AB-INITIO CALCULATIONS OF DENSITY OF STATES FOR Ti-OXIDE

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Electron energy-loss spectroscopy (EELS) has been shown to be a powerful tool to determine not only the chemistry, but also the electronic and atomic structure at grain boundaries by analysing the energy-loss near-edge structure (ELNES).¹ However, as the experimental ability to obtain quality spectra from interfaces with high-spatial resolution is relatively new, the interpretation of ELNES has been mostly qualitative. Here we discuss the ability of ab-initio density of state calculations to perform detailed quantitative analysis at interfaces.

In this methodology, ignoring any multiparticle effects such as excitons, the ELNES can be described as the symmetry projected density of states (DOS) and a matrix element varying slowly with energy. The calculated DOS, which best reproduce the experimental ELNES, are obtained using density functional theory (DFT) in the local density approximation (LDA) (i.e.: Weng et al.²). Traditionally, because a high number of atoms (> 60) is needed to reproduce the periodicity of interface structures, more approximate methods such as the real-space multiple scattering method³ and its equivalent in reciprocal space (KKR-method) were used.⁴ However, norm-conserving pseudopotentials for the (frozen) cores and a mixed-basis of plane waves and atom-centred functions for the valence electrons can be used.⁵ The mixed basis provides the advantage to be efficient even for strongly attractive ionic pseudopotentials, such as oxygen or transition metals. Thus supercells containing up to about 100 atoms, as required for realistic grain-boundary models, can be treated with reasonable effort.

Results were obtained for bulk TiO₂ (rutile). The calculated DOS of all available edges (O-K, Ti-K and Ti-L of TiO₂ in Fig. 1) show a very good agreement to experimental data (Fig. 2) obtained by Brydson et al.⁶ The location (Tab. 3) and the overall shape of the peaks is well reproduced, only the intensity is too low at the second peak, of the Ti-L DOS (Fig. 1b), and too high at the last peak of the O-K DOS (Fig. 1c). The reasons for these discrepancies are still under investigation. However, it is interesting that even at this early stage, these simulations show much better agreement than those obtained by multiple scattering analysis⁷.

The presented calculations reproduce well the experimental ELNES of all edges in bulk TiO₂. Our mixed basis pseudopotential method shows good promise for the calculations of DOS at grain boundaries in near future, particularly when coupled with the atomic resolution experimental capability.

References

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Fig.1: Our (with LDA) calculated DOS of O-K (a), Ti-K(b) and Ti-L_{2,3}(c) edges in TiO₂.

Fig.2: The experimental results of Brydson et al.⁶ with their comparison to theory.

Tab.3: Distances from first peak of our theory and of exp. data of Brydson.⁶

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