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Photoelectron diffraction investigation of the structure of the clean $TiO_2(110)(1\times 1)$ surface

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The surface relaxations of the rutile $TiO_2(110)(1\times 1)$ clean surface have been determined by O 1 s and Ti $2p_{3/2}$ scanned-energy mode photoelectron diffraction. The results are in excellent agreement with recent low-energy electron diffraction (LEED) and medium energy ion scattering (MEIS) results, but in conflict with the results of some earlier investigations including one by surface x-ray diffraction. In particular, the bridging O atoms at the surface are found to relax outward, rather than inward, relative to the underlying bulk. Combined with the recent LEED and MEIS results, a consistent picture of the structure of this surface is provided. While the results of the most recent theoretical total-energy calculations are qualitatively consistent with this experimental consensus, significant quantitative differences remain.

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I. INTRODUCTION

The (110) face of rutile phase TiO_2 is almost certainly the most studied of all oxide surfaces[1–3] and serves as a model surface on which to investigate the range of catalytic applications of this material. Despite this, the simplest related structural problem, namely, the sign and magnitude of the relaxations of the outermost atomic layers of the clean surface in the unreconstructed (1×1) phase, have proved controversial. Until quite recently, there was only one reasonably complete experimental structure determination of this surface[4] [using surface x-ray diffraction (SXRD)], although there have been many theoretical total-energy calculations conducted to identify the minimum energy structure [all but the most recent were reviewed in 2003 Ref. 3]. These theoretical calculations show some significant variations in the optimal values of the surface layer displacements from the locations in an ideally terminated bulk, but none reproduce all aspects of the SXRD experimental study. Clearly, there has been a need for further experimental studies, and two such investigations were reported very recently, one based on quantitative low-energy electron diffraction (LEED),[5] the other using medium energy ion scattering (MEIS).[6] Together with further theoretical calculations,[7] these new investigations appear to resolve some of the most serious inconsistencies, although some distinct quantitative differences between theory and experiment remain.

Figure 1 shows a perspective view of the rutile TiO_2 bulk structure with a (110) surface exposed at the top, the Ti and O atoms in the outermost three repeat layers being numbered following the convention used by Diebold.[3] Atomic displacements, relative to an ideally terminated bulk structure, occur in the positions of atoms several layers below the surface, but the atoms expected to show the most significant effects are those in the surface layer that are undercoordinated relative to those in the bulk. Specifically, these are the bridging O atoms (labeled 3 in Fig. 1) which have only 2 Ti nearest neighbors rather than 3 in the bulk, and the fivefold coordinated surface Ti atoms (labeled 2 in Fig. 1) which lack one of the six O nearest neighbors of the Ti atoms in the bulk. Table I compares the values of the surface relaxations of these atoms as determined by the three existing "complete" experimental structure determinations using SXRD, LEED, and MEIS.

All three experimental studies show that the fivefold Ti atoms at the surface are relaxed inward toward the underlying bulk by about 0.15–0.20 Å, and all agree in the magnitude of this relaxation to within the estimated errors. This effect is also consistently reproduced by essentially all the theoretical total-energy calculations, as shown in Table II which compares theory and experiment for the first three parameters of Table I. Another feature of the results of all three experimental structure determinations listed in Table I is an outward relaxation (away from the underlying bulk) of the sixfold coordinated surface Ti atoms (labeled 1 in Fig. 1) that are bonded to the bridging O(3) atoms. This effect is

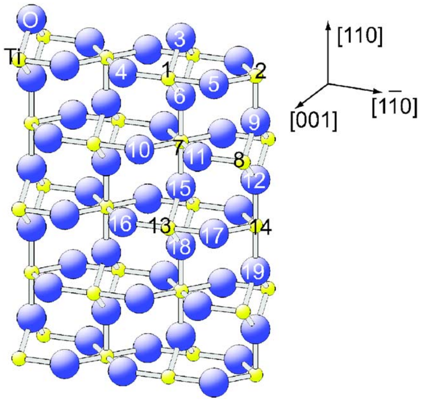

FIG. 1. (Color online) Perspective view of the rutile TiO_2 bulk structure with a (110) surface exposed on the top and the atoms in the outermost three layers numbered following the convention of Diebold. (Ref. 3). The surface displacements of these atoms relative to the ideally terminated bulk structure are given in the tables. Note that, following the usual chemical convention for oxides, the O atoms are shown as the larger spheres in this model.

TABLE I. Displacements of the near-surface Ti and O atoms in $TiO_2(110)$ relative to an ideal bulk-terminated structure according to the three published "complete" experimental structural studies, based on SXRD, LEED, and MEIS. The final column shows the results of this study. Atom numbers are as defined in Fig. 1. Δz values are displacements perpendicular to the surface, defined as positive for an outward relaxation. Δx values are displacement parallel to the surface in the $[1\bar{1}0]$ azimuth.

Atom	Parameter (Å)	SXRD[a]	LEED[b]	MEIS[c]	This study
(1) Ti six-fold	$\Delta z(1)$	0.12±0.05	0.25±0.03	0.19±0.07	0.19(−0.15/+0.10)
(2) Ti five-fold	$\Delta z(2)$	−0.16±0.05	−0.19±0.03	−0.09±0.09	−0.26±0.08
(3) O bridging	$\Delta z(3)$	−0.27±0.08	0.10±0.05	0.13±0.16	0.17±0.15
(4),(5) O in plane	$\Delta z(4,5)$	0.05±0.05	0.27±0.08	0.05	0.00(−0.40/+0.15)
(4),(5) O in plane	$\Delta x(4,5)$	±0.16±0.08	±0.17±0.15	±0.00	±0.05±0.15
(6) O lower bridging	$\Delta z(6)$	0.05±0.08	0.06±0.10	0.10±0.13	0.15±0.15
(7) Ti second layer	$\Delta z(7)$	0.07±0.04	0.14±0.05	−0.06±0.06	0.15(−0.20/+0.15)
(8) Ti second layer	$\Delta z(8)$	−0.09±0.04	−0.09±0.07	−0.09±0.09	−0.21(−0.40/+0.15)
(9) O below five-fold Ti	$\Delta z(9)$	0.00±0.08	0.00±0.08		−0.03±0.08
(10),(11) O second layer	$\Delta z(10,11)$	0.02±0.06	0.06±0.12		
(10),(11) O second layer	$\Delta x(10,11)$	±0.07±0.06	±0.07±0.18		
(12) O second layer	$\Delta z(12)$	−0.09±0.08	0.01±0.17		
(13) Ti third layer	$\Delta z(13)$			0.00±0.07	
(14) Ti third layer	$\Delta z(14)$			−0.02±0.08	
(15) O third layer bridge	$\Delta z(15)$	−0.12±0.07	0.00±0.13		

[a] Reference 4.

[b] Reference 5.

[c] Reference 6.

also reproduced by almost all the theoretical studies shown in Table II.

By contrast, the strong inward relaxation of the bridging O atoms seen in the SXRD investigation $[\Delta z(3) = -0.27 \pm 0.08$ Å$]$ is *not* reproduced by the LEED and MEIS studies that both show a significant outward relaxation of these atoms. Most of the theoretical studies reproduce, at least qualitatively, the SXRD result of an inward relaxation of the bridging O atoms. The near-zero values favored by the work of Swamy *et al.*[7] were cited as evidence of improved theory and/or experiment agreement in the LEED investigation.[5] The very recent density-functional theory (DFT) calculations of Thompson and Lewis[30] for thick (11-layer) slabs seem to be the only ones that show a large (0.23 Å) outward relaxation of the bridging O atoms, more overtly reproducing this trend of the new LEED and MEIS experimental studies.

In addition to the rather complete structure determinations listed in Table I, there have been a few other investigations that have sought to obtain quantitative information on the relative positions of the outermost layer O and Ti atoms, but these provide conflicting information. In particular, one low energy ion scattering study (using 1 keV Li^+) was found to indicate that there was no significant rumpling of the outermost Ti layer (of sixfold and fivefold Ti atoms), no significant change in the height of the bridging O atoms above this layer, but a large (0.6 Å) inward relaxation of this whole layer relative to the bulk.[8,9] However, an ion scattering study using 10 keV O^+ ions[10] led to the conclusion that the sixfold coordinated Ti atoms were ~0.2 Å higher above the surface than the fivefold coordinate Ti atoms (as found in the other experimental and theoretical studies described above), but that the bridging O atoms were relaxed inward to the bulk by ~0.20 Å, broadly compatible with the SXRD result. Support for essentially this same picture with inward relaxation of the bridging O atoms was also obtained in an angle-scan x-ray photoelectron diffraction (XPD) investigation using a novel polarization geometry to enhance the sensitivity to atomic displacements perpendicular to the surface.[11]

Despite recent (somewhat conflicting) claims to the contrary (e.g., Refs. 5 and 30) it seems, therefore, that there is still no clear consensus as to the magnitude, and perhaps even the sign, of the surface relaxation of the $TiO_2(110)$ surface, and particularly that of the bridging O atoms. Both the most recent (LEED and MEIS) experimental studies do clearly favor an outward relaxation of the bridging oxygen atoms, in contradiction to the early SXRD study and to the less complete experimental structural studies using ion scattering and XPD. The most recent theoretical calculations also seem to at least not support this inward relaxation of the bridging O atoms found in all the earlier work, but fail to provide good quantitative agreement. In view of this a new experimental study by a different method certainly has the potential to illuminate the problem further.

Here, we present the results of such a study using scanned-energy mode photoelectron diffraction (PhD). Photoelectron diffraction[12,13] exploits the coherent interference between the directly emitted component of a photoelectron

TABLE II. Comparison of the surface-induced displacements of the outermost layer Ti and O atoms of the $TiO_2(110)(1\times1)$ surface found in experiment (the first three rows of Table I) with the results of a series of theoretical calculations identified by the first-named authors and the method. Abbreviations for the methods are as follows: FP-LAPW (full-potential linear augmented plane wave); LCAO (linear combination of atomic orbitals), PW (plane wave); PP (pseudopotential); LDA (local-density approximation); GGA (generalized gradient approximation); HF (Hartree-Fock); MS-Q and MA are force-field results based on a variable-charge potential and the Matsui-Akoagi model, respectively (Ref. 7).

Atom	Ti six-fold $\Delta z(1)$ (Å)	Ti five-fold $\Delta z(2)$ (Å)	O bridging $\Delta z(3)$ (Å)
SXRD[a]	0.12±0.05	−0.16±0.05	−0.27±0.08
LEED[b]	0.25±0.03	−0.19±0.03	0.10±0.05
MEIS[c]	0.19±0.07	−0.09±0.09	0.13±0.16
This study	0.19(−0.15/+0.10)	−0.26±0.08	0.17±0.15
Harrison FP-LAPW[d]	0.08	−0.23	−0.16
Harrison LCAO[d]	0.23	−0.17	−0.02
Ramamoorthy PW-PP-LDA[e]	0.13	−0.17	−0.06
Bates PW-GGA[f]	0.23	−0.11	−0.02
Lindan[g]	0.09	−0.12	−0.09
Vogtenhuber FP-LAPW[h]	−0.05	−0.18	−0.16
Reinhardt HF-LCAO[i]	0.09	−0.15	−0.14
Swamy LDA[j]	0.22	−0.17	0.01
Swamy HF[j]	0.25	−0.17	−0.01
Swamy MS-Q[j]	0.09	−0.11	0.15
Swamy MA[j]	0.15	−0.07	−0.01
Thompson GGA[k]	0.43	−0.03	0.23

[a] Reference 4.
[b] Reference 5.
[c] Reference 6.
[d] Reference 24.
[e] Reference 25.
[f] Reference 26.
[g] Reference 27.
[h] Reference 28.
[i] Reference 29.
[j] Reference 7.
[k] Reference 30.

wave field emitted from a core level of an atom and the components of the same wave field elastically scattered by the surrounding atoms. This interference provides information on the relative position of the emitter and scatterer atoms. There are two rather distinct ways in which this phenomenon can be exploited. In one, relatively high photoelectron kinetic energies are used (typically ~500 eV or higher) and the angular distribution of the photoelectrons is measured; in this XPD technique, forward scattering dominates and the method is particularly well suited to studying the structure of overlayers involving scatterer atoms higher above the surface than the interface emitter atoms. At lower photoelectron energies (typically ~50–400 eV), backscattering is far more important and measurements of either the angular dependence or the photoelectron energy dependence provide information mainly on the location of scatterer atoms *behind* the emitter relative to the detector. This method is especially well suited to determining the location of adsorbed atoms and molecules on a surface. In truth, neither approach is ideally suited to investigate the structure of clean surfaces, unless there is a measurable shift in the photoelectron binding energy associated with emitter atoms in the surface layer, which is not the case for $TiO_2(110)$. Without this means of identifying the contribution from surface layer emitters, the measured signal is an incoherent sum of the photoelectron diffraction from many near-surface layers. Nevertheless, the XPD experiments of Verdini *et al.*,[11] albeit at relatively low photoelectron energies for this technique (285, 305, and 560 eV) were found to have some sensitivity to the surface structure, and our PhD study at photoelectron energies in the range of ~50–350 eV can be expected to have a somewhat higher degree of surface specificity. As we will show, this is, indeed, the case.

Our use of the PhD technique also involves addressing an issue raised in the earlier LEED study of $TiO_2(110)$,[5] namely, the sensitivity of the results to the description of the atomic scattering within the oxide. In general, the LEED technique is believed to be relatively insensitive to the details of the scattering potentials of the atoms within the surface, the scattering phase shifts being dominated by the contribution from the ion core, a state of affairs which allows the method to be used without requiring any detailed understanding of the valence electronic structure. The report of the recent LEED analysis of the $TiO_2(110)(1\times1)$ surface, however, argues that in order to achieve a successful description of the LEED intensity-energy data, the electron-scattering phase shifts must be obtained from a self-consistent treatment of the atomic potentials. To establish the significance of this effect in our PhD data analysis, we have therefore investigated the influence of using scattering phase shifts obtained in different ways.

II. EXPERIMENTAL DETAILS

The experiments were conducted in an ultrahigh vacuum surface science end station equipped with typical facilities for sample cleaning, heating, and cooling. This instrument was installed on the UE56/2-PGM1 beamline of BESSY II which comprises a 56 mm period undulator followed by a plane grating monochromator.[14] Different electron emission directions can be detected by rotating the sample about its surface normal (to change the azimuthal angle) and about a vertical axis (to change the polar angle). Sample characterization *in situ* was achieved by LEED and by soft-x-ray photoelectron spectroscopy (SXPS) using the incident synchrotron radiation. Both the wide-scan SXPS spectra for surface characterization, and the narrow-scan O 1*s* and Ti 2*p* spectra used in the PhD measurements, were obtained using an Omicron EA-125HR 125 mm mean radius hemispherical electrostatic analyzer, equipped with seven-channeltron parallel detection, which was mounted at a fixed angle of 60° to the incident *X* radiation in the same horizontal plane as that of the polarization vector of the radiation.

A clean well-characterized rutile $TiO_2(110)$ surface was prepared which gave a sharp (1×1) LEED pattern and a Ti 2*p* photoemission spectrum showing only a weak high kinetic-energy shoulder. The main Ti 2*p* peaks are generally assigned to Ti in the 4+ charge state expected for a fully ionic stoichiometric bulk site and in the autocompensated surface (e.g., Ref. 15), while any high-energy shoulder is assigned to Ti in a 3+ state, most commonly attributed to the presence of surface oxygen vacancies. To achieve this surface, the crystal was bombarded briefly with either Ar+ or Ne^+ ions at an energy of 500 eV, followed by annealing in UHV at approximately 830 K. The low-energy side of the Ti 2*p* photoemission peaks showed no sign of any shoulder around a chemical shift of 1.6 eV attributable to surface hydroxyl species.[15]

In the scanned-energy mode photoelectron diffraction technique, one measures the photoemission intensity from a core-level emission in specific directions as a function of the photoelectron energy. Modulations in the resulting spectrum arise from the change in phase of directly emitted and scattered components of the photoelectron wave field as the photoelectron wavelength changes, and can be interpreted in terms of the scattering path lengths and thus the local geometry. The PhD modulation spectra were obtained by recording a sequence of photoelectron energy distribution curves (EDCs) around the O 1*s* or Ti $2p_{3/2}$ peak at 4 eV steps in photon energy in the photoelectron kinetic-energy range of approximately 50–350 eV for each of a number of different emission directions in the polar emission angle range from 0° (normal emission) to 50° in several azimuthal planes. Similar measurements of the Ti $2p_{1/2}$ PhD spectra yielded essentially identical results. Most of the data were recorded in the $[001]$ azimuth but selected data were also taken in the $[1\bar{1}0]$ azimuth and, for the O 1*s* PhD, one spectrum was taken in an intermediate azimuth and polar angle to coincide approximately with a nearest-neighbor Ti backscattering direction for the (known) bulk structure; PhD spectra typically show the strongest modulations when a near neighbor is in this 180° backscattering geometry. The complete set of PhD data used in the analysis presented here was measured in two distinct periods of synchrotron-radiation beam time, on separate samples, but several specific measurements were repeated in the two runs to confirm consistency of the two data sets.

Each of these data sets was processed following our general PhD methodology (e.g., Ref. 12) in which the individual EDCs are fitted by the sum of a Gaussian peak, a step, and a template background extracted from the high kinetic-energy tails of the individual EDCs. The intensity of the fitted peaks is then plotted as a function of kinetic energy $I(E)$. The shape of $I(E)$ contains not only the PhD modulations but longer period variations due to the transmission functions of the monochromator and the analyzer, as well as the variation in the atomic photoionization cross section. These effects are approximated by fitting a spline, $I_0(E)$, through $I(E)$. The PhD modulation function, $\chi(E)$, is then given by

$$\chi(E) = \frac{I(E) - I_0(E)}{I_0(E)}.$$

These PhD modulation spectra form the basis of the structure determination.

III. RESULTS AND STRUCTURE DETERMINATION

Structure determination using PhD data is based on multiple-scattering simulations for trial model structures which are compared with the experimental modulation spectra. These calculations were performed with computer codes developed by Fritzsche[16–18] that are based on the expansion of the final-state wave function into a sum over all scattering pathways which the electron can take from the emitter atom to the detector outside the sample. Key features are the treatment of double and higher-order scattering events by means of the reduced angular momentum expansion and inclusion of the effects of finite energy resolution and angular acceptance of the electron energy analyzer analytically. Anisotropic vibrations for the emitter atom and isotropic vibrations for the scattering atoms are also taken into account. The quality of agreement between the theoretical and experimental modulation amplitudes is quantified by the use of an objective reliability factor (*R*-factor) defined[12,13] such that a value of 0 corresponds to perfect agreement and a value of 1

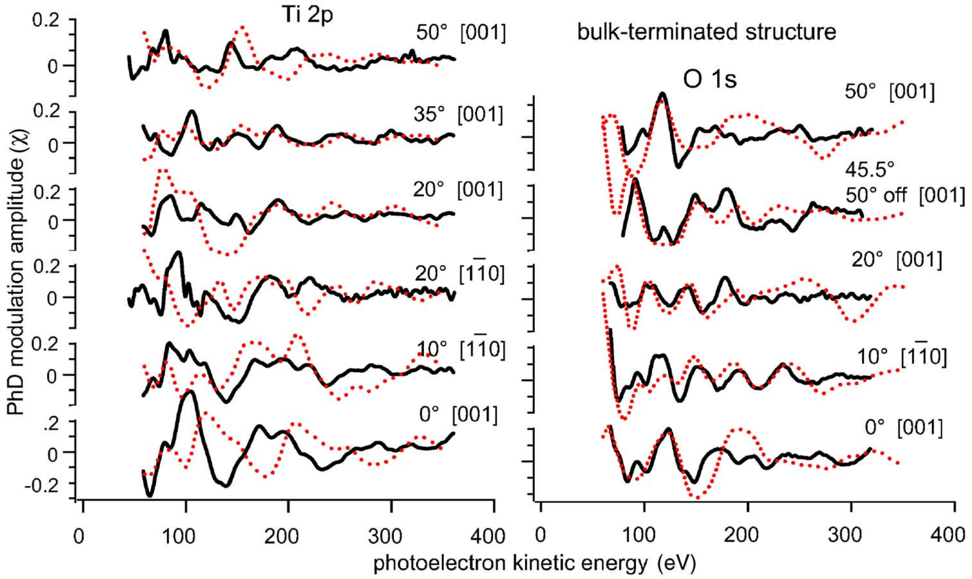

FIG. 2. (Color online) Comparison of the experimental (full lines) Ti $2p_{3/2}$ and O 1 *s* PhD spectra from the $TiO_2(110)(1\times1)$ surface with the results of theoretical calculations (dotted lines) based on a bulk-termination model of the surface structure.

to uncorrelated data. In using PhD to determine an adsorption structure, one usually tests a range of different possible structural models based on different (initially single and distinct) adsorption sites, adjusting the structural parameter variables (initially the adsorbate substrate bonding distances) to obtain the best agreement. In the present case the methodology is necessarily somewhat different. We know that both O 1*s* and Ti 2*p* emitter atoms are located in many (strictly, all) atomic layers of the crystal, but we also know that the deeper lying layers have the bulk crystal structure.

The starting point in the present case was therefore to first calculate the PhD spectra to be expected from an ideally terminated bulk $TiO_2(110)$ surface and compare this with the experimental data. The simulated PhD spectra involved summation of the calculated intensities from each inequivalent O or Ti atom in the near-surface layers, the attenuation in the signal from the deeper layers due to inelastic scattering being already included in the scattering code. Each "layer" in the $TiO_2(110)$ surface comprising, per surface unit mesh, 2 Ti atoms and 2 nominally coplanar O atoms, together with one O atom bridging above and one O atom bridging below. For example, using the labeling of Fig. 1, the outermost layer comprises Ti(1), Ti(2), O(3), O(4), O(5), and O(6). Similarly, the second layer consists of atoms labeled with numbers from 7 to 12. The spacing of these layers in the bulk is 3.25 Å (although the repeat distance is twice as large as the repeat unit is 2 layers). Initially, calculations were run using eight layers of emitters, but subsequently it was found that using only four layers gave essentially the same results, with the addition of further layers having little effect on the calculated PhD spectra, so this smaller number of layers was used in the later structural optimization. Eleven different PhD spectra (six using Ti $2p_{3/2}$ emitters, five using O 1*s* emitters) were available for comparison to the simulated curves. To account for the effect of correlated vibrations, the nearest-neighbor atoms to each emitter were frozen; otherwise, the root-mean-square vibrational amplitudes of the Ti and O atoms were set to 0.070 and 0.066 Å, respectively.[19] All calculations conducted in this structure determination used the scattering phase shifts that had been obtained using the self-consistent methodology described in the LEED study by Lindsay *et al.*[5] These phase shifts will be referred to hereafter as "Lindsay final" or "self-consistent;" the consequences of using different phase shifts will be discussed later in this paper.

Figure 2 shows a comparison of the experimental PhD spectra with those calculated for an ideal bulk termination of the $TiO_2(110)$ surface. The overall *R* factor has a high value of 0.80 indicating a poor level of agreement. Visual inspection (confirmed by *R*-factor values for the individual spectra) shows that the agreement for the O 1*s* spectra is moderate, but for the Ti 2*p* spectra the agreement is very poor. Indeed, for the normal-emission Ti 2*p* PhD spectrum, the theory and experiment are almost in antiphase, consistent with an *R* factor for this spectrum that is >1.0. The implication of this result is twofold. Firstly, the generally poor agreement indicates that a bulk termination is a poor description of the true surface structure. Secondly, it appears that the Ti 2*p* PhD spectra may be more sensitive to the true surface relaxations than are the O 1*s* PhD spectra. One further general remark is that the modulation amplitudes of the experimental spectra are quite low, generally $<20\%$ and some cases barely 10%. For atomic adsorbate emitters occupying high-symmetry sites on a surface PhD modulations in a near-neighbor backscattering direction commonly show modulations amplitudes of $\sim40\%$, and some cases as high as 60%–80%. Adsorbates in multiple adsorption sites or low-symmetry sites, however, lead to much weaker modulations due to the effect of summing the spectra from the many different geometries, the largest modulations for each site occurring in different directions. The present case of multiple emitters in different layers, and in different geometries within the layers, is similar to this case of a complex adsorbate layer, with the consequence that only weak modulations are seen. Weak modulations enhance the importance of experimental noise, and any theoretical deficiencies, and thus lead to best *R*-factor values that are never very low. Nevertheless, we can explore the influence of surface relaxations and determine the best-fit struc-

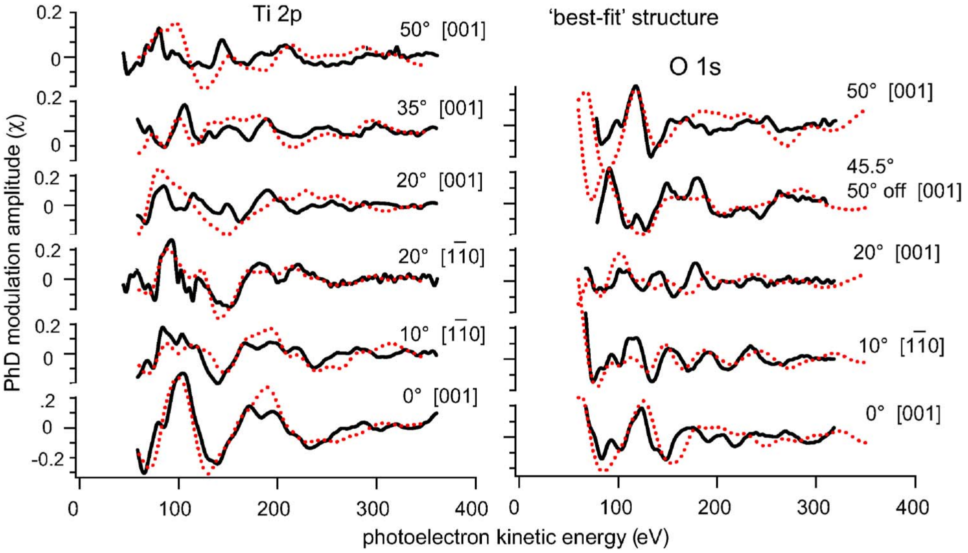

FIG. 3. (Color online) Comparison of the experimental (full lines) Ti $2p_{3/2}$ and O 1 *s* PhD spectra from the $TiO_2(110)(1\times1)$ surface with the results of theoretical calculations (dotted lines) based on the structural model of the surface structure giving the best fit to the PhD spectra. The associated structural parameter values are listed in Table I.

ture. Note that if the resulting R factor is relatively high, this will be reflected in the estimated precision. To estimate the errors associated with the individual structural parameters, we use an approach based on that of Pendry which was derived for LEED.[20] This involves defining a variance in the minimum of the R factor, R_{min}; all parameter values giving structures with R factors less than $R_{min}+\mathrm{Var}(R_{min})$ are regarded as falling within one standard deviation of the "best fit" structure.[21] If R_{min} is large, so is $\mathrm{Var}(R_{min})$, and thus so are the estimated errors.

Before attempting to adjust the many structural parameters (cf. Table I) to determine the best-fit structure, further calculations were performed to simulate the PhD spectra from a series of specific model structure corresponding to the optimum solutions of the previous published structure determinations. The overall R-factor values for these models were found to be 0.85 (SXRD), 0.72 (MEIS), and 0.57 (LEED); similar calculations were also performed for the set of structural parameter values obtained from the theoretical study previously found to be most consistent with the MEIS structure, namely, that obtained using the LCAO method by Harrison *et al.*;[24] the corresponding overall R factor for this structure was 0.55. These initial results clearly show that introducing surface relaxations can significantly improve the fit to the PhD data, and seem to indicate that the (rather similar) LEED and MEIS structures are much better than the SXRD structure, but the overall R-factor values are still poor. Interestingly, these calculations also showed that the normal-emission Ti $2p$ PhD spectrum showed a particularly strong sensitivity to the structural differences in these models. The R-factor values calculated for this spectrum alone were 0.96 (SXRD), 0.97 (MEIS), 0.30 (LEED), and 0.37 (LCAO). Because this spectrum shows the strongest modulations, it is the spectrum that we would expect to be able to reproduce most effectively by our calculations if the correct structural model is identified, and this is also reflected in the large range of R values found.

Careful comparison of the differences in these specific structural models and their associated R-factor values provided an initial guide to determining the ingredients that should give the best fit to the PhD data. In particular, the Ti $2p$ normal-emission spectrum proved to be particularly sensitive to the rumpling of the outermost Ti layer; i.e., the height difference above the underlying substrate of the surface layer sixfold and fivefold coordinated Ti atoms. Armed with this information a new range of model structures was initially tested, initially based on a grid search of structural parameters, but the final structural optimization to locate the minimum R factor was achieved with the help of an adapted Newton-Gauss algorithm, as used in our previous adsorbate studies. The final results of this structural optimization in terms of the best-fit spectra are shown in Fig. 3, while the associated structural parameter values are listed in the final column of Table I. The overall R factor obtained for this structure was 0.35, while the value for the particularly sensitive Ti $2p$ normal-emission spectrum alone was 0.15. The variance in the overall minimum R factor is 0.05, so any structure with a value of $R>0.40$ is formally excluded. On this basis, the best-fit structure found here is formally significantly better than any of the other tested models based on previous structural studies.

Errors in individual parameter values quoted in Table I were also based on this variance, investigating the change in the overall R factor as each structural parameter is varied individually. Note that this method (as commonly used in many other surface and bulk structural techniques) takes no account of coupling between parameters. This neglect of coupling effects may be most serious in the case of these subsurface atoms that have previously been found to suffer some displacement parallel to the surface. Interestingly, in our structural optimization, only displacements perpendicular to the surface were considered, but in checking the precision of all parameters, it was found that a slight improvement in the overall fit was found by including a small lateral displacement of the O(4,5) atoms; this is the solution reflected in Table I and Fig. 3. However, the PhD method is commonly more sensitive to interatomic distances than to the directions of interatomic vectors, so some couplings between displacements perpendicular and parallel to the surface (where these occur) almost certainly exist. We note, however, that for the deeper subsurface atoms, not only the PhD results but also those of the other structural methods have associated estimated errors that render the optimum values of the displacement parameters to be of marginal significance. One further general comment regarding the PhD technique is relevant in assessing the displacements and their associated error estimates in Table I. PhD is intrinsically a local structural technique, providing information on the structural environment of the emitter atom. For an adsorbed layer, this means that the method is far more sensitive to the positions of near-neighbor surface atoms, relative to the adsorbate emitter, than to the positions of these neighbors to the underlying bulk. In the present case, in which we have emitter atoms in many layers of the substrate, this clear distinction is clouded, yet the intrinsic surface sensitivity arising from inelastic electron scattering still means that our results are more sensitive to local distortions in the outermost layers than to the location of these atoms relative to the underlying bulk. For example, we have already noted that the normal emission Ti $2p$ PhD spectrum shows the strongest modulations which appear to be dominated by a single oscillatory period. This is largely attributable to the fact that the fivefold coordinated Ti atom [Ti(2)] lies directly above an oxygen atom [O(9)] in the layer below, so normal emission corresponds to the favored 180° backscattering from this atom. As a result, the precision in the Ti(2)-O(9) distance will be significantly better than in the location of either of these atoms [and especially the O(9) atom] relative to the underlying bulk.

IV. THE INFLUENCE OF DIFFERENT ATOMIC SCATTERING PHASE SHIFTS

In the LEED analysis of the $TiO_2(110)(1\times1)$ surface, Lindsay *et al.*[5] stress the importance of using the correct scattering phase shifts for the Ti and O atoms in order to achieve an acceptable description of the LEED intensity-energy spectra. As these same phase shifts are used in a PhD analysis, this is potentially an important issue for the structure determination we present here. The details of the optimum way to calculate the phase shifts are beyond the scope of this paper, but understanding the implications of different scattering phase shifts on the results of our analysis is important and is described briefly in this section. In all LEED and photoelectron diffraction studies, the atomic scattering is described by a partial-wave expansion. In this formalism (described in any standard text on quantum mechanics: e.g., Ref. 22), the atomic scattering factor for scattering through an angle θ is given by

$$f(\theta) = (2ik)^{-1}\sum_{l=0}^{\infty}(2l+1)(e^{2i\delta_l}-1)P_l(\cos\theta),$$

where k is the electron wave vector, l the angular momentum quantum number, δ_l the associated partial-wave phase shift, and P_l is a Legendre polynomial. The scattering is thus entirely determined by the values of the (energy dependent) scattering phase shift. These are calculated from muffin-tin potentials constructed from atomic potentials truncated at the muffin-tin radius. For an elemental solid such as a metal, the choice of the muffin-tin radius is unambiguous and may be set to half the interatomic distance, but in a compound such as an oxide, an ambiguity exists. As remarked in the Introduction, it is usually assumed that this choice is not critical for LEED and PhD calculations, the scattering in this energy range (~50–350 eV) being dominated by the ion cores, but this conclusion is challenged by the recent LEED study of TiO_2. In this paper, they describe two methods of calculating the phase shifts, one based on a relatively standard approach but making explicit allowance for the ionicity of the compound, the other a more complex method aimed at achieving self-consistency. The details of these methods are described by these authors.[5]

In Fig. 4, we show a comparison of the phase shifts for just the first five partial waves for both Ti and O generated by these authors using these two methods, labeled "Lindsay first" and Lindsay final (self-consistent). Also included in this figure are phase shifts that we had calculated previously using standard methods that took no account of the ionicity nor self-consistency; specifically, the Ti phase shifts were calculated relativistically using the Van Hove-Barbieri program[23] for the bulk rutile structure with muffin-tin radii of 2.3371 a.u. (Ti) and 1.2545 a.u. (O). One surprising feature of this comparison is that the phase shifts calculated by standard methods, taking no particular account of the ionic character of the solid, lie close to those calculated by the self-consistent procedure, whereas those calculated in the initial attempts to fit the LEED data are significantly different, especially for the Ti scattering, but also for the lowest l values for O scattering. Of course, the implication of these differences in the raw partial-wave phase shifts is rather opaque. Rather greater transparency is achieved if we note that we can write the scattering factor in terms of an amplitude and phase,

$$f(\theta) = |f(\theta)|e^{i\phi(\theta)}.$$

This scattering factor phase must be added to any phase difference associated with individual scattering paths in LEED or photoelectron diffraction, so differences in this phase can lead to errors in apparent path lengths and thus the associated structure. For PhD, a particularly important condition is 180° backscattering; so, in Fig. 5, we show the values of $|f(\pi)|$ and $\phi(\pi)$ for the Ti and O atoms as a function of electron energy calculated using the two different sets of phase shifts investigated in the earlier LEED study. The differences are striking, especially for the Ti scattering for which, over much of the energy range, there is a difference in the calculated scattering phase $\phi(\pi)$ of $\sim\pi/2$, while there are also large differences in the magnitude of the scattering factor, also greatest for the Ti atoms. Figure 5 also reveals some differences between the scattering amplitudes and phases derived from the "self-consistent" and "standard" methods, though far less serious than relative to the Lindsay first phase shifts. These differences certainly lead us to expect that the use of the Lindsay first phase shifts will have a profound effect on the calculated PhD spectra, relative to those calculated using the Lindsay final phase shifts, and this is borne out by the subset of simulated PhD spectra shown in Fig. 6. Notice that the effect of changing the phase shifts is far more serious for

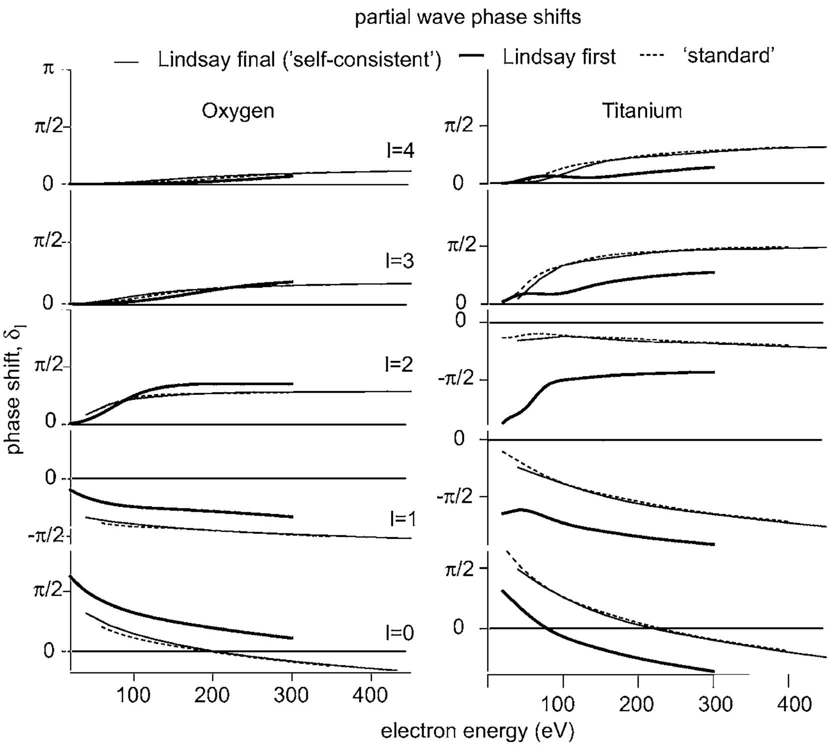

FIG. 4. Comparison of the first five ($l=0$ to $l=4$) partial-wave scattering phase shifts for O and Ti atoms calculated in different ways as described in the text.

the O 1 s PhD spectra than for that recorded using the Ti $2p$ emission. This reflects the fact that the PhD modulations seen in the intensity of photoelectrons emitted from the O atoms is most strongly influenced by the scattering from their nearest-neighbor Ti atoms, and it is the Ti scattering that is most strongly influenced by the choice of scattering phase shifts. By contrast the Ti $2p$ PhD modulations are more strongly influenced by scattering from the O atoms that are the nearest neighbors of the Ti emitter atoms.

In terms of the effect of the two distinct sets of scattering phase shifts used by Lindsay *et al.* in their LEED analysis, our conclusions are thus consistent with theirs; these two sets of phase shifts generate very different simulated intensity-energy spectra and cannot provide equally good descriptions of the scattering data and thus of the surface structure. What is less clear from our analysis, however, is that the use of the self-consistent approach to calculating the scattering phase shifts is entirely necessary. Our own phase shifts, produced

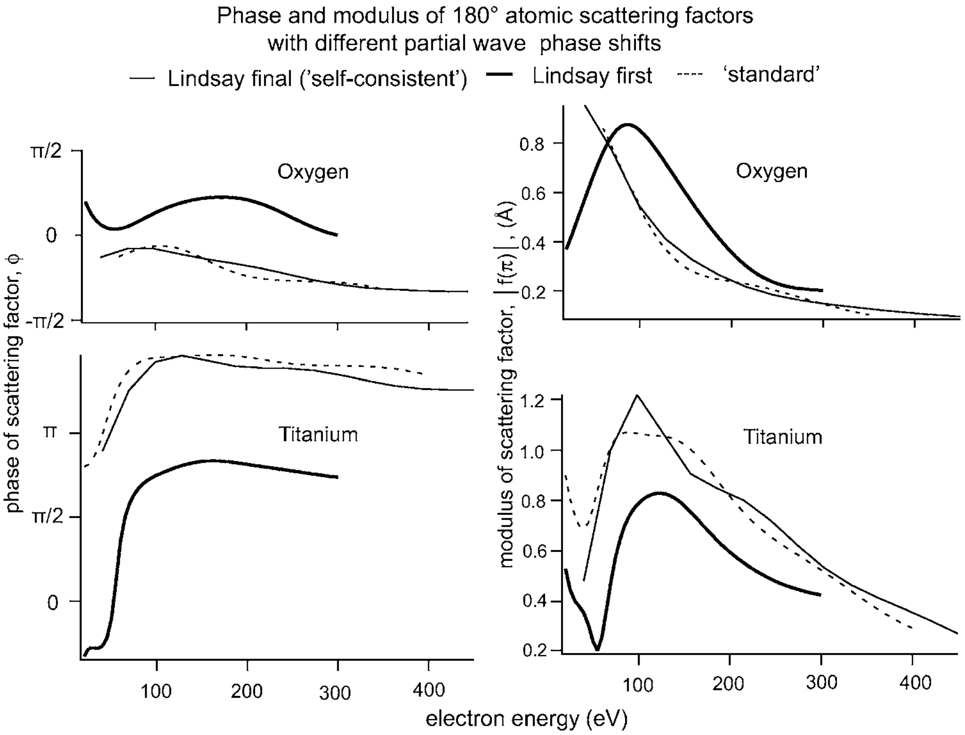

FIG. 5. Comparison of the amplitude and phase of the 180° scattering factor for electron scattering of O and Ti atoms, calculated using the different partial-wave scattering phase shifts as described in the text.

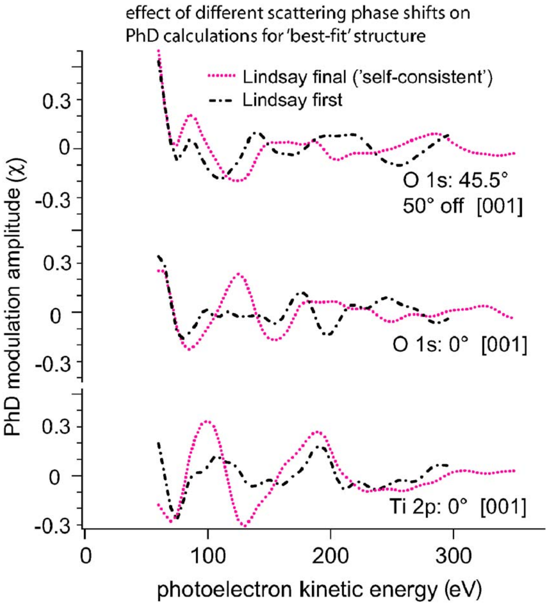

FIG. 6. (Color online) Comparison of calculated PhD spectra from $TiO_2(110)$ for a subset of the emission spectra based on the best-fit structural model but using different scattering phase shifts of the Ti and O atoms.

by the applications of standard methods that take no account of the specific electronic valence structure of the solid yield rather similar phase shifts, and tests varying the muffin-tin radii by significant amounts had rather little effect on them. Indeed, using our standard phase shifts to calculate the set of PhD spectra for the best-fit geometry described above yielded an overall R factor of 0.31, actually slightly lower that that using the self-consistent phase shifts. The real problem in the initial attempts to fit the LEED data seems to have arisen from a set of phase shifts obtained from the use of a rather complex procedure to try to improve on the standard methods, rather than a failure of these standard methods.

V. GENERAL DISCUSSION AND CONCLUSIONS

The primary objective of this study was to provide an independent experimental determination of the details of the surface relaxation of the $TiO_2(110)(1\times1)$ surface using a technique complementary to those previously applied to this system. Our use of scanned-energy mode photoelectron diffraction has achieved this goal and the key structural parameter values are listed in Table I. Despite some limitations in this method when applied to a clean surface, and consequently only modest precision in the structural parameter values, the results do provide valuable additional information which helps to resolve existing controversies in the experimental studies and provides a clear benchmark by which to judge the theoretical modeling of this structure.

The comparison of the structural parameter values of the main experimental studies shown in Table I shows that the signs of all the atomic displacements found in this PhD study are consistent with those of the recent LEED study. The absolute magnitude of all of these displacements are also in agreement with the LEED results within the estimated precision limits, while the MEIS structural parameter values also agree within these limits. Indeed, this statement can be extended to include the SXRD results with one notable exception, namely, the relaxation of the surface bridging oxygen atoms; in this case, our new result confirms the outward relaxation found by LEED and MEIS, whereas the SXRD result showed an inward relaxation. This distinction is certainly significant; the difference between the SXRD relaxation value for the bridging oxygen atoms and those found in the three newer studies are 0.37 ± 0.09 Å (LEED), 0.40 ± 0.18 Å (MEIS), and 0.44 ± 0.17 Å for the present PhD study. Two earlier, less complete, surface structural studies using XPD (Ref. 11) and low energy ion scattering[10] also favored an inward relaxation of the bridging oxygen atoms, but these studies failed to consider the implications of all the near-surface relaxations, so it is not clear that these partial structural solutions are entirely reliable. The balance of experimental evidence now rather clearly favors an outward relaxation of these bridging O atoms. The sign and magnitude of other main relaxations of the surface layer, namely, those of the sixfold and fivefold coordinated surface Ti atoms, are consistent for the four structural studies. Ti atoms are stronger scatterers of x-ray photons, electrons, and ions than O atoms, so it is perhaps not entirely surprising that it is the location of the bridging O atoms that has proved more controversial. Indeed, while the estimated precision in the displacement of the bridging O atoms for the SXRD study is significantly worse than for the Ti atoms, the quoted value of ±0.08 Å is still surprisingly accurate for these weakly scattering atoms. In general, O 1 *s* PhD spectra can be more sensitive to O atomic positions because the modulations seen in such spectra do not rely on the weak scattering from (other) O atoms, but in the present case the inability to distinguish the different O emitter atoms in the surface region cancels out this advantage.

The comparison with many theoretical calculations in Table II shows that, here too, it is the relaxation of the bridging oxygen atoms that has proved the source of the largest qualitative discrepancy with the newest experimental data. In all of the earlier studies of Table I (those labelled Harrison, Ramamoorthy, Bates, Lindan, Vogtenhuber, and Reinhardt), the bridging O atoms are found to relax inward toward the surface, although in two cases the magnitude of this displacement is very small (−0.02 Å). The somewhat later study of Swamy *et al.*[7] investigated several different methods of calculation but concluded that the force-field methods (MS-Q and MA in Table II) yielded results that were mutually inconsistent, and favored the LDA and HF quantum mechanical methods. It is the results of these calculations that were cited in the LEED analysis of Lindsay *et al.*[5] as, together with the new LEED structural data, reconciling experiment and theory, yet while these calculations do not show the significant inward relaxation of the bridging oxygen atoms seen in most of the earlier studies, nor do they find the significant outward relaxation which characterizes the LEED, MEIS, and PhD results. In this regard, the most recent theoretical study of Thompson and Lewis,[30] which postdates the publication of the LEED experimental study, does show a large outward relaxation of the bridging O atoms.

These authors use a rather standard DFT slab calculation computational package Vienna *ab initio* simulation package (VASP) and investigate the convergence of the optimum surface structural parameter values with increasing slab thickness and increased *k*-point sampling density. The results shown in Table II correspond to those from an 11-layer slab (significantly more than previous studies which typically use 3, 5, or 7 layers) and show that the values are almost identical for a 9-layer slab. The results are consistent with the experimentally determined relaxations of the outermost layer Ti atoms and bridging O atoms in terms of sign, yet the displacement of the sixfold Ti surface atom and, to a lesser extent that of the bridging O atoms, are significantly larger than the experimental values, while that of the fivefold Ti atoms is significantly smaller than the experimental value.

In conclusion, our results reinforce the conclusions of the recent LEED and MEIS studies of this surface relaxation where they differ from some of the earlier studies, but also highlight some significant quantitative failures in all current theoretical descriptions of this surface.

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