



**Experiment title:**  
Chemical Bonding in Rutile

**Experiment number:**  
HE-2017

**Beamline:**  
ID15B

**Date of experiment:**  
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**Report:**

The experiment described here has been performed as part of a joint project supported by the Deutsche Forschungsgemeinschaft (DFG) within the priority programme ‘Experimental Electron Density as a Key to Understand Chemical Interactions’. With that objective, the aim of this project is to gain a deeper and more reliable understanding of the chemical bonding in rutile  $\text{TiO}_2$  by investigating its electronic structure experimentally in position and momentum space — separately as well as combined to the density matrix, and supported by theoretical methods. Apart from the systematic innovation of experimental density matrices [1, 2], the special properties of  $\text{TiO}_2$ , the substantial discrepancies between published effective charges of the Ti and O atoms and the necessity also to cover electron–electron correlation are the motivations for the reported experiment.

The high-energy inelastic x-ray scattering experiment has been performed using the dispersion-compensating scanning spectrometer at beamline ID15B with an incident-photon energy of 87.93 keV and a scattering angle of  $173.1^\circ$  [3]. The thus accessible range of the electron-momentum component  $q$  parallel to the scattering vector  $\mathbf{k} = \mathbf{k}_2 - \mathbf{k}_1$  (primary beam 1, secondary beam 2) is  $-22.6 p_0 \leq q \leq +22.6 p_0$  with  $p_0 = h/(2\pi a_0)$  as the atomic momentum unit. The resulting data grid of the off-diagonal distance  $s$  in the pure-position-representation density matrix is as fine as 0.075 Å.

The samples have been rectangular plates 10 mm high, 3 mm wide and 0.7 mm thick, cut from (100)-, (110)- and (001)-oriented single-crystal blanks of 10 by 10 by 0.7 mm<sup>3</sup> and illuminated by the primary beam on an area of 5 by 2.5 mm<sup>2</sup>. In addition to those directions  $\mathbf{R}$ ,  $\mathbf{S}$  and  $\mathbf{T}$ , resp., at the corners of the irreducible  $4\pi/16$  spherical triangle on the unit sphere (Laue class  $D_{4h} = 4/\text{mmm}$ ), we have prepared samples  $\mathbf{C}$  and  $\mathbf{F}$  with surface vectors halfway on the (110)–(001) and (001)–(100) meridians, resp., each composed of five prismatically cut parallel pieces with long axes in the (1,–1,0) and (010) directions, resp. (see Fig. 1).  $q$ -Orientations between those five directions  $\mathbf{R}$ ,  $\mathbf{S}$ ,  $\mathbf{T}$ ,  $\mathbf{C}$ ,  $\mathbf{F}$  have to be reached by rotations of the sample around its three axes such that the tilt of the sample-surface vector with respect to the scattering plane is kept minimum in order to maintain highest momentum resolution. That resolution requirement necessitates different choices of the long sample axis initially perpendicular to the scattering plane for particular desired directions.

The directions of greatest interest lie in the (1,-1,0) plane with an azimuth of 45°, which contains the position-space network of chemical bonds shown in Fig. 3, whose detailed nature we want to elucidate.

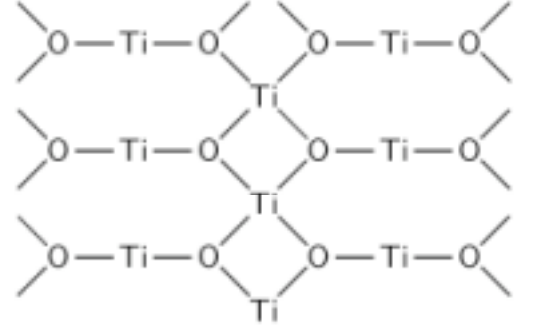
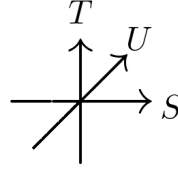
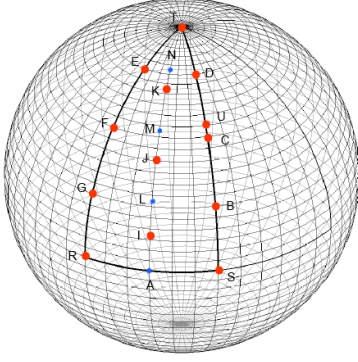


Fig. 1 Measured (red points) and to be measured (blue points) directions in rutile  $\text{TiO}_2$ .

Fig. 2 The main direct and higher-order bonding directions in the (1,-1,0) plane of rutile  $\text{TiO}_2$ .

With the exception of small multiple-scattering effects all necessary corrections have been applied to the measured Compton spectra [4], leading to Compton profiles  $J(\mathbf{q})$  that are normalised to one formula unit of  $\text{TiO}_2$ . The Compton-profile maxima  $J(\theta)$  have a directionally dependent value (therefore the vectorial  $\theta$ ) of approximately 10 electrons/ $p_0$  ( $p_0 = h/2\pi a_0$  is the atomic unit of momentum). In the following our results for the 4 directions  $\mathbf{R}$ ,  $\mathbf{S}$ ,  $\mathbf{T}$ ,  $\mathbf{U}$  of the measured 13 ones are shown as Compton-profile differences  $\Delta J(q)$  exemplarily.

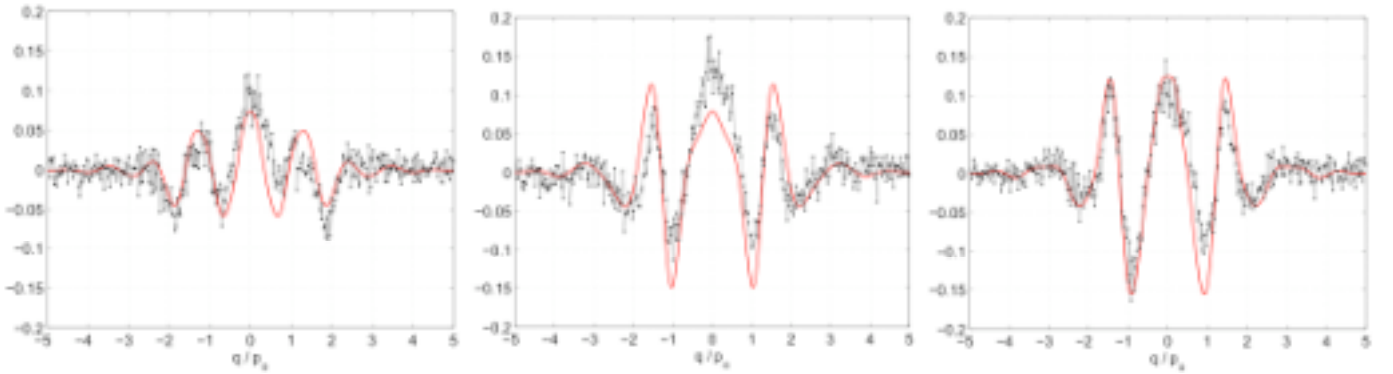


Fig. 3 Measured (black dots with error bars) and calculated (solid-state Hartree-Fock, red line) directional Compton-profile differences  $J(q_T) - J(q_R)$ ,  $J(q_U) - J(q_R)$ , and  $J(q_S) - J(q_R)$ .

We have chosen the  $\mathbf{R} = (100) = [100]$  direction as the reference, since the nearest-neighbour atoms in this direction are connected only via four intermediate bonds and therefore show only small electronic coherence. The spherical atomic contributions cancel in the difference profiles, and the  $\mathbf{R}$  direction adds only little.

The very slow decay of the oscillations in the  $\Delta J(q)$  with increasing  $q$  indicates that highly localised atomic orbitals are contributing to the interatomic coherence = chemical bonding, i.e. 3d orbitals are very visibly involved in chemical bonding in rutile. Formulas of the type  $\text{Ti}^{4+}\text{O}_2^{2+}$  or  $\text{Ti}(\text{Ar}4s^2)^{2+}\text{O}_2^{1+}$  with only 4s covalency, which could agree with measured electron position densities, we can definitely exclude. All three measured anisotropies agree well with our Hartree-Fock calculations, showing, however, also quantitative deviations owing to residual multiple scattering still to be corrected and to the various approximations in the theoretical approach (basis set, electron-electron correlation).

Our results show that the measurements of the blue-point directions and the hopefully soon available CBED data for the position density will enable us to reconstruct the electronic 1-RDM with details that the electron position density alone cannot provide.

## References

- [1] W. Weyrich, in: C. Pisani (ed.), “Quantum-Mechanical Ab-initio Calculation of the Properties of Crystalline Materials”, Springer, Berlin etc. 1996, pp. 245–272, and the list of references cited therein.
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