a_{1g} band (about 1.5 eV in Fig. 2) this is sufficient in this case to admit Mott-Hubbard insulating behavior. It is observed that Ti_2O_3 undergoes a semiconductor to metal transition in the temperature range 200–400 °C, which is accompanied by a large increase in axial ratio.^{5,18} Apparently at zero temperature the LSDA reproduces the high-temperature atomic and electronic structure. One may speculate that this transition is driven primarily by bonding considerations,⁸ and that as the a_{1g} and e_g^π manifolds overlap, the effective bandwidth increases, reducing the importance of correlations.

IV. STOICHIOMETRIC (110) SURFACE OF TiO_2

The atomic structure of the stoichiometric (110) surface of TiO_2 is shown in Fig. 3, which shows the three layer slab used in our supercell calculations. There are two inequivalent Ti atoms in the surface: one is fivefold (atom 2) and the other sixfold coordinated (atom 1), the latter being doubly coordinated to a row of “bridging oxygens” (atom 0). The atomic structure of the surface was calculated by Ramamoorthy, Vanderbilt, and King-Smith⁹ (using the pseudopotential plane-wave LDA method) and we use their relaxed coordinates here. Figure 4 shows the local densities of states in which, as in stoichiometric TiO_2 , the valence band is occu-

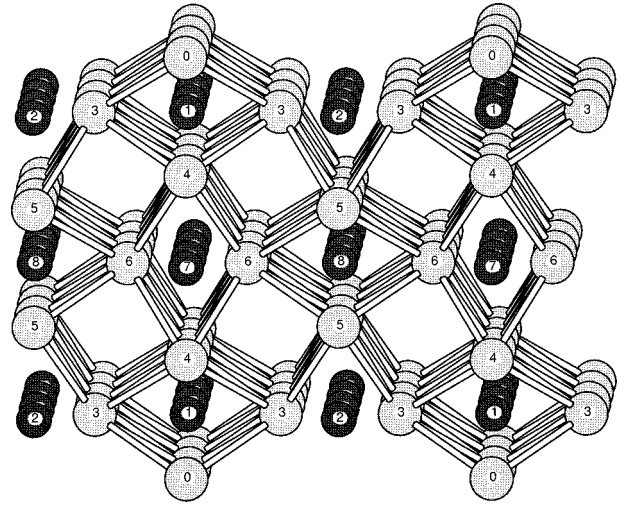


FIG. 3. Atomic structure of the three layer slab used in our calculations on the (110) surface. Lighter atoms are oxygen and darker atoms Ti. Labeling is as used in the text and in Tables 1 and 2. The bridging oxygens (atom 0) are all removed to create the (1×1) reduced surface.

pied by mostly oxygen $2p$ states and the Ti-derived conduction band is unoccupied. The band gap is reduced relative to the bulk crystal, as observed experimentally, and the only other feature we wish to point out here is the electrostatic shift between the fivefold and sixfold Ti atoms, which leads to the states at the bottom of the conduction band being derived from the fivefold Ti atom. These shifts are revealed as affecting both valence and core levels in the large energy range shown. The lowest-lying bands belong to Ti $3p$ states

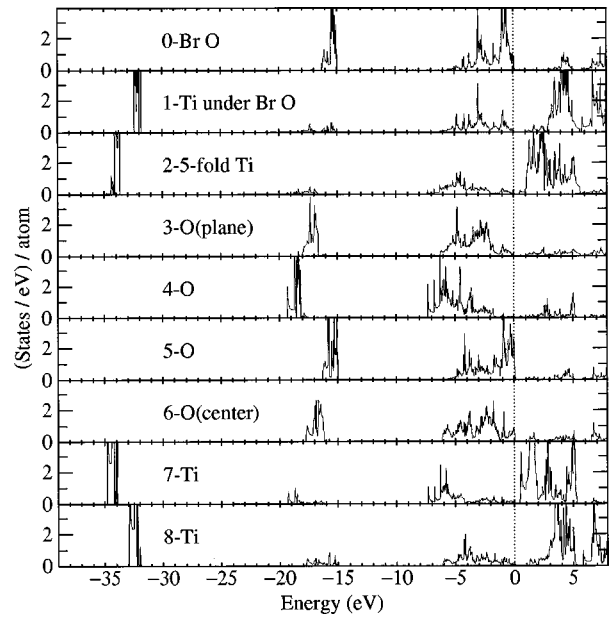


FIG. 4. Mulliken projected densities of states for the stoichiometric (110) surface. A wide energy range is shown in order to indicate the positions of the Ti $3p$ (at around -35 eV) and oxygen $2s$ bands (at around -15 eV). Note the wide dispersion of the Ti $3p$ states. The range allows us to emphasize the electrostatic shifts that arise at the surface.⁴ These shift both core and valence levels and thereby lead to shifts in occupation number or oxidation state of the surface atoms.

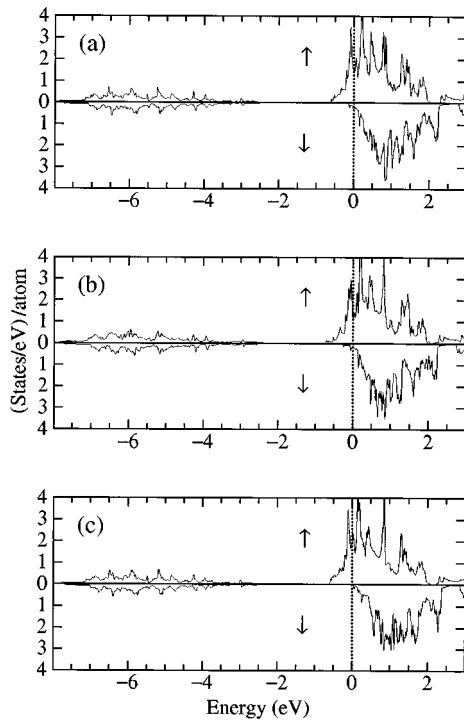


FIG. 5. Spin-up and spin-down Mulliken projected densities of states on the fivefold Ti (atom 2) in the reduced surface. (a) Relaxed atom positions from Ref. 11 in LSDA.¹⁴ (b) Bulk terminated (unrelaxed) atom positions also in LSDA. (c) Relaxed positions in LSDA+GC.¹⁵ This shows the very small effect that both atomic relaxation and gradient corrections (or different exchange-correlation functionals) have on the electronic structure. Note that the gradient corrections have the effect of increasing slightly the exchange splitting in the Ti 3d bands, so that the minority spin band becomes fully unoccupied.

and the dispersion of these is seen to be nearly as large as that of the oxygen 2s bands. They cannot, therefore, justifiably be neglected.

V. REDUCED (110) SURFACE OF TiO_2

This is a surface in which all rows of bridging oxygens are removed. The surface is “reduced” both in the sense that it is oxygen deficient and also in that there are now electrons “donated” from the oxygen ions into the conduction band—in other words, one expects the oxidation state of the surface Ti atoms to be reduced. As a consequence of the removal of the bridging oxygens, the originally sixfold coordinated Ti (atom 1) is now fourfold coordinated. The surface is never realizable in practice but provides a useful theoretical model with which to address the questions posed here, and below we will make a connection to the measured ultraviolet photoemission spectra (UPS) of the reduced TiO_2 (110) surface.

Our LSDA calculations are displayed in Figs. 5 and 6 and in Table II. We have used both bulk terminated atom positions and those quoted by Lindan *et al.*¹¹ after a molecular-dynamics relaxation using the plane-wave Car-Parrinello method. We have also done the calculations with and without gradient corrections. As Fig. 5 shows, the results in all cases are essentially the same. In what follows we concen-

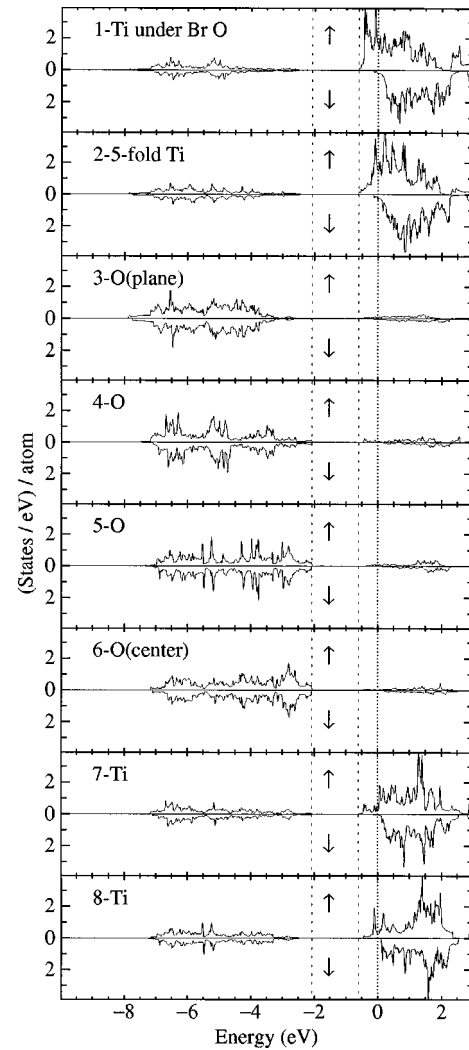


FIG. 6. Spin-up and spin-down Mulliken projected densities of states on all atoms in the reduced surface slab. This figure shows results from relaxed atom positions¹¹ using LSDA [as in Fig. 5(a)]. Note that there is exchange splitting on all the Ti atoms, consistent with a Stoner picture of magnetism (Ref. 19); and essentially no splitting of the occupied oxygen 2p bands.

trate on the results of the relaxed surface using LSDA only.

The stoichiometry of the reduced surface slab that we use is Ti_3O_5 (see Fig. 3). Therefore, there are two electrons to distribute among three Ti atoms (as opposed to one per atom in Ti_2O_3). In a semi-infinite slab one could say that there is one electron to donate per surface Ti atom. This electron might form a localized, spin-polarized state in the Mott-Hubbard limit of $U/W \gg 1$ or it might occupy a delocalized conduction-band state if the bandwidth W dominated the Coulomb repulsion U . In Ti_2O_3 , due to the crystal structure type, the conduction band is split into subbands (Fig. 1) so that there is a pseudogap in the LSDA bands and an actual semiconducting gap in the real crystal. Here, the occupied bandwidth is small and the Mott-Hubbard limit is appropriate. The clear difference between this case and the reduced surface is that in the latter case the Fermi level falls in a region of high density of states. Because of the narrowness of the 3d band the density of states is large enough to allow a Stoner exchange splitting of the band¹⁹ and the development of local moments on the two surface Ti atoms. This is

TABLE II. Oxidation states and magnetic moments on atoms in the stoichiometric and reduced (110) surfaces. Electron transfer in the stoichiometric surface is defined as the difference in Mullikan charge between atoms in the surface and those in bulk TiO_2 (Table I). In the reduced surface, electron transfer is defined as the difference in Mullikan charge between atoms in the reduced surface and atoms in the equivalent positions in the stoichiometric surface. These data then serve to indicate how the “donated” electrons are distributed among the remaining atoms after removal of the bridging oxygens.

Atom	Description	Stoichiometric		Reduced		Moment
		Oxidation state	Transfer	Oxidation state	Transfer	
0	Bridging oxygen	0.60 ⁻	-0.02			
1	Ti under Br O	1.22 ⁺	0.02	1.04 ⁺	0.18	1.2
2	fivefold Ti	1.47 ⁺	-0.22	1.35 ⁺	0.11	0.6
3	Plane layer O	0.70 ⁻	0.08	0.86 ⁻	0.16	0
4	Oxygen	0.69 ⁻	0.07	0.67 ⁻	-0.02	0
5	Oxygen	0.67 ⁻	0.05	0.67 ⁻	0	0
6	Center O	0.67 ⁻	0.05	0.69 ⁻	0.02	0
7	Ti	1.33 ⁺	-0.09	1.39 ⁺	-0.05	0.2
8	Ti	1.35 ⁺	-0.11	1.32 ⁺	0.03	0.2

shown clearly in Fig. 6. Table II shows the oxidation state and magnetic moments of atoms in the stoichiometric and reduced (110) surfaces. The fourth column shows the number of electrons transferred to each atom relative to the bulk TiO_2 . The sixth column shows the number of electrons transferred relative to the stoichiometric surface. These data, therefore, indicate how the electrons left behind after removal of the bridging oxygens are distributed among the remaining atoms. Surprisingly, in the stoichiometric surface, the fivefold Ti atom is in an oxidized state relative to the bulk; that is, its oxidation state is larger than in the bulk (formally greater than Ti^{4+}). Also, the Ti atoms in the central layer are “oxidized”. We can relate these differences in occupancy with a “reduction in covalency” at the surface,⁵ and note that it chiefly affects the five-fold Ti atom exposed on the surface. Although not shown in Fig. 6, we find that the core levels on the two surface Ti atoms are lined up in the reduced surface, unlike in the stoichiometric surface (Fig. 4). We next see that upon removal of the bridging oxygens, the charge is redistributed rather evenly among all the atoms in the top layer, *including the surface-plane oxygens*. The fivefold Ti remains oxidized, but the fourfold Ti atom is now reduced to an oxidation state similar to that in Ti_2O_3 . One could say that the fivefold atom is formally Ti^{4+} whereas the fourfold atom that was under the bridging oxygen is reduced to Ti^{3+} . The Stoner exchange splitting has induced local moments of 1.2 and $0.6\mu_B$ in the LSDA. The minority band is practically empty, and is indeed completely empty in the gradient-corrected LSDA (Fig. 5). The magnetic energy, which is the difference between the total energies in a non-magnetic local-density calculation and in the LSDA, is found to be 0.44 eV per slab containing four surface Ti atoms. This divides roughly into 0.11 eV per spin polarised Ti atom, and may be compared with a spin polarization energy of 0.6 eV for the free atom in LSDA.

This “strong ferromagnetism” was also seen in a recent pseudopotential calculation of this surface,¹¹ from which our relaxed atomic positions have been taken. However, in these calculations the spin-polarized states were found to be split off from the conduction band into the band gap and fully occupied. Their picture is therefore, one of localized mag-

netic moments in a nonmetallic state. The magnetic energy found was 2.8 or 0.7 eV per spin-polarized Ti atom, while the total magnetic moment in the same slab was $5.9\mu_B$ compared to our $4\mu_B$. Since the magnetic energy they find is much greater even than the spin-polarization energy of the free atom, we have to regard this calculation as open to question. We have also carefully checked our calculations in view of this discrepancy by varying both sphere radii and charge-density fit energy without affecting the electronic structure. We have to conclude, therefore, that the difference arises from the pseudopotential method, which may be overestimating magnetic effects by pseudizing the 3d wave functions or through the neglect of the Ti 3p dispersion.

We cannot compare our results directly with the UPS data on the stoichiometric and reduced surfaces of TiO_2 by Sadeghi and Henrich⁵ because it is not clear to what extent our fully reduced (1×1) surface resembles the real case. However, the spectra clearly reveal electronic states just below the threshold at the Fermi energy and above the band gap. The data do not show a gap between these states and the Fermi level, which we may take as a confirmation that these states are not split off into the gap as predicted by the pseudopotential calculations but are, as we suppose, at the bottom of the conduction band. Put another way, at the resolution of the experiment there appears to be no gap between occupied states and the rest of the conduction band.

VI. DISCUSSION AND CONCLUSIONS

The question we are addressing is this. In situations of oxygen-deficient nonstoichiometry in TiO_2 how are the electrons distributed? There are two possible pictures. In the first, localized, picture we imagine electrons donated into localized states on the Ti atoms. We would then expect features such as Hund’s rule magnetic moments and energy, integer atomic charges, and possibly Mott-Hubbard insulators if electron correlations in the Ti 3d shell were large.¹⁷ The other picture involves the existence of a conduction band into which the donated electrons enter and are delocalized. This picture is supported initially by our bulk crystal calculations. In TiO_2 we see that there is strong hybridization or

covalency and that the conduction band is largely Ti 3*d* derived but contains a significant oxygen 2*p* contribution. Calculations of the electronic structure of Ti₂O₃ show that although formally one electron per Ti atom is donated into the conduction band, these are delocalized and there is no spin moment generated. Ti₂O₃ is probably, however, a Mott-Hubbard insulator²⁰ because of the narrowness of the *a*_{1g} band split off by the crystal field due to the distorted octahedra in the corundum structure. In the case of the reduced surface, the 3*d* manifold is rather broader and correlation effects are probably negligible. The width of the conduction band is narrower than in pure Ti, however, so that the higher density of states favors Stoner exchange splitting, unlike in the pure metal.

Although we have not made any assessment of the electron correlation, by doing LDA+*U* calculations, for example, we nevertheless believe that the LDSA gives the correct picture (aside from the usual underestimation of band gaps) except in the rather exceptional case of Ti₂O₃. This is consistent with the conventional understanding that unlike, say, vanadium oxides, the oxides of Ti are not dominated in their electronic structure by electron correlation.⁵ Our calculations are internally consistent in that we find fairly wide 3*d* bands, delocalization of the donated electrons and predictable Stoner exchange splitting in the case where the density of states at the Fermi level is large.

In the case of the reduced (1 × 1) (110) surface we have

predicted strongly spin-polarized conduction-band states as a consequence of the donation of one electron per surface Ti atom. This picture is in contrast to the nonmagnetic Ti₂O₃. Although this calculation is at odds with a previous LSDA result¹¹ we believe it to be the correct one and to be consistent with the UPS spectrum of a reduced TiO₂ surface.

These calculations have revealed the connection between Mulliken and formal charges, and shown how the former are much smaller than the latter due to covalency. We would expect, for example, that x-ray photoemission spectroscopy spectra would give the typical Ti⁴⁺ or Ti³⁺ signals from the two surface atoms in the reduced surface. We have also seen that as a consequence of the much smaller Mulliken charges, the process of reduction does not transfer a whole two electrons per oxygen atom removed, but rather an amount closer to 0.6 electrons.

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