

## Revisiting the surface structure of $\text{TiO}_2(110)$ : A not so simple LEED investigation

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Experimental and theoretical quantitative surface structure determinations, employing state-of-the-art approaches, of *model* metal and semiconductor surfaces, have become generally extremely reliable. 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 immense importance, as oxides are of huge interest with respect to both basic science and industrial applications (e.g. gas sensing, bio-materials, and catalysis). Even the geometry of simple, well-known oxide surfaces remain the subject of debate. A prime example of such uncertainty is the  $1 \times 1$  phase of  $\text{TiO}_2(110)$  [1,2], a prototypical metal oxide surface. Experimentally, the most complete structural study of this surface has been performed using surface x-ray diffraction (SXR) [3]. There have also been a number of theoretical elucidations, utilising a variety of computational approaches (Ref. 2 and refs. therein). However, overall the structural data lacks consistency, with the, at best, semi-quantitative agreement between theory and experiment being of particular concern (see Table 1). Given such a lack of accord for a supposedly well-understood *model* surface, it is appropriate to re-visit the experimental determination of the structure of  $\text{TiO}_2(110)1 \times 1$  (Fig. 1 displays a schematic of this surface).

For this study we have utilised the well-established technique quantitative low energy electron diffraction (LEED-IV). To avoid surface damage during data acquisition, which has previously been observed to occur [4], an ultra-low current LEED optics has been employed. A relatively large data set has been acquired, and IV-curves from eight non-equivalent diffraction beams have been used in the analysis. Elucidation of the structure, utilising these curves, followed the usual approach of generating simulated data for model structures, and then iteratively optimising the geometries to find the best experiment-theory fit [5].

Phase shifts, which describe the interaction of the probe electrons with the ion cores, are a fundamental element of the input for generating simulated IV-curves. Typically, these phase shifts are produced following standard, well-known methodology [5]. Employment of such phase shifts, however, gave rise to no satisfactory fit between experimental and theoretical IV-curves. Given that the prescription used to generate these phase shifts is based simply on a superposition of solutions for neutral atoms, then this failure for  $\text{TiO}_2$ , an ionic-covalent material, is not entirely unexpected. In an attempt to obtain improved experiment-theory agreement, we generated a new set of *self-consistent* phase shifts using a combination of *ab initio* techniques to better mimic the  $\text{TiO}_2$ .

These new phase shifts provide a dramatic improvement in the theory-experiment fit, clearly demonstrating that phase shifts for such systems 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 optimisation. The atomic relaxations obtained for the optimised structure are listed in Table 1, and are compared to those from SXR [3] and recent calculations [2]. It can be seen that the LEED-IV structure is at variance with the earlier studies. As regards divergence from the theoretical results one proposed source is the presence of soft vibrational surface modes [6]. We have tested this possibility by examining the impact of such modes on simulated IV-curves. Calculations at the experimental temperature of  $\sim 140$  K indicate that the addition of these vibrations leave the IV-curves essentially identical. However, at significantly higher temperatures there are clear modifications to the IV-curves, and so in general such modes must be considered when performing structural optimisations.

References

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Figures and Tables

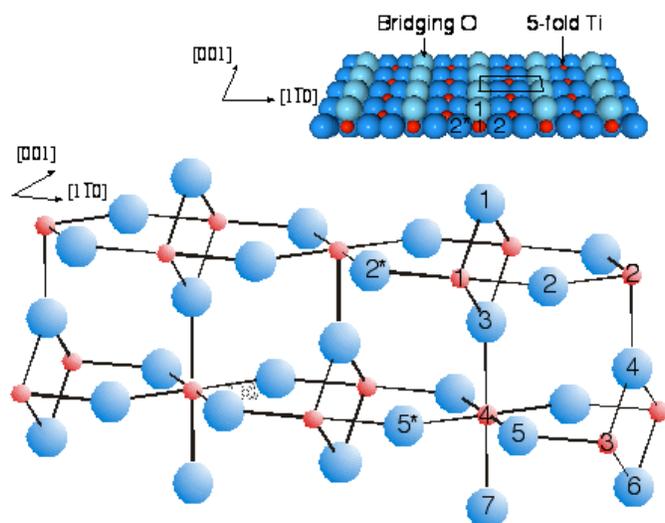


Figure 1. Top is a space filling model of  $\text{TiO}_2(110)1 \times 1$ . Bottom is a ball and stick model of the same surface. In both diagrams, larger (smaller) spheres are oxygen (titanium) ions. The atom numbering is employed below in Table 1.

Table 1. Atomic displacements from the bulk terminated structure of  $\text{TiO}_2(110)1 \times 1$  derived from the *LEED-IV* data. Also listed are values obtained from earlier *SXRD* measurements [3] and recent theoretical calculations, employing *HF* and *DFT-LDA* [2]. Figure 1 shows the location of the atoms, with the symmetry paired atoms denoted as  $2^*$  and  $5^*$ . 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	Displacement (Å)			
	LEED-IV	SXRD	HF	DFT-LDA
Ti (1)	$0.03 \pm 0.03$	$0.12 \pm 0.05$	0.25	0.22
Ti (2)	$-0.40 \pm 0.03$	$-0.16 \pm 0.05$	-0.17	-0.17
Ti (3)	$-0.17 \pm 0.07$	$-0.09 \pm 0.04$	-0.11	-0.11
Ti (4)	$0.07 \pm 0.05$	$0.07 \pm 0.04$	0.13	0.14
O (1)	$-0.12 \pm 0.05$	$-0.27 \pm 0.08$	-0.01	0.01
O (2) [110]	$0.05 \pm 0.08$	$0.05 \pm 0.05$	0.11	0.13
O (2) [ $1\bar{1}0$ ]	$-0.17 \pm 0.15$	$-0.16 \pm 0.08$	-0.06	-0.05
O (3)	$0.01 \pm 0.1$	$0.05 \pm 0.08$	0.02	0.03
O (4)	$-0.05 \pm 0.08$	$0.00 \pm 0.08$	-0.02	-0.02
O(5) [110]	$-0.02 \pm 0.12$	$0.02 \pm 0.06$	0.03	0.02
O(5) [ $1\bar{1}0$ ]	$-0.07 \pm 0.18$	$-0.07 \pm 0.06$	0.03	0.02
O (6)	$0.01 \pm 0.17$	$-0.09 \pm 0.08$	-0.03	-0.02
O (7)	$0.03 \pm 0.13$	$-0.12 \pm 0.07$	0.03	0.03