Spectroscopy in STEM/TEM

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Site-specific ionisation edge fine-structure in the electron microscope

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Channelling for site-selective X-ray analysis was first implemented in 1982 by Spence and Taftø [1]. As a versatile method for chemical analysis, it was rapidly extended to electron energy loss spectrometry (EELS) in the transmission electron microscope (TEM). This technique was called energy loss by channelled electrons (ELCE) [2]. The local chemistry and electronic structure of particular crystallographic sites can be determined by this method. It was, however, rarely used because of instrumental and theoretical shortcomings. For ELCE, not only the incoming but also the outgoing electron wave as well as elastic and inelastic scattering processes have to be considered. As the spectrometer is usually placed off axis, long acquisition times are necessary. Therefore, stability and a high beam intensity are crucial. Only because of recent advances in both numerical simulations and instrumentation, the situation has improved dramatically.

In this work, we present recent results of our measurements and calculations for rutile (TiO_2). The combination of two simulation software packages for treating the elastic and the inelastic scattering is applied. The first package [3] is based on the Bloch wave formalism for treating the elastic scattering, while it uses the mixed dynamic form factor (MDFF) [4] for the description of the inelastic scattering of the fast probe electrons. The second simulation package [5] is used to calculate the cross-density of states and wave functions by means of density functional theory. The obtained data is then used for the calculation of the MDFF mentioned above. The energy loss near edge structure (ELNES) under ELCE conditions depends sensitively on the sample thickness, the specimen tilt [3] and the direction of the momentum transfer vector. Thus, detailed simulations are needed to interpret the experimental spectra.

Figure 1. (left) shows the calculated partial density of states (DOS) of p-character for oxygen, whose superposition gives rise to the fine-structure in the energy loss spectrum. In Figure 1. (right) the unit cell of rutile is shown. The arrows denote the directions of the different p_x-, p_y- and p_z-orbitals. The experimental work was performed on an FEI TECNAI G2 TF20 TEM, operated at 200 kV primary acceleration voltage and an FEI TITAN TEM operated at 300 kV. The acquired O K-edge ELNES at different channelling conditions is shown in Figure 2. (left). Figure 2. (right) depicts the calculated O K-edge ELNES under the same channelling conditions. It is obvious that the experimentally obtained spectra are in excellent agreement with theoretical predictions.

Owing to powerful instrumentation and simulation software, ELCE is transforming from a rather exotic application to a promising method for orbital mapping and site-specific chemistry in crystallography.

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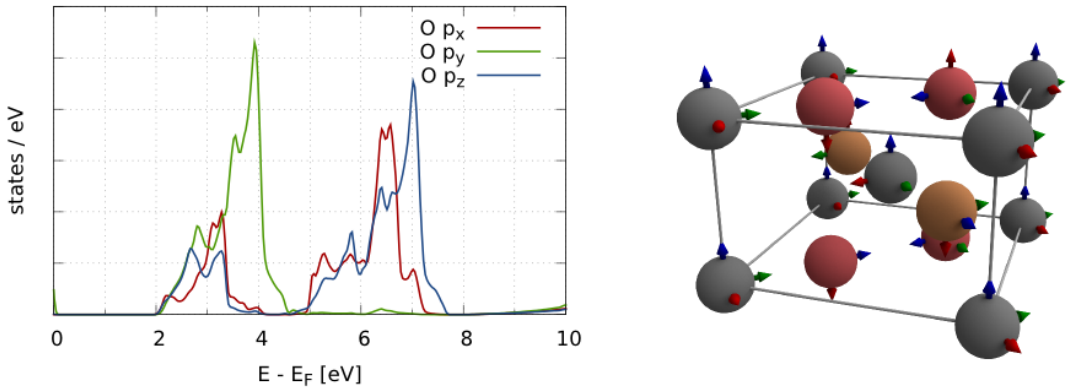

Figure 1. Left: calculated partial DOS of p-character for oxygen. Right: unit cell of rutile (grey: titanium, red/brown: oxygen). The arrows show the directions of the corresponding p_x-, p_y- and p_z-orbitals.

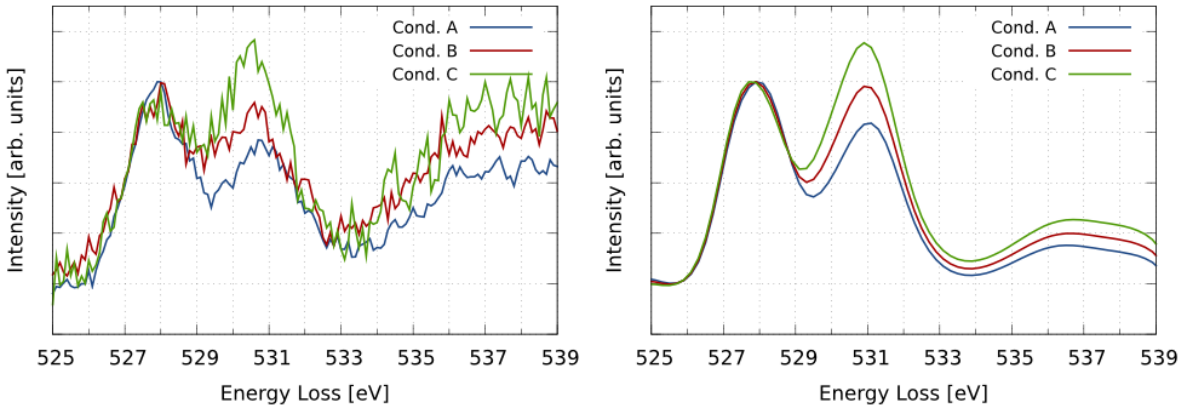

Figure 2. Left: acquired O K-edge ELNES under three different channelling conditions. Right: corresponding calculated spectra. All spectra were normalised to the first peak to facilitate comparison.