

Revisiting the Surface Structure of $\text{TiO}_2(110)$: A Quantitative Low-Energy Electron Diffraction Study

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The relaxation of the prototypical metal oxide surface, rutile $\text{TiO}_2(110)1 \times 1$, has been elucidated using quantitative low-energy electron diffraction. Successful structure determination entailed the development of adjustable parameter free *self-consistent* phase shifts, which provide a more reliable description of the electron scattering than traditional approaches. The resulting optimized structure is remarkably consistent with that emerging from recent state of the art *ab initio* calculations. Additionally, the impact of soft surface vibrational modes on the structure determination has been investigated. It was found that the soft surface mode identified in this study has no significant bearing on the interpretation of the LEED-IV data, in contrast to suggestions in the literature.

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In order to comprehend, and eventually predict, surface properties an essential prerequisite is a detailed knowledge of surface geometric structure. Given this importance, a sizeable catalogue of surface structure determination of *model* single crystal surfaces has been accumulated over the last few decades (see, for example, Ref. [1]). Much of this effort has focused on metal and semiconductor systems, for which confidence in experimental data and their agreement with state-of-the-art calculations is now at a high level. In contrast, to date such work on oxide surfaces often provides rather less satisfactory results. Progress towards more reliable structural data on these surfaces is of particular importance, as oxides are of huge interest with respect to both basic science and industrial applications. Here, the geometry of rutile $\text{TiO}_2(110)(1 \times 1)$ (see Fig. 1 for a schematic of the bulk-terminated structure), a prototypical metal oxide surface, whose precise surface structure remains a topic of some debate [2–4], is determined with the well-established technique of quantitative low-energy electron diffraction (LEED-IV) [5]. Importantly, we examine the impact on the structure determination of both charge transfer in the calculation of scattering phase shifts [5], and of soft surface vibrational modes [6].

The most complete experimental quantitative structure determination of $\text{TiO}_2(110)(1 \times 1)$ currently available emerged from a surface x-ray diffraction (SXRD) study [7]. Theoretical approaches have also been used to elucidate the surface geometry, including *ab initio* techniques based on Hartree-Fock (HF) [3,8] and, density functional theory (DFT) [3,9–11]. Comparison of the surface relaxations reported in these various studies reveal quantitative disparities, with the lack of convergence between experiment and theory being of particular concern. To illustrate this discord atomic displacements derived from the SXRD

study [7], and recent calculations by Swamy *et al.* [3] are displayed in Table I. On this basis, given the importance of $\text{TiO}_2(110)(1 \times 1)$ for fundamental surface studies [4], a further experimental determination of its structure is extremely timely.

LEED-IV measurements, which involve acquisition of diffracted electron beam intensities as a function of the incident electron beam energy (E_p) to produce so-called IV curves for structure determination [5,12], were performed in an ultra high vacuum chamber, having a base pressure of $\sim 1 \times 10^{-10}$ mbar. A LEED optics fitted with a channel plate to act as an image intensifier (MCP-LEED, OMICRON) was employed, to allow diffraction patterns to be recorded with an ultralow incident electron beam current (nA regime). Such a system was utilized, as previously it had been observed that the use of a standard LEED optics

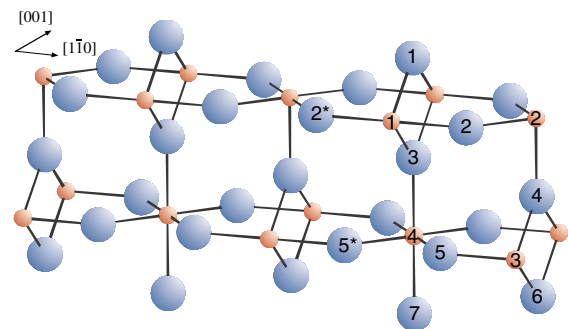


FIG. 1 (color online). Ball and stick model of $\text{TiO}_2(110)1 \times 1$. Larger (smaller) spheres are oxygen (titanium) ions. The numerical labeling of the atoms is employed in Table I for identification purposes. Symmetry paired atoms are denoted as 2* and 5*.

TABLE I. Atomic displacements away from the bulk-terminated structure of $\text{TiO}_2(110)1 \times 1$ resulting from analysis of the LEED-IV data. Also listed are values obtained from previous SXRD measurements [7], and recent theoretical calculations, employing HF and DFT-LDA [3]. Figure 1 provides a key to the identity of the atoms. A negative value indicates that the atom moves towards the bulk for a displacement perpendicular to the surface plane, and in the $[1\bar{1}0]$ direction for a lateral displacement.

Atom	LEED-IV	SXRD [7]	Displacement (\AA)	
			HF [3]	DFT-LDA [3]
Ti(1)	0.25 ± 0.03	0.12 ± 0.05	0.25	0.22
Ti(2)	-0.19 ± 0.03	-0.16 ± 0.05	-0.17	-0.17
Ti(3)	-0.09 ± 0.07	-0.09 ± 0.04	-0.11	-0.11
Ti(4)	0.14 ± 0.05	0.07 ± 0.04	0.13	0.14
O(1)	0.10 ± 0.05	-0.27 ± 0.08	-0.01	0.01
O(2) $[110]$	0.27 ± 0.08	0.05 ± 0.05	0.11	0.13
O(2) $[1\bar{1}0]$	-0.17 ± 0.15	-0.16 ± 0.08	-0.06	-0.06
O(3)	0.06 ± 0.10	0.05 ± 0.08	0.02	0.03
O(4)	0.00 ± 0.08	0.00 ± 0.08	-0.02	-0.02
O(5) $[110]$	0.06 ± 0.12	0.02 ± 0.06	0.03	0.02
O(5) $[1\bar{1}0]$	-0.07 ± 0.18	-0.07 ± 0.06	-0.03	-0.02
O(6)	0.00 ± 0.17	-0.09 ± 0.08	-0.03	-0.02
O(7)	0.01 ± 0.13	-0.12 ± 0.07	0.03	0.03

results in surface damage during the acquisition of LEED-IV data from $\text{TiO}_2(110)(1 \times 1)$ [13].

The $\text{TiO}_2(110)$ sample was prepared *in situ* by cycles of Ar^+ bombardment and annealing at 1000–1100 K until the surface was well ordered and clean, as determined by LEED and Auger electron spectroscopy, respectively. It is known that this preparative prescription gives rise to a number of bridging oxygen vacancies (5% of a monolayer) [4]. However, given their random distribution, they have no impact on this LEED-IV study, which probes only the ordered portions of the surface. Throughout the experiment the $\text{TiO}_2(110)$ sample remained translucent green/blue, indicating a relatively low level of bulk reduction [4]. All of the LEED-IV data were recorded at a substrate temperature of ~ 140 K. To minimize surface contamination, the sample was flashed to ~ 500 K just prior to data acquisition. Auger spectra were never recorded directly prior to collecting LEED-IV curves, due to the possibility of electron beam induced surface damage. For the LEED-IV measurements the incident electron beam was essentially normal to the surface. This geometry was achieved by comparing nominally symmetry-equivalent diffraction beams.

From the set of diffraction patterns, IV curves, having a total energy range of 1660 eV, were extracted for eight nonequivalent integral order beams, i.e., (10), (01), (11), (02), (03), (04), (12), and (13). Determination of structural relaxations from these data involved the usual approach of simulating IV curves for model structures, and then iteratively optimizing the geometry to find the best fit between experiment and theory as measured using the Pendry reliability factor (R_p) [14]. The Barbieri–Van Hove Automated Tensor LEED code [15] and the DL_LEED package [16] were employed for this work.

Simulation of IV curves requires a description of the electron scattering from the surface atoms, which is encap-

sulated in the scattering phase shifts [5,12]. Typically, the scattering potential is generated through a superposition of atomic charge densities, employing the muffin-tin approximation [5,12]. For ionic materials, if nonzero valence free space charge densities can be calculated, phase shifts may then be obtained by estimating the relevant muffin-tin radii and applying Mattheiss’s prescription (with or without an Ewald correction). In general, on the basis that the precise details of the potential are not important for electron diffraction at energies at least 50 eV above the Fermi edge, it is assumed that this approach, although rather elementary, is sufficient. With regards to metal oxides there is a specific problem with the methodology, since it is well known that the O^{2-} ion is unstable in the gas phase and hence the only available starting point is the neutral oxygen atomic solution. Therefore, within oxide materials, the neutral oxygen charge density is used as a starting point, and the orbital occupancies of the neutral atom states are altered to reflect the oxygen’s ionic nature (e.g., Ref. [17]). However, it is important to emphasize that this “ionic oxygen” is simply the neutral oxygen with its occupancy pattern altered rather than being a true representation of the O^{2-} moiety.

Following the above approach phase shifts were generated for this study using the DL_PHASE package [18]. Neutral atomic solutions were calculated and the occupancy of the individual atomic states was altered to generate “ioniclike” solutions. These were then used within a Mattheiss prescription, assuming muffin-tin radii equal to the atomic radii for which the charge densities were generated. Using these phase shifts no satisfactory agreement between the experimental and theoretical IV curves was obtained, with the best R_p being above 0.6. One possible explanation for this is that the charge transfer in TiO_2 gives rise to a scattering potential that deviates significantly from

the atomic superposition even at higher energies. In order to examine this possibility a new scheme for phase shift generation was developed, which accounts more rigorously for the details of the substrate electronic structure, and removes the problem of gas phase O_2^- instability. Importantly, in contrast to the more traditional approach outlined above, our new procedure is *self-consistent* and contains *no adjustable parameters*, and so guarantees reliable and unbiased phase shift generation.

To generate these *self-consistent* phase shifts an *ab initio* calculation of bulk TiO_2 using the CRYSTAL code [19] was used to produce an accurate ground state charge density. The bond critical points were identified and used to partition space into spherical atom centered regions by assigning a muffin-tin radius [4,12] to each of the ions. Values of almost exactly 1 Å were extracted for both Ti and O. Clearly, these numbers do not correspond to either atomic or ionic radii and illustrate that the use of an *ab initio* density is essential in order to assign nonarbitrary radii to the muffin-tins. These muffin-tin radii were then utilized in a self-consistent Korringa-Kohn-Rostoker (KKR) calculation to generate *self-consistent* phase shifts. More specifically, the scalar-relativistic KKR method was applied to bulk TiO_2 . We utilized the local density approximation with the Perdew-Wang [20] exchange-correlation potential. For Brillouin zone integration 726 special points were used and the maximum angular momentum was $l_{max} = 3$. More details on the computational method can be found in Ref. [21]. We note that phase shifts that take into account charge transfer have previously been employed to simulate x-ray absorption spectra [22]. However, unlike our new approach, this procedure utilizes free atomic charge densities, and the muffin-tin radii are not derived from rigorous *ab initio* calculations, introducing uncertainties, which our scheme avoids.

These *self-consistent* phase shifts were used to reanalyze the experimental data. A dramatic improvement in the agreement between the computed and measured data was achieved with the optimum R_P becoming 0.29, indicating an acceptable structural solution. Figure 2 displays plots of the experimental and theoretical IV curves, depicting the best fit. Atomic displacements away from bulk termination are listed in Table I. To verify the importance of employing the *self-consistent* phase shifts, this best-fit structure was used as a starting geometry for an optimization using the original phase shifts. A best value for R_P of 0.64 resulted, clearly demonstrating that phase shifts for systems with ionic-like character need to be calculated with care as self-consistency in the charge distribution can have a significant effect on the fit achieved during the structural optimization.

From comparison of this optimum LEED-IV structure with that derived from SXRD [7], it can be deduced from Table I that the agreement is not quantitatively perfect. Most significant are the differences (Δ) in the displacements of the following atoms: O(1) ($\Delta = 0.37 \pm 0.09$ Å), O(2)[110] ($\Delta = 0.22 \pm 0.09$ Å), Ti(1) ($\Delta = 0.13 \pm 0.06$ Å),

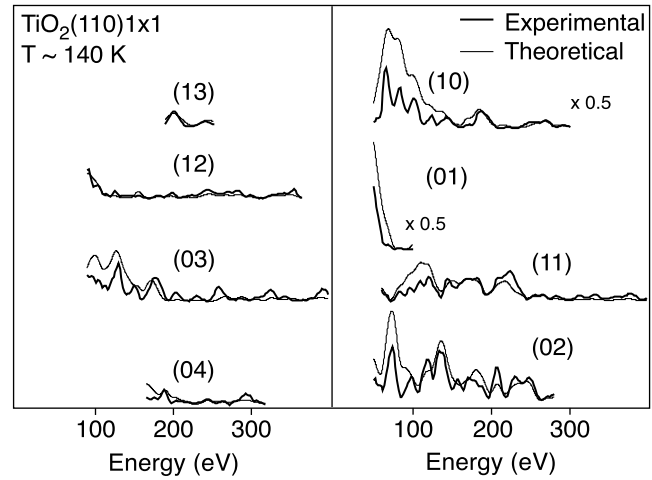


FIG. 2. Comparison of experimental and theoretical LEED-IV data for the best-fit structure. *Self-consistent* phase shifts were employed to generate the simulated curves.

and Ti(4) ($\Delta = 0.07 \pm 0.06$ Å). Currently, the origin of this disparity between the two experimental studies remains uncertain, although it may be related to improvements in surface preparation methodology over the last few years [4]. In contrast, it is clear from Table I that there is rather better agreement between the LEED-IV result and Swamy *et al's* [3] recent HF and DFT calculations. All of the Ti atoms have essentially the same locations in both the experimental work and theoretical calculations, and the only significant differences occur in the displacements of O(1) ($\Delta = 0.11 \pm 0.05$ Å) and O(2)[110] ($\Delta = 0.16 \pm 0.08$ Å) (N.B. HF [3] parameters were used for calculating Δ 's).

It has been suggested that any deviation between the theoretically predicted geometry and that measured may be due to the presence of a soft vibrational mode at the surface [6]. In order to quantify the effects of this mode on the LEED interpretation the full dynamical matrix of the $TiO_2(110)(1 \times 1)$ surface was computed using *ab initio* calculations, and the atomic motions due to the soft mode were included in the simulation of the LEED-IV curves. More specifically, DFT calculations based on the plane-wave, pseudopotential approach [23] with ultrasoft pseudopotentials [24,25], employing the local-density approximation (LDA) functional [26,27], were conducted. A kinetic energy cutoff of 460 eV and a (6,3,1) Monkhorst-Pack grid were found to converge the energy to 0.08 eV per formula unit. The surface was described using a periodic slab of 21 atomic layers with a 10 Å vacuum gap to separate the periodic replicas. The structure was optimized using the BFGS algorithm until the magnitude of the average force on the atoms was less than 0.02 eV/Å and the change in total energy was less than 10^{-6} eV per atom. The dynamical matrix at the Γ point was evaluated using the finite difference approximation with displacements of 0.007 Å, and forced to be symmetric and to satisfy the

infinitesimal translational invariance (see, for example, [28]). Vibrational harmonic frequencies at the Γ point and the relative eigenvectors were then obtained by diagonalizing the resulting dynamical matrix. A surface mode is found at 104 cm^{-1} . This mode involves an inward motion of O(1), Ti(1), O(3) and Ti(4), and an outward motion of Ti(2), O(4), Ti(3) and O(6). The in-plane atoms O(2) and (2*) move outward, too.

To produce simulated IV curves incorporating the calculated vibrational mode, a series of single point LEED calculations at displacements along the eigenvector of the mode were performed. Calculated intensities were combined using the probability distribution of a simple harmonic oscillator. This procedure was conducted at the temperature of the LEED experiment, 140 K, and at a higher, reference temperature of 3825 K, which corresponds to a fivefold increase in the atomic displacements. Comparison of the IV curves generated for a temperature of 140 K with those for a reference structure without the surface vibration (i.e., calculated structure at 0 K) indicates virtually no difference in their profile. Hence such a mode can be discounted as being the source of the small disparity between the structures determined from the LEED-IV and theoretical calculations [3]. At the higher temperature significant differences became apparent. Thus, although in this instance the soft mode has at best minor implications for the interpretation of the LEED-IV data it is clear that such modes must be borne in mind when performing structural optimizations.

In summary, we have performed a fully quantitative LEED-IV study of $\text{TiO}_2(110)1 \times 1$, a prototypical metal oxide surface. The experimentally determined structure and the results of recent HF and DFT calculations [3] are in excellent agreement, with small discrepancies only in the positions of O(1) and O(2). Importantly, we have demonstrated that *self-consistent* phase shifts, generated without adjustable parameters, are required to guarantee a reliable structural solution in such systems. Furthermore, we have explored the significance of soft surface vibrational modes on structure determination, demonstrating that, although for the experimental conditions employed here they are of little consequence, in general, they should be taken into consideration.

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