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The defined adsorption site of sodium on the $TiO_2(1\,1\,0)$–(1×1) surface

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Abstract

The adsorption site of sodium on the $TiO_2(1\,1\,0)$–(1×1) surface was studied by extended X-ray absorption fine structure. For coverage ranging between 0.25 and 0.5 ML, we find that sodium is on an 'in-between' site where it is bound to two bridging oxygen atoms at 2.25 Å and one in-plane oxygen atom at 2.40 Å, in full agreement with DFT calculations. At higher coverage the site becomes an hollow site where the sodium atom is equidistant to the three oxygen atoms at 2.30 Å, while metallic sodium clusters are also formed at the surface.
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1. Introduction

The alkali metal/oxide interaction has important consequences in a variety of fields such as catalysis [1,2], earth sciences and glass science [3,4]. Despite this practical interest, studies in the field are scarce, except several papers dealing with alkali metals on rutile [1,2,5–14]. At low coverage, the work function change and the occurrence of reduced Ti^{3+} [1,2,9] are indicative of an ionic adsorption of alkali metal on $TiO_2(1\,1\,0)$. At higher coverages, the charge transfer per alkali metal adatom decreases, but slower than on metal and semiconductor surfaces [1,2,5]. The charge transfer from adsorbed cesium to $TiO_2(1\,1\,0)$ decreases from unity at low coverage to 12% at saturation, as estimated by metastable electron impact spectroscopy [8].

Defined adsorption sites are often postulated, although their exact description might be far from a consensus as in the case of $Na/TiO_2(1\,1\,0)$ which was much debated [1,10–14]. Having recorded a $c(4 \times 2)$ pattern by low energy electron diffraction (LEED) at a sodium coverage of half a monolayer, Onishi et al. have inferred that adsorbed sodium forms Na_2O moieties with the surface oxygen atoms of rutile. Nerlov et al. made the observation that the binding energy of the Na 2p level was insensitive to coverage within the monolayer range

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[1] and assumed that the chemical environment of the sodium adsorbed on the $TiO_2(1\,1\,0)$–(1×1) surface should be essentially unchanged with increasing coverage. They then suggest that sodium is bound to three oxygen atoms of the surface, either to two bridging oxygen atoms and one in-plane, so-called 'in between' site, or to two in-plane oxygen atoms and one bridging (the 'adjacent' site) [1]. On $TiO_2(1\,1\,0)$–(1×1), the former was firstly favored on the basis of an examination of the expected environment of sodium in the two configurations [1]. At variance, shadowing/blocking measurements were found to better fit the 'adjacent' configuration [11]. A support for the 'in between' arrangement came from theoretical approaches [12,13]. However, although Hartree–Fock cluster calculations predicts a strong bonding of sodium to bridging oxygen atoms and a very weak link to the in-plane oxygen atom [12], ab initio periodic Hartree–Fock [15] and density functional/local density approximation (DFT/LDA) [13] favors a more balanced picture of the sodium–oxygen bonding with distances close to what can be expected for sodium–oxygen bonding distances in bulk compounds.

The present work is aimed at determining the structure of sodium on the $TiO_2(1\,1\,0)$–(1×1) surface by EXAFS measurements. The technique is well suited to examine such a structural environment since the long-range ordering found by Onishi et al. [14] is questionable [1,11]. However, alkali metal surface structures are often difficult to probe in that way. In the present work, we take advantage of the proved efficiency of the SA32 beamline at Super-ACO, the low energy machine of the LURE facility, to probe sodium environment until second and third shell even at coverage lower than a monolayer [3,4]. Models derived from measurements performed at the sodium K-edge, for low and high sodium coverage on $TiO_2(1\,1\,0)$–(1×1) are compared to already published experimental and theoretical models.

2. Experimental and data analysis

The EXAFS experiments were performed in an ultra-high vacuum chamber connected to the SA32 beamline at Super-ACO, the low energy synchrotron radiation machine of the LURE facility, running typically at 800 MeV with an average current of 300 mA. Rutile $TiO_2(1\,1\,0)$ crystals were mounted in the analysis chamber in two perpendicular orientations, so that the surface could be sampled with the photon electric field either along the $\langle 0\,0\,1 \rangle$ bridging oxygen rows or perpendicular to it. The electric field vector is in both cases parallel to the $TiO_2(1\,1\,0)$ plane. The vacuum chamber is equipped with a LEED optics and an Auger electron spectroscopy (AES) analyzer to check surface structures and compositions.

To scan the photon energy range corresponding to the sodium K-edge region, the line is equipped with a beryl $(1\,0\,\bar{1}\,0)$ double-crystal monochromator allowing an energy resolution of about 0.5 eV at 1 keV. The incident flux is monitored through the recording of the total electron yield (TEY) from a 2 μm polyethylene film covered by 700 Å of titanium. The absorption signal is also measured via the TEY inside the UHV chamber. The data analysis follows a now classical scheme. The atomic background is modeled by a spline function and the normalization uses the Heitler formalism where the atomic contribution to the absorption at one given energy E above the edge decreases according to the law:

$$\Delta\mu_{at} = C \cdot [1 - 8(E - E_0)/3E_0]$$

where C is the jump at the edge and E_0 is the edge energy. Then the Fourier transform uses an Hanning window spanning from 2.3 to 7.5 Å^{-1} and the $X(k)$ EXAFS data is k-weighted. Structural parameters are then obtained by a fitting procedure using the FEFFIT code [16], the phase shift parameters being calculated by FEFF7 [17]. From previously published results on the adsorption of sodium on clean SiO_2, this procedure has proved to be highly reliable since, in that case, we could check it on well known model compounds like Na_2O or Na_2SiO_3. It is worth pointing out here that we had to fit two independent polarization experiments with the same structural environment.

The preparation method of the $TiO_2(1\,1\,0)$ surface in vacuum chambers is very well documented. Successive phases of cleaning by Ar$^+$ ions of 500 eV energy, followed by annealing in UHV

at 900 K by means of electron bombardment were performed. The treatment resulted in a clean surface with a good crystallinity. The absence of any carbon and calcium contamination was checked by AES and a sharp (1×1) LEED pattern could be obtained. Ion bombardment and annealing in vacuum convert the stoichiometric rutile sample with pale yellow color into a dark blue defective crystal which electrical conductivity is high enough to avoid charging effects when using the total yield technique to monitor the X-ray absorption (on a very insulating sample, charging could induce distortions of the overall signal). Sodium was evaporated from a well outgassed SAES-Getter source which stability has proved to be reliable. The vacuum level was always kept in the low 10^{-10} Torr range even during the evaporation of sodium.

Two sodium coverages were studied herein, θ_1 and θ_2, in the submonolayer and multilayer ranges, respectively. An absolute measurement of the sodium coverage was not possible in our experimental set-up. The values of θ_1 and θ_2 are discussed below. Two successive experiments were performed at room temperature for each coverage on the two orthogonally oriented samples. Only normal incidence experiments were performed. At grazing incidence, because of the shape of the sample holder and because of a slight (a few tens of mm) displacement of the beam position with the photon energy across an EXAFS scan, we could not be sure to analyze only the TiO_2 surface. For a given series of measurements, equal sodium coverages were deposited on both samples. The size of the surface unit cell of TiO_2(1 1 0) is 2.96×6.49 Å^2, with two surface titanium atoms per unit cell which correspond to 1.04×10^{15} atoms cm^{-2}. This was taken herein as the definition of the monolayer.

3. Results

3.1. Low sodium coverage

The sodium coverage of θ_1 was examined first. It appears at first glance that XAS spectra collected along [0 0 1] and [1 $\bar{1}$ 0] clearly differ from each other (Fig. 1). On the anisotropic TiO_2(1 1 0)
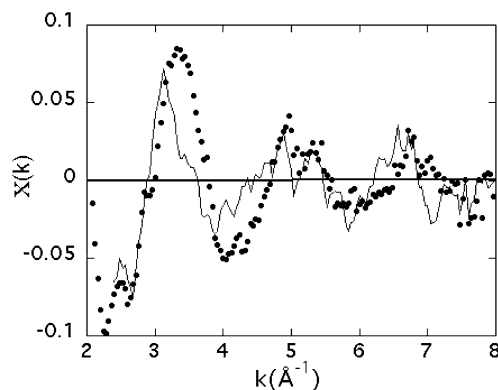

Fig. 1. Raw EXAFS data for the two orientations of the sample versus the photon electric field. ($\cdots$) E//[0 0 1], (—) E//[1 $\bar{1}$ 0].

surface, the occurrence of two different and reproducible XAS profiles along the two main crystallographic directions upon sodium adsorption demonstrates the existence of a defined structural arrangement for sodium. Very similar amounts of sodium were deposited on the two samples, as shown from the relative edge jump $(I - I^0)/I^0$ of the two near edge spectra collected with the electric vector along the [0 0 1] and [1 $\bar{1}$ 0] directions. Samples still exhibited a LEED pattern, although less sharp than that obtained on the clean sample. This is indicative of submonolayer coverage [1]. Finally, the energy position of the edge is identical to that of pure sodium chloride. From the 2 eV shift of the sodium K edge with respect to metallic sodium, it can be inferred that sodium is in a nearly fully ionized state at a submonolayer coverage on TiO_2(1 1 0).

3.1.1. The 'in between' site
The first step of the analysis consisted in the building of model clusters from which the different phase shifts could be calculated by FEFF7. The cluster associated with the 'in between' site is described in Fig. 2. A large enough number of substrate atoms were included in the model to obtain a stable modeling of the Na–O and Na–Ti phase shifts. In order to model the Na–Na phase shifts, the cluster used in FEFF calculations actually involves two sodium atoms on both sides of the bridging oxygen row. According to resonant
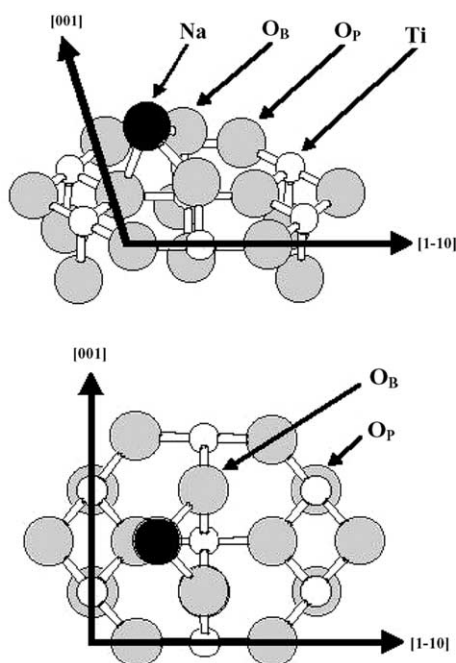
Fig. 2. View of the cluster used for the FEFF calculations. Top: perspective view, bottom: a view along the $[1\bar{1}0]$ axis of the TiO$_2$ surface. O$_B$ and O$_P$ are respectively the so-called 'bridging' and 'in-plane' oxygens of the TiO$_2$ surface.

photoemission experiments [1] and also to theoretical calculations on the stability of the sodium site [13], adsorption of sodium induces a derelaxation of the surface, then the models described in Fig. 2 assume bulk-terminated positions for the titanium and oxygen atoms surrounding the sodium adatom.

The 'in between' model was first fitted on the basis of the calculation which was performed by Albaret et al. [13] for sodium on TiO$_2$(1 1 0) at low coverage (1/8 ML), i.e. with different Na–O distances for bridging and in-plane oxygen atoms. This choice is discussed below. Since the photon electric field is linearly polarized on the horizontal plane, the apparent coordination numbers could be calculated by considering that each neighbor contributes $3\cos^2\Theta$ to the scattered intensity (Θ is the angle between the photon electric field and the bond direction). Finally, the analysis amounts to a fitting procedure which involves only the energy position of the edge and the Debye–Waller factors of each bond. The Fourier transforms were filtered

in R space between 1.2 and 3.3 Å, which includes the two first shells, and the k range spans from 2.6 to 7 Å^{-1}, then it is allowed to fit 6 parameters per EXAFS spectrum. A common value of the energy edge had to be found for the two orientations since they were measured during the same run, and a coherent set of free parameters has to be obtained for these two polarizations. The best results of the fits are given in Table 1 while Fig. 3 shows the corresponding theoretical and experimental Fourier transforms. Because of the very small absorption jump at the edge and because of the limitation of the energy domain, it was assumed that the coordination numbers listed in the following tables could be affected by an error of ±0.3 while distance are accurate within ±0.03 Å.

These results call for two comments. (i) While the distances and the apparent coordination numbers are well defined, the quality of the fit improves when allowing the more remote Na–O distance of the model to vary. This Na–O bond is shifted from 3.8 to 3.6 or 4.5 Å depending on the orientation and it concerns the second peak of the Fourier transform. It is difficult at this stage to definitely attribute the shortening of this distance to a true effect due to a surface relaxation, or to an inaccuracy of the analysis process. Since the discrepancy between expected and fitted distances only affects the more distant atom at 3.8 Å, it likely corresponds to the limit of the modelling of the data. (ii) For both orientations, the introduction of sodium–sodium interactions, with distance set at the geometrical value for both the $[1\bar{1}0]$ and the $[0\,0\,1]$ directions, is rejected by the fitting procedure which returns a very large Debye–Waller factor for these interatomic distance. As a consequence of the absence of sodium–sodium neighbors, the coverage θ_1 must be lower than 0.5 ML since, for geometrical reasons, neighboring sodiums at a distance close to 3 Å would necessarily show up above this coverage (see below).

3.1.2. Other structural models
Because of the limited energy domain beyond the Na K-edge, the determination by EXAFS of a very well defined site is questionable. The above results only prove that the site of the isolated sodium adatom (i.e. low coverage) determined by

Table 1
Best fit results for the local environment of the sodium atom set to a position described in Ref. [13]

Neighbor	E//[0 0 1]			E//[1 1̄ 0]		
	Apparent c.n.	Distance (Å ± 0.03)	DW factor (Å² ± 0.02)	Apparent c.n.	Distance (Å ± 0.03)	DW factor (Å² ± 0.02)
O(B)	2.6	2.25	0.0001	2.1	2.25	0.0001
O(P)	0.0	2.40	0.000001	0.2	2.40	0.0003
Ti(VI)	0.0	2.67	0.001	0.8	2.67	0.02
Ti(V)	1.2	3.34	0.0125	2.	3.34	0.004
O	3.7	3.62 (−0.18)	0.001	2.1	4.5 (0.75)	0.2

The energy edge shift is −5 eV for both pannels. O(B) and O(P) are the bridging and planar oxygens, Ti(V) and Ti(VI) the pentagonal and octahedral titanium. Values in parenthesis are the changes of distances returned by the fitting procedure. The *R*-factor as returned by the fitting program Ref. [16] is 0.02 in average for both orientations.
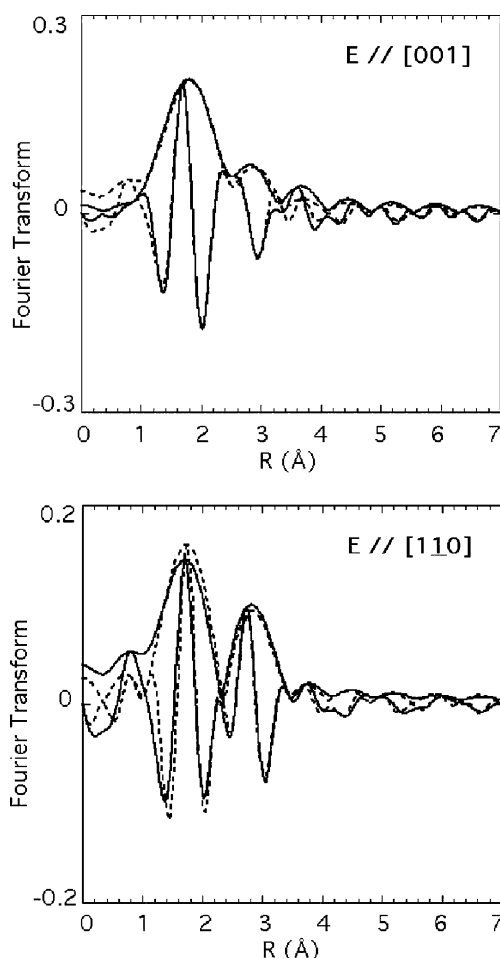

Fig. 3. Experimental (—) and model (- - -) Fourier transforms for the two polarizations for a low sodium coverage described by Table 1.

ab initio density functional calculations is consistent with EXAFS experiments. It is therefore crucial to check whether any other structural solutions, which were claimed from different experimental techniques or theoretical approaches, could also fit the present data.

(1) The 'adjacent' site, where the sodium is bound to one bridging and two planar oxygen atoms, can be considered as an alternative solution to the 'in between site' [1,13]. However, in this case, calculations predict a very short (2.09 Å) Na–O(B) distance and two very long (2.56 Å) Na–O(P) distances [13]. This splitting is not compatible with the EXAFS data. The fitting procedure never reaches reasonable values. Indeed, this structural solution has also been discarded by calculations from energetic considerations [13]. For similar reasons, the theoretical 'in between' model of San Miguel et al. [12] which leads to Na–O(B) distances much lower than the Na–O(P) distance can be rejected too.

(2) In most sodium compounds where sodium is bound to oxygen, the Na–O distance lies close to 2.30 Å, a distance which represents the sum of the two ionic radii. Moreover, all three Na–O distances which were calculated within the 'in between' site corresponding to a coverage of 0.5 ML are actually close to 2.30 Å. The question is to know whether the assumption that the sodium site is well described in the isolated adatom limit. Therefore, an attempt was made to simulate data with a structural model where the sodium atoms are on a hollow site at an equal distance of 2.30 Å, from in-plane and bridging surface oxygen atoms.

Here too, the apparent coordination numbers are well defined by the geometry and the same energy edge shift has to be used for the two analysis. However, the distance between the sodium atom and the substrate atoms could not be kept to their geometrical values and should be allowed to vary. The results for the 'in between' and 'adjacent' sites are shown in Tables 2 and 3, respectively. From a formal point of view, those structural solutions agree pretty well with experiments. The residuals of the fitting procedures are almost equal for all three analysis (Tables 1–3). Therefore, models have to be discussed from their physical meaning. First of all, the fitting of data within the 'in between' model (Table 2) requires a large shift of the edge energy for the two polarizations, which makes this structural solution unlikely. Moreover, assuming that the sodium atoms are at equal distances of three surface oxygen atoms leads for the EXAFS simulation to a relaxation of the TiO_2 surface. It is then possible to compare the sign of the displacements determined herein to the calculated and experimental values [18] found for the relaxation of the clean $TiO_2(1\,1\,0)$ surface. With respect to the moiety involving the sodium atom and its three oxygen neighbors, an increase of the sodium–titanium interatomic distance means an inward displacement of the corresponding titanium atom. All previously published results [18,19] report a negative value of the relaxation of the pentagonal titanium which is 'pushed' inside the bulk lattice, and an outward displacement of the sixfold coordinated titanium. This would lead to an increase of the Na–Ti(V) distance, and a decrease of the Na–Ti(VI) distance, not in line with the values derived from EXAFS shown in Tables 2 and 3. Moreover, the 'adjacent' site (Table 3), can be discarded the Na–Ti(V) distance takes an unrealistic value with respect to the sum of the ionic radii of the two atoms.

Therefore, while in terms of data analysis the solutions presented in Tables 2 and 3 correctly model the data, they lead to questionable numerical values. On the contrary, the site described by Albaret et al. for a low sodium coverage matches almost exactly the EXAFS data recorded at coverage of θ_1, since only a determination of the disorder parameters had to be made (Fig. 3 and Table 1).

Table 2
The structural results when the sodium atom is on the almost hollow 'in between' site with all Na–O distances originally set at 2.30 Å

Neighbor	$E//[0\,0\,1]$			$E//[1\,\bar{1}\,0]$		
	Apparent c.n.	Distance (Å ± 0.03)	DW factor (Å^2 ± 0.02)	Apparent c.n.	Distance (Å ± 0.03)	DW factor (Å^2 ± 0.02)
O	2.5	2.30	0.0000	2.7	2.36 (0.06)	0.000
Ti(VI)	0.			1.	2.79 (0.1)	0.0027
Ti(V)	1.3	3.25 (0.03)	0.008	1.8	3.22 (0)	0.08
O	3.7	3.38 (−0.36)	0.064	2.1	3.74	0.0007

Coordination numbers were fixed during the fitting procedure. The numbers in parenthesis following the distance values are the shifts found by the fitting procedure from the initial geometrical values. *R*-factor is 0.035.

Table 3
Results for the 'adjacent' site in similar conditions as in Table 2

Neighbor	$E//[0\,0\,1]$			$E//[1\,\bar{1}\,0]$		
	Apparent c.n.	Distance (Å ± 0.03)	DW factor (Å^2 ± 0.02)	Apparent c.n.	Distance (Å ± 0.03)	DW factor (Å^2 ± 0.02)
Ti(V)	0.0	2.02		0.75	1.89 (−0.13)	0.0039
O	2.5	2.30 (0)	0.00001	3.	2.30 (0)	0.014
Ti(VI)	1.3	3.20 (0)	0.0046	3.	3.39 (0.19)	0.008
O	1.3	3.28 (0.06)	0.0008	3.	3.47 (0.24)	0.02

$R = 0.03$.

In that sense it could appear as the best model for the sodium adsorption site.

The fact that the Na–O(B) distance is lower than 2.30 Å while Na–O(P) is higher than that value is firmly established by the failure of the attempt of a fit with Na–O(B) = Na–O(P) = 2.30 Å. The error bar (±0.03 Å) accounts for this. The distance Na–O(B) might not differ from Na–O(P) by as much as it is claimed in the present work, but the difference between the two distances is certainly higher than ∼0.1. Such a behavior agrees with the results obtained by first principles calculations for a sodium coverage of 1/4 ML (or 1/8 ML). By comparison with the high sodium coverage θ_2, it is assumed that θ_1 ranges between 0.25 and 0.5 ML (see below). Two types of configurations could be suggested for the filling of the 1/4 ML coverage to 1/2 ML, with either sodium atoms forming Na_2O_2 moieties with bridging oxygen (by clustering two by two with two bridging oxygen atoms) or sodium atoms forming a zig-zag row to maximize the sodium–sodium distance [13]. The absence of any contribution from sodium–sodium distance for the coverage θ_1 favors the latter arrangement, indicating that the coulomb repulsion might be a central ingredient in the ordering of the sodium adlayer.

3.2. High sodium coverage

3.2.1. The hollow site

A multilayer sodium coverage θ_2 has also been examined. A comparison of the relative edge jumps between the two coverages (Fig. 4) shows that the sodium deposited in the θ_2 case is five time that deposited previously. Given the estimation (from LEED and EXAFS results) of 0.5 ML for θ_1, we obtain 2–3 ML for this high sodium coverage. As it will appear, and confirmed by AES experiments (see below) this multilayer consists of both an adsorbed sodium layer at saturation and metallic sodium clusters. The EXAFS will be shown to almost exclusively comes from the adsorbed layer.

Albaret et al. have also modeled the relative stability of different adsorbate configurations upon increasing the sodium coverage. The main evolution from the case where the sodium coverage is very low comes from the fact that the alkali atoms
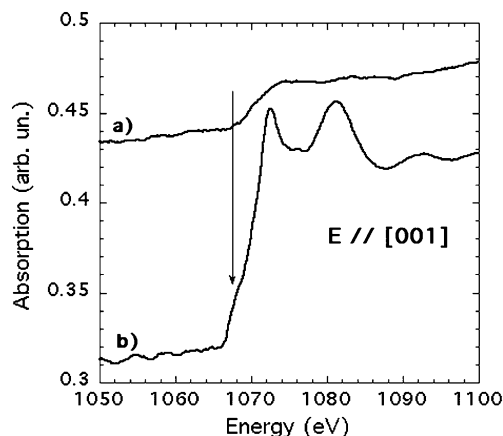

Fig. 4. Near edge structure of sodium for a low coverage (curve a) and for the high coverage (curve b). The amount of sodium is related to the relative jump at the edge and the arrow points to the position of a pre-edge feature which is the signature of metallic sodium.

move toward a nearly perfect 'in between' hollow site where the three interatomic distances with the three first oxygen neighbors are almost equal. This trend to a more symmetric site when the coverage increases is also predicted by either slab calculations [13], cluster calculations or molecular dynamics calculations [19, and references therein], although the numerical values are different. We have then assumed that this perfect hollow site with three Na–O distances equal to 2.3 Å remains the same at full coverage where all sites are occupied. The 'in between' site was definitely favored because the fitting procedure systematically leads to a residual *R*-factor (0.02) lower than that determined in the framework of the 'adjacent' model (*R* = 0.05). All apparent coordination numbers and interatomic distances are again well determined, and for instance, along the direction [0 0 1], one sodium atom has two near neighbors at 2.94 Å (apparent coordination number = 6) while along [1 $\bar{1}$ 0] there is only one neighbor at 3.05 Å with therefore an apparent coordination number equal to 3 (another sodium atom lies farther and it has not been considered). The fitting procedure returns the values listed in Table 4 while the corresponding Fourier transforms are shown in Fig. 5. The changes, in comparison for both directions with the low coverage case, induced by the occupation of all

Table 4
Best fit results for the local environment of the sodium atom in the saturated adsorbed layer, after the theoretical model described in Ref. [13] for the hollow site

Neighbor	$E//[0\,0\,1]$			$E//[1\,\bar{1}\,0]$		
	Apparent c.n.	Distance ($\mathring{A} \pm 0.02$)	DW factor ($\mathring{A}^2 \pm 0.02$)	Apparent c.n.	Distance ($\mathring{A} \pm 0.02$)	DW factor ($\mathring{A}^2 \pm 0.02$)
O(B)	2.5	2.30	0.00001	2.6	2.30	0.0000
O(P)	0.0	2.30	0.00001	0.3	2.30	0.0002
Ti(VI)	0.0	2.71	0.0001	1.	2.71	0.04
Na	6.	2.95	0.020	3.	3.05	0.0002
Ti(V)	1.3	3.18	0.01	1.9	3.16	0.03
O	3.8	3.5 (−0.24)	0.02	2.1	3.5 (−0.24)	0.0035

The energy edge shift is 0.84 eV for both pannels. O(B) and O(P) are the bridging and planar oxygens, Ti(V) and Ti(VI) the pentagonal and octahedral titanium. The figures in parenthesis are the shift returned by the fitting procedure from the geometrical distances.
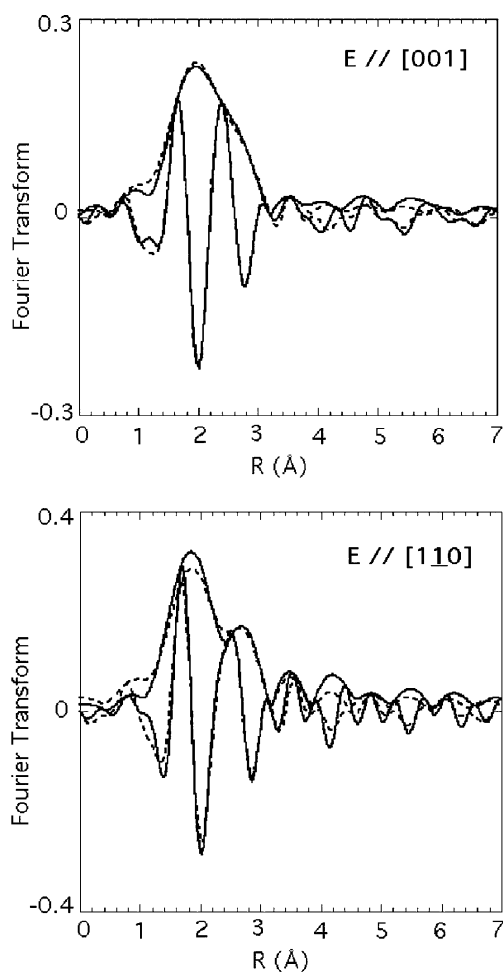

Fig. 5. Experimental (—) and model (- - -) Fourier transforms for the two polarizations for a high sodium coverage described by Table 4. These results have to be compared to those of Fig. 3.

possible sites for the sodium atoms, are well evidenced by the experimental results and the analysis. The experimental results are then fully consistent with the more recent calculations [13].

The results gathered in Table 4 should be compared to those of Table 2 which describe the local structure of the sodium atoms in an 'in-between' site at low coverage. In the case of the large sodium coverage, the modeling of the experimental results does not imply a shift of the interatomic distances as it was the case for θ_1 (except the farthest Na–O at about 3.5 $\mathring{A}$ which will be discussed later).

The simultaneous occurrence of sodium–sodium distances of 3.05 and 2.94 $\mathring{A}$ in the $[1\,\bar{1}\,0]$ and $[0\,0\,1]$ directions, respectively, is consistent with a full occupancy of all the available surface hollow sites of $TiO_2(1\,1\,0)$ surface. This formally corresponds to a maximum coverage of 1.04×10^{15} Na atoms cm^{-2}. As those sodium–sodium distances are much higher than twice the ionic radius of sodium (0.97 $\mathring{A}$), there exists no steric limitation to such a coverage. Notably, a cesium monolayer at saturation on $TiO_2(1\,1\,0)$ contains 6×10^{14} atoms cm^{-2} [2], but a cesium ion is expected to cover an area three times as big as a sodium ion. Therefore, a sodium coverage at saturation 75% higher than that observed for cesium is reasonable.

3.2.2. Coexistence of metallic and ionic sodium

As pointed out by Nerlov et al., photoemission experiments suggest the existence, at high sodium coverage, of metallic sodium which could form disordered metallic clusters. Indeed, in the present case, metallic sodium is expected to show up when

2–3 ML were deposited on the rutile surface. In a similar way, cesium was shown to display a Stranski–Krastanov growth mode on TiO$_2$(1 1 0) [2]. As a matter of fact, Fig. 4 compares the near edge spectra of the very low coverage analyzed in Section 3.1 (curve a) and that of the high coverage (curve b). This last spectrum exhibits at low energy a pre-edge feature, around 3 eV below the main edge, which can easily be attributed to metallic sodium, as shown by previous experiments [3]. The very low Debye temperature of sodium metal, the high disorder of small clusters, which are the most probable agglomeration form for these atoms, and the high interatomic distance in metallic sodium (3.76 Å) might explain the absence of a clear fingerprint for metallic sodium in the EXAFS spectrum, the only signature appearing in the edge jump. given the interatomic distance of 3.76 Å, the EXAFS contribution of metallic sodium could be at the origin of the discrepancy found between geometrical and fitted values of the most distant Ti and O shells above 3.3 Å. However, accounting for this contribution in the fitting procedure would have increased the number of parameters above the allowed limit.
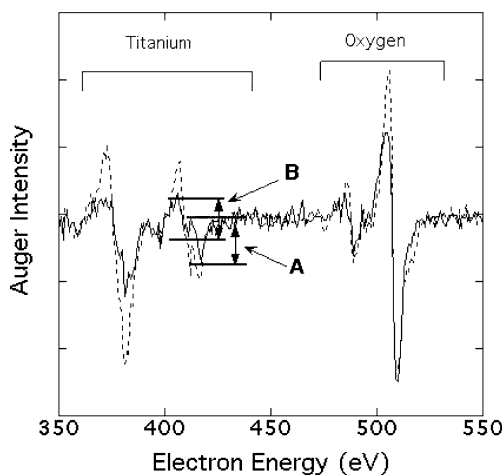

Fig. 6. Titanium and oxygen Auger spectra for the clean TiO$_2$(1 1 0) surface ($\cdots$) and for the same surface covered by about 2 ML of sodium (solid line). The 3d occupation of the Ti surface atoms (Ti^{3+} vs Ti^{4+}) induces a change of the A/B ratio (see Ref. [20]).

A suggestion is to use AES to probe the charge transfer from the sodium adlayer toward the rutile substrate. In titanium dioxide, the Ti LMV spectrum exhibits two peaks whose ratio is closely related to the filling of the 3d states [20,21]. After deposition of about 2 ML of sodium, the oxygen and titanium Auger signals are still present, although their intensities have noticeably decreased with respect to those of the bare rutile surface (Fig. 6). Indeed, the strong increase of the A/B ratio between the two components of the Ti LMV Auger peak upon sodium coverage is indicative of an increase of the Ti^{3+}/Ti^{4+} ratio at the vicinity of the surface [20], or, in other words, of the charge transfer from the alkali metals adatoms to the titanium ions [1,2,9].

4. Discussion

Upon increasing the sodium coverage on TiO$_2$(1 1 0), the EXAFS analysis demonstrates that the sodium site moves from an 'in between' site, where interatomic distances Na–O(B) and Na–O(P) differ by about 0.15 Å, toward a nearly perfect threefold hollow site at saturation, while preserving a similar general geometry. Of paramount importance is the fact that, over all the coverage range which was explored, and even in the presence of additional metallic sodium, the basic geometry of the adsorption site of sodium on TiO$_2$(1 1 0)–(1×1) remains unchanged. Consistent with the earlier suggestion by Nerlov et al. [1] of a unique site for sodium adsorption on the basis of photoemission experiments, this result is also in line with other studies [10,12] for coverages much lower than those which can be explored by EXAFS. Indeed, a totally different view emerges from the bulk of data related to alkali metals on metal and semiconductor surfaces [22,23]. On these surfaces, complex phase diagrams are commonly observed for a given system, including isotropic rings (in the absence of rotational order) [24], phase transitions [25], rotational epitaxy [26], commensurate and incommensurate structures [25]. Defined sites are only observed in particular cases within very narrow coverage ranges. Indeed, the general picture of Gurney [27] which predicts

the occurrence of strong dipoles upon alkali metal adsorption and a further depolarization as dipoles get closer upon increasing coverage, holds in all cases. But, at metal and semiconductor surfaces, the ordering is clearly dominated by adsorbate–adsorbate interactions, while in the present case, the localized bonding and the screening lead to an unique 'in between' adsorption site at any coverage.

The finding of a Na–O distance of 2.30 Å at high sodium coverage shows that sodium is still in an ionic form on the rutile surface. The persistence upon increasing coverage of a some ionic character for alkali metal adsorbed on rutile has already been pointed out [1,2,5,13]. However, as far as interatomic distances are concerned, the ionicity of sodium appears very high even within the saturated adlayer in the presence of metallic sodium. Indeed, in the limit of the isolated adatom, the electron of an adsorbed alkali metal is mainly transferred toward the titanium oxide. Upon increasing coverage, the ionicity of the adatom is partly reduced due to the overlapping between the electronic orbital of neighboring alkali atoms. However, such a process is less effective among oxidized sodium atoms which are tightly bound to the rutile surface that on sodium atoms on, say, metallic surfaces. It might be inferred that this overlapping is even more reduced for the small and deeply adsorbed sodium atom.

5. Conclusions

A direct determination of the sodium adsorption site on a clean $TiO_2(1 1 0)$–(1×1) surface was performed by XAFS. At low coverages, when lateral interactions between sodium adatoms are week, the sodium locates on an 'in between' site with a distance to the bridging oxygens (2.25 Å) shorter than that to the in-plane oxygen (2.4 Å), in agreement with DFT calculations. When the sodium adlayer saturates, all the hollow sites of the $TiO_2(1 1 0)$ surface tend to be occupied by sodium adatoms which still retain a highly ionic character, and the Na–O(B) and Na–O(P) distances become nearly equal. The presence of sodium neighbors

within the adsorbed layer is well evidenced in the EXAFS spectra. The sodium deposited beyond the saturation of the adsorbed layer forms metallic sodium clusters, the signature of which is clearly identified in the near edge spectra.

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