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Alkali-metal–to–substrate charge transfer in $TiO_2(100)c(2\times2)K$

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Resonance photoemission and surface-extended x-ray-absorption fine structure (SEXAFS) have been used to investigate the electron-donor properties of potassium adsorbed on rutile $TiO_2(100)$. Potassium *K*-edge SEXAFS from $TiO_2(100)c(2\times2)K$ shows that K lies in a bridge site, bonding to two oxygen atoms with a K-O bond distance of 2.62 ± 0.03 Å. Resonance photoemission data indicate that K adsorption is accompanied by charge transfer into Ti 3*d* band-gap states which are polaronic in nature. At 0.25 and 0.75 monolayer coverage about $\frac{1}{4}$ of an electron is transferred into Ti 3*d* states for each adsorbed potassium atom.

The nature of the bonding between alkali metals and surfaces of metals and semiconductors continues to be a subject of considerable controversy. Debate hinges on the extent of charge transfer between the alkali metal and the substrate, and hence the origin of the surface dipole established by the alkali metal.[1–8] More recent theoretical work on metals predicts little charge transfer and formation of a polarized covalent adsorbate-substrate bond at ≥ 0.5 monolayer (ML) coverage.[1] At lower coverage, a significant degree of charge transfer has been predicted,[2] more in line with earlier calculations.[3] For semiconductors the theoretical picture is less consistent, with a wide variation in the charge transfer indicated.[4,5] On the experimental front photoemission surface core-level shift (SCLS) spectroscopy has played a key role in the current debate. Results for W(110) have been interpreted as indicating little or no charge transfer,[6] consistent with theory. However, an alternative interpretation of this data has been proposed.[7] SCLS data for semiconductors produces a similarly varied picture which, it has been suggested, arises from the occupation of band-gap states determining the degree of charge transfer.[8]

In this paper we report results which provide direct evidence of charge transfer from an alkali metal to a substrate. We use resonance photoemission[9] to demonstrate that the band-gap state populated on a $TiO_2(100)$ surface by K adsorption has Ti 3*d* character. In addition, we employ surface-extended x-ray-absorption fine structure[10] (SEXAFS) to characterize the adsorption geometry.

Resonance photoemission measurements employed the VG ADES 400 analyzer and toroidal grating monochromator ($15\leq h\nu\leq 90$ eV) on station 6.2 at the Synchrotron Radiation Source, Daresbury Laboratory. Potassium *K*-edge SEXAFS measurements were carried out using a Ge(111) crystal pair in the double-crystal monochromator of station 6.3.[11] A double-pass cylindrical mirror analyzer (CMA) (Physical Electronics Inc.) operated in the nonretard mode was used to record the K *LMM* Auger yield as a monitor of the surface absorption coefficient. The CMA axis was at 90° to the incident photon beam, and measurements were made in normal (90°) and grazing (20°) angles of x-ray incidence. In both geometries the x-ray **E** vector was in the [001] azimuth. Normalization of the SEXAFS (photoemission) data to incident photon flux was accomplished using the electron yield from a thin Al foil (W mesh) placed between the monochromator and the sample chamber. Measurements were carried out at a base pressure of $<1\times10^{-10}$ mbar. During SEXAFS measurements the sample temperature was maintained at ~100 K to reduce Debye-Waller-like damping of the SEXAFS amplitude.[10] The preparation of the clean, stoichiometric $TiO_2(100)1\times1$ surface employed a method described elsewhere.[12] Low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) were used to determine surface order and composition, respectively. Potassium was deposited from a well-degassed SAES getter source as used in an earlier study[13] where we determined that a $c(2\times2)$ ordered overlayer is formed at a K coverage of 0.5 ML.

While photoemission spectra of stoichiometric $TiO_2(100)1\times1$ do not contain band-gap states, the creation of oxygen vacancies gives rise to a characteristic feature at 0.9 ± 0.1 eV binding energy.[12] This corresponds to the reduction of surface Ti atoms, nominally to Ti^{3+}, with the band-gap feature representing Ti 3*d* ionization. A similar effect is observed on $TiO_2(110)$ (Ref. 14) and $SrTiO_3$ (Ref. 15) surfaces. It has been suggested that $TiO_2(110)$ band-gap states,[16] and by implication band-gap states on other TiO_2 and $SrTiO_3$ surfaces, are polaronic in nature. The Ti 3*d* character of the band-gap states is evidenced in resonance photoemission above the Ti $M_{2,3}$ absorption edge, which has a delayed onset with a maximum at about 47 eV.[14]

Shown in Fig. 1 are photoemission spectra which illustrate that adsorption of potassium on $TiO_2(100)1\times1$ results in the occupation of band-gap states having a similar binding energy to those induced by oxygen vacancies. A similar modification was observed following Na adsorption on $TiO_2(110)$.[17] The implication in this case that K reduces surface Ti atoms was tested by monitoring the intensity of the band-gap state through the Ti $M_{2,3}$ resonance. A comparison of a constant initial state (CIS) spectrum of $TiO_2(100)+0.25$ ML K with a CIS spectrum of O-vacancy-induced band-gap states on $SrTiO_3(100)$

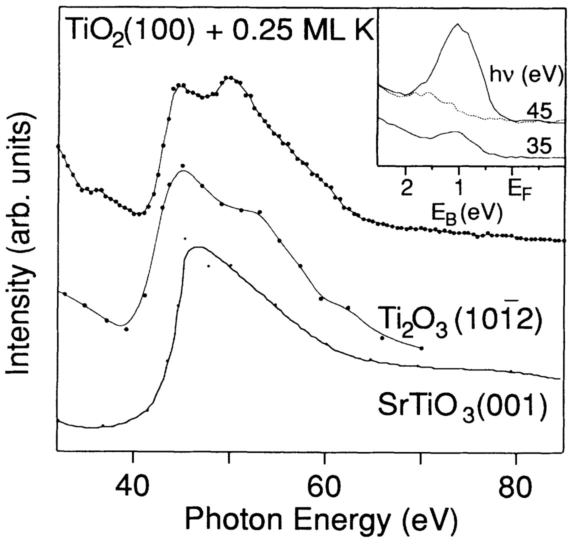

FIG. 1. CIS photoemission spectra of band-gap state intensity through the Ti $3p$ resonance for $TiO_2(100)$+0.25 ML K compared with that for O-vacancy-induced band-gap states on $SrTiO_3(001)$ (Ref. 15) and the $3d$ band of $Ti_2O_3(10\bar{1}2)$ (Ref. 18). The inset shows band-gap state photoemission spectra from $TiO_2(100)$+0.25 ML K; the dotted curve shows the same region of the $TiO_2(100)1\times1$ $h\nu=45$ eV spectrum. Spectra were recorded at 300 K, normal emission, and at a 45° angle of incidence.

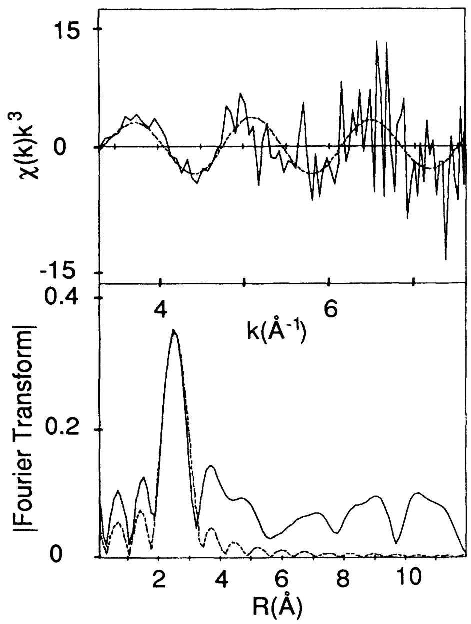

FIG. 3. K *LMM* Auger yield SEXAFS spectra from $TiO_2(100)c(2\times2)$K recorded at an angle of incidence of 20° with the **E** vector in the [001] azimuth. The EXAFS function $\chi(k)$ weighted by k^3 (solid line) and the best fit (dashed line) are compared in the upper part of the figure. The corresponding lower section contains the modulus of the Fourier transform.

(Ref. 15) and the d band of $Ti_2O_3(10\bar{1}2)$ (Ref. 18) is shown in Fig. 1. This comparison clearly evidences the Ti $3d$ character of the band-gap state formed on K adsorption.

The relative intensity of the band-gap feature in the 45 eV photoemission spectrum of $TiO_2(100)$+0.25 ML K can be used to determine the approximate degree of charge transfer to second-layer Ti atoms from each adsorbed potassium atom. To do so we employ a variation on a method previously used to determine the oxygen-vacancy concentration on $TiO_2(110)$ surfaces.[14] In this method the Ti $3d$ and the O $2p$ relative photoemission cross sections are evaluated by comparing the intensities observed in resonance photoemission from $Ti_2O_3(10\bar{1}2)$.[18] We assume charge transfer only into second-layer Ti atoms and that attenuation lengths for Ti $3d$ and O $2p$ features are 10 and 12 Å, respectively.[14] For the 0.25-ML covered surface this simple calculation indicates that about $\frac{1}{4}$ of an electron is transferred into Ti $3d$ states for each adsorbed potassium atom.

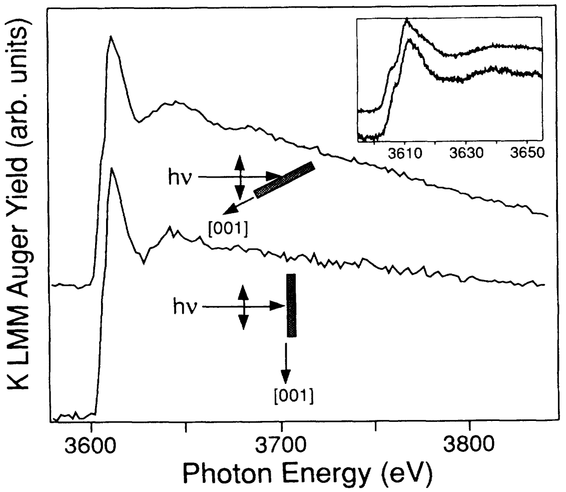

FIG. 2. K *LMM* Auger yield at the K *K* edge from $TiO_2(100)c(2\times2)$K. The spectra were recorded at an angle of incidence of 20° and 90° with the **E** vector in the [001] azimuth. The edge step in the 20° (90°) data is 0.69 (0.71), where the edge step is the difference in count rate above and below the absorption edge divided by the count rate below the edge. The inset shows the corresponding NEXAFS spectra.

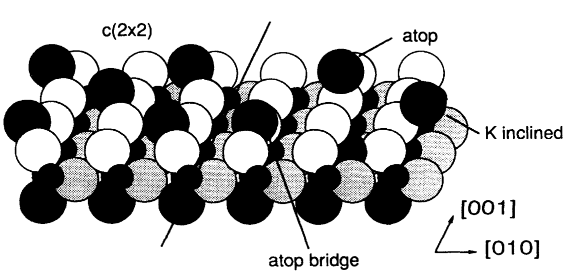

FIG. 4. Model of $TiO_2(100)c(2\times2)$K derived from the SEXAFS data, with K atoms bonded to two bridging oxygens. Atom types are depicted approximately to scale, assuming ionic radii. The alternative K adsorption sites considered in modeling the SEXAFS are also shown. The open and shaded circles represent the first-layer and subsequent-layer oxygen atoms, respectively. Small (large) solid circles represent Ti (K).

TABLE I. The results of single-shell fits to the $TiO_2(100)c(2\times2)K$ SEXAFS data obtained in normal and grazing incidence geometries. The effective coordination numbers and their ratios are compared with those expected for the angled-bridge, atop-bridge, atop, and K-inclined sites. For the angled-bridge and the K-inclined sites the K-O_2 plane and K-O bond angle are at 45° to the surface normal.

Angle of incidence	Experimental	Effective coordination numbers Angled bridge	Atop bridge	Atop	K inclined
90°	2.8 ± 1.0	1.91	1.91	0.0	0
20°	3.2 ± 1.0	2.02	3.80	2.64	1.32
90°/20°	0.88 ± 0.2	0.95	0.5	0	0

On chemical grounds we might expect K to bond to surface oxygen atoms; band-gap states would then be occupied by O-mediated charge transfer from K to Ti $3d$ states. The fact that the band-gap state emission occurs at the same binding energy as that observed when creating O vacancies is consistent with the formation of a self-trapped polaron.[16] In order to investigate the K bonding site we make use of SEXAFS data from the 0.5 ML $c(2\times2)K$ overlayer.

SEXAFS and corresponding near-edge x-ray-absorption fine-structure (NEXAFS) spectra recorded at grazing and normal photon incidence are shown in Fig. 2. Background subtraction and normalization of the grazing incidence data to the edge-jump yields the EXAFS oscillations $\chi(k)k^3$ and their Fourier transform shown as solid lines in Fig. 3. EXAFS spectra were analyzed using EXCURV90, a curve-fitting procedure based on the rapid curved wave computational scheme.[19,20] We test structural models using the ratio of effective coordination numbers obtained from polarization-dependent data, constraining the nonstructural parameters to be the same for all data sets. Successful modeling of the grazing incidence SEXAFS data required a single shell of oxygen neighbors at 2.62 ± 0.03 Å, the analysis routine rejecting models which contained K or Ti backscattering atoms. The NEXAFS (Fig. 2) data are consistent with this result, the spectra being similar to those reported for orthoclase glasses ($KAlSi_3O_8$),[21] in which K has O nearest neighbors.[22] Normal-incidence data were analyzed by constraining the K-O distance and E_0 (8.8 eV) to be that obtained from the grazing incidence data.

Surface-dipole arguments[23] indicate that $TiO_2(100)$ terminates with oxygen atoms, with Ti in the second layer.[23] A picture of the unrelaxed surface of this type is shown in Fig. 4, along with four possible high-symmetry adsorption sites of K on the bridging oxygen atoms. The four-coordinate hollow site can be ruled out on the basis of the SEXAFS-derived K-O bond distance, which is too short to be accommodated by this site. The best fit to the grazing incidence SEXAFS data is shown in Fig. 3. The resulting effective coordination numbers, together with the normal-incidence results are shown in Table I, where they are compared with the theoretical effective coordination numbers for possible adsorption sites. This comparison clearly favors the angled bridge as the K adsorption site, in which the K-O_2 plane is at 45° to the surface normal. An angle between 33° and 50° is consistent with the effective coordination number ratio.

The SEXAFS-derived K-O bondlength for $TiO_2(100)c(2\times2)K$ is close to the sum of the appropriate ionic radii.[24] While the angled-bridge site coordination might be thought of as similar to that in KO_2, the O-O bond distance is more than twice that in the O_2^- anion.[25] While the $c(2\times2)$ surface symmetry could be maintained if the O-O distance decreased in the bridge, the resulting effective coordination numbers are inconsistent with the SEXAFS data. Hence, in this case there is no bulk analog for the local coordination of the alkali-metal atom, in contrast to $TiO_2(110)c(4\times2)Na$ where Na_2O-type units have been proposed on the basis of the surface symmetry and the Na density.[17]

In summary, photoemission results from $TiO_2(100)$-K evidence K $4s\rightarrow$ Ti $3d$ charge transfer. Obtaining direct evidence of charge transfer is possible in this case because the substrate is a reducible d^0 transition-metal oxide and charge transfer results in the occupation of band-gap Ti $3d$ states. The charge-transfer site has K bonding to two oxygen atoms in a bridge configuration.

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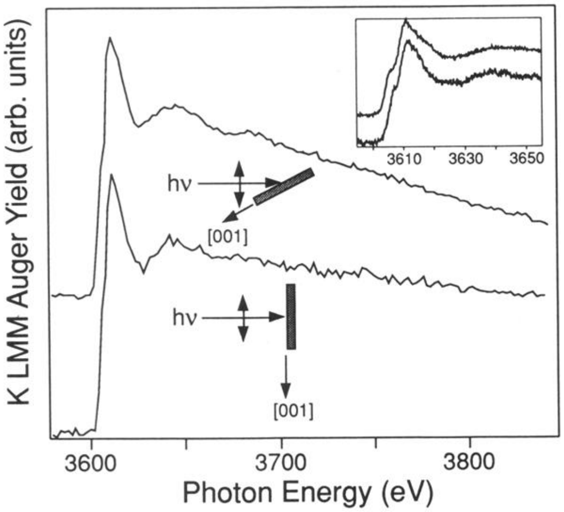

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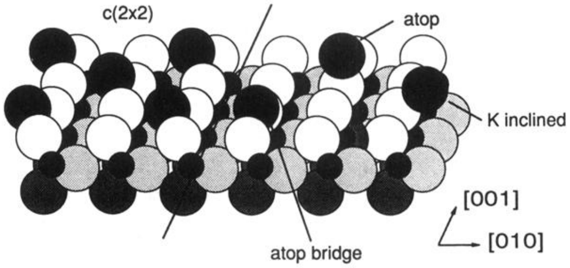

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