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Real-space mapping of electronic orbitals

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ABSTRACT

Electronic states are responsible for most material properties, including chemical bonds, electrical and thermal conductivity, as well as optical and magnetic properties. Experimentally, however, they remain mostly elusive. Here, we report the real-space mapping of selected transitions between p and d states on the Ångström scale in bulk rutile (TiO_2) using electron energy-loss spectrometry (EELS), revealing information on individual bonds between atoms. On the one hand, this enables the experimental verification of theoretical predictions about electronic states. On the other hand, it paves the way for directly investigating electronic states under conditions that are at the limit of the current capabilities of numerical simulations such as, e.g., the electronic states at defects, interfaces, and quantum dots.

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1. Introduction

Electronic states shape the world around us as their characteristics give rise to nearly all macroscopical properties of materials. Be it optical properties such as colour and refractive index, chemical properties such as bonding and valency, mechanical properties such as adhesion, strength and ductility, electromagnetic properties such as conductance and magnetisation, or the properties of trap states: ultimately, all these properties can be traced back to the electronic states in the material under investigation. Therefore, it is not surprising that electronic states are of paramount importance across many fields, including physics, materials science, chemistry and the life sciences. It does come as a surprise, however, that while some of their aspects can be inferred indirectly from macroscopical material properties or some diffraction techniques, the direct observation of individual electronic states in real space so far has succeeded only under very special circumstances (e.g. on an insulating surface using a scanning tunnelling microscope (STM) with a specially functionalised tip [1]) due to both experimental and theoretical challenges. In this work, we endeavour to remedy this situation by using a combination of transmission electron microscopy (TEM), electron energy-loss spectrometry (EELS), and state-of-the-art simulations.

TEM is a well-known technique for studying materials on the nanoscale while EELS adds element-specific information. Both are widely-used on a regular basis in many fields and are readily commercially available. Owing to these two techniques, tremendous progress has been made over the last decade in mapping atom positions with ≈ 10 pm accuracy [2–4], determining charge densities [5–7], and performing atom-by-atom chemical mapping [8–12]. Furthermore, the fine-structures of the spectra allow the determination of the local chemical and structural environment as well as the hybridisation state of the scattering atoms [11–18] in the bulk, which can be substantially different from the surface states probed by STM. This suggests to use the EELS signal to probe the local environment in real-space and map, e.g., crystal fields, conduction states, bonds, and orbitals. Recently, it has been shown on theoretical grounds [19,20] that such real-space mapping of transitions between orbitals on the Ångström scale should indeed be possible, even though the experimental realisation was expected to be extremely challenging.

The method of choice to demonstrate the possibility of this real-space mapping used throughout this work is high-resolution scanning TEM (STEM) together with EELS. In STEM, an electron beam is typically produced by a high-brightness field-emission gun, accelerated to a kinetic energy of the order of 100 keV, and subsequently focused to an Ångström-sized spot on the sample (see Fig. 1c and [21]). Inside the specimen, the probe electrons

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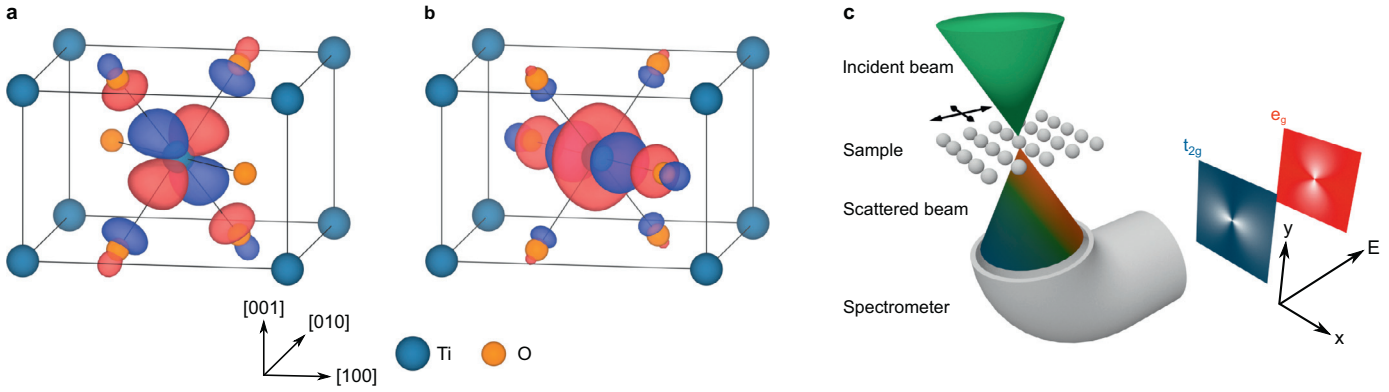

Fig. 1. Maximally-localized Wannier functions in rutile corresponding to unoccupied orbitals of Ti-e_g character ($x^2 - y^2$-like Wannier function (a), z^2-like Wannier function (b)). (c) Sketch of the measurement setup. The incident beam is focused onto and scanned over the sample. It can exchange energy and momentum with the specimen, leading to a mixture of states in the scattered beam. Using a spectrometer comprised of a sector magnet and a subsequent imaging system, maps can be formed of all electrons that have transferred a certain amount of energy E corresponding to transitions to different unoccupied orbitals inside the sample. The blue and red planes symbolize the real-space distribution of the transition probabilities to different final states. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

scatter off the nuclei and sample electrons via the Coulomb interaction.

Scattering by the nuclei is predominantly elastic, i.e., only momentum but no energy is transferred from the lattice (which is assumed to be infinitely heavy) to the probe electron. This gives rise to atomic column contrast in high-resolution TEM, as well as to channeling and dechanneling effects in samples that are thicker than a few tens of nanometres [22,23]. Dechanneling, which can be visualised as a hopping of the electron beam between adjacent columns, destroys the direct spatial correlation between the measured scattering intensity and its point of origin. Consequently, very thin specimens, as well as simulations taking elastic scattering into account, are needed to reduce artefacts and arrive at a reliable interpretation of the data.

Here, the interaction of primary interest is the scattering of the probe electrons on the sample electrons. Both energy and momentum can be transferred between the beam and the sample. Of particular importance for the real-space mapping of electronic transitions is the so-called core-loss regime of energy transfers of $\gtrsim 100$ eV. They trigger an excitation of a sample electron from an initial, occupied core state to a final, unoccupied conduction-band state. The initial states are typically localised in close proximity to the nucleus and are characterised by a large binding energy. Therefore, crystal-field effects are mostly negligible for core states, which typically exhibit atomic character. The final states, on the other hand, lie close to the Fermi energy, and are strongly influenced by the local environment (see Fig. 1a, b).

Due to the strong localisation of the probe beam, it is possible to map the position and energy-dependent transition matrix elements between the initial and the final states using STEM-EELS (see Fig. 1c). If the initial state is known — either from first principles or experiments [24] — it is furthermore possible to obtain both the angular and the radial dependence of the final states [19,25,26] and, thus, bonding information on individual atomic columns [15,27]. To that end, specific transitions can be selected by using a sufficiently narrow energy range.

2. Results

2.1. Experiments

As a model system, we have chosen rutile (TiO_2). It has a relatively simple, tetragonal unit cell and, together with the other titanium oxides, has great practical importance, e.g., in renewable energy and energy storage applications, photocatalysis, or as coating material (for a review, see [28] and other articles published in the same issue). Its tetragonal structure leads to a strong crystal-field splitting. In particular, the different Ti-O bond lengths give rise to a strong asymmetry and splitting [29] of the e_g and t_{2g} states. Most noticeably, the asymmetric shape of the orbitals is rotated by 90° for adjacent Ti atoms due to the crystal symmetry (see Fig. 2). We concentrate here solely on mapping the e_g states since the t_{2g} peak has a much lower intensity. Throughout its narrow energy range [30], there is always a sizeable e_g contribution (see the fitted Gaussian peaks in Fig. 2a), making it impossible to identify an unequivocal t_{2g} signal with todays instruments due to signal-to-noise ratio (SNR) limitations. Also note that in our simulations, the t_{2g} Wannier states are much more localized around the nucleus, which strongly reduces the asymmetry caused by crystal-field effects for t_{2g} states.

A rutile single crystalline sample (MTI corporation) was mechanically thinned down to electron transparency by using the wedge polishing technique with a Multiprep polishing apparatus (Allied High Tech Products Inc.). Further ion milling with a Gentle Mill (Technoorg Linda Ltd.) was performed for ion beam energies in the range of 500–900 eV to remove the damaged regions from the mechanical polishing and provide large, thin, and clean surfaces.

The experiments were performed at 80 kV acceleration voltage on a FEI Titan 80–300 TEM equipped with spherical aberration correctors and a Gatan GIF Quantum Energy Filter. During the experiments, the single-crystalline sample was oriented in [0 0 1] direction and the thickness was determined to be 20 nm using EELS [31,32]. A spectrum image (SI) data cube (see Fig. 2a) was recorded over several unit cells, together with the elastic dark-field (DF) signal (see Fig. 2c). The SI data and the DF signal were acquired simultaneously with a convergence semi-angle of 19 mrad, a GIF collection semi-angle of 20.7 mrad, and a pixel dwell time of 5 ms to maximize the signal while minimizing drift and beam damage artefacts. Optimising the acquisition conditions is essential for acquiring data with sufficient spatial and energy resolution, as well as sufficient SNR for the subsequent data analysis.

The residual lateral drift [33] was corrected using the DF data and the resulting data cube was averaged over 12 unit cells to improve the SNR. Finally, the map corresponding to L_2 transitions with energy transfers in the range 466.6 ± 1 eV was extracted. This corresponds to transitions from initial states with $2p_{1/2}$ character to final states with an energy in the range of 6 ± 1 eV above

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