ESRF

Experiment title:
Reconstruction and oxygen defects in the (100) surface of TiO_2

Experiment number:
S1-30

Beamline:
ID3 (BL7)

Date of Experiment:
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Shifts: 9

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Report:

Since the first report in 1972 [l] the photocatalytic properties of TiO2 (Rutile) have attracted much interest. Although the bulk rutile structure is well understood, almost nothingis known about its surface structures which, however, are intimately related to the catalytic properties [2-4].

The surface x-ray dffraction experiments were performed at the beamline ID3 (BL7) at awavelength of λ=0.76 Å. In total 72 symmetry independent superstructure reflections have been measured, 28 in plane reflections (Old), and 5 superstructure rods extending up to a maximum momentum transfer of about 3 rec. lattice units (a*) normal to the sample surface corresponding to 0.65 $Å^{-1}$. The Fig. 1 shows in the upper part a schematic view of the (1x3) surface unit cell that can be derived from the projected Patterson-function P(w). The solid circles represent Ti-ions, the dotted circle in the center of the unit cell corresponds to a Ti-vacancy.

In the second panel of Fig. 1 we show the calculated (projected) Fourier-synthesis of the electron density, $\rho(y,z)=\Sigma_{kl} |F_{0kl}^{obs}| \cdot \cos[2\pi(ky+lz)+\alpha_{0kl}^{calc}]$, where $|F_{0kl}^{obs}|$ and α_{0kl}^{calc} represent the observed structure factor amplitudes and the calculated phases on the basis of the structure model, respectively. Solid lines correspond to positive maxima in $\rho(y,z)$, negative maxima (dashed lines) are also observed, since only superstructure reflections are included in the Fourier-synthesis [5]. The positive maxima are related to Ti-ions which are shifted laterally out of their (1x1) bulk positions by as much as 0.6-0.7 Å giving rise to the electron density 'dipoles' in $\rho(y,z)$. Using this simplified structure model, neglecting all oxygen contributions to the scattering amplitudes, only insufficient agreement between observed and calculated intensities ($I=|F|^2$) could be obtained.

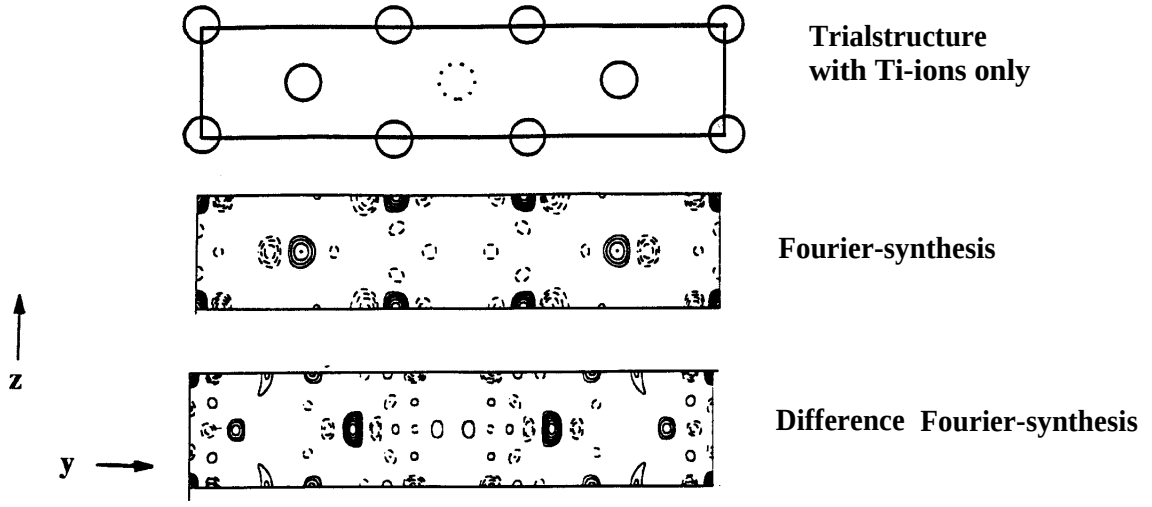

Fig. 1: Structure model including Ti-ions only (top), the corresponding Fourier-synthesis (center) and difference Fourier-synthesis (bottom) of the Ti(100)(3x1) surface structure in a projection along the a-axis of the bulk unit cell. Solid circles represent Ti-ions, positive and negative maxima in the electron density maps are represented' by solid and dashed lines, respectively.

By calculating the difference Fourier-synthesis given by $\Delta\rho(y,z)=\Sigma_{kl}(|F_{0kl}^{obs}|-|F_{0kl}^{calc}|)\cdot\cos[2\pi(ky+lz)+\alpha_{0kl}^{calc}]$ it is possible to obtain an idea about missing parts of the structure as compared to the trial structure. The difference Fourier-synthesis is shown in the third panel of Fig. 1. Due to the high data quality collected at the ESRF it is possible to unambiguously identify intense positive maxima which are related to oxygen-ions. In the final step of the analysis the out of plane data have been included in the structure refinement. Starting with the microfacet (MF) modell suggested by Zschack et al. [6], also the vertical positions of the atoms were allowed to relax from their bulk positions. Large inward relaxations are deduced from a preliminary data analysis leading to a 'flattening' of the micro-facet structure. Current data analysis still concentrates on several open questions such as the simultaneous occurrence of both, the MF and the missing row (MR) structure [6] as well as the presence of an extra oxygen-ion as compared to to original MF-structure, leading to an additionally 6-fold coordinated Ti-ion but to a non-stoichiometic surface.

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